MOLECULAR DESIGN FOR NONPOLAR CHIRAL-AXIAL 
QUADRATIC NONLINEAR OPTICS

by

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Molecular Design for Nonpolar Chiral-axial Quadratic Nonlinear Optics

Abstract

by

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In this thesis the hyperpolarizability of various multi-dimensional molecules is studied theoretically/computationally, with particular focus on the second-rank Kleinman-disallowed (KD) component of the hyperpolarizability. This component, which transforms as a second-rank traceless symmetric tensor, could be utilized in certain chiral-axial molecular alignment schemes to produce a bulk response. Nonpolar chiral-axial systems have been proposed in contrast to polar media, which utilize the vector component of the molecular hyperpolarizability and require parallel alignment of the molecular dipoles. Such parallel alignment of dipoles must be “frozen in” in order to overcome the natural tendency for dipoles to align anti-parallel. This limits the density of chromophores that can be loaded into a polar material. Nonpolar materials do not have such limits in theory. The two geometric classes of molecules that can most easily be incorporated into nonpolar chiral-uniaxial materials are propeller-shaped ($C_3$ or $D_3$ symmetry) and $\Lambda$-shaped ($C_{2v}$ symmetry). This work describes efforts to design molecules within these classes that would be suitable for bulk NLO materials. The sum-over-states (SOS) expression is used to model the molecular hyperpolarizability, and quantum chemical calculations, along with linear absorption data (when available)
provide the necessary parameters to evaluate truncated forms of the SOS expression. A host of chemical and geometric modifications will be considered in order to elucidate important structure/function relationships. Also, the SOS model will be tested in some cases when experimental measurements (via Kleinman-disallowed hyper-Rayleigh scattering) are available.

While a majority of this work focuses on multi-dimensional molecules, a small section deals with the question of optimizing the hyperpolarizability of a one-dimensional system. It is suggested that the recently-proposed idea of “modulated conjugation” as a means for improving intrinsic molecular hyperpolarizability is based on subtle misinterpretations of computational results. Even so, the concept of modulated conjugation may lead to improved hyperpolarizabilities and possible reasons are discussed.
Chapter 1: Introduction

1.1 Introduction to Nonlinear Optics

This thesis describes multi-dimensional organic molecules designed for second-order nonlinear optical (NLO) applications in chiral-axial media. Before describing the background and motivation of the chiral-axial project, a brief introduction to nonlinear optics is presented. For a more thorough introduction to the subject the texts by Boyd\textsuperscript{1} or by Butcher and Cotter\textsuperscript{2} are suggested.

When there is a (time dependent) electric field in matter, the field exerts a force on the charged particles proportional to the electric field strength. In dielectric media the polarization density, denoted $\vec{P}$, describes the average response (or displacement) of these particles to the external electric field. For oscillating electric fields in the UV/Vis region of the electromagnetic spectrum the polarization response is determined mainly by the electrons. Optical frequencies ($\sim 10^{15}$ Hz) are fast compared to “large scale” motions, such as molecular rotations and nuclear vibrations, which consequently cannot follow the quickly changing field. Therefore a large part of materials optics consists of determining the electronic structure and motion in a material. This thesis concentrates on electrons in delocalized $\pi$-orbitals of conjugated organic molecules, which is a significant fraction of the work in non-linear optics. This will be discussed in more detail later.

The typical Coulomb binding forces on electrons are many orders of magnitude stronger than the forces from noncoherent electromagnetic radiation sources, such as
sunlight. Therefore, the assumption that the polarization response is linearly proportional to the applied electric field is reasonable in many cases and amply describes the linear absorption and index of refraction of materials illuminated at low intensity. However, if the intensity of light is increased such that the electric fields are still small compared to the binding force on the electrons (to avoid ionization of the material), yet large enough to push the electrons out of the linear regime, it becomes necessary to go beyond the linear response approximation. This is analogous to stretching a spring past the region where “Hooke’s Law” is a good approximation. In general the polarization response is a (possibly) complicated function of the applied electric field, but in many cases it is useful to consider an expansion of the polarization density in powers of the local electric field:

\[
\vec{P}(t) = \vec{P}^{(0)}(t) + \vec{P}^{(1)}(t) + \vec{P}^{(2)}(t) + \cdots \vec{P}^{(n)}(t) \cdots
\]  

(1.1).

Here each successive order of the polarization is proportional to one more power of the electric field, starting with the zeroth order term, which is independent of the applied field. Determining the consequences of the higher order terms (\(\vec{P}^{(n)}(t), n > 1\)) is the field of nonlinear optics. This field was subject to intense scrutiny starting in the 1960’s, shortly after the development of the laser, which was able to produce coherent optical fields large enough to create deviations from linear response. Prior to the 1960’s only a few nonlinear phenomena were known because they were based on interaction of light with a DC (zero frequency) field, which could be made large more easily. Such DC fields can also result in larger effects as they can be applied for a long time, allowing slow, non-electronic relaxations in the medium to take place and result in relatively large optical changes. One example of such an effect is the linear electro-optic effect, whereby the index of refraction of a material is altered by an applied voltage. A light wave
traveling through such a medium can have its phase altered as a function of the applied voltage. But a vast majority of NLO effects, particularly those having to do with the mixing of several optical fields and which require at least one of the optical fields to be of very high intensity, were discovered using lasers.

A consequence of Maxwell’s equations in dielectric media is that a time varying polarization density will act as a source of radiation. If the polarization is linearly proportional to the electric field (the $\bar{P}^{(1)}(t)$ term of eq. (1.1)), the radiation from the material will be at the same frequency as the perturbing radiation. However, nonlinear polarization terms ($\bar{P}^{(n)}(t)$, $n > 1$) can generate new frequencies not present in the original field(s). These are generally referred to as frequency-mixing or parametric processes. The connection between the polarization response and resultant wave propagation in the medium is made via Maxwell’s wave equation:

$$\nabla \times \nabla \times \vec{E}(t) + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \vec{E}(t) = -\mu_0 \frac{\partial^2}{\partial t^2} \bar{P}(t)$$

(1.2).

The second time derivative of the polarization density acts as a source term for the wave equation. The solution for a linear polarization term leads to the determination of the familiar linear properties of single-photon absorption and index of refraction. Plugging in terms on the right hand side (rhs) of eq. (1.2) that are proportional to higher powers of the electric field results in a multitude of nonlinear effects. Higher-order solutions to the nonlinear wave equation are rather difficult to obtain, and generally built up iteratively using perturbation theory and solving eq. (1.2) for each field involved. Such coupled-wave solutions to eq. (1.2) for low-order polarization terms are discussed in many nonlinear optics texts. The main result is that the total field after interaction with the
nonlinear medium may contain frequencies that are sums or differences of various combinations of the input field frequencies. It is important to keep in mind that the nonlinear wave equation is the governing equation of the propagation of light through the macroscopic medium; and often times this equation adds multiple constraints to be considered beyond simply having a large local response of a given order. For instance, a large second-harmonic response can be generated in a small region of a material (based on the favorable electronic properties of the material for such a conversion process), and yet the second-harmonic wave may fail to grow and propagate through the material if there is (i) significant absorption of the first or second harmonic wave in the material, or if (ii) there is not some way for the second harmonic polarization generated by the fundamental beam and second-harmonic light to stay in phase while propagating (phase matching condition). These types of constraints are important but will not be the focus of this thesis. For now we will move on to discuss the susceptibility tensors that determine the local response to an optical field.

1.1.1 Definition of Optical Susceptibility Tensors

In optics it is convenient to consider the electric field as a superposition of monochromatic waves. This allows simple Fourier transformations from the time domain to the frequency domain. The wave equation (1.2) for the Fourier components simply becomes

\[ \vec{\nabla} \times \vec{\nabla} \times \vec{E}(\omega) + \frac{\omega^2}{c^2} \vec{E}(\omega) = -\mu_0 \omega^2 \vec{P}(\omega) \]  

(1.3),
and its solutions have the same consequences as described for eq. (1.2). In general, the

nth order polarization response is proportional to n electric fields, which are either
distinguishable or indistinguishable (degenerate). The first few orders of the polarization
density are commonly expressed in the frequency domain as

\[ P_i^{(1)}(\omega_\sigma) = \chi_\sigma^{(1)}(-\omega_\sigma; \omega_1) E_j(\omega_1) \]

\[ P_i^{(2)}(\omega_\sigma) = K(-\omega_\sigma; \omega_1, \omega_2) \chi_{ijk}^{(2)}(-\omega_\sigma; \omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2) \]  

\[ P_i^{(3)}(\omega_\sigma) = K(-\omega_\sigma; \omega_1, \omega_2, \omega_3) \chi_{ijkl}^{(3)}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) E_j(\omega_1) E_k(\omega_2) E_l(\omega_3) \]  

(1.4).

In these equations, the relation \( \omega_\sigma = \omega_1 + \omega_2 + \cdots + \omega_n \) holds, where \( \omega_1, \omega_2, \ldots, \omega_n \) are the
frequencies of the “input” fields, and \( \omega_\sigma \) is the “output” frequency. The \( n+1 \) rank tensors
\( \chi_{\sigma \ldots \ldots}^{(n)}(-\omega_\sigma; \omega_1, \omega_2, \ldots, \omega_n) \) describe the strength of the nth-order response to the applied
field(s), and are commonly called susceptibility tensors when expressed in the frequency
domain. In this work we are interested in the second-order, or quadratic susceptibility,
\( \chi_{ijk}^{(2)}(-\omega_\sigma; \omega_1, \omega_2) \), which is responsible for both second-harmonic generation
( \( \omega_1 = \omega_2 = \omega \) and \( \omega_\sigma = 2\omega \) ) and the linear electro-optic effect
( \( \omega_1 = 0, \omega_2 = \omega, \) and \( \omega_\sigma = \omega \) ). The factors \( K \) in (1.4) are included to account for
differing cases where the input fields are either distinguishable or degenerate, and are
defined by

\[ K(-\omega_\sigma, \omega_1, \omega_2, \ldots, \omega_n) = 2^{l+n-m} p \]  

(1.5),

where \( p \) is the number of distinct permutations of \( \omega_1, \omega_2, \ldots, \omega_n \), \( n \) is the order of the
nonlinearity, \( m \) is the number of frequencies \( \omega_1, \omega_2, \ldots, \omega_n \) that are zero, and \( l = 0 \) if \( \omega_\sigma = 0 \)
and $l = 1$ otherwise. For example, second-harmonic generation, characterized by
\[
\chi^{(2)}_{ijk}(-2\omega; \omega, \omega), \text{ gives } K(-2\omega, \omega, \omega) = 2^{i+m-n} p = 2^{1+0-2} \times 1 = \frac{1}{2} .
\]
The mixing of a D.C. field with an optical field (the linear electro-optic effect) gives
\[
K(-\omega, 0, \omega) = 2^{i+m-n} p = 2^{1+1-2} \times 2 = 2 .
\]
Using this K-factor prevents discontinuities in the susceptibilities as the frequency arguments approach zero or become degenerate.

### 1.1.1.1 Permutations and Kleinman Symmetry

Some general remarks can be made concerning the optical susceptibility tensors. First, susceptibility tensors of every order strictly obey intrinsic permutation symmetry, based on time-invariance and causality.\(^2\) This means that the $n!$ possible simultaneous permutations of the $n$ pairs $(j, \omega_j), (k, \omega_k), (l, \omega_l), \ldots$ leave the tensor
\[
\chi_{ijk\ldots}^{(n)}(-\omega_\sigma; \omega_1, \omega_2, \ldots \omega_n)
\]
invariant. For instance, interchanging the pairs $(j, \omega_j)$ and $(k, \omega_k)$ gives
\[
\chi_{ijk\ldots}^{(2)}(-\omega_\sigma; \omega_1, \omega_2) = \chi_{ikj\ldots}^{(2)}(-\omega_\sigma; \omega_2, \omega_1).
\]
If the input fields are identical (as in second-harmonic generation), this symmetry reduces the number of unique tensor elements from 27 to 18 for the third-rank tensor. Note that the first pair of indices and frequencies, $(i, \omega_i)$, are not included in the statement of intrinsic permutation symmetry.

Inclusion of the first pair is known as full permutation symmetry and this is only a valid approximation in regions of low optical loss. In many cases in the literature a further symmetry, known as Kleinman symmetry,\(^3\) is assumed to hold. This conjecture states that the susceptibility tensors are invariant under full permutation of their spatial indices, without the need to also permute their frequency arguments. Kleinman symmetry is only strictly valid when the NLO response is considered at zero frequency; but it is also
commonly assumed for “low” frequencies well removed from any strong material resonances. Many times this assumption leads to only small errors, especially when dealing with quasi-one dimensional molecules, which obey Kleinman symmetry simply because each index can, in effect, take only one value; however, when the frequencies are not all small in comparison to material resonances, the assumption of Kleinman symmetry does not generally hold, and it is a main focus of this thesis to discuss materials with susceptibilities that strongly violate Kleinman symmetry.

1.1.1.2 Spatial Symmetry

Aside from intrinsic permutation symmetry, susceptibility tensors also strictly obey Neumann’s principle, which states that any physical property must be consistent with point-symmetry operations of the medium. Such spatial symmetry requirements can be helpful in reducing the number of tensor components needed to fully describe the system. The most common result of Neumann’s principle is that any even order susceptibility can only be non-zero in a medium that is non-centrosymmetric (i.e. a medium that is not symmetric under \( \vec{x} \rightarrow -\vec{x} \)). Thus certain crystal or molecular symmetries can immediately be discarded as incompatible with non-zero \( \chi^{(2)}_{ijk} \). The requirement of non-centrosymmetry is a necessary but not sufficient condition for a large second-order response. Of the 32 point groups, 11 are centrosymmetric and will not allow quadratic NLO processes. Within the remaining 21 non-centrosymmetric point groups, further symmetry operations can be used to deduce more restrictions on the terms of \( \chi^{(2)}_{ijk} \). For simple symmetries and low-order susceptibilities, the restrictions can often be determined by direct inspection, but for higher-order susceptibilities this becomes less practical and
requires more sophisticated group theoretic formalisms. Symmetry tables for the second and third order susceptibilities can be found in both Boyd\(^1\) and Butcher and Cotter\(^2\) and will not be reproduced here. However, a simple example will be given. Consider the point group \(C_{2v}\), which is the symmetry of many of the \(\Lambda\)-shaped molecules in this thesis. There are four symmetry operations in this group (see fig 1.1): \(E = \) identity; \(C_2 = \) a two-fold rotation; and \(\sigma_1, \sigma_2 = \) single reflections through planes each containing the \(C_2\) axis and that are perpendicular to each other).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1.1}
\caption{The symmetry operations of the \(C_{2v}\) group are depicted on a \(\Lambda\)-shaped object. The coordinate system shown will be adopted throughout this thesis.}
\end{figure}

Applying these operations to the coordinate system in fig. 1.1 gives the transformations
By Neumann’s principle, applying any of these operations to \( \chi^{(2)}_{ijk} \) will not change its value. By simple geometry it can be seen that under the \( C_2 \) operation
\[
\chi^{(2)}_{xyy} \rightarrow -\chi^{(2)}_{xyy}, \; \chi^{(2)}_{xxy} \rightarrow -\chi^{(2)}_{xxy}, \; \chi^{(2)}_{yyx} \rightarrow -\chi^{(2)}_{yyx}, \; \chi^{(2)}_{yyz} \rightarrow -\chi^{(2)}_{yyz}, \; \text{etc.}
\]
Establishing this pattern and using Neumann’s principle, it is clear that all tensor components that have an odd number of \( x \)'s and \( y \)'s combined must be zero. Applying the reflections \( \sigma_1, \sigma_2 \) eliminates components of the form \( \chi^{(2)}_{xyz} \rightarrow -\chi^{(2)}_{xyz}, \; \chi^{(2)}_{xyz} \rightarrow -\chi^{(2)}_{xyz}, \) that is, all terms with subscripts \( (xyz) \) and its permutations must be zero. Therefore, the only nonzero tensors that satisfy Neumann’s principle are the ones with subscripts \((zzz), (zxx), (zyy)\), and their permutations, which is a total of 7 components. This number is further reduced to 5 components for second harmonic generation due to the interchangeability of the last two indices as a result of intrinsic permutation symmetry and degeneracy of the input fields.

### 1.1.2 Microscopic and Macroscopic susceptibilities

In the field of organic nonlinear optics it is common to consider materials design from both the macroscopic and molecular perspectives.\(^9,15,16\) Condensed phases of organic molecules are held together by relatively weak van der Waals forces such that interactions between molecules are usually much weaker than intra-molecular forces. Therefore the oriented molecular gas approximation is used as a way to design organic
materials from molecular building blocks. Within this approximation the molecules in condensed phases do not strongly interact, and the macroscopic response is a superposition of the individual molecular responses. At the microscopic level quantum chemistry can be enlisted to approximately determine the individual molecular NLO responses (see section 1.3). The formulas defining the molecular susceptibilities are the same as eq. (1.4), but usually given different notation:

\[ p^{(1)}_i(\omega_\sigma) = \alpha_{ij}(-\omega_\sigma;\omega_i)E_j(\omega_i) \]

\[ p^{(2)}_i(\omega_\sigma) = K(-\omega_\sigma;\omega_1,\omega_2)\beta_{ijk}(-\omega_\sigma;\omega_i,\omega_2)E_j(\omega_i)E_k(\omega_2) \] \hspace{1cm} (1.7)

\[ p^{(3)}_i(\omega_\sigma) = K(-\omega_\sigma;\omega_1,\omega_2,\omega_3)\gamma_{ijkl}(-\omega_\sigma;\omega_i,\omega_2,\omega_3)E_j(\omega_i)E_k(\omega_2)E_l(\omega_3) \]

The \( K \) factors have been included in this definition for consistency with eq. (1.4), but various ways of defining the molecular (and macroscopic) susceptibility tensors exist, and in practice it is important to state explicitly the formulas used to compute the susceptibilities so that comparisons can be made from group to group. Often the \( K \) factor is absorbed into the susceptibility tensors and factors of 2 or \( \frac{1}{2} \) must be accounted for when making comparisons at second-order. The tensor \( \beta_{ijk}(-\omega_\sigma;\omega_i,\omega_2) \) is termed the molecular hyperpolarizability and is the main focus of this thesis.

Assuming an oriented gas model allows the macroscopic second-order response to be approximated using

\[ \chi^{(2)}_{ijk} \propto N \left\langle \beta_{ijk} \right\rangle = N \left\langle R_{ij}R_{jk}R_{kk} \right\rangle \beta_{ijk} \] \hspace{1cm} (1.8),

where \( N \) is the molecular number density, \( \mathbf{R} \) is the transformation matrix between the molecular and macroscopic frames of reference, and the bracket denotes an orientational average of the molecules. Capital and lowercase subscripts are used to differentiate
between the molecular and macroscopic coordinates, respectively. The constant of proportionality in eq. (1.8) must take into account local field factors. The permutation and spatial symmetry properties/requirements for the macroscopic and molecular tensors are the same, and therefore the model in eq. (1.8) adds some finer detail to the definition of the macroscopic response in this context. More specifically, it says that a non-zero macroscopic response requires non-centrosymmetric molecules to be organized in a non-centrosymmetric bulk alignment pattern. Maximization of the macroscopic response requires further constraints on the molecular hyperpolarizabilities and their possible alignments, which will be discussed in section 1.2.

1.1.3 Quantum Description of Molecular Hyperpolarizability

The benefit of separating a material into microscopic and macroscopic descriptions is that the quantum chemical calculations of susceptibilities are more tractable for a small isolated molecule. We denote the set of wavefunctions of an isolated molecule (subject only to internal Coulomb interactions) by \( \Psi_n(\bar{x}) \). These wavefunctions (indexed by \( n \)) are solutions to the Schrodinger equation \( H\Psi_n = E_n\Psi_n \), and they describe the probability distributions of where each particle in the molecule is most likely to be if the molecule has energy \( E_n \). These many-body unperturbed wavefunctions can be approximately calculated using quantum chemical methods which will be discussed briefly in section 1.3; for now we assume that the unperturbed wavefunctions are “known”. Then nonlinear optical susceptibilities can be derived in terms of these known wavefunctions using standard time-dependent perturbation theory. Under the electric dipole approximation, the optical perturbation is \( H'(t) = e\bar{x} \cdot \vec{E}(t) \), where \( \vec{E}(t) \) is the local
electric (optical) field and $\vec{e}\vec{\chi}$ is the dipole operator. Corrections to this approximation involve either the magnetic field or gradients of the electric field and so are small provided the molecules are small compared to the wavelength of light and velocities are small compared to the speed of light. A derivation of the second-order susceptibility appears in Boyd. However, the expression diverges when one of the input frequencies goes to zero, and is thus unsuitable to describe the electro-optic effect. The original derivation by Orr and Ward does not have this deficiency. They expressed the hyperpolarizability as a sum over the molecular quantum states (SOS) as

$$\beta_{ge}(-\omega_1, \omega_2, \omega_3) = \frac{1}{\hbar^2} I_{1,2} \times \sum_{m \neq g \neq n} \left\{ \frac{\mu^j_{gm} \Delta \mu_{mn}^k \mu^l_{ng}}{(\omega_{mg} - \omega_3)(\omega_{ng} - \omega_1)} + \frac{\mu^j_{gm} \Delta \mu_{mn}^k \mu^l_{ng}}{(\omega_{mg} + \omega_2)(\omega_{ng} + \omega_2)} + \frac{\mu^k_{gm} \Delta \mu_{mn}^j \mu^l_{ng}}{(\omega_{mg} + \omega_2)(\omega_{ng} - \omega_1)} \right\}$$ (1.9),

where $g$ stands for the ground state, $m$ and $n$ label arbitrary excited states,

$$\omega_{ng} = (E_n - E_g)/\hbar, \ \ \mu^j_{ng} = e \langle \Psi^*_n | x_i | \Psi^*_g \rangle = e \int d\vec{x} \ \Psi^*_n(\vec{x}) x_i \ \Psi^*_g(\vec{x}) , \ \Delta \mu_{mn}^j = \mu^j_{mn} - \mu^j_{gg} \delta_{nn},$$

and $I_{1,2}$ is an intrinsic permutation operator that averages the expression over the two permutations of ($\omega_1$, $k$), and ($\omega_2$, $j$), and $\omega_3 = \omega_1 + \omega_2$ holds. The molecular resonance frequencies ($\omega_{ng}$) are treated as complex quantities to keep the hyperpolarizability finite at the resonances. This sum-over-states (SOS) expression is exact if all of the terms in the sum are included, and if all of the molecular parameters can be determined exactly. Neither of these conditions is met in practice, but in many cases a small number of approximately calculated states will give reasonable estimates for the hyperpolarizability tensor components. The quantum parameters in eq. (1.9) indicate the requirements for large hyperpolarizabilities, and their calculation will be discussed in section 1.3.

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1.2 Overview of Chiral-Axial Project

Since the relationship between the molecular hyperpolarizability and macroscopic susceptibility in eq. (1.8) involves a rotational average, it is convenient to consider the decomposition of the hyperpolarizability tensor into rotationally invariant terms. A third-rank tensor transforms as the direct product of three vectors:

\[
\beta_{ijk} \sim 1 \otimes 1 \otimes 1 = 1 \otimes (0 \otimes 1 \oplus 2) = 0 \oplus (1 \otimes 1 \oplus 1) \oplus (2 \otimes 2) \oplus 3
\]

Thus, the decomposition of the hyperpolarizability into rotationally invariant components has the form

\[
\beta_{ijk} = \sum_{L, \sigma} \beta^{(L, \sigma)}_{ijk} = \beta^{(0)}_{ijk} + \beta^{(1,1)}_{ijk} + \beta^{(1,2)}_{ijk} + \beta^{(1,3)}_{ijk} + \beta^{(2,1)}_{ijk} + \beta^{(2,2)}_{ijk} + \beta^{(2,3)}_{ijk}
\]

where the \( L \)-value denotes the irreducible representation of the rotation group. Thus, there is one \( L=0 \) term, three \( L=1 \) terms, two \( L=2 \) terms, and one \( L=3 \) term. The explicit forms of these embedded tensors (as various sums of \( \beta_{ijk} \) contracted with Kronecker delta or Levi-Civita tensors) can be found in Mao’s thesis (ref 14, pp. 46-48). For second-harmonic generation only four terms are non-zero:

\[
\beta^{(SHG)}_{ijk} = \beta^{1s}_{ijk} + \beta^{1m}_{ijk} + \beta^{2m}_{ijk} + \beta^{3s}_{ijk}
\]

The introduction of the “s” or “m” in the superscript is to denote whether the tensors are “symmetric” or of “mixed” symmetry with respect to permutation of indices. The mixed permutation terms (1m and 2m) in eq. (1.12) are Kleinman-disallowed; that is, they are only non-zero when Kleinman symmetry is broken.

Many of the organic molecules that have large hyperpolarizabilities are linear \( \pi \)-electron conjugated systems substituted with electron donors and acceptors at opposite ends. In this case Kleinman symmetry approximately holds (i.e. \( \beta^{1m} = \beta^{2m} \sim 0 \) ) and the
hyperpolarizability tensor has a single dominant diagonal component $\beta_{zzz}$ which is proportional to both the vector ($\beta^{1s}$) and octupolar ($\beta^{3s}$) response. Bulk alignment of the vector ($\beta^{1s}$) response according to eq. (1.8) is straightforward:

$$\chi^{(2)}_{zzz} \sim \left\langle \beta^{1s} \right\rangle \sim \beta_{zzz} \left\langle \hat{z} \cdot \hat{Z} \right\rangle^3.$$  The dipoles must collectively be aligned parallel to each other for maximum response, and most practical NLO devices use this polar alignment (fig. 1.2). However, electrostatic dipole forces favor anti-parallel alignment of dipolar rods, which is centrosymmetric and cancels the vector response in pairs. Parallel alignment must be forced on a system of dipoles by using a strong poling field and “freezing in” rather small (10%) polar alignment in a stabilizing polymer matrix, for instance. The anti-aligning dipole forces increase as chromophore density increases, which puts a limit on the maximum attainable density.\textsuperscript{18} Furthermore, heating of these materials may encourage relaxation to a more stable anti-parallel alignment.

These challenges for engineering dipolar-aligned materials which utilize the $\beta^{1s}$ component of the hyperpolarizability led to the theoretical consideration of nonpolar, chiral-uniaxial materials that instead utilize $\beta^{2m}$.\textsuperscript{9} Nonpolar structures by definition do

\textbf{Figure 1.2} A typical linear “push-pull” organic molecule is shown, which displays a conjugated bridge with a donor (-NH$_2$) and acceptor (-NO$_2$) group at opposite ends: (a) parallel alignment; (b) anti-parallel alignment.
not have a bulk dipole moment, and may therefore have higher intrinsic stability. A chiral-uniaxial material has $D_\infty$ bulk symmetry. The molecular subunits in these materials do not need to be chiral, but they must be aligned along the single bulk symmetry axis in a nonpolar chiral pattern. For SHG there is one unique component of the bulk second-order susceptibility in $D_\infty$ symmetry: $\chi^{(2)}_{xyz} = \chi^{(2)}_{xzy} = -\chi^{(2)}_{yzx} = -\chi^{(2)}_{yxz} \neq 0$, where $z$ is the symmetry axis. This bulk component is only nonzero if Kleinman symmetry is broken. Kleinman symmetry breaking must occur at the molecular level as well. In particular, the component of the hyperpolarizability tensor that transforms as a second-rank pseudo tensor $(\beta^{2m})$ must be nonzero in order to contribute to the bulk susceptibility in $D_\infty$ systems, since $\chi^{(2)}(D_\infty) \sim \{\beta^{2m}\}$.\(^{9,10}\)

The molecular requirements for large $\beta^{2m}$ are most naturally satisfied in propeller-shaped ($D_3$ or $C_3$ symmetry) or $\Lambda$-shaped ($C_{2v}$) molecules.\(^7\) In these cases the respective expressions for $\beta^{2m}$ in terms of the Cartesian components are\(^6\)

$$\beta^{2m}(C_{2v}) \sim (\beta_{zxx} - \beta_{zzz})$$

and

$$\beta^{2m}(D_3, C_3) \sim \beta_{yzy}$$

(1.13),

where $z$ is the two-fold symmetry axis in $C_{2v}$ and the three-fold axis in $D_3$ and $C_3$. The maximized alignment schemes have been worked out previously for these molecular symmetries in $D_\infty$ bulk media.\(^9,10\) For propeller-shaped molecules the maximal alignment requires the molecules to stack with their three-fold rotation axis along the symmetry axis of the $D_\infty$ bulk. Such alignment could be achieved in discotic liquid crystals, for
example. In addition, the chirality requirement means that the propellers must be (at least partially) resolved. The maximal alignment scheme of Λ-shaped molecules requires that their two-fold rotation axis be perpendicular to the bulk-symmetry axis, and the plane of

Figure 1.3 Maximized alignment schemes in $D_\infty$ media; (a) for $C_{2v}$ molecules the $C_2$ axis is perpendicular to the bulk symmetry axis. The maximized rotational angle (about the $C_2$ axis) is $\psi_{\text{max}} = 45^\circ$; (b) for $D_3$ molecules the $C_3$ axis is aligned with the bulk symmetry axis. These figures have been reproduced from ref. 6 with permission.

the molecule should be rotated 45 degrees about the two-fold molecular axis. Since the alignment must be chiral, the molecules must rotate preferentially in one direction. This alignment is not trivial, but could be achieved in helical polymers, or possibly through use of a chiral macromolecular scaffold. Recent results show that an SHG signal was obtained from a chiral-axial system composed of a retinal chromophore covalently bound to a helical bacteriorhodopsin protein which was axially ordered in a lipid bi-layer. The retinal chromophore in that system is not optimized – it has only very approximate $C_{2v}$
symmetry. The authors argue strongly that the NLO response is due primarily to orientation effects – that is, the NLO response results from chiral orientation of the achiral retinal chromophore, as opposed to an intrinsic chiral response from retinal. An apparently more optimized chromophore/macromolecule system can be found in the DNA/cyanine complexes studied by the Armitage group.\textsuperscript{20,21} The $C_{2v}$ symmetric cyanine dye is postulated to bind as dimers to the minor groove of B-form DNA with its $C_2$ symmetry axis perpendicular to the helical axis of the DNA, and twisted roughly 30 degrees about the $C_2$ axis to conform with the minor groove helical pitch. However, Kleinman-Disallowed Hyper Rayleigh Scattering measurements on the DNA/cyanine complex did not show an expected increase in the Kleinman-disallowed SHG signal.\textsuperscript{14} The SHG signal of the complexed system was actually smaller than the pure cyanine signal, suggesting that the cyanine dye does not associate with the DNA minor groove according to the proposed model,\textsuperscript{21} or else the dye becomes disordered due to the high laser power. More work is needed to understand the cause of these results. In any event, more rigid covalent binding between dyes and macromolecules would be preferred.

The development of chiral, conformationally stable, helical foldamers and/or polymers may provide a fully synthetic route to interesting chiral-axial NLO materials. A helical oligomeric foldamer consisting of aromatic $C_{2v}$ naphthalene moieties linked via an iminodicarbonyl spacer has been synthesized.\textsuperscript{22} Chiral side-chains were able to induce circular dichroism in the absorption spectrum of the naphthalene chromophore. X-ray crystallography suggests that the naphthalene units have their $C_2$ axis roughly perpendicular to the helix axis, and they are twisted approximately 20-30 degrees about their $C_2$ axis. Other helical foldamers containing small aromatic $C_{2v}$ substituents have
been reported, but in most cases (including the naphthalene mentioned above) these substituents are not optimized NLO-phores, and the helical pitch of many foldamers is far removed from the ideal 45 degree angle for Kleinman-disallowed response.\textsuperscript{23,24,25}

The development of optimized chiral-axial materials must therefore proceed at both the macroscopic and microscopic levels. The macroscopic level will most likely require advances in synthetic chemistry that must be developed in the laboratory. Optimization of the Kleinman-disallowed molecular response has been an active area of experimental and theoretical research by the Petschek and Singer groups at Case Western Reserve University, and also by the Twieg group at Kent State University. This thesis seeks to add to the theoretical research and design of optimized chromophores for $L=2$ Kleinman-disallowed hyperpolarizability through symmetry analysis and quantum chemical computations. The goal of this effort involves rationalization of previous experimental results, as well as proposing more molecules for investigation.

1.3 Molecular Design Strategies and Calculation of Hyperpolarizabilities

The sum-over-states (SOS) equation (1.9) gives an exact expression for all off the Cartesian components of the $\beta_{ijk}$ tensor for all possible input and output frequencies. All of the parameters can in principle be determined computationally. In addition, it is a simple matter to obtain values for some of the transition energies and ground to excited state transition moments from a linear absorption spectrum. The experimentally
determined molar absorption coefficient ($\varepsilon$, in $M^{-1}cm^{-1}$) can be related to the transition moments ($\mu_{0n}$) according to

$$|\mu_{0n}|^2 = 0.009\lambda_{0n} \int \varepsilon_{0n}(\lambda) \lambda^{-2} d\lambda$$

(1.15),

where $\varepsilon_{0n}(\lambda)$ is the molar absorption coefficient of the $n$th excited state, $\lambda_{0n}$ is the peak wavelength, all wavelengths are in $10^{-9}$ m, and the transition moment is in Debye. A gross estimate of this integral for $\Delta\lambda_{0n}/\lambda_{0n} \sim 10\%$ is $|\mu_{0n}|^2 \approx 10^{-3} \varepsilon(\lambda_{0n})$. Therefore, a maximum molar absorption coefficient of 100,000 (typical of strongly absorbing dyes) yields a transition moment of about 10 Debye (see fig. 1.4).

**Figure 1.4** Sample molar absorption curve. Two clear peaks can be seen which result from two separate quantum transitions. By integrating to find the area under each peak the magnitude of the molecular transition moments $|\mu_{01}|$ and $|\mu_{02}|$ can be determined. This spectrum was recorded by Guilin Mao. The molecule is malachite green.

As in most perturbation calculations, a truncated form of eq. (1.9) must be used in practice. The number of states in the sum needed to represent the hyperpolarizability sufficiently well is highly dependent on the molecule under study. The convergence of
the sum-over-states is expected to be more rapid as the oscillator strength (linear absorption) of the first (lowest-energy) excited state increases relative to the rest of the excited states, and as the separation in energy between the first excited state and the second excited state increases. The oscillator strength sum rule can be an indicator of the size of the lowest-energy oscillator strength compared to the rest of the excited states:

$$\frac{2m}{e^2 \hbar} \sum_{n=1}^{\infty} E_n(\mu_{n0})^2 = \sum_{n=0}^{\infty} f_{n0} = N$$  \hspace{1cm} (1.16)$$

Here \( m \) is the electron mass, \( e \) the charge, and \( N \) is a measure of the number of valence electrons in the molecule, usually defined as twice the number of double or triple bonds. However, experience shows that a single low-lying excited state will rarely come close to saturating this sum rule. For most molecules of interest, \( N \approx 15-30 \), while a single (large) oscillator strength rarely exceeds \( f_{n0} \approx 2 – 3 \). Therefore, a low-lying state with large oscillator strength hardly guarantees that there will not be other states nearby with similarly large (or larger) oscillator strengths which may strongly affect the hyperpolarizability. It is therefore much safer to rely on convergence of the truncated SOS due to the increasing energy denominators. Even with these uncertainties, considering only the ground and first excited state (the two-level model\(^{27}\)) has been a common and often successful practice in the literature, especially when quasi one-dimensional molecules are being examined far from resonance. The two-level model for a one-dimensional molecule off-resonance (i.e. all input and output frequencies = 0) reduces to

$$\beta_s^{(2\text{level})} = 3(\mu_{01})^2 \Delta \mu_{01} / E_{01}^2$$  \hspace{1cm} (1.17)$$
This approximation has been the impetus behind most design strategies for molecules to be incorporated into poled materials, which utilize the symmetric $L=1$ vector component of the hyperpolarizability ($\beta^{01}$). A large $\beta_0^{(2\text{level})}$ is obtained in molecules with strong linear absorption, which is proportional to $(\mu_0)^2$, and large charge transfer between the ground and first excited state. Therefore, one-dimensional charge transfer molecules are constructed by placing electron donating and electron withdrawing groups at opposite ends of the molecule to reinforce each other and create a large net movement of charge ($\Delta\mu_{01}$) between the ground and first excited state.

For $L=2$ Kleinman-disallowed hyperpolarizabilities it is necessary to have large off-diagonal tensor components (for examples see eqs. (1.13) and (1.14)). For $\Lambda$-shaped molecules an analogue of eq. (1.17) can be obtained by substituting eq. (1.9) into eq. (1.13), yielding

$$\beta_2^{(2\text{level})} \sim (\mu_{01}^2) \Delta \mu_0^2 \mathcal{F}$$

(1.18),

where $\mathcal{F}$ is a dispersion term that depends on the type of process (i.e. SHG, EO, etc.) and has the property $\mathcal{F} \rightarrow 0$ as the input frequencies $\omega_1, \omega_2 \rightarrow 0$. Therefore there is no strictly off-resonant expression for this Kleinman-disallowed component as was the case in eq. (1.17). Furthermore, we note in this case that the transition moment must be perpendicular to the charge-transfer symmetry axis (i.e. a “B-type” excited state); if the transition moment is parallel to the charge-transfer axis (A-type state) the two-level term vanishes. This provides the most basic design strategy for Kleinman-disallowed hyperpolarizabilities in $\Lambda$-shaped molecules; low-lying B-type states with strong absorption strength and large charge transfer are expected to make important
contributions. No dipolar two-level term exists for propeller-shaped molecules; instead the simplest term in the SOS requires three levels. However, it is possible to consider $D_3$ molecules as “supra-molecules” composed of three $\Lambda$-shaped propellers joined at their apices, which allows us to write a microscopic to “macroscopic” relation as

$$\chi_{\text{SOS}}^{(2)} \sim \beta^{2m}(D_3) \sim \langle \beta^{2m}(C_{2v}) \rangle.$$ Then the design strategy for $D_3$ molecules simply becomes optimization of the $\Lambda$-shaped propellers (according to eq. (1.18)) along with the requirement that the propellers are joined at their apices in such a way that the twist angle is close to the optimum of 45 degrees. This is of course a bad approximation for highly coupled propellers, in which case the twist angle will most likely be small (less than 30 degrees); but even in this case, the suggestion that the individual propellers should have strongly absorbing B-type states with large charge transfer is reasonable, and commonly results in states appropriate to the more complicated sum in $D_3$.

In this thesis eq. (1.18) will be used as a foundational design strategy; however, multi-level calculations using the SOS will also be considered as well. A plethora of quantum chemical codes are available for computing the ground and excited state parameters of interest. The basis of many such calculations (and all calculations in this thesis) is the Hartree-Fock Roothaan set of equations.

### 1.3.1 Hartree-Fock Roothaan Equations

The author has found the work on electric structure calculations by Springborg$^{28}$ to be a very good resource, and many of the following arguments are adapted from this text. Let

$$\Psi \equiv \Psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_n, \vec{X}_1, \vec{X}_2, \ldots, \vec{X}_m)$$

define the many-body wavefunction of an isolated
molecule, where \( n \) is the number of electrons and \( m \) the number of nuclei. The time-independent, spin-independent, non-relativistic Schrödinger equation for a molecular system is given by

\[
(T_e + T_N + V_{e-e} + V_{N-N} + V_{e-N})\Psi = E\Psi
\]  

(1.19)

where \( T_e = -\sum_{i=1}^{n} \frac{1}{2} \nabla_i^2 \) and \( T_N = -\sum_{i=1}^{m} \frac{1}{2} \nabla_i^2 \) are respectively the electron and nuclei kinetic energy operators, and the Coulomb interactions for electron-electron, nuclei-nuclei, and electron-nuclei pairs are respectively

\[
V_{e-e} = \sum_{i \neq j=1}^{n} |\mathbf{x}_i - \mathbf{x}_j|^{-1}, \quad V_{N-N} = \sum_{i \neq j=1}^{m} Z_i Z_j |\mathbf{X}_i - \mathbf{X}_j|^{-1}
\]

and

\[
V_{e-N} = -\sum_{i=1}^{m} \sum_{j=1}^{n} Z_i |\mathbf{X}_i - \mathbf{x}_j|^{-1}, \quad \text{where } Z \text{ is the atomic number, and atomic units are employed. Since nuclei are much heavier than electrons it is common to assume that their motions are decoupled (the Born-Oppenheimer approximation) and use the following product wavefunction:}
\]

\[
\Psi(\mathbf{x}, \mathbf{X}) = \Psi_e(\mathbf{x}; \mathbf{X}) \times \Psi_N(\mathbf{X})
\]

(1.20).

The argument for the electronic wavefunction is meant to indicate an explicit dependence on the electronic coordinates, while the nuclear coordinates are treated as an adjustable “parameter”. Substituting eq. (1.20) into eq. (1.19) gives

\[
E\Psi_e\Psi_N = H\Psi_e\Psi_N = \Psi_N(T_e + V_{e-e} + V_{e-N})\Psi_e + V_{N-N}\Psi_e\Psi_N
\]

(1.21)

where we have assumed \( T_N \Psi_N(\mathbf{x}; X) \Psi_N(\mathbf{X}) = \Psi_e(\mathbf{x}; \mathbf{X}) T_N \Psi_N(\mathbf{X}) = 0 \) since the kinetic energy of the “fixed” nuclei should be small compared to the rest of the terms. The form of eq. (1.21) allows us to define the electronic Schrödinger equation as

\[
(T_e + V_{e-e} + V_{e-N})\Psi_e = E_e(\mathbf{X}) \Psi_e(\mathbf{x}; \mathbf{X})
\]

(1.22).
The electronic energy is

\[ E_e = \int d\vec{x}_1 d\vec{x}_2 \cdots d\vec{x}_n \Psi_e \left( -\sum_{i=1}^{n} \frac{1}{2} \nabla_{\vec{x}_i}^2 + \sum_{i=1}^{n} \sum_{j=1}^{m} \frac{Z_j}{|\vec{X}_j - \vec{x}_i|} + \sum_{i>j=1}^{n} \frac{1}{|\vec{x}_i - \vec{x}_j|} \right) \Psi_e \]  

(1.23),

and the total energy is

\[ E = V_{N-N}(\vec{X}) + E_e(\vec{X}) \]  

(1.24).

Under these approximations the iterative procedure is straightforward: (1) Pick a set of nuclear coordinates, \( \vec{X} \); (2) Solve eqs. (1.22)-(1.23) for the electronic wavefunction and total electronic energy; (3) Calculate the total energy using eq. (1.24); (4) Calculate the energy gradient with respect to the nuclear coordinates and make appropriate changes to the nuclear coordinates (and repeat (1)-(3)) until the energy is minimized. However, solving (1.22) is not trivial. To make progress the independent electron approximation is employed, so that the multi-electron wavefunction is expressed as

\[ \Psi_{HF} = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(\vec{x}_1) & \psi_1(\vec{x}_2) & \cdots & \psi_1(\vec{x}_n) \\ \psi_2(\vec{x}_1) & \psi_2(\vec{x}_2) & \cdots & \psi_2(\vec{x}_n) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_n(\vec{x}_1) & \psi_n(\vec{x}_2) & \cdots & \psi_n(\vec{x}_n) \end{vmatrix} \]  

(1.25)

The functions \( \psi_1(\vec{x}_1), \psi_2(\vec{x}_2), \ldots \psi_n(\vec{x}_n) \) are called molecular orbitals, and the determinant form (called a Slater determinant) guarantees that the many-electronic wavefunction will be anti-symmetric with respect to interchange of any two electrons. Each of the molecular orbitals describes the probability distribution of a single independent electron in the molecule. Substituting eq. (1.25) into eq. (1.23) leads to the Hartree-Fock energy:

\[ E_{HF} = \sum_{i=1}^{n} \int d\vec{x}_i \psi_i^*(\vec{x}_i) h(\vec{x}_i) \psi_i(\vec{x}_i) + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} \left\{ \int d\vec{x}_1 d\vec{x}_2 |\psi_i(\vec{x}_1)|^2 r_{12}^{-1} |\psi_j(\vec{x}_2)|^2 - \int d\vec{x}_1 d\vec{x}_2 \psi_i^*(\vec{x}_1) \psi_j(\vec{x}_2) r_{12}^{-1} \psi_j^*(\vec{x}_2) \psi_i(\vec{x}_2) \right\} \]  

(1.26),
where \( h(\vec{x}_i) = -\frac{1}{2} \nabla^2 \psi_i - \sum_{k=1}^{m} Z_k |\vec{x}_i - \vec{X}_k|^{-1} \) and \( r_{ij}^{-1} = |\vec{x}_i - \vec{x}_j|^{-1} \). Functional minimization of this Hartree-Fock energy with respect to the molecular orbitals (enforcing the orthonormal constraint \( \int d\vec{x} \psi_i^* \psi_j = \delta_{ij} \)) leads to the Hartree-Fock equations for the molecular orbitals:

\[
\begin{align*}
 h(\vec{x}_i)\psi_i(\vec{x}_i) & + \sum_{j \neq i} \left[ \int d\vec{x}_2 |\psi_j(\vec{x}_2)|^2 r_{ij}^{-1} \right] \psi_j(\vec{x}_i) \\
 & - \sum_{j \neq i} \left[ \int d\vec{x}_2 \psi_j^*(\vec{x}_2) \psi_i(\vec{x}_2) r_{ij}^{-1} \right] \psi_j(\vec{x}_i) = \varepsilon_i \psi_i(\vec{x}_i)
\end{align*}
\] (1.27).

This equation must be solved iteratively by substituting an initial set of orbitals into the left hand side (lhs) and generating new orbitals until self-consistency is reached. The second term on the lhs of eq. (1.27) is called the Coulomb term, as it describes the effect on \( \psi_i \) of the average potential created by the rest of the electrons. This mean-field term does not fully account for the electron-electron interactions, and is the main “error” in the Hartree-Fock method. Various post Hartree-Fock schemes exist for trying to recover this lost electron correlation energy. The third term results from the anti-symmetric form of the Slater determinant and is called the exchange term. It accounts for the fact that electrons with the same spin avoid each other (thus lowering their Coulomb repulsion) consistent with Pauli’s exclusion principle.

It is notationally convenient to define \( J_j(\vec{x}_i) = \left[ \int d\vec{x}_2 |\psi_j(\vec{x}_2)|^2 r_{ij}^{-1} \right] \) and \( K_j(\vec{x}_i)\psi_i(\vec{x}_i) = \left[ \psi_j^*(\vec{x}_2) \psi_i(\vec{x}_2) r_{ij}^{-1} \right] \psi_j(\vec{x}_i) \) so that eq. (1.27) can be written in the condensed eigenvalue form

\[
F(\vec{x}_i)\psi_i(\vec{x}_i) = \varepsilon_i \psi_i(\vec{x}_i)
\] (1.28).
where
\[
F(\vec{x}_j) = h(\vec{x}_j) + \sum_j (J_j(\vec{x}_j) - K_j(\vec{x}_j))
\] (1.29)
is the Fock operator. Most computational strategies for solving the Hartree-Fock equation make the Linear Combination of Atomic Orbitals (LCAO) ansatz for the molecular orbitals. Each molecular orbital is expanded in a basis set of all the atomic orbitals within the molecule:
\[
\psi_j(\vec{x}_j) = \sum_{k=1}^{N_h} c_{k,j} \phi_k(\vec{x}_j)
\] (1.30), where \(N_h\) is the number of atomic orbitals (\(\phi_k\)) in the expansion. Substitution into eq. (1.28) and subsequent integration yields the matrix form
\[
\int d\vec{x}_j \phi_j^* \left( F \sum_{k=1}^{N_h} c_{k,j} \phi_k = \epsilon_i \sum_{k=1}^{N_h} c_{k,i} \phi_k \right) \rightarrow \sum_{k=1}^{N_h} F_{jk} c_{j,k} = \epsilon_j \sum_{k=1}^{N_h} S_{jk} c_{k,j}
\] (1.31),
where \(F_{jk} = \int d\vec{x}_j \phi_j^*(\vec{x}_j) F(\vec{x}_j) \phi_k(\vec{x}_j)\) and \(S_{jk} = \int d\vec{x}_j \phi_j^*(\vec{x}_j) \phi_k(\vec{x}_j)\). Equation (1.31) is the self-consistent Hartree-Fock Roothan equation, and it is the starting point for many quantum chemistry calculations. In order to solve these equations four types of integrals must be computed:
\[
S_{ij} = \int \phi_i^*(\vec{x}) \phi_j(\vec{x}) d\vec{x}
\]
\[
T_{ij} = \int \phi_i^*(\vec{x}) \left[ -\frac{1}{2} \nabla^2 + \frac{Z}{|\vec{x} - \vec{x}_k|} \right] \phi_j(\vec{x}) d\vec{x}
\]
\[
V_{ij} = \int \phi_i^*(\vec{x}_1) \left[ -\sum_k \frac{Z_k}{|\vec{x}_1 - \vec{X}_k|} \right] \phi_j(\vec{x}_1) d\vec{x}_1
\] (1.32)
\[
V_{ij\alpha\beta} = \int \phi_i^*(\vec{x}_1) \phi_j^*(\vec{x}_2) \left[ \frac{1}{|\vec{x}_1 - \vec{x}_2|} \right] \phi_\alpha(\vec{x}_1) \phi_\beta(\vec{x}_2) d\vec{x}_1 d\vec{x}_2
\]
The most chemically realistic form for the atomic orbitals are Slater-type orbitals (STO’s) centered on each atom:

\[
\begin{align*}
\varphi_{1s}(\zeta_1, r) &\sim \exp(-\zeta_1 r) \\
\varphi_{2s}(\zeta_2, r) &\sim r \exp(-\zeta_2 r / 2) \\
\varphi_{2p_x}(\zeta_2, r) &\sim x \exp(-\zeta_2 r / 2) \\
\end{align*}
\]

(1.33)

In practice Slater-type orbitals are each represented by a least squares fit of a linear combination of a small number of Gaussian-type functions with appropriate symmetry. This is done because Gaussian-type functions can be integrated much more rapidly than Slater-type. Choosing an atomic basis set is thus a balance between minimizing computation time while still retaining chemical realism. The two-center \( V_{ijkl} \) integrals are by far the most time-consuming to compute. There are \( \sim (N_b)^4 \) such integrals, and for most mid-sized organic molecules \( N_b \sim 10^2 \sim 10^3 \). Methods which compute all of the integrals in (1.32) are termed \textit{ab initio}, whereas methods which neglect (or partially neglect) some of the \( V_{ijkl} \) integrals are termed \textit{semi-empirical}. Semi-empirical methods will also generally parameterize many of the integrals both for computational efficiency and in order account approximately for neglected terms and other approximations. This is done by fitting the results to specific types of data for specific molecules. This limits their applicability to other situations. However, the relatively small number of atom types (C, O, N, H) and bonding motifs in many organic molecules allows semi-empirical methods to have moderate success in computing a small number of molecular properties across a broad spectrum of molecules. Semi-empirical methods are thus invaluable tools for screening large sets of molecules, and in some contexts perform equally well or better.
than \textit{ab initio} methods, which may take substantially more computational time – particularly for large molecules.

\subsection{1.3.2 Post Hartree-Fock Configuration Interaction}

The self-consistent solution to the Hartree-Fock Roothan equations (1.31) will yield atomic orbital coefficients \(c_{k,j}\) which define the molecular orbitals \(\psi_i\) according to eq. (1.30). The atomic orbital basis sets normally include more orbitals than electrons in order to maintain spherical symmetry. For example, a carbon atom basis set may contribute a 2s atomic orbital and three 2p atomic orbitals, which can accommodate 8 electrons even though there are only 4 electrons in the \(n=2\) level for C. This leads to a number of unoccupied (virtual) molecular orbitals, which can be used to improve the Hartree-Fock ground state calculation and to reasonably calculate molecular excited states. This is the basis of the \textit{Configuration Interaction} (CI) calculation. In CI, the electronic wavefunction is expanded as a linear combination of Slater determinants that are formed by moving electrons from the original filled Hartree-Fock orbitals into the unfilled orbitals:

\begin{equation}
\Psi_{\text{CI}} = a_0 \Psi_{HF} + \sum_i a_i (P_i \Psi_{HF})
\end{equation}

with \(\sum_i |a_i|^2 = 1\). The operator \(P_i\) acts on the Hartree-Fock wave function to generate all possible configurations between the original occupied and unoccupied Hartree-Fock orbitals. These are often referred to as Configuration State Functions (CSF’s), and the coefficients \(a_i\) will be termed configuration coefficients. In practice the number of configurations is so large that restrictions must be placed on the number considered. This
can be accomplished in two ways: (1) restrict the types of CSF’s to those generated by moving only one (or at most a few) electron(s) at a time, e.g. Configuration Interaction Singles (CIS), Configuration Interaction Singles/Doubles (CISD), etc.; or (2) restrict the number of occupied and unoccupied orbitals that are allowed to exchange electrons, and “freeze” the rest of the orbitals. This defines a subset of the Hartree-Fock orbitals called the active space. The more configurations considered in eq. (1.34) the closer the calculation should come to recovering the electron correlation energy not accounted for in Hartree-Fock, which was due to using only one Slater determinant. In theory the exact wavefunction could be represented by a linear combination of a complete set of Slater determinants, so the more Slater determinants used in (1.34) the closer one gets to the exact wavefunction. The Multi-Configuration Self-Consistent Field (MCSCF) method is a variation of the CI method in which not only the configuration coefficients of eq. (1.34) are optimized, but the starting Hartree-Fock orbitals are also allowed to change. Therefore, MCSCF should perform better than a comparable (same active space size) CI calculation because MCSCF has more parameters to adjust. But this altering of the reference orbitals can make MCSCF excited state calculations more difficult to interpret, and convergence can be slow and problematic. In the end, the ability to calculate excited states within the CI and MCSCF methods makes them of interest for nonlinear optical calculations. The following example illustrates some of the quantum chemical concepts for calculating nonlinear optical properties described above, and provides graphical representation to aid in interpretation of the results.
1.3.3 Sample Calculation of a Λ-shaped Molecule and Discussion of Molecular Orbitals.

To illustrate the concepts described in sections (1.3-1.3.2) a sample calculation on malachite green (fig. 1.5) is presented. The calculations were performed with Gaussian03 and the results visualized using Chem3D 9.0. First the AM1 semi-empirical method is used to optimize the nuclear coordinates. The AM1 method is parameterized for calculating molecular geometries. The atomic basis set used is VSTO-3G, which stands for Valence Slater-Type Orbitals. The 3G indicates that each VSTO (i.e. 1s for H, and 2s, 2p for C and N) is represented by an expansion of 3 Gaussian functions. Again, this is done for computational reasons: it is numerically faster to integrate multiple Gaussian functions than a single Slater-Type function. The two core 1s electrons in each C and N atom are not a part of the valence basis. Each C and N contributes 4 atomic orbitals (a 2s-type and three 2p-types), and each H contributes a single 1s-type atomic orbital, for a total basis size of $23 \times 4 + 2 \times 4 + 25 = 125$ atomic basis functions. Thus, each molecular orbital will be represented by 125 atomic orbital coefficients (see eq. (1.30)), and there are 125 such molecular orbitals. Each C contributes 4 valence electrons, each N has 5, and each H has 1, for a total of 127 valence

![Figure 1.5 Molecular structure of malachite green](image-url)
electrons. The positive molecular charge lowers this number to 126 valence electrons, which occupy the lowest 63 orbitals. A sampling of the resultant molecular orbitals is shown in fig 1.6. The highest occupied molecular orbital (HOMO) is used as a reference point for the occupied orbitals. Similarly, the lowest unoccupied molecular orbital (LUMO) is used as a reference for the unoccupied orbitals. We note that the orbitals in fig 1.6 can be categorized according to their two-fold rotational symmetry. Those orbitals that change sign under two-fold rotation are called B-type, whereas the orbitals that are invariant under rotation about the two-fold axis are termed A-type. Using the AM1 optimized nuclear coordinates, a post Hartree-Fock configuration interaction singles (CIS) calculation was carried out using another semi-empirical method, ZINDO/S, which is parameterized to reproduce ground to excited state energy gaps and ground to excited state transition moments of small benzene-like molecules. In general

Figure 1.6 Selected Hartree-Fock molecular orbitals of malachite green calculated with the AM1 semi-empirical parameterization using a VSTO-3G basis.
the CIS method has a major deficiency – it does not recover any of the ground state electron correlation energy because according to Brillouin’s Theorem, singly excited configurations do not mix with the ground state. This is problematic for the \textit{ab initio} determination of energy gaps between ground and excited states using CIS, and therefore \textit{ab initio} methods almost always employ the Configuration Interaction Singles/Doubles (CISD) at minimum. However, since ZINDO/S is parameterized to experimental energy gaps (from spectroscopic measurements), the difficulty is much less severe. The parameterization indirectly accounts for some of the ground state correlation energy. In Gaussian03 the basis set for ZINDO/S is VSTO-6G, which uses 6 Gaussians functions to represent each orbital. Despite this difference (6G vs. 3G), along with the entirely different parameterization than AM1, the frontier orbitals (those near the HOMO/LUMO gap) generated by ZINDO/S are qualitatively similar to those shown in fig 1.6; so reference to fig. 1.6 will be made to interpret the CIS results instead of displaying the actual ZINDO/S orbitals. The active space of the CIS calculation included all 125 molecular orbitals. The number of single electron configurations is the product of the number of occupied and unoccupied orbitals: \(63(\text{occ.}) \times 62(\text{unocc.}) = 3906\). Depending on the symmetry of the excited state, some of the configuration coefficients may be identically zero. An A-type excited state is made up of configurations in which the orbitals that are exchanging the electron have the same symmetry (i.e. \(\psi_A \rightarrow \psi_A\) or \(\psi_B \rightarrow \psi_B\)), whereas a B-type state excited state requires the electron to be exchanged between orbitals of opposite symmetry (\(\psi_A \rightarrow \psi_B\) or \(\psi_B \rightarrow \psi_A\)). Since about half the orbitals are A-type and half are B-type, each excited state will have roughly \(3906 / 2 \approx 1950\) configuration coefficients. The lowest-lying excited state has a very
dominant configuration with coefficient $a_{63\rightarrow 64} = 0.965$. The next largest coefficient is $a_{62\rightarrow 65} = 0.145$. These configurations represent transitions between orbitals of opposite symmetry (see fig 1.6), so the first excited state is B-type. Because this first excited state has dominant $\text{HOMO} \rightarrow \text{LUMO}$ character it is rather easy to “see” the implications for NLO (recall eq. (1.18)). In this case the charge transfer can be approximated as
\[
\Delta \mu_{01} \sim \int d\vec{x} \, z \left( |\psi_{\text{HOMO}}|^2 - |\psi_{\text{LUMO}}|^2 \right); \text{ and the transition moment can be approximated as}
\]
\[
\bar{\mu}_{01} \sim \int d\vec{x} \, \psi_{\text{HOMO}} \vec{x} \psi_{\text{LUMO}} = (\mu_{01}^x, \mu_{01}^y, 0) = (\mu_{01}^x, 0, 0). \]
To understand why the $z$-component of the transition moment is zero, consider what happens to the integral under the two-fold rotation:
\[
\int d\vec{x} \, \psi_{\text{HOMO}} \vec{x} \psi_{\text{LUMO}} \rightarrow \int d\vec{x} \, (\psi_{\text{HOMO}})(-x, -y, z) (-\psi_{\text{LUMO}}). \]
Since the LUMO changes sign but $z$ does not, the $z$-component of this integral must be zero. We further assume that the $y$-component is small (zero) because the molecule is rather flat and the $x$-direction is much larger than the $y$-direction. The second excited state calculated with ZINDO/S has a dominant CIS coefficient of $a_{62\rightarrow 64} = 0.92$. The next largest coefficient for the second excited state is $a_{60\rightarrow 64} = 0.25$. These configurations represent transitions between orbitals of the same parity with respect to two-fold rotation, which classifies an A-type excited state. Again, because there is a single dominant configuration, the NLO parameters can be considered
\[
\Delta \mu_{02} \sim \int d\vec{x} \, z \left( |\psi_{\text{HOMO-1}}|^2 - |\psi_{\text{LUMO}}|^2 \right) \text{ and}
\]
\[
\bar{\mu}_{02} \sim \int d\vec{x} \, \psi_{\text{HOMO-1}} \vec{x} \psi_{\text{LUMO}} = (0, 0, \mu_{02}^z). \]
In this case only the $z$ component of the transition moment is non-zero, which again can be seen from considering the transformation
\[
\int d\vec{x} \, \psi_{\text{HOMO-1}} \vec{x} \psi_{\text{LUMO}} \rightarrow \int d\vec{x} \, (-\psi_{\text{HOMO-1}})(-x, -y, z) (-\psi_{\text{LUMO}}). \]
These calculations show that the two lowest-lying excited states in malachite green are well-approximated by $HOMO \rightarrow LUMO$ and $HOMO-1 \rightarrow LUMO$ single electron transfers, respectively. The lowest-lying excited state has a transition moment perpendicular to the charge transfer axis (B-type), while the next state has a transition moment parallel to the charge transfer axis (A-type).

The types of frontier orbitals (those near the HOMO/LUMO gap) seen in fig. 1.6 are characteristic of organic NLO molecules. Large transition moments are the result of electron transitions between delocalized $\pi$ orbitals. These orbitals result due to extended conjugation of double and/or triple bonds. Generally $\pi$-electrons (p-type orbitals perpendicular to the plane containing conjugated atoms) are much more mobile than other electrons, including $\sigma$-electrons (p-type orbitals that are directed in the plane of the atoms and thus more strongly participating in localized bonding interactions). This is the motivation for starting from an underlying $\pi$-conjugated structure. Addition of donor or acceptor groups can be used to direct the charge transfer of the relatively neutral $\pi$-conjugated structure. In the case of malachite green, the two amine groups (-N(CH$_3$)$_2$) act as donors, biasing the $\pi$-type charge distribution of the electron in the HOMO towards the phenyl amine rings (as opposed to the unsubstituted phenyl). The central carbon atom bears much of the positive charge, and thus acts as a $\pi$-electron acceptor, as can be seen from the large $\pi$ orbital over the central carbon in the LUMO. The concepts described in this section will be employed (explicitly or implicitly) throughout a majority of this thesis.
1.4 Introduction to this Thesis

Work on the chiral-axial project described in this thesis has required a significant collaborative effort among the groups of Dr. Twieg, Dr. Singer, and Dr. Petschek. Dr. Twieg’s group at Kent State has synthesized several molecules for characterization. Dr. Singer’s group has performed the Kleinman-Disallowed Hyperpolarizability (KD-HRS) measurements, and I have worked along with Dr. Petschek to both analyze the experimental results in light of quantum chemical calculations and to propose better molecules for Kleinman-Disallowed hyperpolarizability. Our collaborative efforts have resulted in 4 manuscripts, 2 of which have been published to date. These manuscripts make up chapters 2-4 of this thesis, and generally contain both the synthetic chemistry and optical characterization. The manuscripts have been preserved in their original form for completeness sake, but the synthetic portions are not a focus of this thesis and can be neglected / skimmed without loss of continuity.

Chapter 2 describes truxenone derivatives, which have a three-fold rotational symmetry (fig. 1.7). Truxenones are planar molecules and should be suitable for octupolar NLO ($\beta^{3\omega}$), while conversion of $R_3 = O$ to the bulkier group $R_3 =$ dicyanomethylene causes a propeller-like distortion of the molecule, and opens the possibility for a nonzero Kleinman-disallowed ($\beta^{2m}$) component. The chapter is divided into two sections. The first contains truxenone derivatives with amine donors at the $R_1$ position and $R_2 = H$. This work was published in Chemistry of Materials. The second section contains hexaalkoxy derivatives ($R_1 = R_2 = OR$) which are expected to more readily form discotic liquid crystals. The mesogenic behavior of these derivatives is examined.
Chapter 3 was published in *Tetrahedron Letters*.\textsuperscript{34} It describes triarylnapthylmethyl carbocation molecules with either propeller or $C_2$ symmetry. Their synthesis and spectroscopic properties are reported, and their prospects for NLO are briefly discussed. Some of the molecules in this chapter will be studied more in depth for their NLO properties in chapter 5.

\textbf{Figure 1.7} General structure of truxenone derivatives.

\textbf{Figure 1.8} Triarylmethyl carbocation derivatives.
Chapter 4 discusses synthesis and properties of several Λ-shaped phenanthrenequinone derivatives. Quantum chemical calculations describe the nature of the low-lying excited states, and their implications for KD-hyperpolarizabilities.

![Figure 1.9 Phenanthrenequinone derivatives.](image)

Chapter 5 contains quantum chemical calculations of various chemically diverse Λ-shaped compounds. A series of TAMC’s is discussed (fig 1.8), along with many other types of molecules, including bis(styryl) substituted compounds. Geometric and chemical effects are investigated, and spectroscopic and charge transfer calculations are presented to give indication of prospects for KD-hyperpolarizabilities. Two-level and multi-level SOS calculations are discussed, and comparison to experimental data is made where available.

Chapter 6 is a deviation from the discussion of Kleinman-disallowed hyperpolarizabilities. This chapter considers the idea of “modulated conjugation” and the recent claims about this concept for maximizing the off-resonant hyperpolarizability of one-dimensional molecules. Section 6.2 was published as a comment in *Optics Letters.*

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1.5 References


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Chapter 2: Truxenone Derivatives for Nonlinear Optical Applications

2.1 Synthesis and Characterization of New Truxenones for Nonlinear Optical Applications

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\textbf{ABSTRACT:} The synthesis of several new truxenones and one tris(dicyanomethylene) derivative substituted by different amines at positions 4, 9 and 14 are reported. A complete characterization of the NLO properties of representative derivatives was carried out by Hyper Rayleigh Scattering and the major electronic effects and the influence of the structural modifications on the NLO properties have been examined. Due to their $C_3$ symmetry and their large first hyperpolarizability, the chiral versions of the tris(dicyanomethylene) truxone derivatives are of interest for second-order nonlinear optics in uniaxially aligned chiral media.
KEYWORDS: Nonlinear optics; Hyper-Rayleigh Scattering, Hyperpolarizability, Multipolar, $C_3$ symmetry.

2.1.1 Introduction.

Truxenone, diindenon[1,2-a;1',2'-c]fluorene-5,10,15-trione, and related truxene derivatives have been known for well over a century but have only relatively recently attracted attention as building blocks for functional materials. During the last two decades a number of studies have reported the exploitation of different truxenone or truxene derivatives involving their mesomorphic, electrochemical and nonlinear optical properties. A main source of interest in the truxenones as a component or precursor for functional materials derives mainly from the presence of the three identical carbonyl functional groups disposed in the plane of the molecule with overall $C_{3h}$ symmetry. As such, the truxenone molecule is formally comprised of three fluorenones that share a common central benzene ring and serves as a rigid template for further modification permitting creation of derivatives with threefold rotational symmetry.

Multidimensional chromophores as functional nonlinear optical materials have been the focus of research in two-photon absorption and parametric nonlinear optics. The research presented here has been undertaken in order to identify chromophores that can be aligned in thermally stable axially aligned chiral media, which can result in large second order nonlinear optical tensors. Such materials will prove to be valuable alternatives to conventional second order NLO materials such as electro-optical media created by electric field poling. Truxenones and their derivatives are of interest for this and other applications as a consequence of their multidimensionally delocalized electrons and their potential to form columnar liquid crystal media. The central benzene ring in
truxenone fused to three carbonyl groups on the five-membered rings functions is a strong electron-withdrawing unit and the substitution of the truxenone in positions 4, 9 and 14 by donor groups will create a multipolar NLO active truxenone. The $C_{3h}$ symmetry gives the truxenones and truxenes an octupolar character, which, as in the case of two-photon absorption, is likely to result in more efficient non-linear optical properties than the corresponding dipolar molecules. No synthesis has previously been reported of any truxenone derivatives with a donor substituent on the immediate periphery of the truxenone unit. Only the study of Lambert et al. reports the preparation and NLO characterization of truxenone derivatives linked to various donor groups via an intervening phenylethynyl bridge. It is well known that an ethynyl bridge is not very efficient for the transfer of the $\pi$ electrons, diminishing the NLO potential of this kind of molecule. Here we report the synthesis of some truxenones and derivatives of truxenone that are directly substituted on the immediate periphery by different amine donor groups.

2.1.2 Experimental Section

**Instrumentation.** Proton nuclear magnetic resonance ($^1$H NMR) spectra and carbon nuclear magnetic resonance ($^{13}$C NMR) spectra were recorded on a Bruker Avance-400 (400 MHz) or Inova-500 (500 MHz) NMR spectrometer. Chemical shifts for protons are reported in parts per million (CDCl$_3$ $\delta$ 7.25). Chemical shifts for carbon are reported in parts per million downfield from added tetramethylsilane. The $^{13}$C-NMR data are not available for those compounds having poor solubility. Elemental analysis for carbon, hydrogen, and nitrogen was determined on a Leco CHNS-932 instrument. Melting points were measured on a TA Instruments DSC 2920 operating at 10 °C/min under nitrogen or
by using a polarizing optical microscope equipped with a Mettler FP82HT heating stage attached with a Mettler FP90 temperature controller operating at 10°C/min. The mass spectroscopy was performed on a Bruker Daltonics Esquire 3000+ with an APCI ion source. The IR spectra were recorded on a Bruker Optics Vector 33. The microwave reactions were performed with the CEM Discover station at maximum power (300W) in a pressure vessel provided by CEM.

**Materials.** Commercial reagents were obtained from commercial vendors; 5-fluoroindanone was obtained from TCI, while the amines and other reagents were purchased from Sigma Aldrich, Acros or Lancaster. All the reagents were used as received with the exception of pyridine, which was distilled from calcium hydride at 760 Torr and chlorobenzene, which was dried over molecular sieves (3Å). The flash chromatographies were performed on silica gel (60Å, 70-230 mesh).

**2,2-dibromoindan-1-one.** In a 100 ml round-bottom flask with magnetic stirbar, 1-indanone (5.00 g, 37.9 mmol) was dissolved in 100 ml of chloroform. Under strong agitation, bromine (12.10 g, 75.8 mmol) diluted in chloroform (5 ml) was slowly added and stirring was continued for an additional 1 hour. Any excess of bromine was removed by bubbling nitrogen through the solution during 1 hour. The solvent was removed under vacuum and the solid product was washed with a small quantity of ethanol. 9.0 g (82%).

\[ ^1H \text{NMR (CDCl}_3\text{)} \delta: 7.97 (d, J=7.6Hz, 1H), 7.75 (t, J=7.6Hz, 1H), 7.52 (t, J=7.6Hz, 1H), 7.42 (d, J=7.6Hz, 1H), 4.31 (s, 2H). \]

\[ ^13C \text{NMR (CDCl}_3\text{)} \delta: 192.7; 147.1; 136.9; 129.0; 126.6; 126.0; 56.8; 52.3. \]

IR (cm\(^{-1}\)): 2922; 1716, 1598, 1465, 1421, 1266, 1208, 1100. mp: 133 °C (Lit. 131-134 °C) \(^8\). MS: m/z 288.80, 290.80, 292.80 (M + H)\(^+\). MS-MS (290.80), m/z: 209.90, 211.80, 131.1.
**5,6-dimethoxyindan-1-one.** In a 100 ml round-bottom flask with magnetic stirbar, P₂O₅ (1.20 g, 8.5 mmol) and methanesulfonic acid (12.00 g, 125.0 mmol) were mixed and heated at 110 °C for 30 min. Next, 3-(3,4-dimethoxyphenyl)propionic acid (2.00 g, 9.5 mmol) was added all at once and stirring was continued for 15 min. After cooling to room temperature, the reaction mixture was poured into 200 ml of water, and extracted with ethyl acetate (200 ml) and dichloromethane (100 ml). The organic layers were combined and dried over magnesium sulfate. The solvent was removed under vacuum and the product was purified by flash chromatography (hexane/ethyl acetate). 1.25g (68%). ¹H NMR (CDCl₃) δ: 7.18 (s, 1H), 6.89 (s, 1H), 3.97 (s, 3H), 3.91 (s, 3H), 3.06 (t, J=5.4Hz 2H), 2.68 (t, J=5.4Hz 2H). ¹³C NMR (CDCl₃) δ: 155.6, 150.6, 149.5, 130.0, 116.9, 107.6, 104.3, 56.4, 56.2, 36.7, 25.7. IR (cm⁻¹): 2964, 2924, 2852, 1718. mp 117-119 °C (Lit. 118-120 °C). MS: m/z: 193.0 [M + H]⁺ MS-MS (193.0), m/z: 151.0.

**2,2-dibromo-5,6-dimethoxyindan-1-one.** In a 100ml round-bottom flask with magnetic stirbar, 5,6-dimethoxyindan-1-one (1.00 g, 5.2 mmol) was dissolved in 40 ml of chloroform. Under strong agitation, bromine (1.67 g, 10.4 mmol) diluted in chloroform (5 ml) was slowly added and stirring was continued for 1 hour. The excess of bromine was removed by bubbling nitrogen through the solution during 1 hour. The solvent was removed under vacuum and the product was recrystallized from methanol. 1.04 g (58%). ¹H NMR (CDCl₃) δ: 7.32 (s, 1H), 6.80 (s, 1H), 4.24 (s, 2H), 4.01(s, 3H), 3.96 (s, 3H). ¹³C NMR (CDCl₃) δ: 191.7, 157.5, 150.5, 142.6, 121.4, 107.2, 106.3, 57.2, 56.6, 56.3, 52.3. IR (cm⁻¹): 2963, 2855, 1711, 1568, 1507, 1268, 1222, 1109. mp 131 °C. MS: m/z 348.8, 350.8, 352.70 [M + H]⁺ MS-MS (350.8), m/z: 269.9, 271.8, 191.0. Calculated for C₁₁H₁₂Br₂O₃: C, 37.53%; H, 3.44%. Found: C, 38.00%; H, 3.03%.
5,6-dimethoxyindan-1,3-dione. In a 100 ml round-bottom flask with magnetic stirbar, 5,6-dimethoxyindan-1-one (1.00 g, 5.21 mmol) was dissolved in a mixture of acetic acid (50 ml) and water (10 ml) and the reaction mixture was cooled in an ice bath. Chromium trioxide (3.68 g, 36.8 mmol) was added in small portions over 1 hour and then the cooling bath was removed and the mixture was stirred for an additional 24 hours. Isopropanol (10 ml) was added and the mixture was stirred for an additional 30 min. The reaction mixture was poured into 200 ml of water, and extracted with dichloromethane (2×100 ml). The solvent was removed under vacuum to give the product, which was used without further purification. 0.56 g (52%). ¹H NMR (CDCl₃) δ: 7.34 (s, 2H), 4.04 (s, 6H), 3.20 (s, 2H). ¹³C NMR (CDCl₃) δ: 196.6, 155.8, 138.4, 103.2, 56.7, 44.7. mp: 265 °C dec. (Lit. 267 °C)¹⁰. MS: m/z: 207.0 [M + H]⁺. MS-MS (207.0), m/z: 191.0, 165.0.

2,3-dihydro-cyclopenta[b]naphtalen-1-one. In a 250 ml round-bottom flask with magnetic stirbar, α,α',α',α''-tetrabromo-o-xylene (30.00 g, 71.0 mmo l) was dissolved in dry DMF (150 ml) and then 2-cyclopenten-1-one (5.82 g, 71.0 mmol) and NaI (70.00 g, 466.6 mmol) were added. The reacti on mixture was heated at 80 °C overnight. After cooling to room temperature, the solution was poured into an ice/water mixture (400 ml), and decolorized by addition of sodium bisulfite. A brown/yellow precipitate appeared which was removed by suction filtration. The crude product was purified by flash chromatography. 2.92 g (23%). ¹H NMR (CDCl₃) δ: 8.31 (s, 1H), 7.97 (m, 1H), 7.88 (s, 1H), 7.85 (m, 1H), 7.58 (m, 1H), 7.49 (m, 1H), 3.31 (m, 2H), 2.79 (m, 2H). ¹³C NMR (CDCl₃) δ: 207.7, 147.9, 137.2, 134.7, 132.3, 130.4, 128.6, 127.9, 126.1, 124.9, 124.4, 58.4, 36.9. IR (cm⁻¹): 3349, 2964, 2924, 2852, 1740, 1680. mp 135 °C (Lit. 140-141
°C)\(^{11}\). MS: m/z 183.0 [M + H]\(^+\). MS-MS (183.00), m/z: 165.00 (-H\(_2\)O), 155.0 (-CO), 141.0 (-CH\(_2\)CO).

**2,2-dibromo-3-hydrocyclopenta[b]naphtalen-1-one.** In a 100 ml round-bottom flask with magnetic stirbar 2,3-dihydrocyclopenta[b]naphtalen-1-one (1.00 g, 5.5 mmol) was dissolved in 30 ml of chloroform. Under strong agitation, bromine (1.76 g, 11.0 mmol) diluted in chloroform (5 ml) was slowly added and stirring was continued for 1 hour. The excess of bromine was removed by bubbling nitrogen through the solution during 1 hour. The solvent was removed under vacuum and the product was recrystallized from ethanol. 1.1 g (59%). \(^1\)H NMR (CDCl\(_3\)) \(\delta\): 8.55 (s, 1H), 8.03 (d, J=7.5Hz, 1H), 7.89 (d, J=7.5Hz, 1H), 7.82 (s, 1H), 7.69-7.57 (m, 2H), 4.43 (s, 3H). \(^13\)C NMR (CDCl\(_3\)) \(\delta\): 192.2, 139.8, 138.1, 133.1, 130.7, 130.0, 128.2, 127.2, 124.7, 58.5, 52.1. IR (\(\text{cm}^{-1}\)): 3021, 2963, 2924, 2855, 1744, 1643, 1367. mp 161 °C. MS: m/z 338.8, 340.8, 342.8 [M + H]\(^+\). MS-MS (340.80), m/z: 259.90, 261.80 (-HBr), 181.10 (-Br). Calculated for C\(_{13}\)H\(_8\)Br\(_2\)O: C, 45.92%; H, 2.37%. Found: C, 46.40%; H, 2.48%.

**Dimethyl 2,3-naphthalenedicarboxylate**\(^12\). In a 100ml round-bottom flask with magnetic stirbar, 2,3-naphthalenedicarboxylic acid (1.50 g, 7.0 mmol) was dissolved in methanol (15 ml) and thionyl chloride (3.30 g, 28.0 mmol) was added slowly. The reaction mixture was heated under reflux for two hours and after cooling to room temperature the solvent was removed under reduced pressure. The mixture was dispersed in water (200 ml) and extracted with ethyl acetate. The solvent was removed under vacuum, and the product (a colorless oil which solidifies after standing at 4 °C) was used without further purification. 1.66 g (98%). \(^1\)H NMR (CDCl\(_3\)) \(\delta\): 8.28 (s, 2H), 7.95-7.93
(m, 2H), 7.66-7.64 (m, 2H), 3.98 (s, 6H). $^{13}$C NMR (CDCl$_3$) δ: 167.57, 133.22, 129.85, 128.77, 128.49, 128.39, 61.49.

2-hydrocyclopenta[b]naphtalen-1,3-dione. Sodium hydride dispersed in mineral oil (60%, 0.50 g, 10.4 mmol) was placed in a two-neck flask under nitrogen. A solution of dimethyl 2,3-naphthalenedicarboxylate (1.66 g, 7.0 mmol) in ethyl acetate (10 ml) was slowly added and the reaction mixture was heated under reflux for 4 hours. After cooling to room temperature, the solid was filtered off, washed with a mixture of ethanol/ diethyl ether (1/1, 10 ml) and then dispersed into a hot solution of hydrochloric acid (2%, 200 ml) and stirred for a few minutes during decarboxylation. After cooling to room temperature the solid crude product was filtered off and purified by flash chromatography (hexane/ethyl acetate). 0.69 g (52%). $^1$H NMR (CDCl$_3$) δ: 8.53 (s, 2H); 8.16-8.13 (m, 2H); 7.77-7.74 (m, 2H), 3.40 (s, 2H). $^{13}$C NMR (CDCl$_3$) δ: 197.7; 138.2; 136.4; 130.7; 129.7; 124.3; 46.7. IR (cm$^{-1}$): 2964, 2924, 2856, 1706, 1613, 1246, 1183. mp 221 °C (dec). (Lit. 136 °C dec). MS: m/z 197.0 [M + H]$^+$ MS-MS (197.0), m/z: 179.0, 152.1.

2,2-dibromo-5-fluoroindan-1-one. In a 100ml round-bottom flask with magnetic stirbar, 5-fluoroindan-1-one (1.00 g, 6.7 mmol) was dissolved in 25 ml of chloroform. Under strong agitation, bromine (2.13 g, 13.3 mmol) was slowly added and stirring was continued for 1 hour. The excess of bromine was removed by bubbling nitrogen through the solution during 1 hour. The solvent was removed under vacuum and the product was washed with a small amount of ethanol. 1.38 g (70%). $^1$H NMR (CDCl$_3$) δ: 7.98 (dd, J=8.4Hz, J’=5.2Hz, 1H), 7.22 (m, 1H), 7.11 (m, 1H), 4.30 (s, 2H). (Lit. 7.87-7.81 (m, 1H), 7.49-7.41 (m, 2H) 3.49 (s, 2H)). $^{13}$C NMR (CDCl$_3$) δ: 191.0; 169.6; 167.0; 150.1 (d, J=41.6Hz); 129.2 (d, J=33.6Hz); 117.4 (d, J=80.0Hz); 113.0 (d, J=70.0Hz); 56.1;
In 100 ml round-bottom flask with magnetic stir bar, 5-bromoindan-1-one (2.00 g, 9.5 mmol) was dissolved in 30 ml of chloroform. Under strong agitation, bromine (3.04 g, 19.0 mmol) was slowly added and stirring was continued for 1 hour and then nitrogen was passed through the reaction mixture during 1 hour. Residual solvent was removed under vacuum and the yellowish solid product was washed with a small amount of ethanol. 2.35 g (67%). \(^1\)H NMR (CDCl\(_3\)) \(\delta\): 7.83 (d, \(J=7.5\) Hz, 1H), 7.67 (d, \(J=7.5\) Hz, 1H), 7.62 (s, 1H), 4.28 (s, 2H). \(^1^3\)C NMR (CDCl\(_3\)) \(\delta\): 191.7, 148.7, 132.7, 129.8, 129.3, 127.7, 126.3, 55.8, 51.9. IR (cm\(^{-1}\)): 2962, 2924, 1701, 1506, 1368, 1218. mp: 94 °C (Lit. 93 °C). MS: m/z 366.7, 368.7, 370.8, 372.8. MS-MS (370.80), m/z: 287.9, 289.7, 291.7, 209.0, 210.9.

**Truxenone.** In a 100 ml round-bottom flask with magnetic stir bar, indan-1,3-dione (2.50 g, 17.0 mmol) was added to methanesulfonic acid (40 ml). The mixture was heated at 110 °C for 3 hours. After cooling to room temperature, the reaction mixture was dispersed in water (300 ml) and the crude product was filtered off. The product was dissolved in hot propylene carbonate (75 ml) and after cooling was isolated by suction filtration. This material was then recrystallized from 2-picoline. 1.73 g (79%). \(^1\)H NMR (CDCl\(_3\)) \(\delta\): 9.32 (d, \(J=7.2\) Hz, 3H), 7.90 (d, \(J=7.2\) Hz, 3H), 7.72 (t, \(J=7.2\) Hz, 3H), 7.60 (d,
J=7.2Hz, 3H). IR (cm⁻¹): 2922, 2856, 1703, 1606, 1567, 1459, 1317, 1271. mp > 400 °C (Lit. mp > 350 °C)¹⁴. MS: m/z 384.9 [M + H]⁺. MS-MS (384.9), m/z: 356.0, 191.0.

**4,9,14-trifluorotruxenone.**

**Method A**

The 2,2-dibromo-5-fluoroindan-1-one (0.25 g, 0.8 mmol) was placed in an adapted microwave vessel and irradiated for 2 min at maximum power (300 W). After cooling to room temperature, the reaction mixture was mixed with dichloromethane (2×10 ml) and the product was filtered off. 19.6 mg (16.6%)

**Method B**

The 2,2-dibromo-5-fluoroindan-1-one (1.00 g, 3.3mmol) was placed in a 25 ml round-bottom flask equipped with a magnetic stir bar and heated in an oil bath at 220 °C until gas evolution ceased (ca 1 hour). The mixture was cooled to room temperature, dispersed in dichloromethane (25 ml), sonicated for 5 min and then the product was filtered off, and washed two more times with dichloromethane (25 ml). The product obtained was used without further purification. (97.2 mg, 20.6%)

¹H NMR (CDCl₃) δ: 9.06-9.02 (m, 1H); 8.00-7.97 (m, 1H), 7.10-7.00 (m, 1H). IR (cm⁻¹): 2916, 2851, 1702, 1595, 1572, 1460, 1460, 1212. mp >400 °C. MS: m/z 438.9 [M + H]⁺. MS-MS (438.9), m/z: 410.9. Calculated for C₂₇H₉F₃O₃: C, 73.98%; H, 2.07%. Found: C, 73.80%; H, 2.06%.

**4,9,14-tribromotruxenone.** The 2,2,5-tribromoindan-1-one (3.00 g, 8.1 mmol) was placed in a 25 ml round-bottom flask equipped with a magnetic stirbar, and heated in an oil bath at 220 °C until gas evolution ceased (ca 1.5 hour). The mixture was cooled to room temperature, dispersed in dichloromethane (25 ml), sonicated for 5 min and then
the product was filtered off, and washed two more times with dichloromethane (25 ml). The product obtained was used without further purification. 0.51 g, (30%). $^1$H NMR (CDCl$_3$) $\delta$: 9.39 (s, 1H), 8.36 (d, J=7.6 Hz, 1H), 7.72 (d, J=7.6 Hz, 1H). IR (cm$^{-1}$): 2924, 2854, 1737, 1601, 1563, 1457, 1375, 1203. mp 395 °C (dec). MS: m/z 618.4, 620.4, 622.4, 624.4. MS-MS (622.4), m/z: 618.4, 620.3, 592.4, 541.6, 513.6. Calculated for C$_{27}$H$_9$Br$_3$O$_3$: C, 52.21%; H, 1.46%. Found: C, 51.70%; H, 1.47%.

4,9,14-Tris(pyrrolidino)truxenone. In a 25 ml round-bottom flask with magnetic stirbar was placed 4,9,14-trifluorotruxenone (90 mg, 0.2 mmol), potassium carbonate (ca 2 g) and anhydrous dimethyl sulfoxide (30 ml). Pyrrolidine (1.4 g, 20 mmol) was added and the reaction mixture was heated overnight at 100 °C under nitrogen. After cooling to room temperature, the reaction mixture was poured into water (200 ml) and the precipitated product was filtered off and dried. 61.6 mg (51%). $^1$H NMR (CDCl$_3$) $\delta$: 8.73 (d, J=2.4 Hz, 3H), 7.67 (d, J=8.0 Hz, 3H), 6.49 (dd, J=8.0 Hz, J’=2.4 Hz, 3H), 3.60-3.57 (m, 12H), 2.12-2.01 (m, 12H). HRMS: Calculated for [M + Na]$^+$: m/z 614.2420. Found: m/z 614.2421.

4,9,14-Tris(diethylamino)truxenone. In a 25 ml round-bottom flask with magnetic stirbar was placed 4,9,14-trifluorotruxenone (100 mg, 0.23 mmol), potassium carbonate (ca 3 g) and anhydrous dimethyl sulfoxide (10 ml). Diethylamine (2 ml, 20.0 mmol) was added and the reaction mixture was heated at 100 °C under nitrogen overnight. After cooling to room temperature, extraction several times with dichloromethane, the product was obtained as a dark red solid. 27.8 mg (20%). $^1$H NMR (CDCl$_3$) $\delta$: 8.73 (d, J=2.4 Hz, 3H), 7.67 (d, J=8.0 Hz, 3H), 6.49 (dd, J=8.0 Hz, J’=2.4 Hz, 3H), 3.57 (q, J=7.2 Hz, 12H), 1.27 (t, J=7.2 Hz, 18H). $^{13}$C NMR (CDCl$_3$) $\delta$: 190.2, 153.6, 145.0, 144.9,
132.3, 125.9, 123.7, 111.6, 111.5, 51.8, 31.7, 29.7, 27.5, 26.8. IR (cm\(^{-1}\)): 2984, 2923, 2880, 2827, 1683, 1611, 1573, 1484, 1399, 1266, 1228, 1101. mp 300 °C (dec). MS: m/z 598.2. Calculated for C\(_{39}\)H\(_{39}\)N\(_3\)O\(_3\): C, 78.36%; H, 6.58%; N, 7.03%. Found: C, 78.40%; H, 6.25%; N, 7.64%.

4,9,14- Tris(dibutylamino)truxenone. In a 25 ml round-bottom flask with magnetic stirbar was placed 4,9,14-trifluorotruxenone (44 mg, 0.1 mmol), potassium carbonate (ca 3 g) and anhydrous dimethyl sulfoxide (10 ml). Dibutylamine (2 ml, 12.0 mmol) was added and the reaction mixture was heated at 100 °C under nitrogen overnight. After cooling at room temperature, the reaction mixture was poured into water (200 ml), and extracted with dichloromethane. The product was purified by flash chromatography and recrystallized from hexane. 21.4 mg (27%). \(^1\)H NMR (CDCl\(_3\)) \(\delta\): 8.94 (d, J=2.4Hz, 3H), 7.69 (d, J=8.0Hz, 3H), 6.61 (dd, J=8.0Hz, J’=2.4Hz, 3H), 3.55 (t, J=7.6Hz, 12H), 1.77-1.72 (m, 12H), 1.54-1.48 (m, 12H), 1.03 (t, J=7.6Hz, 18H). \(^13\)C NMR (CDCl\(_3\)) \(\delta\): 190.4, 153.8, 145.0, 126.1, 123.8, 111.7, 51.5, 29.8, 20.5, 14.2. IR (cm\(^{-1}\)): 3118, 2947, 2903, 2855, 1689, 1613, 1576, 1501, 1460. mp 206 °C. MS: m/z 766.0 [M + H]\(^+\) MS-MS (766.0), m/z: 710.0, 654.0. Calculated for C\(_{51}\)H\(_{63}\)N\(_3\)O\(_3\): C, 79.96%; H, 8.29%; N, 5.49%. Found: C, 79.45%; H, 8.26%; N, 5.85%.

4,9,14-Tris(dihexylamino)-truxenone. In a 25 ml round-bottom flask with magnetic stirbar was placed 4,9,14-trifluorotruxenone (100 mg, 0.2 mmol), potassium carbonate (ca 3 g) and anhydrous dimethyl sulfoxide (10 ml). Dihexylamine (3 ml, 13.0 mmol) was added and the reaction mixture was heated at 100 °C under nitrogen overnight. After cooling at room temperature, the reaction mixture was poured into water (200 ml), and extracted with dichloromethane. The product was purified by flash chromatography and
recrystallized from hexane. 35.1 mg (16%). $^1$H NMR (CDCl$_3$) $\delta$: 8.92 (d, $J=2.0$Hz, 3H), 7.66 (d, $J=8.0$Hz, 3H), 6.59 (dd, $J=8.0$Hz, $J'=2.0$Hz, 3H), 3.55-3.51 (m, 12H), 1.77-1.72 (m, 12H), 1.50-1.37 (m, 18H), 0.93 (t, $J=7.6$Hz, 18H). $^{13}$C NMR (CDCl$_3$) $\delta$: 190.2, 153.6, 145.0, 144.9, 132.3, 125.9, 123.7, 111.6, 111.5, 51.8, 31.7, 29.7, 27.5, 26.8, 22.7, 14.1. IR (cm$^{-1}$): 3077, 2946, 2902, 2856, 1689, 1613, 1576, 1501, 1460. mp 137 °C. MS: m/z 934.1 [M + H]$^+$ MS-MS (934.1), m/z: 850.1, 766.0, 708.0. Calculated for C$_{63}$H$_{87}$N$_3$O$_3$: C, 80.98%; H, 9.38%; N, 4.50%. Found: C, 80.35%; H, 9.29%; N, 4.41%.

4,9,14-Tris-(S)-(+)-2-Pyrrolidinemethanol-truxenone. In a 100 ml round-bottom flask with magnetic stirbar was placed 4,9,14-trifluorotruxenone (100 mg, 0.2 mmol), potassium carbonate (ca 2 g) and anhydrous dimethyl sulfoxide (30 ml). (S)-(+) -2-Pyrrolidinemethanol (1ml, 10 mmol) was added and the reaction mixture was heated at 100 °C under nitrogen overnight. After cooling to room temperature, the reaction mixture was poured into water (200 ml) and the precipitated product was filtered off and washed with hot 2-picoline and dried. 141 mg (92%). This compound was used for subsequent reactions without further purification. $^1$H NMR ($d_6$-DMSO) $\delta$: 8.42 (s, 3H), 7.34 (d, $J = 8.4$ Hz, 3H), 6.53 (d, $J = 8.4$Hz, 3H), 4.89 (b, 3H), 3.90 (s, 3H), 3.58-3.40 (m, 6H), 2.11-2.01 (m, 18H). IR (cm$^{-1}$): 3368, 2951, 2874, 1679, 1607, 1572, 1496, 1363, 1275, 1226, 1153, 1104, 1040, 1008, 883, 802, 760, 667, 570. mp 201 °C. MS: m/z 682.0.

4,9,14-Tris-(S)-(+) -(2-hexyloxymethyl-Pyrrolidin-1-yl)-truxenone. In a two neck flask, 4,9,14-Tris-(S)-(+) -2-Pyrrolidinemethanol-truxenone (0.10 g, 0.2 mmol) and NaH (50% in mineral oil) (0.10 g, 2.0 mmol) were dispersed in dry THF (20 ml) under N$_2$, then iodohexane (1.0 ml, 6.7 mmol) was slowly added and the reaction mixture was heated under reflux overnight. After cooling to room temperature, the excess of NaH was
neutralized by addition of water. Then the mixture was poured into water, extracted with dichloromethane and purified by flash chromatography on silica gel (CH$_2$Cl$_2$/EtOAc is 9:1) giving red gel. 55 mg (39%). $^1$H NMR (CDCl$_3$) δ: 8.76 (d, J = 1.6 Hz, 3H), 7.62 (d, J = 8.4 Hz, 3H), 6.59 (dd, J = 1.6 Hz, J' = 8.4Hz, 3H), 4.20 (s, 3H), 3.75-3.41 (m, 18H), 2.21-2.06 (m, 12H), 1.61 (m, 6H), 1.40-1.28 (m, 18H), 0.91 (t, J = 6.8 Hz, 9H). $^{13}$C NMR (CDCl$_3$) δ: 190.5, 152.6, 145.0, 144.7, 132.1, 125.7, 124.3, 112.7, 112.2, 71.7, 70.2, 58.6, 48.9, 31.7, 29.8, 28.8, 25.8, 23.1, 22.7, 14.1. IR (cm$^{-1}$): 3114, 2926, 2856, 1684, 1606, 1575, 1497, 1468, 1363, 1320, 1275, 1224, 1184, 1160, 1101, 1005, 974, 889, 801, 761, 725, 667, 581. MS: m/z 934.1 [M + H]$^+$ MS-MS (934.1), m/z: 850.1, 766.0, 708.0. Calculated for C$_{60}$H$_{75}$N$_3$O$_6$: C, 77.14%; H, 8.09%; N, 4.50%. Found: C, 76.93%; H, 8.47%; N, 4.02%.

4,9,14-Tris-(R)-(+) -Pyrrolidinotruxenone. In a 100 ml round-bottom flask with magnetic stirbar was placed 4,9,14-trifluorotruxenone (0.20 g, 0.5 mmol), potassium carbonate (ca 8 g) and anhydrous dimethyl sulfoxide (60 ml). R-(+)-3-hydroxypyrrolidine (1.0 g, 11.5 mmol) was added and the reaction mixture was heated at 100 °C under nitrogen overnight. After cooling to room temperature, the reaction mixture was poured into water (800 ml) and the brown precipitated product was filtered off and washed with hot 2-picoline and ethanol respectively, and then dried in vacuum. 0.26 g (89%). The product was used for alkylation reaction without further purification. $^1$H NMR ($d_6$-DMSO) δ: 8.55 (s, 3H), 7.53 (b, 3H), 6.57 (b, 3H), 5.07 (b, 3H), 4.51 (s, 3H), 3.59 (m, 6H), 3.35 (m, 6H), 2.16-2.03 (m, 6H). IR (cm$^{-1}$): 3339, 2915, 2853, 1672, 1606, 1569, 1503, 1470, 1379, 1329, 1274, 1226, 1164, 1098, 1011, 978, 880, 853, 800, 759, 663. mp > 400 °C. MS: m/z 640.0 M$^+$. 67
**4,9,14-Tris-(R)-(+)-(3-propoxy-pyrrolidin-1-yl)truxenone.** In a two neck flask, 4,9,14-Tris-(R)-(+)-Pyrrolidinotruxenone (0.10 g, 0.2 mmol) and NaH (50% in mineral oil) (0.10 g, 2.0 mmol) were dispersed in dry THF (20 ml) under N₂, then iodo propane (1.0 ml, 10.0 mmol) was slowly added and the reaction mixture was heated under reflux overnight. After cooling to room temperature, the excess of NaH was neutralized by addition of water. Then the mixture was poured into water, extracted with dichloromethane and purified by flash chromatography on silica gel (CH₂Cl₂/EtOAc is 9:1) giving red solid. 73 mg (59%). ¹H NMR (CDCl₃) δ: 8.68 (d, J = 2.0 Hz, 3H), 7.64 (d, J = 8.4 Hz, 3H), 6.51 (dd, J = 2.0 Hz, J’ = 8.4 Hz, 3H), 4.27 (s, 3H), 3.77-3.61 (m, 12H), 3.50 (t, J = 6.8 Hz, 6H), 2.29-2.16 (m, 6H), 1.64 (m, 6H), 0.95 (t, J = 7.6 Hz, 9H). ¹³C NMR (CDCl₃) δ: 190.4, 152.5, 144.9, 144.5, 132.0, 125.7, 124.8, 113.0, 112.3, 78.0, 71.0, 46.8, 31.1, 23.2, 10.7. IR (cm⁻¹): 2960, 2931, 2854, 1683, 1607, 1574, 1504, 1470, 1380, 1332, 1274, 1229, 1179, 1102, 1011, 976, 883, 799, 760, 664, 610, 580. mp 258 °C. HRMS: Calculated for [M + H]⁺: m/z 766.3856. Found: m/z 766.3858.

**4,9,14-Tris(dibutylamino)-1,6,11-tris(dicyanomethylen)e-truxane.** In a 100 ml round-bottom flask with magnetic stirbar, 4,9,14-tris(dibutylamino)truxenone (100 mg, 0.1 mmol) and malonitrile (100 mg, 1.5 mmol) were dispersed into dry chlorobenzene (30 ml) and placed under nitrogen. TiCl₄ (0.3 ml, 2.7 mmol) and a solution of pyridine (2 ml) in chlorobenzene (10 ml) were slowly added to the reaction mixture at room temperature. The reaction mixture was heated under reflux and the reaction progress was followed by TLC. After 6 hours of heating, the reaction was cooled, poured into water (200 ml) and extracted with dichloromethane. The organic layer was dried over magnesium sulfate and the solvent removed under reduced pressure. The product was
purified by flash chromatography (hexane/dichloromethane). 78.0 mg (66%). $^1H$ NMR (CDCl$_3$) δ: 8.25 (d, $J = 9.2$ Hz, 3H), 6.96 (d, $J = 2.4$ Hz, 3H), 6.68 (dd, $J = 9.2$ Hz, $J' = 2.4$ Hz, 3H), 3.54-3.39 (m, 12H), 1.79-1.69 (m, 12H), 1.53-1.42 (m, 12H), 1.05 (t, $J = 7.2$Hz, 18H). $^{13}C$ NMR (CDCl$_3$) δ: 162.1, 152.0, 142.4, 142.3, 134.8, 128.0, 123.7, 115.4, 114.8, 113.2, 110.4, 77.3, 68.8, 51.7, 29.7, 20.4, 13.9. IR (cm$^{-1}$): 2980, 2925, 2879, 2831, 2212, 1601, 1534, 1404, 1357, 1222. mp 323 °C (dec). MS: m/z 910.0 MS-MS (910.0), m/z: 853.9, 797.9, 726.9. HRMS: Calculated for [M + H]$^+$: m/z 910.5284. Found: m/z 910.5266.

2.1.3 Synthesis

A variety of methods are known to prepare the parent truxenone molecule but the majority of them fall into two main categories as seen in Figure 2.1.1: first, the trimerization of an indane-1,3-dione$^{15}$ (directly or from an indane-1,3-dione precursor or dimer,$^{16}$ method A) and, second, the condensation or trimerization of an inden-1-one derivative (often involving a dihalogenated precursor$^{17,18}$ method B).

![Figure 2.1.1](image)

**Figure 2.1.1.** The two main precursors for the preparation of the truxenones derivatives: an indane-1,3-dione (method A) or the 2,2-dibromoinden-1-one (method B).
The functionalization of the benzene rings in truxenones may result from the condensation/trimerization of already pre-functionalized precursors, such as the conversion of 5-bromoindan-1-one to 4,9,14-tribromotruxenone. Surprisingly, the post-functionalization of the benzene ring(s) in truxenone appears not to have been reported. The preparation of ring annulated truxenones by trimerization of ring annulated indan-1-one or indan-1,3-dione derivatives is rare. Such systems with extra annulated rings usually arise by the condensation/trimerization of the same types of precursors but with the extra rings already present, as in the case of the preparation of 6H-trinaphtho[2,3-a:2',3'-f:2",3"-k]trindene-6,13,20-trione or from conversions of other polycyclic aromatics with the appropriate symmetry, as in the case of the oxidation of decacyclene to give 1,6,11-truxone tricarboxylic acid.

In addition to our main objective, which is the preparation of truxenones substituted in positions 4, 9 and 14 by amine donor groups, we have also made several attempts to incorporate alkoxy groups about the periphery of the truxenone. Both 5,6-dimethoxyindan-1-one and 5,6-dimethoxyindan-1,3-dione were considered as appropriate precursors as the presence of two alkoxy groups may provide several advantages: first, they can increase the solubility of the final truxenone, as well as the propensity to form liquid crystalline phases, and second, in the case of the preparation of the truxenone by method A, the number of isomers produced is limited to one (by comparison, trimerization of the 5-methoxyindan-1,3-dione could result in four different truxenone isomers which would be very difficult to separate). The 5,6-dimethoxyindan-1-one is prepared via intramolecular Friedel-Crafts acylation of the 3-(3’,4’-dimethoxyphenyl)propionic acid by a known procedure. The 5,6-dimethoxyindan-1-one
can then be directly converted to the 5,6-dimethoxyindan-1,3-dione by benzylic oxidation with a \( \text{Cr}^{+6} \) reagent in good yield (52%).\(^\text{10}\) Numerous systems for the conversion of an indan-1,3-dione to a truxenone are known\(^\text{14}\), the most common being trimerization of the indan-1,3-dione in sulfuric acid.\(^\text{21}\) We have found that substituting methanesulfonic acid for sulfuric acid often provides better results. While the application of this approach to 2-hydrocyclopenta[b]naphthalene-1,3-dione to produce \([3,a,4], [8,a,9], [13,a,14]\)-tribenzotruxenone (\(R^1\) and \(R^2 = o\)-phenylene in Table 2.1.1) was successful, unfortunately this method failed when applied to 5,6-dimethoxyindan-1,3-dione. In either acidic or basic media the 5,6-dimethoxyindan-1,3-dione could not be converted to the truxenone as the starting material was either completely degraded (acid media) or recovered (basic media). In this last case, the deactivation of the carbonyl group by the presence of a donor (methoxy groups) could explain this different of behavior.

All attempts to create the desired hexaalkoxytruxenones from the halogenated dialkoxyindan-1-one precursors were also not productive. When we used 2,2-dibromo-5,6-dimethoxyindanone or 2,2-dibromo-3-hydrocyclopenta[b]-6′,7′-dimethoxynaphtalen-1-one as truxenone precursors, the analysis of the reaction mixture by mass spectroscopy showed the complete consumption of the starting material, but without any formation of the corresponding truxenone.
Table 2.1.1. Overview of all the truxenones synthesized here from indan-1,3-dione derivatives in methanesulfonic acid (110 °C, 3 hours).

<table>
<thead>
<tr>
<th>R¹</th>
<th>R²</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMe</td>
<td>OMe</td>
<td>-</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>79%</td>
</tr>
<tr>
<td>o-phenylene</td>
<td></td>
<td>21%</td>
</tr>
</tbody>
</table>

In contrast, in the case of the 2,2-dibromo-5-haloindan-1-ones, the reaction does provide the corresponding 4,9,14-trihalotruxenones, albeit in a modest yield of 20 to 30% (Table 2.1.2).

Table 2.1.2. Summary of the attempts to prepare truxenones from inden-1-one derivatives via the sequence of bromination (Br₂) and pyrolysis (220 °C).

<table>
<thead>
<tr>
<th>R₁</th>
<th>R₂</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMe</td>
<td>OMe</td>
<td>-</td>
</tr>
<tr>
<td>H</td>
<td>Br</td>
<td>30</td>
</tr>
<tr>
<td>H</td>
<td>F</td>
<td>21</td>
</tr>
</tbody>
</table>

The halogenated materials employed in this study could be synthesized from the 3-halodihydrocinnamic acids due to a preference in the regiochemistry of the intramolecular acylation. With the appropriate 5-haloindan-1-ones in hand, they were converted to a 2,2-dibromo-5-halo derivatives, which were subsequently pyrolyzed by the method described by Lambert et al.⁷ to give the respective trihalotruxenone. When we
prepared the precursor 2,2-dibromo-5-fluoroindan-1-one, we noted that Tatsugi and Izawa\textsuperscript{13} obtained this compound from the bromination and oxidation of indan-1-one with NBS-DMSO when they prepared indane-1,2,3-triones. However, the m.p. and NMR data between our compounds are not in consistency (see experimental section). The x-ray crystallography study showed our compound has the expected structure\textsuperscript{22}.

The ability to synthesize the truxenones substituted by fluorine at positions 4,9,14 combined with the fact that the carbonyl substituted central ring activates aromatic nucleophilic substitution\textsuperscript{23,24,25} provides an alternative route for the preparation of the truxenones substituted by an amine donor group. We have realized the triple nucleophilic substitution of the 4,9,14-trifluorotruxenone with some secondary amines including acyclic versions such as dibutylamine and dihexylamine as well as cyclic amines such as pyrrolidine and the chiral secondary amines L-(+)-prolinol and R-(+)-3-pyrrolidinol. The results obtained are summarized in Table 2.1.3.

The difference of yields from these reactions is due to a number of reasons. On the one hand, the longer the alkyl tail of the secondary amine the lower is its nucleophilic activity. On the other hand, the presence of shorter tail lengths results in lower solubility of the product in common organic solvents that complicates the workup of the reaction.
Table 2.1.3: Overview of all the 4,9,14-tris(dialkylamino)truxenones obtained by nucleophilic substitution of the 4,9,14-trifluorotruxenone.

<table>
<thead>
<tr>
<th>R</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>NEt₂</td>
<td>20</td>
</tr>
<tr>
<td>NBu₂</td>
<td>27</td>
</tr>
<tr>
<td>NHex₂</td>
<td>16</td>
</tr>
<tr>
<td>-N</td>
<td>51</td>
</tr>
<tr>
<td>-OH</td>
<td>92</td>
</tr>
<tr>
<td>-N-OH</td>
<td>68</td>
</tr>
</tbody>
</table>

Substitution of the acyclic dibutylamine and dihexylamine by the different pyrrolidines should provide better NLO properties than their corresponding acyclic secondary amine due to increased electron donation\(^{26}\). Unfortunately, simple pyrrolidines also result in a dramatic decrease of the solubility of the compounds in common organic solvents and complicates their implementation and even the measurement of the NLO properties. To circumvent these problems we used the chiral amino alcohols L-(+)-prolinol and R-(+)-3-pyrrolidinol. The free alcohol group permits the addition of a long alkyl chain by means of an ether linkage so as to increase the solubility as shown in Scheme 2.1.1.
For any ultimate use as nonpolar electro-optic media at least two further major features are sought from these materials. First of all, the symmetry of the truxenone must be broken to remove a plane of symmetry, i.e., the plane containing the three ketones and the overall π-system of truxenone must be forced into a propeller shape, yielding a chiral character \((C_{3h} \text{ to } C_3)\). Removal of this plane of symmetry creates two enantiomers, right-handed and left-handed propellers, which ultimately could be separately created by a chiral synthesis or resolved following achiral synthesis. Figure 2.1.2 shows how the molecular geometry changes when a truxenone is converted to its tris(dicyanomethylene) derivative. Second, the molecules must have axial alignment. The truxenones, and the propeller shaped derivatives derived from them, would appear to be good candidates to form discotic liquid crystals which will self assemble to provide the desired macroscopic organization. Currently, liquid crystals with a planar truxenone core (carbonyl groups at positions 5,10,15) appear to be unknown but there are numerous examples of discotic liquid crystals that contain the truxene core (three methylene groups at positions 5,10,15); these include a series of 2,3,7,8,12,13-hexaesters\(^{27}\) and 2,3,7,8,12,13-hexaethers\(^{38}\). There are examples of propeller shaped discotic liquid crystals, but those with twisted cores
appear to be restricted to metal containing chelates wherein the coordination sphere about the metal establishes the propeller geometry.\textsuperscript{29} Such molecules typically relax quickly and thermally between the two enantiomers (right-handed propellers and the left-handed propellers). While such enantiomers can be synthesized and then resolved e.g. by chemical reactions in a chiral environment, the only example we know of which has been resolved in this way has a chromophore which does not have sufficiently large hyperpolarizability to result in interesting nonlinear optical susceptibilities\textsuperscript{30}. Other discotic liquid crystals with thioether tails are nonplanar but the distortions in the aromatic part of the molecule are small.\textsuperscript{31}

\textbf{Figure 2.1.2:} Left: A nearly planar truxenone core (AM1 geometry optimization). Right: The dicyanomethylene substituents (which replace the ketones in the truxenone) interact with the adjacent benzene rings and twist the molecule into a propeller geometry (RHF optimization using SBKJC basis). For simplicity, both molecules are shown with dimethylamino donor groups.

Truxenone itself is a planar $C_{3h}$ molecule wherein there is little or no steric interaction between the carbonyl group(s) and the hydrogen atom(s) on the adjacent rings. However, when methylene carbon atoms bearing additional substituents replace the carbonyl oxygens, the entire molecule becomes distorted and assumes a nonplanar $C_3$ symmetry. This is the case for the known tris-5,10,15-(dicyanomethylene) derivative of the parent truxenone\textsuperscript{32} as well as for the tris-5,10,15-(fluorinylidene) compound.\textsuperscript{33} The
dicyanomethylene group is a well known acceptor group in NLO materials and as such it could serve a dual role here as an acceptor group and also the source of nonplanarity due to the interactions of the nitrile group(s) with the adjacent donor-substituted ring(s). Quantum chemical Restricted Hartree-Fock (RHF) calculations were carried out to examine the influence of the dicyanomethylene groups and the results confirmed that the equilibrium geometry is nonplanar. These optimization calculations were done with GAMESS\textsuperscript{34}, using the SBKJC basis with an effective core potential and assuming a three-fold rotation axis. It is, in principle, possible to have another isomer of the tris(dicyanovinyl) compound: not all the dicyanovinyls need to be on the same side of the fused ring structure. Consistent with the observation that only one isomer is obtained, GAMESS calculations (semiempirical AM1) confirm that the unsymmetrical isomer has significantly (7.4 mH or 4.6 kcal/mole) higher energy. This is enough of a difference to make the product predominantly that shown, as is observed experimentally, at least if the reaction is approximately an equilibrium reaction.

The conversion of parent truxenone to its tris(dicyanomethylene) derivative was accomplished using a pyridine-TiCl\textsubscript{4} system.\textsuperscript{35} This method has been applied here to the tris(dibutylamino)truxenone in order to prepare its tris(dibutylamino)tris(dicyanomethylene) derivative in 66% yield. This derivative now has the requisite propeller symmetry and it is a racemic mixture of two propeller enantiomers (or diastereomers in the cases when chiral amines were employed). Unfortunately, none of the amine substituted tris(dialkylamino)truxenones or their tris(dicyanomethylene) derivatives prepared in this study were mesogenic. All these compounds possessed
simple crystal to isotropic transitions and in some cases the clearing transition was not reversible due to decomposition.

![Chemical structure](image)

**Scheme 2.1.2.** Transformation of the 4,9,14-tris(dibutylamino)truxenone (Trux-3NBu$_2$) to its tris(dicyanomethylene) derivative (Trux-6CN-3NBu$_2$) by the reagent system pyridine-TiCl$_4$.

### 2.1.4 Linear and NLO Properties

We have previously described the molecular and bulk properties required for axially aligned chiral second-order nonlinear optical media.$^5$ When the molecular first hyperpolarizability tensor $\beta_{ijk}$ is expanded in terms of rotationally invariant tensor components, the figure of merit of the Kleinman-disallowed component that transforms as a second rank tensor of mixed symmetry contributes to the nonlinear optical response of chiral uniaxial media. We have developed the method of Kleinman-Disallowed Hyper Rayleigh Scattering (KD-HRS) in order to measure the figures of merit for all of the rotationally invariant tensor components.$^{36}$ As this technique is able to characterize rotationally invariant figures of merit of the hyperpolarizability tensor, it provides considerably more information than electric field induced second harmonic generation (measuring the Kleinman allowed vector component) and 90 degree hyper-Rayleigh
scattering which (generally) results in only two numbers which are then interpreted as giving the vector and octupolar Kleinman allowed components.

The solubility of many truxenones in most common solvents is so small that measurements with our HRS set-up were not possible for some of the compounds. For this reason, the characterization of $\beta_{ijk}$ using KD-HRS was carried out only on the more soluble homologs for which the amino groups are diethylamino (Trux-3NEt$_2$), dibutylamino (Trux-3NBu$_2$), prolinoxypropyl (Trux-3POPr) and 3-pyrrolidinoxyhexyl (Trux-3POHex), and one tris(dicyanomethylene) derivative (Trux-6CN-3NBu$_2$).

The choice of the wavelength of the probe beam was guided by the absorption spectra of the different compounds. In Figure 2.1.3 is seen the UV-Vis spectrum of Trux-3NBu$_2$ (truxenone substituted with three dibutylamino groups, which is representative of all the truxenones substituted by an amino group) and the spectrum of its tris(dicyanomethylene) derivative (Trux-6CN-3NBu$_2$).

![Absorption spectra of Trux-3NBu$_2$ (solid line) and Trux-6CN-3NBu$_2$ (dashed line) obtained in dichloromethane solution.](image)

Figure 2.1.3. Absorption spectra of Trux-3NBu$_2$ (solid line) and Trux-6CN-3NBu$_2$ (dashed line) obtained in dichloromethane solution.
Unlike typical dipolar NLO molecules with a single, high transition dipole moment, clear charge transfer band, these spectra are very structured and show multiple absorption peaks, with the lowest lying peak relatively weak. This relatively weak lowest lying absorption in Trux-3NBu$_2$, which seems to be a mixture of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, is also observed in the parent 9H-fluoren9-one molecule$^{37}$ and 3-dimethylamino-9H-fluoren9-one$^{38}$. In addition weak, low-lying $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions are confirmed by our own ZINDO calculations on this molecule. Results of a ZINDO/S all singly excited configuration interaction calculation (done with Gaussian03$^{39}$) on Trux-6CN-3NBu$_2$ suggest that the weak low-lying absorptions are due to $\pi \rightarrow \pi^*$ transitions only. For both truxenone molecules mentioned above the weak $\pi \rightarrow \pi^*$ transitions result mainly from poor HOMO-LUMO overlap. The calculations on Trux-6CN-3NBu$_2$ show two doubly degenerate (E-type) excited states with oscillator strengths greater than 1 in the wavelength range shown in Figure 2.1.3. The calculations also predict two more doubly degenerate and one nondegenerate (A-type) excited states with moderate oscillator strengths between 0.3 and 0.6. Many other weak transitions are also predicted in this range. The CIS calculation is not good enough to capture all the richness of the excited states (and thus allow assignments of all of the bands in Figure 2.1.3 to be made), but it does suggest that multiple strongly absorbing excited states are concentrated in a relatively small wavelength band, and also confirms that the most strongly absorbing degenerate (E-type) states are not the lowest lying excited states. For good Kleinman allowed non-linear optical behavior, strongly absorbing low-lying E-type states are preferred. For efficient Kleinman disallowed non-linear optical behavior ($\beta_{2,mm}$ second rank tensor susceptibility), such low-lying states, preferably with an additional
strongly absorbing non-degenerate A-type state, are best. These molecules can be thought of as linear chromophores coupled together through the common central ring. Given that the excited states have large amplitude on the (strongly accepting) central ring carbons, the three mutually interacting arms of the molecule yield a complicated excited state structure. The numerous states observed experimentally and in ZINDO calculations clearly shows that this is an over simplified picture: other electronic states must contribute. This suggests that future theoretical and synthetic work can improve the properties of such molecules.

Due to these broadband absorption properties, the KD-HRS experiment cannot be done in the visible wavelength range. Thus, measurements were performed with the fundamental at 1560nm. The experimental setup and analysis, which determine the four rotational invariants of the hyperpolarizability $\beta$ tensor, are discussed in a previous paper. Although the selected truxenones have good solubility in most common solvents, we have preferred to make the measurements in benzene rather than halogenated solvents like chloroform or dichloromethane. In fact, when the compounds are measured in chloroform solutions, there is an obvious degradation of the compounds with the irradiation time as evidenced by a color change and by a difference in the two photon fluorescence emission spectra before and after irradiation. When the experiments were carried out in benzene solution, neither degradation nor changes in fluorescence were observed.

Since the hyperpolarizabilities of the solvents are too small to be measured in our setup, the external reference method$^{40}$ has been used here. Disperse Red 1(DR1) was chosen as the reference because it is one of the most studied NLO chromophores and its
Rotational invariants can be directly related to the EFISH measurements by the relationship, $\beta_{1ss} = \sqrt{\frac{3}{5}} \beta_{\text{EFISH}}$. The $\beta_{1ss}$ and $\beta_{3ss}$ are the well-known polar and octupolar figures of merit, respectively. Previous EFISH measurements give the hyperpolarizability values as $\beta_{\text{EFISH}} = 125 \times 10^{-30}$ esu at 1360nm (see ref 38, p. 489). A two-level model has been used to estimate the $\beta$ value of the Disperse Red 1 at 1560nm.

The rotational invariants of the hyperpolarizability tensors of the molecules measured (Table 2.1.4) are listed in Table 2.1.5.

All the amine substituted truxenones studied show appreciable hyperpolarizability values. The large Kleinman-disallowed components ($\beta_{1mm}$ and $\beta_{2mm}$) indicate breaking of Kleinman symmetry for these multidimensional materials. We also note that the values of $\beta$ increase when we change from dibutylamino or diethylamino to pyrrolidino derivatives. In fact, it is well known that amongst dialkylamino groups that pyrrolidine provides one of the strongest donor effects, which we anticipated would slightly lower the transition energies and increase the transition moments relative to the derivatives with an acyclic amino group. For this reason, the Kleinman allowed hyperpolarizabilities of the compounds containing this cyclic amino group were expected to be larger than the compounds containing an acyclic amino group, as both these effects would increase the sum over states expression for the Kleinman allowed hyperpolarizabilities, particularly in the region for which both the fundamental and second harmonic are below the lowest lying absorption energy of the molecule.
<table>
<thead>
<tr>
<th>Truxenones</th>
<th>Tris(dicyanomethylene) derivative</th>
</tr>
</thead>
<tbody>
<tr>
<td>R=</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>Trux-3NEt₂</td>
</tr>
<tr>
<td>N</td>
<td>Trux-3NBu₂</td>
</tr>
<tr>
<td>OC₆H₁₃</td>
<td>Trux-3POHex</td>
</tr>
<tr>
<td>N</td>
<td>Trux-3POPr</td>
</tr>
<tr>
<td></td>
<td>Lambert’s compound</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1.4. Structure of all the truxenones and the tris(dicyanomethylene) measured by KD-HRS in this study as well as the phenylethynyl bridged truxenone synthesized by Lambert et al.
Table 2.1.5. Rotational invariants (in units of $10^{-30}$ esu) measured by KD-HRS at 1560 nm. The calculated depolarization ratio is determined from KD-HRS measurements while the experimental depolarization ratio is directly determined from 90 degree HRS measurements.

Contrary to our expectations, linear absorption data suggests that the low-lying ground to excited state transition moments are slightly decreased (by $\sim$5% on average) when going from the acyclic to cyclic amino donors, and there is virtually no change in
energy. Thus, there must be some other cause for the increase of the hyperpolarizabilities of the pyrrolidino derivatives, most probably an increase in transition moments between excited states. The similar value obtained for \textbf{Trux-3POPr} and \textbf{Trux-3POHex} indicates also that the alkoxy chains introduced to improve the solubility of the compounds have, as anticipated, little influence on the NLO properties. The large improvement observed between \textbf{Trux-3NBu}_2 and \textbf{Trux-6CN-3NBu}_2 was also expected, due to the fact that the substitution of the carbonyls by dicyanomethylene groups will enhance the withdrawing influence of the central ring, and by consequence should lower the excitation energies and increase the transition moments. The twisting of the core due to the dicyanomethylene group will offset some of the gain in the transition moments polarized in the plane (E-type), but will increase transition moments polarized along the C\textsubscript{3} axis (A-type), hence increasing all of the rotationally invariant components of the hyperpolarizability tensor.

The large vector components ($\beta_{1ss}$ and $\beta_{1mm}$) suggest non-planar structures with a non-zero dipole. The large $\beta_{2mm}$ components, which require a special axis in the molecule (more precisely a non-zero second rank traceless symmetric pseudotensor), are of interest for second-order nonlinear optics in uniaxially aligned chiral media. If the molecules are considered to be planar, the only special axis in these molecules as shown (and as suggested by careful molecular modeling) is the three-fold rotation axis perpendicular through the plane of the central benzene ring, in which plane the electrons contributing the nonlinear optical response move. With the naïve $C_{3h}$ symmetry for the triketone, the additional mirror symmetry is consistent with a traceless symmetric second rank tensor and not a traceless symmetric second rank pseudotensor. Thus, there must be
conformational or other fluctuations of the ketones away from their putative symmetry, in order to result in these non-zero root mean square (RMS) averages. These fluctuations seem to be intrinsic to the triketone molecules as the HRS for the Trux-3NEt₂ has very comparable vector and pseudotensor contributions in two different solvents: benzene and 1,4-dioxane.

In fact, quantum chemistry calculations suggest that, while the ring system is very close to planar, the amines are somewhat non-planar, with their two alkyl substituents slightly out of the plane of the π system. This small change, which also results in small motions out of plane of other atoms, is not expected to make the optically responsive part of these molecules particularly non-planar – the small deviations from planarity primarily involve optically non-responsive atoms. However, there do seem to be rather low energy vibrations in the triketones, which result in out of plane twisting of the molecules. These may be the source of these symmetry-disallowed contributions. These unexpected fluctuations are not expected to contribute to the nonlinear susceptibility in a chiral uniaxial condensed phase so the magnitude of the nonlinear optical tensor in such a phase made from the tris(dicyanomethylene) is less certain. The large hyperpolarizability components obtained for all these truxenones indicate interest in these molecules for future NLO applications.

The depolarization ratio is often determined in standard HRS measurements. Thus, it is a useful check of results to calculate the depolarization ratio from the rotational invariants in KD-HRS measurements. In a standard 90 degree HRS experiment the depolarization ratio is defined as $D_{zz}^{xx} = \frac{I_{\perp}}{I_{\parallel}}$, where the $I_{\perp}$ and $I_{\parallel}$ represent the second harmonic scattering intensity when the incident and outgoing polarization states are
orthogonal and parallel to each other, respectively. In the KD-HRS experiment we can express the $I_\perp$ and $I_\parallel$ in terms of the rotational invariants and therefore calculate the depolarization ratio. In Table 2.1.5, we compare the value calculated in this manner from KD-HRS measurements to those determined directly from 90 degree HRS measurements as an internal consistency check on our measurements. The reasonable agreement in Table 2.1.5 between the calculated and measured values of this ratio provides confidence in our results. However, the putative symmetry of the triketone compounds would suggest a depolarization ratio of 2. This overall disagreement with this expected value is another reflection of the fluctuations away from the putative symmetry leading to non-zero vector components.

The determination of the rotational invariants and the depolarization ratios allow us, by using the relation (1), to calculate the corresponding $\beta$ value in nonpolarized Hyper Rayleigh Scattering experiments ($\beta_{\text{unpolarized}}$) and then compare our results with those in the literature. In fact, Lambert et al also found large hyperpolarizabilities in similar phenylethynyl bridged truxenone derivatives (which gives $\beta_{\text{ref}} = \sqrt{8/21} \times 355 \times 10^{-30}$ esu = $219 \times 10^{-30}$ esu at 1500 nm, for a molecule for which the lowest energy absorption maximum is at 508 nm), using unpolarized Hyper Rayleigh Scattering (HRS), i.e. no polarizer for the second harmonic scattering.

$$\beta_{\text{unpolarized}} = (\beta_{1ss} \times \sqrt{3} + 2/\sqrt{7} \times \beta_{3ss}) \times \sqrt{(1 + 1/D_{zz})} \quad (2.1)$$

The calculated $\beta$ values in unpolarized Hyper Rayleigh Scattering (the experimental depolarization ratios are used for calculation) are listed in Table 2.1.6 and compared to
the previous results obtained by Lambert et al ($\beta_{\text{ref}}$). Since our measurements are done at 1560nm and theirs at 1500nm, a simple calculation using the two-level model gives a reference $\beta_{\text{ref}}$ equal to $204 \times 10^{-30}$ esu. In Table 2.1.6 the absorption peaks refer to the lowest energy peaks since all the truxenones present multiple absorption peaks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\beta_{\text{unpolarized}}$ ($\times 10^{-30}$ esu)</th>
<th>$\beta_{\text{unpolarized}} / \beta_{\text{ref}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lambert’s sample</td>
<td>508</td>
<td>204</td>
<td>1</td>
</tr>
<tr>
<td>Trux-3NBu$_2$</td>
<td>465</td>
<td>212</td>
<td>1.04</td>
</tr>
<tr>
<td>Trux-3Net$_2$</td>
<td>461</td>
<td>247</td>
<td>1.21</td>
</tr>
<tr>
<td>Trux-3POPr</td>
<td>455</td>
<td>326</td>
<td>1.60</td>
</tr>
<tr>
<td>Trux-3POHex</td>
<td>459</td>
<td>316</td>
<td>1.55</td>
</tr>
<tr>
<td>Trux-6CN-3NBu$_2$</td>
<td>582</td>
<td>327</td>
<td>1.60</td>
</tr>
</tbody>
</table>

Table 2.1.6. Characteristics of different truxenone derivatives, where $\lambda_{\text{max}}$ is the maximum absorption of the lowest energy absorption peak; $\beta_{\text{unpolarized}}$ is the unpolarized hyperpolarizability values calculated from rotational invariants by the relation (I), and $\beta_{\text{unpolarized}} / \beta_{\text{ref}}$ is the ratio between the unpolarized hyperpolarizability values of the compound and that of Lambert’s compound.

If the results obtained for Trux-3NBu$_2$ and Trux-3NEt$_2$ are similar, the three other compounds show a large improvement of the $\beta$ value and then of the NLO properties of this kind of material. In general, it would be expected that the closer we get to a resonance the larger the expected hyperpolarizability. This is less clear in these truxones as in general it seems that states, which have larger extinction coefficients, also have higher energies. This fact is expected from symmetry and heuristic chemistry and confirmed by ZINDO/S quantum chemistry calculations. If we think of three excited states on each part of the molecule and suppose that these states “spread out” over the molecule in a symmetric way, (e.g. in a way transforming according to the $A$ rather than
the $E$ representation of $C_3$) then in the $C_{3h}$ symmetry appropriate to the ketones this state will have no transition dipole moment to the ground state. This, in turn, implies that there is no absorption, or rather that there should be absorption only through symmetry violating transitions, vibrations, etc. Moreover, ZINDO calculations suggest – and this seems likely from the linear absorption data but is harder to discern from heuristic chemistry – even low-lying states which have symmetry allowed transitions have relatively small absorption cross-sections: the strong absorption maximum is associated with a relatively high lying state. As it is generally expected that states which contribute strongly to the linear absorption also contribute strongly to the non-linear hyperpolarizability, it is not clear that the lowest energy absorption maximum is the peak relevant to understanding the hyperpolarizabilities. Nevertheless we see that all these molecules have in common the fact that they have relatively weak low-lying absorptions. In the end, the larger hyperpolarizabilities of the molecules synthesized for this work confirms our belief that the direct connection between the rigid $\pi$ system in the center and the donors, rather than the phenylethynyl connection used by Lambert et al results in improved non-linear optical properties.

2.1.5 Conclusion

The synthesis of several new truxenones substituted by different amino groups at positions 4, 9 and 14 has been accomplished exploiting aromatic nucleophilic substitution reactions of the new fluorotruxenone precursors. One of these aminotruxenones was successfully converted to its nonplanar dicyanomethylene derivative. For representative materials in this series a complete characterization of NLO properties was carried out by
Kleinman-Disallowed Hyper Rayleigh Scattering (KD-HRS). The major electronic effects and the influence of the structural modifications on the NLO properties have been examined experimentally and theoretically. Due to their trigonal symmetry and the large first hyperpolarizabilities that have been determined, these compounds are of interest for second-order nonlinear optics in uniaxially aligned chiral media. In order to fully exploit these materials, further effort dedicated to the interesting and challenging optical resolution of the diastereomeric materials remains to be pursued. We also believe that with appropriate molecular design, e.g. the addition of other donor groups, significant improvements to the hyperpolarizabilities can be made, and the strongly absorbing states can be shifted closer to the lowest lying absorptions, or the lowest lying absorptions can be made to absorb more strongly. The addition of such donor groups, with appropriate alkyl chains, should also allow the formation of liquid crystalline states, which are of interest for our ultimate goal of forming chiral axial phases by self-assembly. Such alignment is particularly of interest for resolved chiral chromophores as this would allow the unambiguous measurement of Kleinman disallowed average nonlinear optical susceptibilities.

**Acknowledgements**

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2.2 Synthesis of Discotic Hexaalkoxytruxenones for Nonlinear Optical Applications

Lionel Sanguinet, Zhiyong Yang, Jarrod C. Williams, Robert J. Twieg
Guilin Mao, Kenneth Singer, Greg Wiggers, Rolfe Petschek

2.2.1 Introduction

Multipolar molecules, quadrupoles and octupoles, have been increasingly examined as alternatives to the more conventional dipolar push-pull chromophores as nonlinear optical (NLO) materials. In the search for more efficient NLO chromophores, this alternative approach from simple dipolar systems involves expanding the charge transfer from one to two or three dimensions by connecting donor and acceptor groups with a variety of spatially extended $\pi$ conjugation. Such higher-dimensional networks, where the connectivity between active groups is central or lateral, have been proposed and studied for more than a decade\textsuperscript{41,42}. The influence of chromophore dimensionality has also been examined for a growing number of other optical phenomena. For example, Cho \textit{et al.}\textsuperscript{43} has observed a linear relationship between two-photon absorption (TPA) cross section values and the first hyperpolarizability of a multipolar NLO chromophore and Lahankar, \textit{et al} has studied electronic interactions in branching chromophores.\textsuperscript{44} With the goal of identifying a good multipolar NLO candidate, Feng \textit{et al.}\textsuperscript{45,46} have reported a theoretical investigation on some truxene and truxenone derivatives. In fact, the truxene ring system has been known for well over a century\textsuperscript{1} and over the last two decades it has been the
subject of a number of relevant studies. The properties of truxenes, including their thermal stability\textsuperscript{47}, electrochemistry\textsuperscript{48}, and mesomorphic behavior\textsuperscript{49} are all leads for further applications in other diverse areas as electronic materials\textsuperscript{50}. While truxenes have been examined in nonlinear optics in the field of two-photon absorption\textsuperscript{51}, Lambert \textit{et al} have also highlighted the promising first hyperpolarizabilities of their triketone derivatives: the truxenones.\textsuperscript{7}

The central rings of planar truxenes and, much more so, the truxenones, are good electron acceptors and the $C_{3v}$ symmetry results in charge transfer in a minimum of two dimensions. When disubstituted carbon atoms replace the carbonyl oxygens in truxenone, the entire molecule becomes sterically congested and it distorts to nonplanar propeller shaped $C_3$ symmetry. The charge transfer dimension then evolves from two to three dimensions. This $C_3$ symmetry is found in the known tris-5,10,15-(dicyanomethylene) derivative of the parent truxenone\textsuperscript{35} as well as for the tris-5,10,15-(fluorinylidene) compound.\textsuperscript{33} The practical implementation of these multipolar chromophores requires their ultimate incorporation into chiral materials\textsuperscript{52} - polymers or thin films - that are subsequently processed. To simplify the processing, we propose here to develop a new family of truxenone derivatives, which should possess large optical nonlinearities and also spontaneously self assemble as discotic liquid crystals and thus assist in the essential macroscopic alignment.

\subsection*{2.2.2 Synthesis}

The preparation methods for simple truxenones and truxenes are well known. The major approaches are based on an aldol trimerization of an indane-1,3-dione (directly or from a precursor or dimer)\textsuperscript{53} and from an indan-1-one, for the truxenones and the truxenes
respectively. A second method to prepare some truxenones directly involving the pyrolysis of a 2,2-dihalogenated derivative of an indan-1-one has also been reported\(^{49,18}\) (Scheme 2.2.1). Since there has been recent renewal of interest in these molecules as potential intermediates for the synthesis of fullerenes,\(^{54,55,56}\) additional methods of preparation of truxenone continue to be developed.

![Scheme 2.2.1](image_url)

*Scheme 2.2.1.* The two main preparation routes of truxenones proceed from either an indan-1,3-dione (route A) or from a 2,2-dibromoindan-1-one (route B).

Functionalization of the benzene rings in truxenones results from the condensation/trimerization of already pre-functionalized precursors\(^{57}\), as in the case of conversion of 5-bromoindan-1-one to 4,9,14-tribromotruxenone. Surprisingly, the post-functionalization of the benzene ring(s) in truxenone appears to not have been reported. For this reason we initially sought a synthetic strategy involving the incorporation of the donor group(s) early in the synthesis. We also have to consider what influence these donating group(s) might have on both the electronic properties of the molecule and also on its liquid crystal behavior. While dialkylamino groups are certainly excellent donor groups, they appear in liquid crystalline materials only relatively rarely. We have recently reported the synthesis of a variety of amine substituted truxenones with large multipolar nonlinearities but we have observed no mesogenic properties amongst any of them.\(^{58}\) As far as liquid crystal properties go, alkoxy groups are often a better choice. In fact, it is
well established that for the parent truxene, six alkoxy chains about the periphery at the 2,3,7,8,12,13-positions are sufficient to introduce liquid crystal behavior. As such, we embarked on this study with the expectation that the analogous hexaalkoxy truxenones would also be liquid crystalline.

Both 5,6-dimethoxyindan-1-one and 5,6-dimethoxyindan-1,3-dione were considered as suitable precursors for the preparation of discotic truxenones. The presence of two alkoxy groups was seen as advantageous in two ways: first, two tails (vs. a single tail) on each external benzene ring will enhance the likelihood of mesogenic behavior of the final truxenone, and second, at least in the case of the preparation of the truxenone by method A, the number of isomers produced would be limited to one. In comparison, the condensation of 5-methoxyindan-1,3-dione by method A could give four different isomers which would be very difficult to separate. The 5,6-dimethoxyindan-1-one itself was prepared via an intramolecular Friedel-Crafts acylation of 3-(3’,4’-dimethoxyphenyl)propionic acid by a known procedure. Subsequent bromination, producing the 2,2-dibromo-5,6-dimethoxyindan-1-one, was accomplished under standard conditions. Of course, the successful use of any of these methoxy substituted precursors is predicated by the necessity to ultimately convert the methoxy groups to the larger alkoxy groups.

Our first attempt to create 3,4,8,9,13,14-hexaalkoxytruxenones by the pyrolysis of 5,6-dialkoxy substituted 2,2-dibromoindan-1-one precursors was not productive. When we applied the method developed by Lambert et al. to 2,2-dibromo-5,6-dimethoxyindanone, the analysis of the pyrolysis product mixture by mass spectroscopy showed the complete consumption of the starting material but revealed only trace
amounts, at best, of the desired 3,4,8,9,13,14-hexamethoxytruxenone. In contrast, the pyrolysis of both 2,2,5-tribromoindan-1-one and 2,2-dibromo-5-fluoroindan-1-one provides modest (20-30%) yields of the respective trihalotrunxenone.\textsuperscript{58} As such, the pyrolytic method applied to 2,2-dibromo-5,6-dimethoxyindan-1-one appears to be incompatible with this more acid sensitive material. The deprotection of the methoxy groups by the HBr liberated by the reaction and the oxidation of the resulting phenolic compound could be an explanation for the failure here.

Fortunately, other methods for the conversion of an indan-1,3-dione to a truxenone are known. The 5,6-dimethoxyindan-1-one can be directly converted to the 5,6-dimethoxyindan-1,3-dione by benzylic oxidation with a Cr\textsuperscript{+6} reagent in a good yield (52\%).\textsuperscript{10} (Scheme 2.2.2). In the literature the most common conditions for the direct trimerization of an indan-1,3-dione involve the use of sulfuric acid.\textsuperscript{21} In our hands, we have found the substitution of methanesulfonic acid for the sulfuric acid often provides better results. Unfortunately, the extension of this method to 5,6-dimethoxyindan-1,3-dione did not provide the desired product as the starting material is consumed but no 3,4,8,9,13,14-hexamethoxytruxenone is obtained. Much to our surprise, the implementation of the complementary classical method for the conversion of indan-1,3-diones to truxenones in basic media (pyridine for example) also failed when applied to 5,6-dimethoxyindan-1,3-dione. In this case the starting material was recovered unchanged.
Subsequently, we concentrated our efforts on the utilization of acidic media for the trimerization of 5,6-dimethoxyindan-1,3-dione with the intention of increasing the electrophilic character of the carbonyl. One method tested involved the utilization of silica and microwave irradiation in the solid state.\cite{59} This method did result in a reasonable yield of the dimethoxyindan-1,3-dione dimer (1) but the desired hexamethoxytruxenone trimer was not produced to any significant extent. Another approach examined involved the utilization of a Lewis acid to enhance the electrophilic character of the carbonyl group\cite{60}. In this case we examined a system of titanium tetrachloride in pyridine. Under these conditions, the reaction of 5,6-dimethoxyindan-1,3-dione produced a complicated mixture. The analysis by MS of the crude product reveals the presence of three major compounds: dimer (1), trimer (2) and truxenone (3), wherein the dimer product usually predominated (Scheme 2.2.3).

\textbf{Scheme 2.2.2.} Transformation of 3-(3’,4’-dimethoxyphenyl)propionic acid into either 5,6-dimethoxyindan-1,3-dione or into a 5,6-dialkoxyindan-1-one with longer tails.
Scheme 2.2.3. Structure of the dimer (1), trimer (2) and the truxenone (3) resulting from the condensation of the 5,6-dimethoxyindan-1,3-dione.

Perhaps solubility issues may play a role here, should the six methoxy groups not solubilize the truxenone precursors sufficiently. In an attempt to circumvent this potential problem, we have also examined the reaction of 5,6-dibutoxyindan-1,3-dione in the titanium tetrachloride / pyridine system. This method results in the production of 3,4,8,9,13,14-hexabutoxytruxenone in a very low yield (4%) that was unacceptable for further studies.

To improve the synthesis of the hexaalkoxytruxenones we examined a new approach based on the post-functionalization of the hexaalkoxytruxenes. Fortunately, a reasonable synthesis for the mesogenic 2,3,7,8,12,13-hexalkoxytruxenes has already been reported involving the trimerization of 5,6-dialkoxyindan-1-ones in polyphosphate ester (PPE). Conversion of the hexaalkoxytruxene to the analogous hexaalkoxytruxenone would then require an oxidation at each of the three methylene sites. Numerous methods are known for the oxidation of the single bis-benzylic site in fluorene to give fluorenone\textsuperscript{61,62,63}. After several attempts, we found that a mixture of activated manganese
dioxide and potassium permanganate was a useful oxidant to convert the truxenes to truxenones in acceptable yields (Scheme 2.2.4). With this reagent we have synthesized three new truxenones, with either six butoxy, octyloxy or dodecyloxy groups, in acceptable yields (39-65%). Unfortunately, the extension of this method for preparation of hexamethoxytruxenone from hexamethoxytruxene was not possible, again due to solubility problems. In this case the reaction appears to lead to a mixture of partially oxidized compounds that have resisted separation by crystallization or chromatography. Another useful, and perhaps still more reliable, oxidation system, especially for the substrates with longer alkoxy tails, is a mixture of pyridinium dichromate and 70% t-butylhydroperoxide that we have adopted more recently for the truxene to truxenone conversion.64

Truxene itself is a planar C₃ₙₘ molecule wherein there is little or no steric interaction between the carbonyl group(s) and the hydrogen atom(s) on the adjacent rings. However, when the methylene carbon atoms bearing additional substituents replace the carbonyl oxygens, the entire molecule becomes distorted and it assumes a nonplanar C₃ propeller symmetry. This is the case for the known tris-5,10,15-(dicyanomethylene)
derivative of the parent truxenone as well as for the tris-5,10,15-(fluorinyldiene) compound. The dicyanomethylene group is a well known acceptor group in nonlinear optical materials and as such it could serve a dual role here as an acceptor group and also the source of nonplanarity due to the interactions of the nitrile group(s) with the adjacent donor-substituted ring(s).

The conversion of parent truxenone to its tris(dicyanomethylene) derivative has already been accomplished using a pyridine / TiCl₄ system. This method has been extended here (Scheme 2.2.5) to all the hexaalkoxytruxenones described above. These molecules possess the requisite propeller symmetry of interest for nonpolar electrooptics.

Scheme 2.2.5. Conversion of hexaalkoxytruxenones to their corresponding tris(dicyanomethylene) derivatives (R = C₄H₉, C₈H₁₅, C₁₂H₂₅).

2.2.3 Linear Absorption

The UV-visible absorption spectra of truxene-6OC12, trux-6OC12, and trux-6CN-6OC12 are seen in Figure 2.2.1. Each of these molecules has several closely-spaced excited states, roughly corresponding to strongly coupled excited states on each leg of the molecule, leading to relatively broadband absorption characteristics. The red shifts
relative to truxene-6OC12 due to the carbonyl and dicyanomethylene substitutions follow our expectations, as dicyanomethylene is a stronger acceptor than the carbonyl group. In order to examine the nature of the excited states, the ZINDO/S Configuration Interaction Singles (CIS) routine in Gaussian03 was used to calculate first ~20 excited states of these molecules. Optimized geometries were calculated with the AM1 semi-empirical Hamiltonian, and the non-planarity of trux-6CN-6O12C was confirmed (see Figure 2.2.2).

![Absorption Spectra](image)

**Figure 2.2.1:** Absorption spectra ($C_6H_6$) showing the influence of substitution at the methylene position.
All of the molecules exhibited a general characteristic of having weak lowest-lying transitions. In the Truxene-6OC12 parent compound, the two lowest lying excitations (with calculated wavelengths of 337 nm and 326 nm) have $\pi \rightarrow \pi^*$ character and are predicted to be optically inactive within the $C_{3h}$ point group. One or both of these states is likely responsible for the very weak absorption seen near 375 nm. The low energy absorption tail in the Truxene-6OC12 spectrum (from about 450 nm to 550 nm) seems to be the result of several optically forbidden transitions; two transitions similar to those in the truxene with $\pi \rightarrow \pi^*$ character, and three additional ones with $n \rightarrow \pi^*$ character, associated with the lone pairs on the ketone oxygens. Furthermore, the first optically allowed E-symmetry $\pi \rightarrow \pi^*$ transition, predicted to be at 392 nm, has a calculated oscillator strength of only 0.1, and is mainly composed of a HOMO $\rightarrow$ LUMO transition. This is not surprising as a similar behavior is known in the HOMO $\rightarrow$ LUMO transition of the parent 9H-fluoren9-one molecule. The optical transitions in the tris-dicyanomethylene compounds are similar to those in the tris-ketones, except that no $n \rightarrow \pi^*$ transitions are predicted in the range of interest. The long wavelength tail from 525 nm to 625 nm in the Trux-6CN-6OC12 molecule is mainly the result of an E-

**Figure 2.2.2:** (a) The geometry of the Trux-6O core is nearly planar, whereas (b) the Trux-6CN-6O core shows deviation from planarity. Calculations were performed with Gaussian03.
symmetry HOMO → LUMO $\pi \rightarrow \pi^*$ transition with a calculated oscillator strength of 0.2: there is in addition an A-symmetry excited state with slightly lower energy. Given the symmetry ($C_3$) this state is (weakly) allowed. These weak transitions are not expected to play a major role in determining the NLO response of the molecules.

The strongest absorbing transitions in all of the truxenes, ketones and the tris(dicyanovinyl) derivatives of these molecules are E-type $\pi \rightarrow \pi^*$ transitions originating from complicated CIS states that contain multiple configurations involving approximately the 5 highest occupied molecular orbitals and 5 lowest unoccupied molecular orbitals. It is not surprising that the strongly absorbing states should be E-type because this corresponds to absorption of light polarized in the plane of the molecule because the plane in which the $\pi$ electrons are delocalized is close to the plane perpendicular to the rotation axis e.g. in the plane containing the two transition dipoles that transform like the E representation. The ZINDO calculations reproduce the main features and trends from the data in Figure 2.2.1 reasonably well. The ratio of the oscillator strengths of the two longest wavelength absorptions for Trux-6CN-6OC12 is predicted to be almost 2:3. For the Truxenone-6OC12 molecule, the calculations suggest that each of the two large peaks in the spectrum is mainly composed of two separate E-type transitions that are too close in wavelength (i.e. within 20 nm) to be resolved experimentally. Thus, the shoulders on both of the main peaks most likely come from electronic transitions and not from some type of vibrational structure. The ratio of the combined oscillator strengths of the two longer wavelength transitions to the two shorter wavelength transitions is calculated to be 4:3, which is very close to the ratio of the heights of the two peaks from the measured spectrum. In both of the donor-substituted
derivatives the overall transition energies calculated by ZINDO are about 15-20% higher than experiment. Finally, for the Truxene-6OC12 molecule, the first strong E-type state is predicted to be at 323nm, in close agreement with the data. The ratio of oscillator strengths between this state and the next large E-type state is calculated to be about 1:1. With confidence that we can calculate the oscillator strengths of the lowest lying excited states in these molecules, we can analyze the hyperpolarizabilities using the quantum mechanical sum-over-states (SOS) model, which requires excited state – excited state transition moments not available from experiment.

2.2.4 Nonlinear Optical Properties

Low-lying states with E-type symmetry make strong contributions\textsuperscript{65} to the SOS expression for an in-plane octupolar hyperpolarizability. \( \beta_{xxx} = -\frac{1}{3} \beta_{xxy} \), which is the dominant component of the octupolar \(( \beta_{3xx} )\) term. In this contribution, the three states include the ground state and two states belonging to an E-type excited state, which states can be either identical or simply degenerate. For the Kleinman-disallowed \( \beta_{xyz} \) component (which determines \( \beta_{2nm} \)), 3-states are required for contributions, which must include an excited A-type state in addition to the ground state and (both components of) a degenerate E-type excited state. Our ZINDO calculations predict that the dicyanomethylene-substituted compound has an A type excited state (\( f \sim 0.3-0.4 \)) sandwiched between the two lowest strong E-type states. The existence of this A-type state probably causes the asymmetric lineshape near 400nm for trux-6CN-6OC12 in Fig 2.2.1, and makes Kleinman-disallowed hyperpolarizabilities feasible. In contrast,
Kleinman-disallowed hyperpolarizabilities are expected to vanish by symmetry for planar truxenones, for which this A-type excitation will be electric dipole forbidden.

The method of Kleinman-Disallowed Hyper Rayleigh Scattering (KD-HRS) developed by our group permits the measurement of the figures of merit for all of the rotationally invariant components of the first hyperpolarizability tensor.\textsuperscript{36} Since this technique is able to characterize all of the figures of merit for the rotationally invariant tensor components, it provides significantly more information than electric field induced second harmonic generation (EFISH, measuring the Kleinman allowed vector component) and 90 degree hyper-Rayleigh scattering (standard HRS, measuring only vector and octupolar Kleinman allowed components). Experimental details including the depolarization ratio experiment are described in our previous paper. Our experiments were done in benzene solution at 1560nm and a 50°C bath was used to ensure that the sample solutions remained completely dissolved and homogeneous.

The KD-HRS method was performed on three different hexadecyloxy derivatives: truxene-6OC12, trux-6OC12, and trux-6CN-6OC12. However, analysis of the results suggests that the SHG signal was contaminated by a fluorescent background in each of the samples. The depolarization ratios ($I_\perp / I_\parallel$) at 90 degrees were all close to 1, instead of the theoretical value of 2/3 for molecules in which $\beta_{3ss}$ is the dominant hyperpolarizability. Given that some of these molecules have and the others approximate symmetries for which $\beta_{3ss}$ is the only allowed hyperpolarizability, this lack of agreement is surprising. Upon re-examining the emission spectra we believe that there was significant three-photon absorption induced fluorescence competing with the SHG signal. The depolarization ratio near 1 suggests that the fluorescence is mostly unpolarized, and
at least of the same order of magnitude as the SHG, if not larger. We encountered similar theoretical problems in reconciling earlier measurements of aminotruxenone molecules. In both cases our measurements of the hyperpolarizability of planar $C_{3h}$ molecules resulted in Kleinman-disallowed and vector components that were of similar magnitude to the octupolar component of the rotationally averaged hyperpolarizability tensor - but symmetry considerations suggest that the octupolar component should be much larger than the other components for all of the planar molecules, since the Kleinman-disallowed and vector components are symmetry forbidden in $C_{3h}$. Furthermore, in the tris(dicyanomethylene) compounds, which have only $C_3$ symmetry, the Kleinman-disallowed components are not symmetry forbidden, but because their deviation from planarity is not extreme (see fig 2.2.2), we would expect these Kleinman-disallowed hyperpolarizabilities to be modest compared to the octupolar component; however, our measurements yielded Kleinman-disallowed components comparable to the octupolar components.

To rule out the possibility that our results were affected by material impurities, some of the hexaalkoxy truxenone samples were re-synthesized and more rigorously purified. The highly purified samples showed very similar absorption spectra, but exhibited significantly more fluorescence when excited at 1560nm, completely overwhelming the SHG signal and making determination of the hyperpolarizability tensor even less certain, suggesting that the purification removed an unknown fluorescence quencher. Attempts at making time-resolved measurements at 800nm to separate the SHG from fluorescence failed because there was considerable absorption at the second harmonic frequency for trux-6CN-6O12C and trux-6O12C. Truxene-6O12C does not
have large absorption at 400nm, but the hyperpolarizability still proved unmeasurable due to resonantly enhanced two-photon fluorescence that dominated the signal. Attempts were also made to make measurements at wavelengths longer than 1560nm to shift the SHG peak relative to the Stokes-shifted fluorescence peaks, but the overall decrease in signal to noise made extracting the hyperpolarizabilities impossible.

To place an upper bound on the SHG signal from a highly purified sample of trux-6CN-6OC12, we compared emission intensity at 90 degrees to that of DR1, which has little fluorescence and a known hyperpolarizability. For equal molar concentrations the truxenone signal at the second harmonic wavelength (780nm) was about 2.5 times that of the DR1 signal (which is primarily SHG). Considering that the peak of the fluorescence emission spectrum was near the SH frequency and that the noise in the truxenone measurement was about ¼ the size of the DR1 signal, a reasonable estimate for the upper bound for the unobservable SHG portion of the trux-6CN-6O12C HRS signal is ~1 times that of DR1. Thus, we would expect the various rotational invariants of the hyperpolarizability tensor for this molecule to be at most $60 \times 10^{-30} \text{ esu}$. Calculations of the octupolar and vector components of the hyperpolarizability tensor by means of the SOS model (including ~20 states) yielded $|\beta_{1\sigma}| \approx |\beta_{3\sigma}| \sim 40 \times 10^{-30} \text{ esu}$ at 1560nm. Calculations of the planar truxenones yielded slightly reduced values for the octupolar components, and the rest of the components were assumed to be small (~zero) due to symmetry. The Kleinman-disallowed component of interest for the dicyanomethylene compound was also calculated by the SOS model to be $|\beta_{2nm}| \sim 5 \times 10^{-30} \text{ esu}$. Clearly significant improvement requires molecules that have larger transition moments to the low-lying excited states. Possibly these values of $\beta$ could be measured by HRS if a
good fluorescence quencher can be added or if a clear and unambiguous way to separate out the fluorescence background can be found. However, significant fluorescence is not unexpected in molecules like these in which the optically responsive electrons are largely confined to rigid parts of the molecule.

2.2.5 Mesogenic Properties

The 4,9,14-dialkylaminotruxenones we examined in our previous paper do not possess any liquid crystal behavior. On the other hand, some truxenes are already well known in the literature as discotics when they were hexasubstituted by alkoxy, alkanoyloxy or \( p \)-alkoxybenzoate chains. We have examined these truxenes for comparison to their new truxenone analogs described here.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( K_1(K_2) \rightarrow D_{ho} )</th>
<th>( D_{ho} \rightarrow I )</th>
<th>Decomposition Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Truxene-6OC4</td>
<td>88 (114)</td>
<td>( c )</td>
<td>330</td>
</tr>
<tr>
<td>Truxene-6OC8</td>
<td>65 (85) (66 (86) ( a ))</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>Truxene-6OC12</td>
<td>62 (68) (67 (73) ( a ))</td>
<td>231</td>
<td>230 ( a )</td>
</tr>
<tr>
<td>Truxenone-6OC4</td>
<td>96</td>
<td>( c )</td>
<td>325</td>
</tr>
<tr>
<td>Truxenone-6OC8</td>
<td>58</td>
<td>( c )</td>
<td>353</td>
</tr>
<tr>
<td>Truxenone-6OC12</td>
<td>49 (50 ( b ))</td>
<td>289</td>
<td></td>
</tr>
<tr>
<td>Trux-6CN-6OBu</td>
<td>( c )</td>
<td>( c )</td>
<td>288</td>
</tr>
<tr>
<td>Trux-6CN-6OC8</td>
<td>( c )</td>
<td>( c )</td>
<td>327</td>
</tr>
<tr>
<td>Trux-6CN-6OC12</td>
<td>( c )</td>
<td>( c )</td>
<td>300</td>
</tr>
</tbody>
</table>

Table 2.2.1. Phase transitions temperatures and the decomposition temperatures (in °C) obtained by DSC at 10 °C/min under nitrogen. (a) Literature transition temperatures. Ref. . (b) Phase change temperatures were obtained by polarizing optical microscopy at 10 °C/min. (c) A phase transition was not observed due to decomposition of the sample.
The truxenones substituted by six alkoxy chains, each with eight or more carbons, possess the desired mesogenic behavior. The studies of these hexaalkoxytruxenones by DSC indicate that these compounds possess an exceptionally large mesomorphic range (Table 2.2.1). For example, the hexaoctyloxytruxenone has a discotic phase encompassing almost 300°C. However, it also appears that these hexasubstituted truxenones are not very stable at their very high clearing temperatures. This instability makes it difficult to prepare good specimens for examination by polarizing microscopy since the isotropic phase is not readily accessible without concomitant decomposition. In most cases, the difficulties in observing the clearing point for these compounds are just an issue of thermal stability. Only in the case of the truxenone with six dodecyloxy chains has the isotropic phase been clearly observed by polarizing optical microscopy without significant thermal degradation. However, this measurement required observation under a nitrogen atmosphere. Under these conditions, the transition between the two phases of this liquid crystal could be clearly observed. The pictures presented below (Fig. 2.2.3), show the optical textures observed for truxenone-6OC12 below and above the crystal to discotic transition. As the textures are very similar, the assignment of the discotic phase of the Trux-6OC12 as $D_{ho}$ is made in analogy to the assignment of the analogous Truxene-6OC12.
Figure 2.2.3. Textures observed for Trux-6OC12 at 11.5°C (crystalline) and 53.9°C ($D_m$) by polarized optical microscopy. The sample was placed between a glass slide and a cover glass without any surface treatment, heated briefly above 289°C (clearing temperature) under nitrogen and then cooled down.

While the hexaalkoxytruxenones possess clear-cut liquid crystal behavior their tris(dicyanomethylene) derivatives do not appear to be mesogenic. Unfortunately, and as before in the case of the truxenone precursors, full analysis of these tris(dicyanomethylene) derivatives with a polarizing optical microscope is even more difficult due to their poor thermal stability at the elevated temperatures where clearing occurs. As was observed for the corresponding truxenones, and in spite of working under an inert atmosphere, the samples decomposed significantly before reaching any unambiguous clearing point. The DSC analyses of the tris(dicyanomethylene) derivatives also show no clear phase transition(s) prior to their decomposition around 300 °C.

In general, it is anticipated that these tris(dicyanomethylene) derivatives should be less liquid crystalline than the tris(ketones) for at least two reasons. First, sterically, the central “disc” is thicker and consequentially harder to pack. Hence, when we replace the ketones with dicyanomethylenes we would expect to need longer flexible chains which might compensate to increase the relative volume of the region of flexible chains
surrounding the columns of hard-core mesogens. Second, we expect that the non-flat nature of the tris(dicyanomethylene) derivatives should decrease the \(\pi\)-stacking interactions, again decreasing the tendency to form liquid crystals. Finally, the tris(dicyanomethylene)s are somewhat more polar, suggesting stronger intermolecular interactions. Countering these effects is the fact that the tris(dicyanomethylene)s are a mixture of both enantiomers, which is generally easier to accommodate in a liquid crystalline phase than in a crystal. Almost all crystals formed by cooling from liquid or liquid crystalline mixtures are purer than these fluids. While there are counterexamples, they are rare\(^{66}\). This is because, in general, the entropy of mixing is larger in the liquid and so will depress the clearing point in this and other mixtures. However, this last effect is not expected to be a large influence. Hence this decreased mesogenicity of the tris-dicyanomethylene relative to the tris ketones is not unexpected, although we had not anticipated the magnitude of the difference. Preliminary experiments with the behavior of the Trux-6CN-6OC12 in solvents suggest that lyotropic columnar liquid crystal phases may form in these mesogens. This, together with the geometric need to accommodate a thicker central core suggests that additional volume of flexible tails relative to the wider central cores may result in thermotropic columnar phases.

### 2.2.6 Conclusion

A new synthesis of hexaalkoxytruxenones has been developed which relies on the oxidation of hexaalkoxytruxene precursors. The hexaalkoxytruxenones with octyl and dodecyl tails have very broad discotic phases. In contrast, the tris(dicyanomethylene) derivatives of these ketones did not possess any mesogenic activity even with the longest
alkyl chains. The thermal instability of these materials at their clearing points complicates the full characterization of their full phase transition behavior. The nonlinear optical properties of representative hexaalkoxytruxenes, hexaalkoxytruxenones and the tris(dicyanomethylene) derivatives of the hexaalkoxytruxenones could not be unambiguously determined experimentally due to a strong fluorescence background. However, upper bounds on the hyperpolarizabilities have been established and SOS calculations suggest modest values in line with the experimental upper bound.

**Acknowledgements**

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Chapter 3: Triarylnaphtylmethyl Carbocations

3.1 Synthesis and spectral characterization of bisnaphthylmethyl and trinaphthylmethyl cations

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Abstract—Cationic triaryl methane dyes containing one, two or three naphthalene moieties have been prepared. Their synthesis and preliminary spectral, nonlinear optical and theoretical characterization are reported here. The major electronic and steric hindrance effects of the 1,4-linked naphthalene have been examined by comparison of the UV-Vis absorption of the 1,4-linked and 2,6-linked series. © 20085 Elsevier Science. All rights reserved

Triarylmethane cations (TAMCs) such as Crystal Violet have been the subject of numerous investigations of their physical and photophysical chemistry.\textsuperscript{1,2} The applications for these dyes range from biochemistry\textsuperscript{3} to optical data storage\textsuperscript{4}. We are interested here in their properties as nonlinear optical (NLO) chromophores and especially their multipolar properties.\textsuperscript{5} In order to increase the first hyperpolarizability of Crystal Violet, researchers have modified TAMC structures by incorporation of different heterocycles,\textsuperscript{6} as well as stilbene\textsuperscript{7} and phenylethynyl groups.\textsuperscript{8} At the same time, there
have been attempts to shift the main absorption band to the near infrared. TAMCs with multiple naphthyl groups have been described but often not isolated and fully characterized. An objective of this study has been the synthesis of some bisnaphthyl and trinaphthylmethane cations and the comparison of their UV/Vis spectra with those of some well-known TAMCs.

### 3.1.1 Synthesis

TAMC synthesis can be accomplished by two main methods. The first route involves the reaction between a bis-dialkylaminoketone and an arene or heterocycle in the presence of \( \text{POCl}_3 \). The second synthetic pathway involves the use of the bis-dialkylaminoketone and an organolithium reagent to form the corresponding carbinol, followed by ionization after treatment with an inorganic acid such as perchloric acid. The experience of most investigators indicates that the latter route is more useful and can be extended to the synthesis of many TAMCs. In any case, for either route, we must prepare the requisite naphthyl derivatives related to Michler’s ketone, bis(6-pyrrolidinonaphtalen-2-yl) methanone (1) and bis(4-pyrrolidinonaphtalen-1-yl) methanone (2) in Scheme 3.1.

**Scheme 3.1**: Synthetic pathway for the preparation of the bisnaphthylmethyl and trinaphthylmethyl cations.

The synthesis of such diarylketones has been described and usually requires a multistep synthesis. We have successfully employed a one step method developed by
Olah et al.\textsuperscript{15} based on the reaction between an aryllithium reagent and N-carboethoxypiperidine. The synthesis of ketone 1 starts from 6-bromo-2-naphthol which is transformed into 6-bromo-2-naphthalamine by a Bucherer reaction, alkylation with 1,4-diodobutane to provide 6-bromo-2-pyrrolidonaphthalene and, finally, conversion to an organolithium reagent and reaction with N-carboethoxypiperidine to form the ketone 1 in good yield (56%) and useful overall yield (22%).

The preparation of ketone 2 proved to be more problematic. The first challenge was the preparation of 4-bromo-1-naphthalamine. Direct reaction of 1-naphthylamine with elemental bromine resulted in a complex mixture of mono, di- and polybromination products\textsuperscript{16}. Amongst the bromination reagents examined 2,4,4,6-tetrabromo-2,5-cyclohexadien-1-one proved to be the most effective to produce the desired 4-bromopyrrolidinonaphthalene.\textsuperscript{17} In contrast to the case of ketone 1, the organolithium derivative of 4-bromopyrrolidinonaphthalene afforded ketone 2 in poor yield (<10%). This difference in reactivity between the 1,4- and 2,6-naphthyl isomers can be explained by the greater peri steric demands in the 1,4-isomer. To circumvent this problem we modified our strategy and used instead 1-bromo-4-fluoronaphthalene to give bis(4-fluoronaphthalen-1-yl) methanone. The pyrrolidine donors were next introduced by aromatic nucleophilic substitution. The two approaches examined for preparation of ketone 2 are described in Scheme 3.2.

The preparation of the bisnaphthyl and trinaphthylmethyl cations has been performed by reaction between the ketones 1 and 2 with an organolithium reagent and then treatment of the reaction mixture with perchloric acid (Scheme 3.1). We have used organolithium reagents obtained by bromine-metal exchange from 4-bromopyrrolidinobenzene, 4-bromopyrrolidonaphthalene, 6-bromo-2-pyrrolidonaphthalene, or by acid/base reaction from phenylacetylene and 1-(4-
It is important to note that even if the carbinol can be prepared, in some cases the isolation of the cationic salt is not possible, as in the cases when Ar is either a phenyl, an ethynylphenyl or a 1-(4-ethynylphenyl)-pyrrolidine. In successful cases the carbocation was isolated in a yield between 42 and 80%.

Scheme 3.2: Two synthetic strategies for the preparation of bis(4-pyrrolidonaphtalen-1-yl)methanone i/ 2,4,4,6-tetrabromo-2,5-cyclohexadien-1-one, CH₂Cl₂, –10°C, ii/ n-BuLi, THF, –78°C, N-carboethoxypiperidine, iii/ pyrrolidine, DMSO, reflux.

3.1.2 Spectral Characterization

It is known that the modification of a donor group in a charge transfer chromophore can have a large influence on the UV-Visible spectrum. Thus, within a series of triarylmethyl cations, the substitution of the dimethylamino group by most dialkylamino or cycloaliphatic amine groups causes a red shift of the main absorption band due to increased electron donation.¹⁸

The substitution of 4-pyrrolidonophen-1-yl by 4-pyrrolidononaphthalen-1-yl also produces a bathochromic shift as charge transfer through the naphthalene is more facile than in benzene due to the difference in resonance energy. At the same time, the annulated ring in the 1,4-substituted naphthalene will be a steric obstacle to planarity of the cation contributing to a hypsochromic effect. These two effects are in opposition. Comparison of the UV-Vis spectra of the molecules with one, two and three 1,4-linked
(transverse) naphthalene moieties (bPN14, bN14P and tN14 respectively) indicates that the electronic contribution is dominant, as increased bathochromic shifts are observed with each 1,4 naphthalene addition.

<table>
<thead>
<tr>
<th>Compound</th>
<th>PG</th>
<th>tP</th>
<th>bPN14</th>
<th>bN14P</th>
<th>tN14</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda_{\text{max}} ) (( \varepsilon ))</td>
<td>( (8.96 \times 10^4) )</td>
<td>( (6.98 \times 10^5) )</td>
<td>587 ( (6.98 \times 10^5) )</td>
<td>662 ( (4.10 \times 10^5) )</td>
<td>701 ( (3.88 \times 10^5) )</td>
</tr>
<tr>
<td>( \Delta \lambda )</td>
<td>49</td>
<td>77</td>
<td>119</td>
<td>131</td>
<td>137</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>bN14N26</th>
<th>bN26N14</th>
<th>bPN26</th>
<th>bN26P</th>
<th>tN26</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda_{\text{max}} ) (( \varepsilon ))</td>
<td>( (5.21 \times 10^4) )</td>
<td>( (2.9 \times 10^5) )</td>
<td>( (8.47 \times 10^4) )</td>
<td>( (6.81 \times 10^4) )</td>
<td>( (9.83 \times 10^4) )</td>
</tr>
<tr>
<td>( \Delta \lambda )</td>
<td>148</td>
<td>162</td>
<td>148</td>
<td>124</td>
<td>141</td>
</tr>
</tbody>
</table>

**Table 3.1.** Spectroscopic properties of TAMC chromophores in ethanol solution (ca 1.10 M). \( \lambda_{\text{max}} \) is given in nm, \( \varepsilon \) in mol\(^{-1}\)cm\(^{-1}\), and \( \Delta \lambda \) represents the full width at half maximum in nm.

To better understand this behavior, we performed a series of *ab initio* geometry optimizations and molecular orbital calculations (RHF and MCSCF) with GAMESS\(^{(19)}\). The geometry of the molecules was optimized using RHF theory with an effective core potential and the Stevens/Basch/Krauss/Jasien/Cundari (SBKJC) basis. For **bPN14** (2 phenyls, 1 transverse naphthalene) and **bN14P** (1 phenyl, 2 transverse naphthalenes) we find that the unsubstituted phenyl(s) become more planar (a 29° twist for phenyls in bPN14 and a 26° twist for the phenyl in bN14P, as compared to ca 33° for the phenyls in tP), whereas the 1,4 naphthyl substituents are rotated 45°-50°. MCSCF calculations show
that the first excited states of these molecules are well approximated by the transfer of one electron from the HOMO to the LUMO of the RHF ground state. The HOMO in each of these molecules is on the naphthyl substituents, while the LUMO is mainly concentrated on the central carbon and also spreads to the phenyl(s) (Figure 2). Thus, raising the energy of the HOMO through 1,4 naphthyl substitution is offset by the decreased conjugation, but the increased conjugation of the phenyl(s) lowers the LUMO slightly, leading to overall moderate red shifts.

The substitution of a pyrrolidine group (in tP) by a hydrogen (in Pyrrolidine Green, PG) results in a red shift of about 36 nm. Akiyama et al explain this by the observation that all highly symmetrical molecules have a degeneracy of their HOMO and the substitution of one pyrrolidine group by one hydrogen breaks this degeneracy and decreases the transition energy. More specifically, calculations show that while the H-substituted ring in PG has a torsion angle of ca 45°, the unsubstituted phenyls become more conjugated (torsion angle of 29°). MCSCF calculations show that the HOMO is spread over the unsubstituted phenyls and the LUMO has moderate representation there as well. It results that the increased conjugation of these phenyls decreases amount of energy needed to transfer an electron to the LUMO.

The variations in the absorption bands of the TAMCs can also be explained by the calculations. The UV-Vis spectra of the TAMCs are composed mainly of two bands (x and y) which calculations show are HOMO to LUMO and HOMO-1 to LUMO transitions respectively. In PG, the large twist angle of the H-substituted phenyl leads to the large bathochromic shift of the y-band. This separation of x and y-bands is not seen in bN14P (and possibly bPN14 and others as well), where the phenyl along the y axis is much more conjugated. This is supported by MCSCF calculations which suggest that the x and y bands of bN14P are only separated by 18nm.
Just as the enhancement of the donor group may induce a bathochromic shift, the extension of the conjugated pathway may act in the same direction. The substitution of a phenyl by a 2,6-linked naphthalene (longitudinal naphthalene) moiety extends the conjugated bridge, but does not introduce the steric effect characteristic of the transverse naphthalene. Calculations show that the twist of the longitudinal naphthalenes in all of the compounds studied does not deviate much (±5°) from the 33° twist of the phenyls in tP. Nevertheless, the electronic effect in this kind of 2,6-linkage is smaller than seen previously. There are red shifts with the addition of longitudinal naphthalene moieties, ca 100 nm between tP (3 phenyls) and bPN26 (two phenyls, one longitudinal naphthalene) and ca 200 nm between tP and tN26 (three longitudinal naphthalenes). In contrast to the transverse naphthalene substitutions, where each additional substitution produces a greater red shift, this is not the case for the longitudinal systems, as compound bN26P possesses a band at shorter wavelength than bPN26. The reason for this is not completely understood. In general, the smaller steric effect in the 2,6 naphthyls suggests that the degeneracy of the HOMO and HOMO-1 is less important in this system. We believe the
results for the 2,6 napthyls are a consequence of the LUMO in these molecules being less concentrated on the central carbon and more spread out onto the napthyl rings. This conjugation, of course, lowers the energy of the LUMO and hence the excitation energy of the molecules. Thus the red-shifts in the 2,6 napthyls are primarily related to a decrease in the energy of the LUMO.

A common effect of the extension of the aromatic core in the naphthalene derivatives is a broader absorption band than in the triphenylmethyl cation series that typically have a width (at half height) between 50 and 80 nm. On the other hand, in the TAMCs where at least one naphthalene moiety is incorporated, this value increases to a range between 119 and 141 nm. This expansion of the bandwidth results in absorption tailing into the near infrared, especially in the case for tN26.

To understand the influence of these structural modifications on the NLO properties, we have undertaken a series of measurements of the first hyperpolarizability of these new TAMCs by the Time-Correlated Single Photon Counting 45° hyper-Rayleigh scattering (TCSPC-45°-HRS) technique. The TCSPC method distinguishes HRS from two-photon fluorescence in the time-domain, resulting in improvement of the accuracy of measurements of Kleinman-disallowed components. This measurement permits the figure of merit of this kind of compound for chiral axial nonlinear optical media\textsuperscript{21}. The measurements of these second order non-linear optical properties are more sensitive to the nature, symmetry and overlap between the various orbitals (see Figure 3.2). The results obtained for the compound bN14P and two other classical TAMCs are summarized in Table 3.2.
Figure 3.2. Singly occupied orbitals in the first excited state of BN14P (a) lower lying (RHF HOMO) SOMO, (b) higher lying (RHF LUMO) SOMO. Note the large charge transfer in the y (symmetry axis) direction, which produces a large NLO response. Graphics were made using Molekel software.

<table>
<thead>
<tr>
<th>β_{1se}</th>
<th>β_{1mm}</th>
<th>β_{2mm}</th>
</tr>
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<tr>
<td>393 ± 30</td>
<td>226 ± 19</td>
<td>655 ± 35</td>
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<td>255 ± 21</td>
<td>337 ± 32</td>
<td>429 ± 26</td>
</tr>
<tr>
<td>200 ± 17</td>
<td>275 ± 27</td>
<td>360 ± 23</td>
</tr>
</tbody>
</table>

Table 3.2. Absolute value of the rotational invariants of the hyperpolarizability (10^{-30} esu) obtained from TCSPC-45°-HRS.

We see that bN14P possesses better nonlinear properties than Crystal Violet in both the dipolar and the Kleinman disallowed parts, due to a large charge transfer from the ground to first excited state. This indicates the potential of these new bisnaphthyl and trinaphthylmethyl cations for NLO applications.

Acknowledgments
This work was financially supported by NSF grant DMR-0308701.
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Chapter 4: Phenanthrenenquinone Derivatives for NLO Applications

4.1 Synthesis and Properties of 3,6-disubstituted 9,10-Phenanthrenequinone Derivatives

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Abstract: A series of 3,6-disubstituted-9,10-phenanthrenequinone derivatives (3,6-dihalo-, 3,6-N,N-dialkylamino-, 3,6-bis(4-N,N-dialkylaminophenylvinyl) and 3,6-bis(4-N,N-dialkylaminophenylethynyl)) have been synthesized and characterized. In some cases these \textit{o}-quinones were further reacted with \textit{o}-phenylenediamine derivatives. The linear optical properties for each series were measured and compared to ZINDO spectroscopic calculations, and the implications for their nonlinear properties are discussed with the goal of elucidating the most important structure-function relationships. Differences in conjugation connectivity, electron density, planarity and geometry of the charge-transfer pathways were found to have a pronounced effect on the overall properties.
4.1.1 Introduction

Organic molecules and polymers with π-conjugated structures have been extensively studied for both fundamental and diverse practical reasons such as electronic and photonic applications, including nonlinear optical (NLO) materials, liquid crystal displays, solar cells and organic light emitting diodes (OLEDs). It has been demonstrated that conjugated phenylvinylene and phenylacetylene compounds have remarkable optical and electronic properties due to the multiple conjugation pathways and especially as the identity, number and location of donor/acceptor groups are varied and the conjugation between donor and acceptor groups is tuned. Such compounds provide a structural basis for studying the effect of functional group substitution by tuning the donor/acceptor groups and thus give useful information for design of organic molecules having specifically tailored properties.

During the past few decades much effort has gone into the design of dipolar push-pull chromophores as NLO materials, especially for electro-optic (EO) applications. We have long been interested in such conjugated donor/acceptor systems and recently have sought to explore two-dimensional chromophores for use in nonpolar chiral materials. In contrast to dipolar-aligned materials, nonpolar chiral materials do not require the thermodynamically unfavorable mutual orientation of molecular dipoles which tends to decay over time and ultimately limits practical chromophore loading densities. Instead, chiral materials can be made from a uniaxial alignment of chiral molecules ($D_3, C_3$, etc. symmetry groups), or from achiral molecules ($C_2$, symmetry, for example) aligned in a chiral fashion, and in theory there are no thermodynamic limits on chromophore densities. Molecules suitable for use in such chiral materials must possess appreciable
Kleinman-disallowed hyperpolarizabilities. Derivatives of 9,10-phenanthrenequinone (PQ) attracted our attention due to both their approximate $C_{2v}$ symmetry and their relatively low lying B-type excited states (involving a transition moment perpendicular to $C_2$ axis), the latter predicted by preliminary semi-empirical quantum chemistry calculations. For promising Kleinman-disallowed hyperpolarizabilities in $C_{2v}$ molecules a low-lying B-type excited state accompanied by large charge transfer is critical. In this article, we describe the synthesis of a series of donor/acceptor functionalized 3,6-disubstituted 9,10-phenanthrenequinone derivatives, including 3,6-bis-$N,N$-dialkylaminophenanthrenequinone (I), 3,6-bis(phenylvinyl)phenanthrenequinones (II), and 3,6-bis(phenylethynyl)phenanthrenequinones (III) (Scheme 4.1, here D is often an electron donor group, such as NR$_2$). In some cases these diketones have been subsequently reacted with a variety of $o$-phenylenediamines, thus providing a comparable group of new phenazine derivatives.

Scheme 4.1 functionalized 3,6-disubstituted 9,10-phenanthrenequinone derivatives

![Scheme 4.1](image-url)
4.1.2 Synthesis

3,6-dihalophenanthrenequinones. The 3,6-dihalophenanthrenequinones are the key intermediates required here for the preparation of 3,6-disubstituted phenanthrenequinone derivatives with extended π-conjugation and donor groups. The 3,6-dibromo-9,10-phenanthrenequinone (3,6-DBPQ), used in the coupling reactions with alkenes and alkynes, was readily obtained by direct bromination of phenanthrenequinone with Br₂ in nitrobenzene according to the literature method. The 3,6-DBPQ could then be converted directly, albeit in low yield, to the corresponding 3,6-difluoro derivative. Thus, by reacting 3,6-DBPQ with CsF in anhydrous DMSO, we obtained the 3,6-difluorophenanthrenequinone (3,6-DFPQ). This reaction did not go to completion as monitored by GC and provided a mixture of 3,6-DBPQ, 3,6-DFPQ and the intermediate 3-bromo-6-fluoro-9,10-phenanthrenequinone. Attempts to force this reaction to completion did not provide more 3,6-DFPQ product and unknown side reactions intervened instead. Therefore, the reaction was usually intentionally stopped short of completion and the mixture obtained was used directly for subsequent reactions without purification. Alternatively, pure 3,6-DFPQ could be isolated from this mixture in 34% yield by chromatography. The related preparation of the new compound 3,6-diiodophenanthrenequinone (3,6-DIPQ) from 3,6-DBPQ proved even more difficult. The reaction of 3,6-DBPQ with KI was performed in the presence of Cu(I) as catalyst and provided 3,6-DIPQ in very low yield (21%). Just as in the case of the previous bromine to fluorine exchange, this replacement of bromine by iodine was complicated by unknown side reactions and the reaction could not be forced to provide enhanced yields.
3,6-N,N-dialkylaminophenanthrenequinones. Much recent research has been concerned with the conversion of arylhalides to arylamines.\textsuperscript{12} There was no evidence, even at elevated temperature, for the production of any 3,6-N,N-dialkylaminophenanthrenequinone \textbf{I} by direct reaction of 3,6-DBPQ with excess N,N-dialkylamine using the classical copper catalyzed procedures of arylhalide amination with base additives. As already noted, treatment of 3,6-DBPQ with cesium fluoride in DMSO provided a mixture of products containing 3,6-DFPQ (along with intermediate 3-bromo-6-fluorophenanthrenequinone and starting 3,6-DBPQ). This mixture could be used directly in a subsequent aromatic nucleophilic substitution reaction by addition of N,N-dialkylamines to prepare the 3,6-dialkylamine substituted phenanthrenequinone derivatives (\textbf{I}) in useful yields (Scheme 4.2, Table 4.1).

\textbf{Scheme 4.2.} Synthesis of 3,6-substituted phenanthrenequinones (\textbf{I})\textsuperscript{a}

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {\textbf{I}};
\node (b) at (-2,1) {\textbf{II}};
\node (c) at (2,1) {\textbf{III}};
\node (d) at (0,-1) {\textbf{IV}};
\draw[->] (a) -- (b) node[midway,above] {a};
\draw[->] (b) -- (c) node[midway,above] {c};
\draw[->] (c) -- (d) node[midway,above] {b};
\end{tikzpicture}
\end{center}

\textsuperscript{a} Reaction conditions: (a) CsF, DMSO, 90 °C, (b) K\textsubscript{2}CO\textsubscript{3}, amines, 100 °C, using a mixture containing 3,6-DFPQ, (c) KI, Cul, HMPA.
Table 4.1 Synthesis of 3,6-dialkylamino phenanthrenequinone derivatives (I)

<table>
<thead>
<tr>
<th>Product</th>
<th>Amines</th>
<th>Reaction Time (h)</th>
<th>Yield (%)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>la</td>
<td><img src="HN" alt="HN" /></td>
<td>7</td>
<td>33</td>
</tr>
<tr>
<td>lb</td>
<td><img src="HN" alt="HN" /> <img src="OH" alt="OH" /></td>
<td>6</td>
<td>28</td>
</tr>
<tr>
<td>lc</td>
<td><img src="HN" alt="HN" /></td>
<td>6</td>
<td>58</td>
</tr>
<tr>
<td>ld</td>
<td><img src="HN" alt="HN" /> <img src="OH" alt="OH" /></td>
<td>7</td>
<td>38</td>
</tr>
</tbody>
</table>

\(^a\) Isolated yield based on 3,6-DBPQ.

From these reactions, the 3-bromo-6-aminated PQ derivative was sometimes isolated in addition to the desired 3,6-diamino PQ derivatives. For example, in the case of the preparation of 3,6-bis-N,N-dibutylamino PQ, the 3-bromo-6-N,N-dibutylamino PQ was isolated in 20% yield, which was separated easily from the desired 3,6-bis-N,N-dibutylamino PQ product by column chromatography.

3,6-bis(N,N-dialkaminophenyl-4-vinyl)phenanthrenequinones (II) The well known Heck reaction,\(^{13}\) the palladium mediated cross-coupling between alkenes and \(sp^2\)-halides, was utilized in this study. For the preparation of compounds of type II, the Heck reaction was used for the coupling of 3,6-DBPQ with styrenes (Scheme 4.3). The reactions were carried out in the presence of Pd(OAc)\(_2\) as catalyst with the addition of a triarylphosphine ligand under nitrogen protection. In our reactions, tri-\(\rho\)-tolylphosphine proved to be a successful added ligand which was necessary to minimize the formation of palladium black. The reactions could be monitored easily by GC, TLC, or MS by observing the
consumption of the 3,6-DBPQ. It was found that the reactions did not occur at a useful rate unless heated above 100 °C (Table 4.2). In some preparations a small component of the product appeared to contain cis isomers but these could be removed by a combination of chromatography and crystallization.

Scheme 4.3. Synthesis of 3,6-bis(N,N-dialkylphenyl-4-vinyl)phenanthrenequinone (II) 

\[
\begin{align*}
\text{NH}_2 & \xrightarrow{a} \text{NR}_2 & \text{H} & \xrightarrow{b} \text{NR}_2 & \text{NR}_2 & \xrightarrow{c} \text{NR}_2 & \xrightarrow{d} \text{NR}_2 \\
(\text{II})
\end{align*}
\]

\(a\) Conditions: \(R = \text{Bu, C}_{12}\text{H}_{25}\). (a) RI, K₂CO₃, DMSO, 80 °C ¹⁴; (b) POCl₃, DMF, r.t. ¹⁵; (c) MePPh₃Br/BuLi, THF, DMSO, -20°C - r.t. ¹⁶; (d) 3,6-DBPQ, Pd(OAc)₂, tri-o-tolylphosphine, Et₃N, DMF, 110 °C ¹⁷.

Table 4.2 Synthesis of 3,6-vinyl-\(\pi\)-conjugated substituted 9,10 phenanthrenequinones (II)

<table>
<thead>
<tr>
<th>Product</th>
<th>Arylstyrene</th>
<th>Reaction Time (h)</th>
<th>Yield (%) (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIₐ</td>
<td>((\text{H}_3\text{C})_3\text{C})</td>
<td>14</td>
<td>57</td>
</tr>
<tr>
<td>IIₖ</td>
<td>((\text{C}_4\text{H}_9)_2\text{N})</td>
<td>48</td>
<td>40</td>
</tr>
<tr>
<td>II₇</td>
<td>((\text{C}<em>{12}\text{H}</em>{25})_2\text{N})</td>
<td>48</td>
<td>57</td>
</tr>
<tr>
<td>II₈</td>
<td>(\text{N})</td>
<td>5</td>
<td>50</td>
</tr>
</tbody>
</table>

\(a\) Isolated yield, calculated based on 3,6-DBPQ.
3,6-bis(N,N-dialkylaminophenyl-4-ethynyl)phenanthrenequinones (III) Terminal acetylenes are very valuable intermediates in the Sonogashira cross coupling reactions and were utilized here for the preparation of 3,6-bis(N,N-dialkylphenyl-4-ethynyl)phenanthrenequinone (III). We prepared the electron donor functionalized aryl acetylenes by taking advantage of the Sonogashira reaction of trimethylsilylacetylene (TMSA) and a 4-halo-N,N-dialkylaniline followed by the easy conversion of the protected acetylene to the corresponding free acetylene.\textsuperscript{18} The N,N-dialkylaniline halides react with TMSA in the presence of catalytic amount of a palladium and copper cocatalyst in a secondary or tertiary amine solvent to give trimethylsilylethynylarenes in high yields. The resulting trimethylsilylethynylarenes were easily converted to the corresponding terminal arylacetylenes under mild conditions in near quantitative yields by treatment with potassium carbonate in methanol (Scheme 4.4).

The general synthetic strategy for the phenylacetylene series relied on the Sonogashira cross-coupling reaction.\textsuperscript{19} This method has been used successfully for the preparation of numerous interesting molecules and is recognized as a universal method for such coupling reactions.\textsuperscript{20} The target molecules of type III were prepared by coupling the terminal arylacetylenes with 3,6-DBPQ in the presence of bis(triphenylphosphine)palladium dichloride catalyst and copper(I) iodide in DMF solution containing a secondary amine as shown in Scheme 4.4. The coupling reactions were monitored by gas chromatography, TLC, and/or MS to determine reaction progress and the yields and conditions are listed in Table 3. Generally, the coupling reactions were slow below 50 °C and only proceeded with acceptable yields at elevated temperatures, typically around 110 °C. The products were purified by flash chromatography on silica
gel, but the monoadducts were not easily separated from the desired double adduct product. The formation of diacetylene by-product from the copper catalyzed oxidative coupling reactions between acetylenes was also observed and while this product could be easily separated by flash chromatography on silica gel, its formation was sometimes a major factor affecting the yield. For example, this by-product was isolated in 56% yield during the preparation of compound \textbf{III}b and thus diminishing the yield of \textbf{III}b.

\textbf{Scheme 4.4.} Synthesis of 3,6-bis(N,N-dialkylphenyl-4-ethyl)phenanthrenequinones (\textbf{III})

\begin{align*}
\text{Scheme 4.4.} \quad & \text{Synthesis of 3,6-bis(N,N-dialkylphenyl-4-ethyl)phenanthrenequinones (III)} \\
& \text{a} \\
\end{align*}

\begin{align*}
\text{a Conditions: } & R = \text{C}_2\text{H}_5, \text{C}_4\text{H}_9, \text{C}_{12}\text{H}_{25}. \quad \text{(a) } \text{RI, K}_2\text{CO}_3, \text{DMF, 90 °C}  \quad 21; \quad \text{(b) } \text{TMSA, Pd(PPh}_3\text{)_2Cl}_2, \text{CuI, (i-Pr)}_2\text{NH, r.t.}  \quad 22; \quad \text{(c) } \text{K}_2\text{CO}_3, \text{MeOH, r.t.}  \quad 21; \quad \text{(d) } \text{3,6-DBPQ, Pd(PPh}_3\text{)_2Cl}_2, \text{CuI, Et}_3\text{N, DMF, 100 - 110 °C.} \\
\end{align*}

\begin{table}[h]
\centering
\caption{Synthesis of 3,6 phenylethynyl phenanthrenequinones (\textbf{III})}

<table>
<thead>
<tr>
<th>Product</th>
<th>Arylacetylene</th>
<th>Reaction time (h)</th>
<th>Yield (%)$^a$</th>
</tr>
</thead>
</table>
| \textbf{III}a | $\begin{array}{c}
\text{NH}_2 \\
\text{NR}_2
\end{array}$ | 24 | 21 |
| \textbf{III}b | $\begin{array}{c}
\text{NH}_2 \\
\text{NR}_2
\end{array}$ | 17 | 38 |
| \textbf{III}c | $\begin{array}{c}
\text{NH}_2 \\
\text{NR}_2
\end{array}$ | 26 | 27 |
| \textbf{III}d | $\begin{array}{c}
\text{NH}_2 \\
\text{NR}_2
\end{array}$ | 18 | 23 |
| \textbf{III}e | $\begin{array}{c}
\text{NH}_2 \\
\text{NR}_2
\end{array}$ | 48 | 11 |

$^a$ Isolated yield, calculated based on 3,6-DBPQ.
As will be described later, it proved difficult to characterize the multipolar nonlinear optical properties of molecules in classes II and III because of their multiphoton induced fluorescence properties. We therefore sought to synthesize another class of molecules which might exhibit less fluorescence.

3,6-substituted dibenzo[a,c]phenazines (IV)  Representative o-quinone compounds in classes II and III were further reacted with nitro substituted 1,2-phenylenediamines in acetic acid under reflux, giving the corresponding 3,6-substituted dibenzo[a,c]phenazines (IV) (Scheme 4.5) These nitro substituted heteroaromatic compounds were anticipated to have weaker fluorescence since the nitro group has a well known and dramatic effect on quenching single photon fluorescence. Alternatively, compounds in Class IV could also be prepared by reacting the diamine and 3,6-DBPQ first and then coupling the intermediate nitro substituted 3,6-dibromodibenzo[a,c]phenazine with the appropriate styrene or phenylacetylene (Scheme 4.5). However, these substances proved to have low solubility and were not convenient for use as synthetic intermediates. Unfortunately, and to our surprise, even the nitro substituted adducts IV (Table 4.4) possessed significant multiphoton fluorescence that again complicated the nonlinear optical experiments needed to determine hyperpolarizabilities. The linear optical properties and electronic structure of compounds in Class IV will be discussed later, along with compounds from Classes I-III.
Scheme 4.5. Synthesis of 3,6-substituted-dibenzo[a,c]phenazines (IV)

\[ \text{(II or III)} \rightarrow \text{(IV)} \]

\( R_1 = \text{H or NO}_2; R_2 = \text{acetylene or styrene with donor groups.} \)

Table 4.4 Synthesis of 3,6-disubstituted-dibenzo[a,c]phenazines (IV)

<table>
<thead>
<tr>
<th>Product</th>
<th>( R_1 )</th>
<th>( R_2 )</th>
<th>Reaction Time (h)</th>
<th>Yield (%)(^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV(a)</td>
<td>H</td>
<td></td>
<td>48</td>
<td>28</td>
</tr>
<tr>
<td>IV(b)</td>
<td>NO(_2)</td>
<td>((\text{H}_3\text{C})_3\text{C})</td>
<td>6</td>
<td>87</td>
</tr>
<tr>
<td>IV(c)</td>
<td>H</td>
<td>((\text{C}_4\text{H}_9)_2\text{N})</td>
<td>3</td>
<td>76</td>
</tr>
<tr>
<td>IV(d)</td>
<td>NO(_2)</td>
<td>((\text{C}_4\text{H}_9)_2\text{N})</td>
<td>4</td>
<td>24</td>
</tr>
<tr>
<td>IV(e)</td>
<td>NO(_2)</td>
<td>((\text{C}<em>{12}\text{H}</em>{25})_2\text{N})</td>
<td>4</td>
<td>72</td>
</tr>
<tr>
<td>IV(f)</td>
<td>NO(_2)</td>
<td></td>
<td>6</td>
<td>87</td>
</tr>
<tr>
<td>IV(g)</td>
<td>NO(_2)</td>
<td>((\text{C}_4\text{H}_9)_2\text{N})</td>
<td>4</td>
<td>24</td>
</tr>
</tbody>
</table>

\( ^a \) Isolated yield.
4.1.3 Optical Properties and Electronic Structure Calculations

To investigate the molecular first hyperpolarizability tensor, $\beta_{ijk}$, of the PQ compounds in classes II-IV the method of Kleinman-Disallowed Hyper Rayleigh Scattering (KD-HRS)$^{25}$ was employed. Since this technique is able to characterize all of the rotationally invariant figures of merit of the hyperpolarizability tensor, it provides considerably more information than either (or both) electric field induced second harmonic generation (EFISH), which only measures the Kleinman allowed vector component, and conventional 90 degree hyper-Rayleigh scattering, which (is generally interpreted as) providing only the Kleinman allowed vector and octupolar components. However, in the wavelength range 1200 – 1600 nm, the diketone compounds in classes (II) and (III) possessed multiphoton fluorescence signals that were too large to permit separation of the SHG signal from the dominant fluorescence background, even though the $\Phi_F$ (single photon fluorescence quantum yields) of IIb and IIId were measured to be only in the range of 0.03-0.04 (measured in toluene solution compared to a reference DCDHF$^{26}$ dye). Attempts at measurements at longer wavelengths (1600-1800 nm) were also unsuccessful, as the HRS signal to noise was significantly decreased. Furthermore, our hope that the nitro-substituted phenazine derivatives would have enough fluorescence quenching to allow for a pure SHG signal to be obtained did not materialize, as those compounds also had unmeasurable SHG in the 1200-1600 nm range. Therefore, to understand the NLO properties of these molecules we considered the linear absorption spectra along with ZINDO-calculated transition moments and charge transfers. These parameters allow us to make inferences about the NLO through the sum-over-states model.$^{27}$
The UV-Vis absorption spectra of some representative compounds are shown in Figure 4.1. The 3,6-disubstituted conjugated PQs (Classes II-IV) show the presence of two strong absorption bands \( \varepsilon > 10^4 \text{ M}^{-1}\text{cm}^{-1} \). For those compounds with N-donor substituents, the first the low energy (long wavelength) band appears at 540 ± 25 nm, and the high energy (short wavelength) band is located around 375 ± 25 nm. For those compounds without donor substituents, the low energy band is at 400 ± 15 nm and the high energy band is around 300 ± 10 nm. The 3,6-halogen substituted PQs (Class I) show the presence of two main absorption peaks at 335 ± 10 nm and 430 ± 5 nm, respectively, and also a relatively low intensity peak near 525 nm. Figure 4.1(a) shows significant red shifts of 150 nm and 50 nm respectively for the two bands of IIIa when substituted with an amine donor (IIIc). These large shifts are characteristic of all the compounds from classes II-IV upon addition of an amine donor. Changing the alkyl tail length on these amine donors has very little effect on the electronic properties, as expected. For example, the \( \lambda_{\text{max}} \) of IIIc-e are very close at 530 ± 5 nm (the absorption wavelengths and molar extinction coefficients are listed in Table 4.7). It can be seen from Figure 4.1(a and b) that the 3,6-substituted phenanthrenequinones conjugated through double bonds have longer (~25 ± 5 nm) maximum absorption wavelengths than their counterparts conjugated via triple bonds. For example, \( \lambda_{\text{max}}(\text{IIb}) > \lambda_{\text{max}}(\text{IIIId}) \) and \( \lambda_{\text{max}}(\text{IVd}) > \lambda_{\text{max}}(\text{IVg}) \). Within class IV the lowest energy absorption peak of the single nitro compounds is red shifted by about 30-40 nm with the addition of a second nitro acceptor group (compare IVc and IVd in Fig 4.1b, for example). The second (higher energy) peak is largely unaffected,
Figure 4.1. UV-Vis absorption spectra of representative 3,6-substituted phenanthrenequinone compounds in CH$_2$Cl$_2$. 
indicating that this transition is not directly related to electrons near the nitro groups. Analogous molecules in groups III and IV have nearly the same transition energies and oscillator strengths, except that the higher energy peak is broadened in the group IV molecules, possibly indicating the presence of a new excited state not seen in the group III molecules.

The excited state symmetries of the lowest lying states, together with their transition moments and charge transfer in these compounds are of paramount interest for nonlinear optical characterization. As mentioned previously, excited states (with large oscillator strengths) polarized perpendicular to the dipole axis are required for \( C_{2v} \) molecules in order to maximize Kleinman disallowed molecular hyperpolarizabilities in the sum-over-states formalism. A further requirement is that the excited states are at low enough energy to benefit from resonant enhancement, since away from resonance the Kleinman disallowed components go to zero. Finally, it is important that the charge transfer between the ground and excited state is significant. Semi-empirical ZINDO/s configuration interaction singles (CIS) calculations\(^{28}\) were performed on representative molecules from each group to better understand the nature of the excited states. All filled and valence orbitals were used in the CIS calculation. Molecular geometries were optimized using the semi-empirical AM1 Hamiltonian (more rigorous geometry optimization using the \textit{ab initio} Hartree Fock method with SBKJC basis was carried out on a subset of the molecules but the oscillator strengths and energies of the subsequent ZINDO calculations differed by < 10% from the AM1 case, which did not justify performing the more rigorous calculations on these large molecules). In the compounds II/III/IV without the amine donors these ZINDO calculations predicted the lowest lying
transition wavelengths moderately well (within 15%), but only predicted red shifts upon adding an amine donor of approximately 10-20 nm for both the lowest energy peak and the second peak. It is not clear whether there are significant solvent effects that are not accounted for in the calculation, or whether the strength of the amine donor is not well parameterized in ZINDO. Nevertheless, ZINDO was still able to make reasonable calculations of the strength and symmetries of the transition moments (which do not depend as much on solvent effects). From these calculations it is clear that the lowest energy \( \pi \rightarrow \pi^* \) transition in molecules from Groups I-III has B-type symmetry – but with a very weak oscillator strength. In figure 4.1(a) this weak peak \((\approx 0.05)\) can be seen for molecule Ia near 525nm. In Ia this small transition moment is mainly the result of a poor HOMO-LUMO overlap (see Figure 4.2), as the HOMO\( \rightarrow \)LUMO transition accounts for over 85% of the excited state. This state has moderate charge transfer (~4-5 D, calculated by ZINDO), given the size of the molecule. Increasing the conjugation length (groups II and III) with extended phenylvinyl and phenylacetylene creates two nearly degenerate highest occupied \( \pi \) orbitals that spread out along the conjugation path (further away from the central phenanthrenequinone ring system). These orbitals have similar spatial profiles but opposite symmetry with respect to rotation about the symmetry axis of the molecule. The LUMO remains mostly unaffected, as compared to Group I.
Unlike Group I, the lowest lying excited state in II and III is not dominated by a single CI transition, but rather composed of contributions from both the HOMO $\rightarrow$ LUMO and HOMO-2 $\rightarrow$ LUMO transitions (see fig 4.3 for orbitals). The HOMO-2 is concentrated on the phenanthrenequinone ring, and is very similar to the HOMO of Group I molecules. Coupled with the minimal representation of the HOMO on the phenanthrenequinone core, this leads to a very weak transition moment, and in fact this lowest-lying B-type state cannot be seen in Figure 4.1(a) for molecule IIIa (it would be expected between 450 – 500 nm), or IIb/IIIc (it would be expected between 550 – 600 nm and is probably buried by the tail of the stronger absorption near 525 – 550 nm). This structure of the molecular orbitals contributing to the lowest excited state also results in slight or no increase in the charge transfer as compared to Ia.

Our calculations show that the two main transition peaks observed in molecules II and III are composed of CIS states with multiple electronic configurations composed of transitions from the 5 highest and 5 lowest unoccupied $\pi$ orbitals. One of these states is

**Figure 4.2.** HOMO and LUMO of Ia (calculated with MOPAC, with the alkyl chains truncated), showing the B-type symmetry and with very limited regions of overlap between these two orbitals which results in a weak oscillator strength for this transition.
Figure 4.3: Frontier orbitals for IIIc. The lowest-lying B-type state has CIS coefficients of 0.72 and 0.50 for the HOMO $\rightarrow$ LUMO and HOMO-2 $\rightarrow$ LUMO transitions respectively, which results in small oscillator strength.

A-type and the other B-type, but ZINDO does not provide unambiguous ordering of these two states, as the predicted energies are nearly degenerate in all cases. The dominant contributions, which make up about 50% of the state in each case, are HOMO-1 $\rightarrow$ LUMO and HOMO-2 $\rightarrow$ LUMO for the A-type and B-type states, respectively (refer to the representative orbitals in fig. 4.3). To investigate this further, an MCSCF calculation was performed with GAMESS$^{29}$ on molecule IIIc. The SBKJC basis was used with an active space consisting of the five highest occupied and five lowest unoccupied $\pi$ orbitals from a previous RHF run. The MCSCF calculation was
an equally weighted average of the ground and first three excited states, and like the ZINDO calculation, the results suggest that the second and third excited states are nearly degenerate (i.e. they differ by only about 10nm) in the gas phase. This lends more evidence that there are solvent effects which may change the energies of these two excited states in very different ways (possibly related to the different excited state charge transfers). At any rate, comparison of the experimental oscillator strengths of these two states with the ZINDO calculations suggests that the lower energy state is (surprisingly) B-type and the higher energy is A-type for molecules II/III (see Table 4.5 for assignments).

Assuming these predictions of B-type states with moderate oscillator strengths are accurate, the lack of strong SHG in the HRS signal is indicative of small charge transfer between the ground state and these B-type excited states. The charge transfer calculated with ZINDO for these states is about 5 D at most. This is not that surprising since the HOMO-2 is not spread out over the conjugation path, but rather localized on the phenanthrenequinone ring. These moderate B-type transition moments, and the fact that the transition moments and charge transfer do not extend from the phenanthrenequinone core onto the 3,6-substituents that extend the conjugation of the molecules indicates less potential for these dyes based on this core.
Table 4.5 Comparison of experimental oscillator strengths and transition energies with ZINDO calculations. Symmetries predicted by ZINDO (A-type or B-type) are also given. In some cases calculated oscillator strengths of the two nearest transitions are given when experimental peaks were not completely resolved. Experimental oscillator strengths were determined using $f = 0.043 \int \epsilon(v) dv$, where $v = \lambda^{-1} (cm^{-1})$, and $[\epsilon] = M^{-1} cm^{1}$. For the symmetric (dinitro) group IV molecules with amine donors (IVd and IVg) the structure of the three highest occupied orbitals are nearly identical (in both energy and shape) to those of the analogous group II/III molecules. However, the LUMO of group IV molecules extends from the top of the phenanthrene core to the nitro acceptors, and is about 0.5 ev lower in energy than in II/III (see Figure 4.4). ZINDO predicts that the lowest lying B-type $\pi \rightarrow \pi^*$ transition has small oscillator strength ($f \sim 0.1$), with two main CI contributions similar to the group II/III molecules (i.e. HOMO $\rightarrow$ LUMO and HOMO-2 $\rightarrow$ LUMO). Unlike the group I-III molecules, the
predicted charge transfer is now quite large (9D in IVg compared to 2.9D in IIIc), resulting from the larger separation of the nitro acceptors from the phenanthrene core. However, the small oscillator strength still makes this state of little consequence in the sum-over-states model. There are predicted 3 strong transitions (each with \( f \sim 1 \)) in the UV-Vis range. Unlike the group II/III molecules, the calculations suggest that the lowest energy strong transition unambiguously has A-type symmetry. This A-type transition has smaller charge transfer than in the analogous lowest-lying A-type transition in IIIc (2.3D for IVg compared to 6.3D for IIIc). This results because, in addition to the HOMO-1 \( \rightarrow \) LUMO transition, there is mixing in of a transition localized on the dibenzo-phenazine core which has little charge transfer. The remaining two transitions, one of A and one of B symmetry, are predicted to be nearly degenerate, and most likely make up the broad peak seen near 350 – 400nm (evidence of 2 peaks in this region is most clearly seen in the spectrum for IVg). Although the A-type lowest energy state is not necessarily desirable for Kleinman disallowed hyperpolarizabilities, the B-type state near 350-400 nm is predicted by ZINDO to have a rather large charge transfer of \( \sim 9 \) D, and it is surprising that a moderate SHG signal could not be observed, unless the fluorescence background is quite large for these symmetric phenazine compounds.
Figure 4.4 The LUMO of IVg has significant charge delocalization away from the phenanthrene core, resulting in large charge transfer but weak oscillator strength for the lowest-lying B-type state. The HOMO, HOMO-1, and HOMO-2 are nearly identical to those of IIIc (Fig. 4.3).

4.1.4 Conclusion

We have synthesized a series of \( \pi \)-conjugated 3,6-bis(N,N-dialkylaminophenyl-4-ethynyl)phenanthrenequinones and conjugated 3,6-bis(N,N-dialkylaminophenyl-4-vinyl)phenanthrenequinones to compare their linear optical properties and to develop structure-function relationships. Also, we have performed spectroscopic and molecular orbital calculations and considered their implications for the potential 2\(^{nd}\) order Kleinman-disallowed hyperpolarizabilities in these molecules. Overall, these compounds have low fluorescence yields, but apparently the multiphoton cross-sections are strong enough that the induced fluorescence masks the SHG signal, making it impossible to determine the molecular hyperpolarizabilities by the KD-HRS method in the 1200-1600 nm region without a fluorescence separation technique. The calculations coupled with
SOS considerations suggest that the group II/III molecules do not have states with the combined large oscillator strength and large charge transfer states that were expected. The symmetric group IV compounds with amine donors do have a strong B-type state with large charge transfer, but it is not the lowest energy state. It would be expected that a strong SHG signal could be obtained if the incoming laser frequency was more in resonance with this state (i.e. near 900 nm), but the broad absorption of the low-energy A state did not permit measurements in that regime.
4.2 References


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Chapter 5: Two-level and Multi-level SOS

Calculations of $\Lambda$-shaped Molecules

5.1 Spectroscopic and Charge-transfer Calculations of $\Lambda$-shaped Molecules for Kleinman-Disallowed Quadratic Nonlinear Optics

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Abstract: Molecules with actual or approximate $C_{2v}$ symmetry are considered for quadratic chiral axial nonlinear optical applications. Molecular orbital calculations (Ab initio MCSCF, and semi-empirical ZINDO/S) were used to evaluate the nature of the excited states, and the implications for the hyperpolarizability are discussed using the standard sum-over-states (SOS) formalism. Many of these molecules are shown to have strong $\pi \rightarrow \pi^*$ low-lying excited states with transition moments perpendicular to the $C_2$ axis and moderate charge transfer, thus showing potential for appreciable $L=2$ Kleinman-disallowed hyperpolarizabilities.
5.1.1 Introduction

Most organic materials designed for electro-optic or frequency doubling applications rely on polar ordering of one-dimensional donor-π-acceptor, or “push-pull” molecules. Polar ordering is usually achieved by electric field poling of guest-host systems of chromophores doped into or covalently bonded to polymers. In terms of the electro-optic effect, efforts aimed at synthesizing such polymeric materials have made good progress in lowering the half-wave voltage to near or below 1V.\textsuperscript{1,2} However, polar order is susceptible to thermal relaxation, which can decrease the macroscopic quadratic nonlinear optical effects as the chromophore dipoles become less aligned, and ultimately limit the chromophore loading densities.\textsuperscript{3} Much effort has gone into creating systems with highly stable polar order.\textsuperscript{4,5,6,7,8} As an alternative to polar materials, non-polar chiral uniaxial (\(D_\infty\)) symmetry) materials have been proposed.\textsuperscript{9} These materials incorporate multidimensional chiral (\(C_n\) or \(D_n\)) or non chiral (\(C_{2v}\)) molecules into a chiral uniaxial (“chiraxial”) alignment scheme that minimizes molecular dipole interactions while still implying a collective second-order response. From an oriented molecular gas perspective, this can be achieved by stacking chiral propeller-shaped molecules (\(C_n\) or \(D_n\), \(n \geq 3\)) along their symmetry axis, or by designing supramolecular structures that align nonchiral (\(C_{2v}\)) molecules along a helical path with their dipole axis pointing radially and their transverse axis twisted along the helix direction. Recent results of second harmonic generation (SHG) measurements from a bacteriorhodopsin film suggest that the nonlinear response from that film is mainly due to the chiral macromolecular orientation of achiral retinal chromophores, as opposed to an intrinsic molecular chirality.\textsuperscript{10} This provides motivation for designing more optimized chromophores to be incorporated into
helical/chiral supramolecular structures. Such structures are consistent with two possible hyperpolarizability tensors: a (very small) tensor which is completely antisymmetric under interchange of the two electrical fields and the resultant polarization and another tensor of mixed symmetry under this interchange, e.g. that is symmetric under some interchanges, antisymmetric under others. This latter hyperpolarizability is consistent with electro-optics and frequency doubling and is the subject of this paper.

This mixed symmetry violates Kleinman (index permutation) symmetry and requires that electrons are delocalized in at least two directions in the molecules\textsuperscript{9,11} so all of the usual one-dimensional polar molecules are not candidates. In addition, the breaking of Kleinman symmetry requires that the perturbing light not be too close to zero frequency, but rather near resonances. This requirement is easily satisfied for organic chromophores in the uv/visible regions, and for SHG this suggests the possibility of utilizing resonantly enhanced Kleinman disallowed hyperpolarizabilities for anomalous dispersion phase matching,\textsuperscript{12} provided the electronic states are spaced in such a way that there is a transparency window at both the fundamental and second harmonic. In fact, most practical chromophores for non-linear optics are used in the vicinity of resonances.

The most promising molecular symmetries for chiraxial NLO are \( \Lambda \)-shaped (\( C_{2v} \) or \( C_2 \)) or propeller-shaped (\( C_3 \) or \( D_3 \)). Attempts at designing chiral propeller-shaped molecules have met with some difficulty because of somewhat contradictory design constraints whereby large transition moments both perpendicular and parallel to the symmetry axis are desired, as the relevant molecular tensor component for chiraxial systems is \( \beta_{xyz} \).\textsuperscript{13} Maximizing this requires a large (~45\(^\circ\)) angle between the blades of the propeller and the rotation axis of the propeller. This is difficult if conjugation is to be
maintained between the center of the molecule; moreover it makes the overall shape of the molecule less consistent with the formation of liquid crystal phases. Thus, while there are multiple octupolar molecules with large $L=3$ quadratic hyperpolarizabilities, a majority of these molecules are largely or completely planar, and thus unsuitable for large $L=2$ hyperpolarizabilities. There are a variety of metallo-organics with appropriate geometry, such as, the trimeric styryl-bipyridyl complexes having $D_3$ symmetry (first suggested by Hilton et al and later characterized through hyper-Rayleigh scattering by Maury et al to have a large off-resonant quadratic response). This may be a fruitful approach to designing propeller complexes for KD hyperpolarizabilities, since these must be highly non-planar propellers due to the nature of the ligand-metal bond (see fig. 5.1), although resolving them into single enantiomers may require chiral substituents in the molecule because the enantiomers are likely to interconvert thermally. The propellers in that study are formed by three $C_{2v}$ styryl-bipyridyl ligands complexed to a central metal atom. There is typically rather little conjugation through the metal atom; or, at least the change in the electronic structure does not typically allow for direct (linear) coupling between the excited states on the ligands. Thus the primary issue for the hyperpolarizability, and the focus of this paper, is optimizing the Kleinman-disallowed $L=2$ component of the hyperpolarizability in approximately planar $C_{2v}$ molecules, as this seems the most interesting symmetry group for molecules with large KD hyperpolarizability.
Studies of the NLO properties of \( \Lambda \)-shaped molecules abound in the literature, but relatively few deal explicitly with the Kleinman-disallowed hyperpolarizability. The general structural motif for nonlinear optical \( \Lambda \)-shaped molecules is a “push-pull” concept, with either a \( \pi \)-electron acceptor at the apex of the molecule and donor-capped legs, or vice versa, and with a \( \pi \)-conjugated bridge in between the donor/acceptor pairs (fig 5.2). As in the case of one dimensional molecules, there seems to be a competition between charge transfer and oscillator strength of low-lying excited states that should be balanced in order to optimize the NLO response. Apart from tuning donor/acceptor strengths and varying the conjugation bridge, in two dimensions the angle between donors and acceptors emerges as another critical parameter. This “\( 2\theta \) angle” was studied systematically by Yang and Champagne where in most cases a strong correlation was shown between this angle and the ratio \( \beta_{xxx} / \beta_{zzz} \) at zero frequency.

**Figure 5.1**: Propeller-shaped (\( D_3 \)) complex with \( C_{2v} \) ligands is expected to exhibit nonplanar geometry consistent with Kleinman-Disallowed hyperpolarizabilities.
In this paper we will explore these parameters for a variety of $\Lambda$-shaped molecules in the context of producing optimized $L=2$ Kleinman-disallowed hyperpolarizabilities.

![Figure 5.2: Schematic representations of a $\Lambda$-shaped molecule showing placement of donors and acceptors and definition of $2\theta$.](image)

### 5.1.2 Theory

It has been shown previously that the third rank hyperpolarizability tensor applicable to an SHG experiment, $\beta_{ijk}(-2\omega,\omega,\omega)$, can be decomposed into four irreducible rotational invariants (two $L=1$ components, one $L=2$ component, and one $L=3$ component).\textsuperscript{9,11,50}

For poled materials the symmetric $L=1$ (vector) component is utilized, but for chiraxial systems optimization of the $L=2$ component is necessary. The expressions for all four rotationally invariant figures of merit for molecules with $C_{2v}$ symmetry (assuming $z$ is the $C_2$ axis of symmetry, and assuming all elements containing components perpendicular to the $x$-$z$ plane of the molecule are small, i.e. $\beta_{yz}$ and $\beta_{zy} = 0$) are\textsuperscript{50}
\[
\beta_{1s}^2 (C_{2v}) = \frac{1}{15}\sqrt{3} |3\beta_{zzz} + 2\beta_{xxx} + \beta_{xxx}|^2
\]

\[
\beta_{1mm}^2 (C_{2v}) = \frac{1}{3\sqrt{3}} |\beta_{xxx} - \beta_{xxx}|^2
\]

\[
\beta_{2mm}^2 (C_{2v}) = \frac{1}{3\sqrt{5}} |\beta_{xxx} - \beta_{xxx}|^2
\]

\[
\beta_{3ss}^2 (C_{2v}) = \frac{2}{15\sqrt{7}} \{3|\beta_{zzz}|^2 + 8|\beta_{xxx}|^2 + 2|\beta_{xxx}|^2
+ \text{Re}[8\beta_{xxz}^* \beta_{xxz} - 6\beta_{xxz}^* \beta_{zzz} - 3\beta_{zzz}^* \beta_{xxz}^*]\}
\]

Here the numerical subscripts (1,2,3) label the $L$ value, while the $s$ or $m$ tells whether the rotational invariant is “symmetric” or “mixed” with respect to permutation of indices. The $1ss$ and $3ss$ terms are commonly referred to as vector and octupolar, respectively. The $1mm$ and $2mm$ components are only non-zero when Kleinman symmetry is broken (i.e. for multidimensional molecules away from zero frequency and near a resonance). The vanishing of these terms under Kleinman symmetry is readily apparent.

Using time dependent perturbation theory, the electronic portion of the molecular hyperpolarizability tensor for a second-order process can be expressed as a sum over the excited electronic states (SOS):

\[
\beta_{ij} (-\omega_\sigma; \omega_2, \omega_{\delta}) = \frac{1}{\hbar^2} I_{1,2} 
\times \sum_{nm} \left\{ \frac{\mu_{nm}^i \Delta \mu_{nm}^j \mu_{nm}^k}{(\omega_{ng} - \omega_{ng})(\omega_{ng} - \omega_{\delta})} + \frac{\mu_{nm}^i \Delta \mu_{nm}^j \mu_{ng}^k}{(\omega_{ng} + \omega_2)(\omega_{ng} + \omega_{\delta})} + \frac{\mu_{nm}^i \Delta \mu_{nm}^j \mu_{ng}^k}{(\omega_{ng} + \omega_2)(\omega_{ng} - \omega_{\delta})} \right\} \tag{5.2}
\]

where \( g \) stands for the ground state, \( m \) and \( n \) label arbitrary excited states, \( \omega_{nm} = (E_n - E_m) / \hbar \), \( \mu_{nm}^i = e \langle \psi_n | r_i | \psi_m \rangle \), \( \Delta \mu_{nm}^i = \mu_{nm}^i - \mu_{gg}^i \delta_{nm} \), and \( I_{1,2} \) is a permutation operator that averages the expression over simultaneous permutation of
\( \omega_1 \leftrightarrow \omega_2 \) and \( j \leftrightarrow k \). Within the SOS calculation, contributions to the hyperpolarizability tensor can be separated into two-level terms and three-level terms. Two-level (dipolar) terms arise from coupling of the ground state to a single excited state via \( \mu_{\text{gn}} \Delta \mu_{\text{mn}} \mu_{\text{ng}} \). Three-level terms result from coupling of the ground state to two excited states via \( \mu_{\text{gm}} \mu_{\text{ma}} \mu_{\text{ng}} \). For \( C_{2v} \) molecules the ground state to excited state transition moments will be either along the symmetry axis (A-type), which we will call the z-direction in this work, or perpendicular to z, along the x-direction (B-type). Dipole-operator matrix elements between excited states will be in the z-direction if the symmetries of the excited states are the same, and along the x-direction if the symmetries are opposite. The Kleinman disallowed (KD) components (1mm and 2mm) of the hyperpolarizability (see eq. (5.1)) are expected to be optimized through dipolar contributions from B-type excited states with large charge transfer. While charge transfer states with A-type symmetry contribute to the vector and octupolar figures of merit through dipolar terms, they only affect the KD components through three level terms when coupled with a strong B-type state. Therefore, strong B-type states are fundamental for large KD hyperpolarizabilities.

The simplest approximation for the KD components is given by the two level model,\(^{53}\) which includes the ground state and a single B-type excited state. For SHG this is

\[
\left| \beta_{2,mm}^{(2L)}(-2\omega,\omega,\omega) \right| = \left( \frac{144}{5\hbar^8} \right)^{1/4} \frac{\left( \mu_{01}^* \right)^2 \Delta \mu_{01} \omega^2}{(\omega_{01}^2 - \omega^2)(\omega_{01}^2 - 4\omega^2)} \tag{5.3}
\]

For electro-optic applications this can be converted via

\[
\left| \beta_{2,mm}^{(2L)}(-\omega,\omega,0) \right| = \left( \frac{1}{3} \right) \left| \beta_{2,mm}^{(2L)}(-2\omega,\omega,\omega) \right| \left[ \frac{(\omega_{01}^2 - 4\omega^2) / (\omega_{01}^2 - \omega^2)}{\omega_{01}^2 - \omega^2} \right] \tag{5.4}
\]
Some studies of \( \Lambda \)-shaped molecules report on the non-resonant off-diagonal component of the hyperpolarizability tensor, \( \beta_{zzz}(0) \).\(^{31,33,39,46}\) Assuming the validity of the two level approximation, this can be used to estimate the 2mm component via

\[
\left| \beta_{2mm}^{(2L)}(-2\omega,\omega,\omega) \right| = \left| (144/5)^{1/4} \beta_{zzz}^{(2L)}(0) \left[ \omega^2 \omega_{10}^2 / ((\omega_{10}^2 - \omega^2)(\omega_{10}^2 - 4\omega^2)) \right] \right| \quad (5.5). 
\]

We note that it is reasonable to suppose that large \( \Lambda \)-shaped molecules are less likely to be well described by a two level model. These larger molecules have more and more closely spaced states that may contribute to the hyperpolarizability. This is particularly true if the coupling between the two “legs” of the \( \Lambda \) is weak, in which case the molecule is more appropriately viewed as two rod-like molecules, neither of which has KD contributions to the hyperpolarizability. Seeing this near cancellation in a SOS model requires including both (nearly degenerate) excited states formed by the weak coupling of the excited states localized on each leg.

While our focus is on the 2mm KD component of the hyperpolarizability, we point out that a single B-type excited state will also contribute to the vector (1ss) hyperpolarizability with a relative magnitude for SHG of

\[
\left| \beta_{2mm}^{(2L)} / \beta_{1xx}^{(2L)} \right| = (240)^{1/4} (\omega / \omega_{10})^2 = 3.9 (\omega / \omega_{10})^2. \quad \text{This ratio approaches ~4 near resonance,}
\]

but in practice is usually much smaller, as most \( \Lambda \)-shaped molecules also have low-lying dipolar A-type states that increase the vector component relative to the KD component.

In the absence of very strong coupling between the symmetric “legs” of a \( \Lambda \)-shaped molecule it would be expected that a narrow angle \((2\theta < 90 \text{ degrees}) \) will favor the diagonal component of the hyperpolarizability tensor, whereas a wider angle favors the off-diagonal components (and ultimately the 2mm component). Within the two level
model (eq. (5.3)) we can derive a simple geometric optimization condition for the 2mm component of an uncoupled bis(dipolar) \( \Lambda \)-shaped molecule.\(^{27}\) We consider two identical dipolar molecules, each with a dominant low-energy charge transfer excited state, joined together at an apex. Adding their transition moments in phase yields an A-type state, whereas adding them out of phase gives a B-type state. Reducing the \( 2\theta \) angle between the dipoles will make the projection of each dipole along the symmetry axis larger. This will monotonically increase both the A-type transition moment and the charge transfer in the \( z \)-direction, and lead to increasing the \( \mu^2 \Delta \mu \) product, which is proportional to \( \cos^3(\theta) \). However, widening the angle will increase the B-type transition moment (perpendicular to the symmetry axis) but reduce the charge transfer along the symmetry axis. For the B-type state we have \( \mu^2 \Delta \mu \sim \sin^2(\theta) \cos(\theta) \), and this is maximum near 110 degrees. From this angular dependence (see figure 5.3) we see that putting together two dipolar molecules at this maximum angle gives a \( \mu^2 \Delta \mu \) product for the B-type state that is roughly the same size as the diagonal \( \mu^2 \Delta \mu \) product for only one of the constituent dipoles. More precisely, the density of the \( \mu^2 \Delta \mu \) product is reduced by a factor of \( 1/(\sin^2(55)\cos(55)) = 2.6 \) when going from one to two dimensions, even with optimal alignment. The situation may be more complicated when the dipoles are strongly interacting, but the general expectation that the density of the \( \mu^2 \Delta \mu \) product of a two-dimensional molecule is smaller than for a related one-dimensional molecule is expected to hold in most cases on geometric grounds; although it may also be that there are differences in the competition between the charge transfer and the transition moments.
with moderate coupling. However, in the bulk it is hoped that a higher order parameter for non-polar alignment along with resonant enhancement will help overcome this factor.

![Graph](image)

**Figure 5.3**: Comparison of $\mu'\Delta\mu$ for the A-type and B-type states of a bis(dipolar) $\Lambda$-shaped molecule as a function of angular alignment. The maximum for the B-type state is about half that of the A-type state.

Furthermore, the expectation that $\Lambda$-shaped molecules may have multiple important states contributing to the hyperpolarizability should be examined, as this may also help increase the two-dimensional KD response. It is known that highly symmetric molecules (e.g. $D_3$, $C_{3v}$, etc.) give rise to degenerate excited states in which a minimal state SOS model must include at least three-levels; but the failure of the two-level model has been shown in less symmetric (linear and $C_2$ symmetry) molecules as well. Therefore, while the two-level model will be used as a means of defining a figure of merit for comparing a large set of molecules, we will also present discussion of more complicated multi-state models in this report.
5.1.3 Materials

We will first look at a series of triarylmethyl carbocation molecules (TAMC’s) synthesized in our group. (fig. 5.4) These molecules consist of a central carbocation substituted with various -aryl groups (phenyl, phenylethynyl, naphthyl, phenylstyril) and in most cases terminated with amine donors. We will consider molecule 1 as the most basic structure within this class. This molecule is a malachite green analogue where the dimethylamino donors of malachite green have been replaced by the cyclic pyrrolidine donor to slightly enhance the electronic properties. Malachite green (MG) has two prominent absorption peaks in the UV/Vis. It has been known for a long time (first from polarized fluorescence studies\textsuperscript{56}) that the longest wavelength (\~615 nm) transition moment of MG is perpendicular to the symmetry axis (the so-called “x-band” of absorption, corresponding to a B-type excited state), while the weaker absorption near

![Figure 5.4: Triarylmethyl carbocations synthesized by our group. Pr = pyrrolidine = \textbullet N.](image-url)
420nm is polarized parallel to the symmetry axis (often labeled “y-band” absorption in the literature). The existence of a lowest-lying B-type excited state prompted experimental investigation of MG through Kleinman-disallowed hyper-Rayleigh scattering. The KD-HRS results showed KD components of the hyperpolarizability comparable to the vector component, and this led to the study of more TAMC’s. More recently the synthesis and spectral characteristics were reported for \( \textbf{1} \) and \( \textbf{2} \), along with other TAMC’s with \( \text{C}_2 \) symmetry, including two dinaphthylmethyl carbocations (\( \textbf{6} \) and \( \textbf{7} \)) which were expected to have improved Kleinman disallowed hyperpolarizabilities compared to \( \textbf{1} \) because of their extended conjugation through the naphthyl units (see chapter 3)\(^{47} \). Using the Time-Correlated Single Photon Counting Kleinman-Disallowed 45° HRS (TCSPC- KD HRS) technique, appreciable Kleinman-disallowed figures of merit were reported for \( \textbf{1} \) and \( \textbf{6} \)\(^{47} \), but data for \( \textbf{7} \) could not be attained at the 795nm setup due to prohibitively high levels of resonantly enhanced multiphoton induced fluorescence emission at the second harmonic that could not be temporally separated from the SHG signal. Synthesis of \( \textbf{4} \) and \( \textbf{5} \) has been undertaken (unpublished) which are expected to have large charge transfer due to extended conjugation along the symmetry axis, and \( \textbf{3} \), which is expected to have improved charge transfer and redshift over \( \textbf{1} \) due to increased planarity and resonance destabilization. Results of TCSPC-KD HRS have been reported\(^{48} \) for \( \textbf{2} \) and \( \textbf{5} \) which will be discussed, but \( \textbf{3} \) and \( \textbf{4} \) could not be measured due to their red-shifted linear absorption which interfered with the 795 nm fundamental wavelength.

Calculations on another set of TAMC’s (\( \textbf{8}-\textbf{12} \)) that were expected to be good prospects for KD hyperpolarizabilities will be presented (fig 5.5). These differ from the
first set of TAMC’s by addition of a nitro group (8-11), ring-locking (10,11), or extension of conjugation length via styryl substituents (12).

![Molecular structures of modified TAMC’s](image)

**Figure 5.5:** Molecular structures of modified TAMC’s

Next we will present calculations on a variety of molecules (13-25) that seem to have good spectroscopic and geometric properties for strong KD hyperpolarizabilities. These molecules are either previously synthesized (as found from literature searches), or at least seem plausible to synthesize. Within this class of molecules we will consider structure and function relationships and molecular orbital calculations that will help guide future rational design of chromophores for optimal KD hyperpolarizabilities. A majority of these molecules (12-21, 25) contain diene or styryl conjugated pathways between donor and acceptor groups. Diphenylcyclopropene is also investigated as a pathway for charge transfer with remarkable properties in certain contexts (22, 23).
We remark that there are a number of conformers possible for most of these molecules resulting from the relative rotation of the two “legs” of the Λ around their long axis. In some of the molecules (such as 13) we expect that changes in conformation can occur thermally and yet more obviously in the presence of light, which may result in singlet or triplet excited states that allow interconversion of various double bonds. In others (such as 14) the various different conformers seem likely to interconvert only in the presence of light, if at all, and to be likely mixed products of many synthesis techniques. In all cases, consistent with our prior calculations, we believe that the optical properties of most conformers will be similar, with the exception of the dramatic trans-cis isomerization of
the ethylene bridge (shown in fig. 5.7(d)). We have calculated only the properties of the conformers most closely resembling the (planar) symmetric geometric structures shown in fig 5.6.

**Figure 5.7:** Some of the possible conformations of 14 are shown: (a),(b), and (c) should have similar conformation energy and similar optical properties, whereas (d) is a higher energy conformation that will have larger changes in linear and nonlinear properties.

Lastly we consider 3- and 5-carbon symmetric cyanine molecules that have been measured with TCSPC-KD HRS\(^{48}\) (fig 5.8). These molecules have very little “bend” to them, so their charge transfer is expected to be small. Nevertheless the measured KD hyperpolarizabilities of the 5-carbon cyanines are rather substantial, and possible reasons for this are investigated.
5.1.4 Calculation Techniques

For molecules with many electrons it is not desirable/feasible to do \textit{ab initio} electronic structure calculations to screen a large set. Recent studies show that for gas phase calculations, the semi-empirical ZINDO\textsuperscript{57} configuration interaction singles (CIS) calculations along with the sum-over-states (SOS) expression (eq. (5.2)) give similar results for non-resonant hyperpolarizabilities as finite-field calculations for both Hartree-Fock and DFT methods over a wide range of molecular structures.\textsuperscript{58} Furthermore, results from Coe et al\textsuperscript{59} comparing spectroscopic calculations of benzothiazolium salts between INDO and TD-DFT suggest that there is no clear evidence as to which method is more accurate at predicting hyperpolarizabilities within the SOS framework. In addition, our own experience shows that both charge transfer and transition moment calculations with ZINDO produce similar results as more rigorous \textit{ab initio} MCSCF calculations (described below). Therefore we have chosen to screen all molecules in this study using the ZINDO/SOS method.\textsuperscript{60} The molecular geometries were optimized using the semi-empirical AM1 Hamiltonian\textsuperscript{61} with Gaussian03.\textsuperscript{62} The ZINDO package within
Gaussian03 was used with default parameters for calculation of excited states, and the RhoCI density was used to calculate excited state dipole moments. The CIS active space included all filled and valence orbitals. For a small subset of the molecules additional *ab initio* multi-configuration self-consistent field (MCSCF) calculations were done with GAMESS to calculate changes in dipole moments between the ground and low-lying excited states. Such calculations, in which a variational principle on the energy is used, allow both the single particle wavefunctions and the occupations within an active space of orbitals to be varied. Our procedure was to optimize the geometries using the Restricted Hartree Fock method, and the SBKJC basis with effective core potential (ECP). The RHF orbitals of the optimized geometry were then used as the starting orbitals for the MCSCF calculation. The MCSCF active space varied slightly from molecule to molecule, but between 4-6 occupied and 4-6 valence orbitals were used. All orbitals in the active space had effectively solely $\pi$ character. Within this active space, all possible configurations were allowed. For “fairness” both the ground and excited state properties were calculated using MCSCF calculations with identical geometries and active spaces.

5.1.5 Results I: Two-level Figure of Merit

In order to take into account the differing sizes of these molecules we define a parameter $R = \mu^2 \Delta \mu / N$, where $N$ is twice the number of double or triple bonds. We have chosen to exclude the energy in the definition of this figure of merit because at zero frequency the KD responses are zero so the term “off resonance” in this context has less meaning than when talking about the vector or octupolar response, where zero frequency is used as
a standard. Figures of merit involving the excitation energies are inevitably more complicated than a single number in this situation. In the following, \( R \) values are reported for the two (or few) lowest lying excited states of these \( \Lambda \)-shaped molecules. Usually this includes both an A-type and B-type excited state; but only the \( R \) values for the B-type states contribute to the two-level expression for the 2mm component of interest, whereas \( R \) values for A-type states contribute to the 1ss and 3ss components.

**Molecules 1-7**

All of the TAMC’s exhibit various degrees of twisting about the central carbon atom, and are therefore not strictly \( C_{2v} \) symmetric. However, the deviation from planarity is relatively small compared to the other two dimensions of the molecules, and it is estimated that the \( C_{2v} \) approximation will introduce errors in calculated hyperpolarizabilities of only a few percent. For all TAMC’s besides 6 and 7 only one conformation was considered; but for 6 and 7 three conformations are plausible (the ones drawn in fig 5.4, plus either one or both of the napthyl units rotated by 180 degrees about the bond to the central carbon). The AM1 calculations suggest that the energy difference between the three conformations for each of these molecules is less than \( \frac{1}{2} \) kcal mole\(^{-1}\) and therefore it is probable that all three exist in solution. For our calculations we report on the two symmetric conformations of each of these molecules (the conformations implied in fig 5.4 will be labeled 6a, 7a herafter, while the conformations with both naphthyls rotated by 180 degrees will be labeled 6b and 7b).
The results of the ZINDO/s and MCSCF calculations for compounds 1-7 are summarized in table 5.1. The common reference dye Disperse Red 1 is included in the list for comparison. As expected, each of these TAMC’s had a strong B-type and a strong A-type excited state in the visible region. The electronic states of interest had
rather simple “single electron” character, i.e. a CIS coefficient of \( |a_{n \rightarrow m}|^2 \approx 85 - 90\% \) or more for the HOMO \( \rightarrow \) LUMO or HOMO-1 \( \rightarrow \) LUMO transitions respectively. The energies and relative strengths of the transitions depend on the details of the molecular orbitals for each molecule (see figure 5.9), but roughly the B-type state results from movement of an electron delocalized over the symmetric “legs” towards the central (positively charged) carbon, while the A-type state results from movement of an electron delocalized strongly over the aryl substituent along the symmetry axis towards the central carbon. Thus the charge transfer is in opposite directions for the lowest lying A and B-type excited states in these TAMC’s. We note here that this type of electronic structure is not well-approximated by the non-interacting bis(dipolar) model, since in that model both the A and B states originate from electrons in the same region of the molecule having opposite phase. In the case of these TAMC’s there is a third donor substituent directly attached to the central carbon along the symmetry axis that strongly influences the lowest-lying A-type state, and moderately affects the B-type state. In any case, the roughly 120 degree angle between the symmetric legs and the central electron-accepting carbon atom in these molecules seems close to optimum geometric alignment (\( \approx 110 \) degrees) for the B-type transition, as discussed earlier. The strong representation of the LUMO on the central carbon of each of these molecules coincides with the resonance structure which places the positive charge on this central carbon. In all cases, this resonance structure maximizes the aromatic stabilization and is therefore the most important/stable resonance structure for these TAMC’s.
(1) 

HOMO-1
(-11.16 ev)

HOMO
(-10.41 ev)

LUMO
(-4.72 ev)

(2) 

HOMO-1
(-10.29 ev)

HOMO
(-9.90 ev)

LUMO
(-4.49 ev)

(3) 

HOMO-1
(-10.31 ev)

HOMO
(-10.22 ev)

LUMO
(-4.90 ev)
(4)

HOMO-1 (-10.68 ev)  
HOMO (-10.33 ev)  
LUMO (-4.84 ev)

(5)

HOMO-1 (-10.22 ev)  
HOMO (-9.83 ev)  
LUMO (-4.66 ev)

(6a)

HOMO-1 (-10.13 ev)  
HOMO (-9.73 ev)  
LUMO (-4.52 ev)
Figure 5.9: The two highest occupied (HOMO, HOMO-1) and single lowest unoccupied (LUMO) molecular orbitals, computed with MOPAC within the Chem3D Ultra suite. The Pyrrolidine group was simplified to NMe₂ to speed up computation.

The single naphtyl substituent of molecule 2 causes a slight decrease in the transition moment of the B-type state (HOMO-1 → LUMO) as compared to the B-type state in 1 (HOMO → LUMO), as well as a hypsochromatic (“blue” or increased energy) shift (~40nm). This is mainly due to steric effects of the bulky 1,4 substituted naphthyl group, which raise the energy of the LUMO. Despite steric crowding, the napthyl group acts as a better acceptor (compare the LUMO of 1 and 2), which increases the charge transfer and ultimately the NLO response. The A-type state in 2 has significant bathochromatic (“red” or decreased energy) shift compared to 1 due to the strong concentration of electron density on the naphthylamine group (HOMO), which has much higher energy than the electron on the bare phenyl group of 1 (HOMO-1). Furthermore, the HOMO-1 of 1 is delocalized over the entire molecule, which lowers its energy even more, and is the main reason why there is such a large energy difference between the A and B states in that molecule. The A and B states of 2 are much closer in energy, and in fact the ZINDO calculations suggest that the A-type is lower in energy.
It is known that fluorene analogues of TAMC dyes, formed by directly bridging two phenyl amine groups together (see molecule 3 for an example, fig. 5.10 for a schematic), exhibit very large bathochromic shifts in their linear absorptions, compared to non-bridged TAMC’s. The fluorene ring system lowers the energy of the LUMO significantly by bringing the central carbon acceptor in plane with the bridge-forming carbons (C1 and C2 in fig. 5.10) that bear a moderate portion of the LUMO density.

![Figure 5.10](image)

**Figure 5.10** Carbons C1 and C2 are bridged together to form the fluorene analogue (b) of a TAMC (a). The central five membered ring system in (b) is formally anti-aromatic and causes a dramatic bathochromatic shift.

Furthermore, the central charged 5-carbon ring is now anti-aromatic, so that the energy of the HOMO is raised because 4 of the carbon atoms which bear significant HOMO density are now part of the central destabilized anti-aromatic ring. It is this combined lowering of the LUMO energy and raising of the HOMO energy that gives this molecule its extreme bathochromatic shift. In 3 the lowering of the LUMO energy is slightly counteracted by the opposing amine donor along the symmetry axis (the \( R'' \) position in fig. 5.10). If this amine donor is replaced by H the LUMO is lowered to -5.15 ev (as compared to -4.90 ev for 3, see fig. 5.9). Thus the fluorene analogue of malachite green (not pictured) is even more red-shifted than 3, with its lowest lying absorption red-shifted by another ~100 nm to 955 nm. Calculations confirm that the low-lying state in
3 and other TAMC fluorene analogues is B-type. However, this B-type transition moment in 3 is about 2 times smaller than in 1. This can be partly explained through geometric effects. The $2\theta$ angle between the central carbon acceptor and amine donors in 1 is $\sim$113 degrees, but only $\sim$90 degrees in 3, which should reduce the B-type state transition moments by a factor of roughly 0.85. The remaining decrease is directly related to unfavorable changes in the HOMO/LUMO overlap. The increased planarity of 3 has only modest effects on the charge transfer. In fact, taken by itself the increased planarity of the bridged phenylamines slightly lowers the charge transfer, as evidenced by the fact that the B-type state of the MG fluorene analogue is actually calculated to have smaller charge transfer ($\Delta\mu = 2.8 \text{ D}$) than 1. This seems to be a result of the LUMO density increasing on the carbons that are linked together to form the bridge (C1 and C2 in fig. 5.10), e.g. with the relative destabilization of the charged resonance structure. Despite this effect, the charge transfer in 3 is slightly greater than in 1 because the unbridged phenylamine group in 3 is only twisted $\sim$32 degrees out of plane (compared to $\sim$39 degrees for the bare phenyl of 1) due to increased conjugation caused by the amine. This structural effect encourages more density of the LUMO on the unbridged phenyl, which increases charge transfer overall. In terms of the KD NLO response, the $R$-value of the lowest B-type state is not impressive. However, SHG measurements in the 1400-1680 nm range show a large response,\textsuperscript{48} which must be attributed mainly to the three level term which couples the lowest lying A and B states. This warrants further investigation theoretically and experimentally (and will be discussed in Section 5.1.6).

Relative to 1, the extended conjugation of molecules 4-7 results in bathochromic shifts of the absorption of both the A and B-type states and generally increases the charge
transfer. For 4 and 5 this is partly the result of a reduction in steric hindrance from
replacing the phenyl with phenylethynyl. The twist angle for the phenylamine legs in 4
and 5 is calculated to be roughly 27 degrees, as compared with 29.5 degrees for 1. The
interaction of the acetylene bond with the central carbon in 4 and 5 also lowers the energy
of the LUMO and increases the charge transfer since there is moderate representation of
the LUMO on the acetylene bond, which acts as an acceptor. As was the case when
comparing the fluorene analogue of malachite green with 3, the replacement of an amine
group in 5 with H to give 4 lowers the LUMO energy, causing a larger bathochromatic
shift in the B-type state of 4 than in 5. Overall the effect of the ethynyl linkage increases
the $R$ value for the B-type state of both 4 and 5. The A-type state in 5 is directly
enhanced by the ethynyl linkage and (much more so) the amine donor, which leads to a
~200 nm bathochromatic shift over the analogous A-type state in 1. The $R$ value for this
A-type state is exceptional, exceeding DR1. The lack of amine donor in 4 causes this
compound to have only a moderate change in the energy of the A-type state (~70 nm)
compared to 1. In 6 and 7 the delocalization of the HOMO mainly over the
naphthylamine donors causes a significant raising of the HOMO energy as compared to
1, leading to a moderate redshift of the B-type state. The extended conjugation of the
naphthylamines causes increased charge transfer as well since more of the HOMO is
further away from the central carbon. Overall this increases the B-type $R$-value in 7, but
not for 6, because 6 is sterically crowded, and because the amine group in 6 is closer to
the central carbon than in 7, both of which leads to a rather large reduction of the B-type
transition moment in 6 as compared to either 7 or 1. Thus, the conjugation and geometry
in the 2,6 substitution pattern of the napthylene in 7 is superior to the 1,4 substitution.
pattern in 6. Despite the lower $R$ value, the measured KD hyperpolarizability of 6 is larger than 1, which implies that three level contributions may be important. The lowest-lying A-type states of 6 and 7 are significantly red-shifted (~200 nm) with respect to 1 due to the addition of an amine donor which drastically raises the energy of the HOMO in each case. For both of these molecules this brings the A-type state to near (accidental) degeneracy with the B-type state and causes more obvious potential breakdown of the two-level model.

The compounds with the largest calculated $R$ values were 5 and 7a, with $R=32.2$ and 32.8 respectively. These molecules represent two different strategies for optimizing the properties of the frontier orbitals—either extension of the conjugation pathway along the symmetry axis of the molecule (5), or extension along the legs of the molecule (7a).

**Molecules 8-12**

Calculations on molecules 8-12 explored further modifications of these TAMC’s, with the results summarized in table 5.2. A nitro group was added to molecules 1 and 4 along the symmetry axis (giving 8 and 9), but this produced very little (10%) increase in the charge transfer of the lowest lying B-type state, and thus had insignificant effect on the $R$ values. This is because the spatial distribution of charge of the LUMO in 8 and 9 is virtually unchanged with respect to 1 and 4, still mainly represented on the central carbon in each molecule. It is the LUMO+1 that is strongly affected by the nitro group, but this orbital is far removed from the LUMO in energy and has significant influence only on higher energy states.
The main effect of the nitro group on the HOMO-1, HOMO, and LUMO is roughly a uniform lowering in energy, which produces A and B states of similar energy as 1 and 4 (confirmed through experiment and calculation). Therefore, this nitro substitution may affect higher energy transitions, but has relatively minor impact on the frontier orbitals and low-lying transitions in these carbocations. A bridged fluorenyl version of 9 has been prepared in the literature and has remarkably long wavelength absorption (1096 nm). This lowest-lying excited state is B-type and has a similar large reduction in transition moment as other fluorene analogues, such as 3. ZINDO calculations suggest that the fluorene analogue of 9, which is fully planar, does not have large HOMO \( \rightarrow \) LUMO charge transfer, since a majority of the LUMO is still concentrated on the central carbon. Thus, in all of these cases the nitro acceptor is effectively screened and does not strongly interact with the central carbon to induce more charge transfer as was hoped. Heuristically, this lack of effect on the LUMO may be traced to the improbability of the resonance structure shown in fig. 5.11.

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Table 5.2: Spectroscopic and two-level figure of merit calculations for 8-12. \(^a\) Literature values (if available). \(^b\) Calculated with ZINDO/s in gas phase. \(^c,d\) Calculated with ZINDO/s, in Debye units. \(^e\) See ref. 66. \(^f\) See ref. 67. \(^g\) See ref. 68.
Figure 5.11: This resonance structure of 8 implying charge transfer to the nitro group is improbable. Analogous resonance structures for 9-11 lead to similar conclusions regarding the electron-accepting ability of the nitro group in those compounds.

This highlights the difficulty of producing a B-type state with large charge transfer through adding nitro acceptors along the symmetry axis or through increased planarity.

Another approach to increase charge transfer through increased planarity met with similar results. The modification of the symmetric rotamers 7a,b to give 10 and 11 via an oxygen ring-closure leads to a modest bathochromic shift in the lowest B-type state of each molecule but a decrease in charge transfer. This bathochromic shift results mostly from the increase in planarity of the naphthyl units with the central carbon, which lowers the energy of the LUMO by about twice as much as it lowers the HOMO (fig 5.12). This oxygen bridge does not cause nearly as much red shift as the direct C-C connection in the fluorene analogues: the central hetero-cyclic ring is now formally aromatic, stabilizing the HOMO. The transition moments of the B-state are actually increased (as opposed to decreasing significantly in the flourene-bridged compounds). This occurs despite rather small decreases in the 2θ angle for each oxygen-bridged compound. Comparison of the HOMO and LUMO of 7a and 10 and 7b and 11 respectively shows that the π-orbital on oxygen is not highly occupied in either of these frontier orbitals for 10 or 11, and therefore these orbitals are similar to 7a,b. The main influence of the oxygen is structural, and since the spatial distribution of the HOMO/LUMO is similar with or
without the oxygen bridge, the increased planarity increases the transition moment. The rigidity of the closed ring system causes the nitrophenyl group to twist out of plane roughly 60 degrees in 10 and 11. This further decouples the frontier orbitals of the nitrophenyl group from the central carbon and limits charge transfer (both 10 and 11 are reduced as compared to 7a,b). Thus the combination of nitro acceptor and ring-locking does not produce the desired result in the B-type state of either molecule.

The lowest lying A-type state in 10 and 11 have strong HOMO-1 $\rightarrow$ LUMO character. This transition has moderate oscillator strength in 11, but vanishingly small in 10 due to poor orbital overlap. The first moderately strong A-type transition for 11 (recorded in table 5.2) has multiple contributing configurations but is dominated by a HOMO-2 $\rightarrow$ LUMO transition. Overall this ring closure modification has removed the near degeneracy of the A/B states in 7a,b but in terms of the quantum parameters the $R$ values have both decreased because of reduced charge transfer.

It is clear from the above examples that successful modification of the LUMO is very difficult in these TAMC’s. However, the HOMO can easily be modified through structural changes or extension of conjugation. In 12 the conjugation was extended away from the central carbon through a styryl bridge ending with an amine donor. This resulted in an exceptional B-type state, again dominated by a HOMO $\rightarrow$ LUMO transition (fig. 5.13). The HOMO-1 for this molecule is very similar (spatially) to the HOMO but with opposite parity with respect to rotation about the symmetry axis, and of slightly (~0.2 ev) higher energy. The relative size of the B/A transition moments can be rationalized by the simple geometric arguments of the bis(dipolar) model. The $2\theta$ angle is 128 degrees, so the expected ratio of transition moments B:A is $\tan(64) = 2.05$. The
calculated value is 2.15. The nearly equal charge transfer in the B and A-type states also
follows the expectations of the bis(dipolar) model. Thus, we see behavior more closely
approximating the bis(dipolar) model as the legs of the TAMC are extended.

(10)

(11)

Figure 5.12: Frontier orbitals of 10 and 11.
Figure 5.13: Frontier orbitals of 12 responsible for the lowest-lying B-type state.

Molecules 13-25

Based on the promising results from 12, we have considered other molecules with similar geometric structure, with results summarized in Table 5.3 below. Molecule 13 has a similar structure to 12 and the roughly 2:1 ratio between the B and A-type states is preserved. Calculations on a “monomer” version of 13 (i.e. NMe₂ – stilbene – NO₂) gave an R-value of 57.5. Based on this calculation the predicted R-value for 13 with a 2θ of 128 degrees is 20.4, and the bis(dipolar) model is almost exact. The similar energies for the A and B states is a result of nearly degenerate LUMO/LUMO+1, which are concentrated on the nitrostyryl group but have opposite phase. Bridging two carbons to form 14 does not strongly alter the optical properties. The decrease in ratio of the B to A-
Table 5.3: Spectroscopic and two-level figure of merit calculations for 13-25. \(^a\) Literature values (if available). \(^b\) Calculated with ZINDO/s in gas phase. \(^c,d\) Calculated with ZINDO/s, in Debye units. \(^e\) See ref . \(^f\) Estimation based on ref 37. The molecule in that study has a diazo bridge instead of ethylene. \(^g\) See ref 45. \(^h\) See ref . Only one peak can be resolved experimentally due to near degeneracy.

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</table>

type transition moment and the slight increase in charge transfer are rationalized by the decrease in \(2\theta\) from 128 to 98 degrees. Solvochromatic properties of 14 were studied by Kuo et al\(^{38}\) and used to estimate NLO properties through the two-level model. However, in that work the lowest-lying transition moment was assumed to be A-type, and this was (wrongly, we believe) used to calculate the diagonal component of the hyperpolarizability. They measured a transition moment of 12.25D and used the McCrea
equation\textsuperscript{70} to determine the excited state dipole moment. Along with a calculated MOPAC ground state dipole moment they determined the charge transfer to be 5.6 D. This is all consistent with our ZINDO calculations for the B-type state, but not the A-type state, which has a much weaker transition moment. Thus we expect a moderately large KD component for this molecule.

The KD hyperpolarizability of an azo-bridged analogue of 15 has been reported at 780nm and 1340nm.\textsuperscript{37} Our ZINDO calculations suggest nearly degenerate lowest-lying A and B-type states (resulting from nearly degenerate HOMO/HOMO-1 both localized on the styryl-amine legs), but this is not easy to discern from the experimental spectrum\textsuperscript{37} which shows a rather symmetric but broad (\sim 150nm fwhm) peak at 500nm. Assuming the B-type state is at 500nm, the two-level approximation gives values for the 2mm component of the hyperpolarizability of \(77.5 \times 10^{-30} \text{ esu}\) and \(26 \times 10^{-30} \text{ esu}\) for 780nm and 1340nm, respectively. The experimental values are given as \(167 \times 10^{-30} \text{ esu}\) and \(180 \times 10^{-30} \text{ esu}\), respectively. However, there is potentially a large margin of error in the long wavelength (1340nm) data point in that work, as the experimental ratio of the 1mm to 2mm component is very different from the expected value of \(~1.14\) for a \(C_{2v}\) molecule (see Eq (5.1)).

The effects of bridging two carbons together to form 16 are deleterious to the lowest B-type state. This is not mainly the result of a change in \(2\theta\), or in changes to the HOMO/LUMO, but rather a result of large changes in the HOMO-2 orbital that mixes into the lowest-lying B-type state via a HOMO-2 \(\rightarrow\) LUMO transition. This orbital is localized on the central ring system and has very poor oscillator strength to the LUMO, which is strongly localized on the dicyanovinyl fragment (fig. 5.14).
Figure 5.14 Frontier orbitals that describe a majority of the lowest lying B-type state of 16. The CIS coefficients are 0.61 and 0.72 for the HOMO-2 → LUMO and HOMO → LUMO transitions respectively.

The localization of this orbital close to the LUMO also keeps the charge transfer from increasing significantly as well, and thus the \( R \)-value for this B-state is very small. We have obtained similar results for other analogous strongly accepting ring systems (such as phenanthrenequinone and fluorenone) attached with 3,6 styryl-donor legs (see chapter 4).

The planar carbazole ring system is not plagued by such poor oscillator strength and we therefore sought to explore a different acceptor system attached to a carbazole core to compare with 14. A nonsymmetric version of 17 appears in the literature\(^{71}\) (with only a single polyene bridge), and it seems reasonable to suggest a symmetric version can be synthesized by starting from the symmetric carbazole 3,6 carbaldehyde precursor. The
meta position of the dicyanomethylene group (as compared to the para position of the nitro group in 14) causes an effective increase in the $2\theta$ angle, which increases the transition moment but lowers the charge transfer of the B-type state. This change pushes the $2\theta$ angle to about 114 degrees, closer to the optimum than in molecule 14. Furthermore, the polyene/dicyanomethylene structure has better absorption density than the nitrostyryl group, which overall increases the $R$ value of 17 as compared to 14. In addition, the absorption of the B-type state in 17 should be redshifted – ZINDO predicts a 30 nm shift from 14 – possibly approaching 500 nm. The nonsymmetric version is reported to absorb at 472 nm.\(^{71}\) Other 3,6 acceptor-substituted carbazole derivatives appear in the literature, including 3,6 bis(1-methyl-4-vinylpyridinium)\(^{72}\) and 3,6 bis(1-sulfonyl-4-vinylbenzene),\(^ {35}\) which would be expected to have similar linear and nonlinear properties as the carbazole derivatives described here.

Molecule 18 has been synthesized and characterized via Stark spectroscopy and also TD-DFT, CPHF, and FF-DFT computations.\(^ {45}\) Using the TD-DFT results from that work ($\mu = 10.9 \text{D}, \Delta\mu = 10.6 \text{D}$) gives an $R$ value for the lowest lying B-state that is about 20% higher than our ZINDO results. The Stark spectroscopic data in that work suggests a yet higher $R$-value of about 2.8 times our ZINDO value. This results from a very large measured charge transfer of 23.6 D. However, this result seems to us inconsistent based on the fact that the charge transfer in the monomer was measured to be 16.3 D\(^ {45}\) and it would be expected that the charge transfer should decrease for geometric reasons in the bis(dipolar) molecule, even in the presence of strong coupling. Despite these disagreements, all of these results suggest that this molecule would be very promising for KD hyperpolarizabilities.
Synthesis of di(nitrostyryl)-substituted indoloindole (molecule 19) is not reported in the literature. An indoloindole analogue of 19 with a diazo bridge between the indoloindole and nitrophenyl has been prepared, but the yield of the symmetric di-substituted molecule was anomalously low, and thus only the mono(diazo nitrobenzene)-substituted compound was characterized. That compound had moderately strong low-lying absorption at 526nm, and the di-substituted compound would be expected to be have a bathochromatic shift to the 550-600nm range. Calculations on molecule 19 show a large charge transfer (8.7 D) for the lowest-lying B state. This can be traced to the relatively small \(2\theta\) angle of about 75 degrees. The large \(R\)-value in this case is quite exceptional since the \(2\theta\) angle is far from optimum.

The well-known (dicyanomethylene)pyran derivative DADB (20) has been characterized experimentally by EFISH and theoretically by ZINDO/SOS calculations to have large nonresonant vector hyperpolarizability \((\beta \sim 135 \times 10^{-30} \text{ esu})\). Our ZINDO spectroscopic calculations are in full agreement with those of Longjun et al in terms of the transition energies and oscillator strengths they reported. However, in their report they considered the vector hyperpolarizability only, which is proportional to \(\beta_{zzz} + \beta_{zxx}\) off resonance. They concluded that the A-type state was the most dominant/important in determining the vector NLO response, which is true, but this gives the impression that the B-type state should have a much smaller \(R\) value. However, that is not the case, since \(\beta_{zzz} \sim 3R\) whereas \(\beta_{zxx} \sim R\). Even with this consideration the inferred ratio of the \(R\) values between the A and B states in that report is still 1.5-2 times larger than our ratio of 14/10.3. This suggests that there may be disagreements between our calculated charge transfers and theirs, but it is not clear why this occurs since the rest of our calculations are
in strong agreement. Independent of these apparent disagreements, we expect this molecule to possess reasonable KD hyperpolarizability for SHG of about $|\beta_{2nm}| \approx 100 \times 10^{-30}$ esu at 1064nm according to the two-level model. This molecule is clearly not an optimal electronic structure for the KD response or the vector response, but it has been included for comparison and also because it has been a popular NLO-phore because of its very high thermal stability. Finally, this molecule is of some pedagogical interest because, as pointed out by Longjun et al.,\(^{34}\) the dicyanomethylene group acts as a mild donor in the A-type state. However, in the B-type state (not considered by Longjun et al), the dicyanomethylene acts as an acceptor and the styryl amine legs are the donors. Thus the charge transfer of the A and B type states is in opposite directions.

Other molecules with the dicyanomethylene group were considered. In \textbf{21-23} much larger charge transfer in the B type states is calculated compared to the A states. The origin of this difference is highlighted in figure 5.15, where a large difference in electron density on the dicyanomethylene carbon is seen between the nearly degenerate HOMO and HOMO-1 of \textbf{21}. Plausible resonance structures (figure 5.16) help explain this complicated dual donor/acceptor character of the dicyanomethylene group for compounds \textbf{21-23}. When dicyanomethylene is attached to diphenylaminecyclopropene (\textbf{22}) the calculated charge transfer of the B-type state is 14.6 D, but only 3.8 D for the A-type state. Replacing the amines with the more strongly accepting cyano group (\textbf{23}) increased charge transfer to an unprecedented 17.9 D and also lowered the energy of the B-type state relative to the A-type state.
Figure 5.15: Frontier orbitals of 21 and 22. In 21 the A and B type states result mainly from HOMO → LUMO and HOMO-1 → LUMO transitions, respectively. In 22 the A and B type states result from predominantly HOMO → LUMO+1 and HOMO → LUMO transitions, respectively.

Figure 5.16: (a)-(c) Resonance structures which suggest the dual nature of the di(cyanomethylene) group as both electron acceptor and electron donor in 21. (d)-(f) Resonance structures stabilized by aromaticity of the propenylium ring; (d) and (e) are consistent with the B-type state. (g) Structure showing dual nature of the di(cyanomethylene) group in 22 and 23. Note that the negative charge is unlikely to be shared with the other cyclopropene carbons; (f) and (g) taken together lead to an A-type state with no net charge transfer, consistent with the calculations.
The synthesis of 21 is not reported in the literature but the related structure 2,5-bis(benzylidene)cyclopentanone was reported to have a large $d$-coefficient for SHG in the solid state. Compounds iso-electronic to 22 have been reported in the literature with either dicyanomethylene or carbonyl at the apex, and with para-hydroxyl substituents instead of alkylamines. The dicyanomethylene-hydroxyl compound has an intense low-lying peak absorption that ranges from 477 nm in methanol to 521 nm in benzene, which corresponds well to the energies of the A-type states in 22 and 23. A majority of this peak should be composed of the A-type state, which has much higher oscillator strength than the B-type state. The large absorption of the A-type state could prohibit resonant access to the B-type state, so lowering the energy of the B-type state (via cyano acceptors, compound 23) may be desirable. Other acceptors, such as nitro groups, might lower the energy of this B-type state even more with respect the A-type state.

As a final note, the geometric similarity between compounds 22, 23, and the TAMC 1 might suggest that molecules analogous to the TAMC’s but with a cyclopropenium cation instead of a single central carbenium might produce compounds with larger charge transfer than the TAMC’s. This may be expected because the cyclopropenium cation creates more room between each of the three aryl substituents and lowers the steric hindrance, producing nearly planar molecules (fig 5.17).

![Figure 5.17](image_url) Structure of triarylcyclopropenyl cations.
However, it was shown that such TAMC analogues have drastic hypsochromatic shifts compared to their TAMC counterparts. Such a shift is often accompanied by reduced charge transfer, which was confirmed by our ZINDO calculations on a cyclopropenium analogue of 1. Therefore, these molecules are not expected to have improved KD hyperpolarizabilities with respect to TAMC’s.

Calculations on 24 show large charge transfer and modest transition moment for the lowest-lying B-type state. The $R$ value for this state is surprisingly large considering the narrow (~60 degrees) $2\theta$. In 25, the effects of extending the conjugation to form an "X-shaped" chromophore, in which the connection between two chromophores at an angle $2\theta$ to each other is made in the middle rather than at the ends of the chromophore, were examined. The ZINDO calculations suggest exceptional $R$ values based on very large charge transfer. However, this calculation should be treated with caution as it is unclear whether the ZINDO parameterization is reasonable for such a large conjugated system. Nevertheless, these results suggest the possibility of increasing $R$ through this type of system, which warrants further investigation.

**Molecules 26-29**

Symmetric cyanine molecules (Fig 5.8) with a polymethine chain represent an interesting class of chromophores with a large effective $2\theta$. This type of geometry limits the charge transfer and the size of the A-type transition moments, but allows for very large B-type transition moments, both ground to excited state as well as large excited state absorption cross-sections, which have been found experimentally. The electronic structure of these molecules is relatively straightforward. The lowest lying state is B-type with large
oscillator strength, and mainly results (~90%) from a single electron HOMO → LUMO transition (fig 5.18).

This transition results in small charge transfer as the orbitals mostly oscillate between adjacent carbons on the polymethine chain. The $R$ values are given in table 5.4 where comparison to experimental KD-HRS measurements is made.

Table 5.4 Spectroscopic and two-level figure of merit calculations for 26-29.  

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<tr>
<td></td>
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<td>$\lambda^b$</td>
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<td>$\Delta\mu_{gn}^d$</td>
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<td>$R$</td>
<td>$</td>
<td>\beta_{2mm}</td>
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<td>26</td>
<td>540</td>
<td>515 (B)</td>
<td>11.8</td>
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<td></td>
<td>550</td>
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<td>-3.6 (-0)</td>
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<td>0.6</td>
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<td>27</td>
<td>645</td>
<td>575 (B)</td>
<td>14.6</td>
<td>1 (-0.8)</td>
<td>20</td>
<td>10.7</td>
<td>168</td>
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<td>360</td>
<td>350 (A)</td>
<td>1.8</td>
<td>-2.9 (-2.0)</td>
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<td>0.5</td>
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<tr>
<td>28</td>
<td>560</td>
<td>490 (B)</td>
<td>11.7</td>
<td>-1.4 (-1.2)</td>
<td>18</td>
<td>10.6</td>
<td>29</td>
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<tr>
<td></td>
<td>325</td>
<td>350 (A)</td>
<td>1.2</td>
<td>2.9 (-2.1)</td>
<td></td>
<td>0.2</td>
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<td>29</td>
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<td>555 (B)</td>
<td>14.3</td>
<td>-1.8 (-1.1)</td>
<td>20</td>
<td>18.4</td>
<td>255</td>
<td>111</td>
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<tr>
<td></td>
<td>345</td>
<td>350 (A)</td>
<td>1.5</td>
<td>2.2 (2.3)</td>
<td></td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
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</table>

$^a$ Literature value, ref 48.  
$^b$ Calculated with ZINDO/s in gas phase.  
$^c,d$ Calculated with ZINDO/s, in Debye units.  
MCSCF charge transfer calculations are reported in parenthesis.  
The MCSCF active space size was $4 \times 4$.  
$e$ In units of $10^{-30}$ esu; measured at 795 nm (KD-HRS); typical error bars are ~10-20%; see ref 48, p. 119.  
Note: in table 4.3 of this reference there is a copy error, and the data for molecules labeled DiSc(3) and DiCc(5) should be switched (Private communication).  
The data reported in the above table corrects this error.  
$^f$ In units of $10^{-30}$ esu, at 795 nm; calculated with 2 level model (eq. (5.3)) using ZINDO transition moments but experimental transition energies.
The two-level results for 26 and 28 are in good quantitative agreement with the measurements. However, considering the rest of the comparisons in table 5.4 and table 5.1, it is clear that the two-level model is not necessarily a faithful predictor of trends for KD-HRS measurements. In a larger context, Mao has shown the common failure of the two level model for corroborating the various ratios of the four irreducible components of the hyperpolarizability tensor (see eq. (5.1)) in data obtained for his thesis. In the next section multi-level calculations are explored on a subset of the molecules in this report and compared to HRS data when available.

5.1.6 Results II: Multi-level SOS Calculations

In addition to low-lying B-type states, many of the molecules described in this report have low-lying A-type states with relatively strong absorption (refer to tables 5.1-5.4) which can make important contributions in the sum-over-states expression for the hyperpolarizability. For the KD components this requires a moderate transition moment between the B and A-type excited states. When using the SOS formalism to calculate hyperpolarizabilities there are two important types of errors to consider: (1) truncation errors and (2) errors in determining the various quantum parameters. Both types of errors are often mingled together in a typical SOS calculation. To get a feel for how errors in quantum parameters affect the hyperpolarizability we can consider variations of the two-level parameters in equation (5.3):
\[
\frac{\delta \beta_\mu}{\beta} = 2 \frac{\delta \mu}{\mu}
\]
\[
\frac{\delta \beta_{\Delta \mu}}{\beta} = \frac{\delta (\Delta \mu)}{\Delta \mu}
\]
\[
\frac{\delta \beta_{\omega_{10}}}{\beta} = 2 \frac{\delta \omega_{10}}{\omega_{10}} \times \left(1 - \left(\frac{\omega}{\omega_{10}}\right)^2\right)^{-1}
\]

(5.6)

By far the most important errors are those associated with determining the transition frequencies. These errors can be reduced in the non-resonant (\(\omega \to 0\)) limit; but any quasi-resonant calculation of the hyperpolarizability will fail miserably without careful referencing of the theoretical calculation to the experimental transitions.

Of the 9 molecules (1, 2, 3, 5, 6, 26-29) in this report that have been characterized by resonantly enhanced KD-HRS, we believe we have the most complete/unambiguous information concerning the quantum parameters of molecule 1. The linear absorption spectrum is shown in figure 5.19. Well-separated A and B-type states can be integrated

![Figure 5.19](image_url)

**Figure 5.19** Molar absorption curve of molecule 1 showing the two lowest energy excited states, along with their symmetry designations.
to determine the ground to excited state transition moments. Close to resonances a
damping parameter is also required to model the dispersion accurately. The common
phenomenological homogeneous damping term that describes the full-width half-max
(fwhm) of the linear absorption peaks was used, leading to the replacement
\[ \omega_{0,i} \rightarrow \omega_{0,i} - i \gamma_i \]
in the SOS expression for the hyperpolarizability.

Using these experimental data eliminates some of the potential calculation errors
and allows us to test the truncation errors of the SOS more rigorously. Figure 5.20
compares Mao’s KD-HRS data for molecule 1 with various truncated SOS models. The
calculations do not include any adjustable parameters. From figure 5.20 it is clear that the
data points at 795 nm require a 3-level description at minimum; there is an important
two-photon resonance from the lowest-lying A-type state at \( 2 \times 420 = 840 \) nm. The SHG
at 795 nm is also in moderate resonance with the single-photon resonance of the B-type
state at 630 nm. It is evident from this figure that including states beyond the 3-level
model does not change the SOS results significantly. Finally, we add that a more realistic
(inhomogeneous) damping model would possibly bring the SOS results closer to the data
near the two-photon resonance at \( 2 \times 630 = 1260 \) nm, though such an analysis would be
quite involved for a three-state system.\(^{78,79}\)
Figure 5.20 Dispersion of the 1ss and 2mm hyperpolarizability for SHG calculated with the SOS truncated at 2, 3, and 20 levels for molecule 1.
A summary of the parameters used in the three-level model is given in table 5.5.

<table>
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<th>Exp.</th>
<th>Calc.</th>
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</thead>
<tbody>
<tr>
<td>$\lambda_{gb}$</td>
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</tr>
<tr>
<td>$\lambda_{ga}$</td>
<td>420 X</td>
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<td></td>
</tr>
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<td>$\Delta\mu_{ga}$</td>
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<td></td>
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<tr>
<td>$\gamma_s$</td>
<td>0.3 X</td>
<td></td>
</tr>
</tbody>
</table>

**Table 5.5** A summary of all parameters used in the three-level model, denoting whether the parameter was determined by experiment or calculation (ZINDO). The 1ss component uses all of these parameters, while the 2mm does not depend on $\Delta\mu_{ga}$. The wavelengths are in nm; the dipole/transition moments are in Debye, and the damping parameters are in $10^5\text{rad s}^{-1}$.

The only other molecule from Mao’s data that was measured at multiple quasi-resonant frequencies is 3. The dispersion curve for this molecule is seen in figure 5.21, which was generated using the excited state energies and damping parameters from the linear absorption spectrum (of the first 4 excited states, as recorded in table 5.1) and calculating the rest of the parameters with ZINDO.
Figure 5.21 Dispersion of the 1ss and 2mm hyperpolarizability for SHG calculated with the SOS truncated at 2, 3, and 20 levels for molecule 3.

From these figures we see that Mao’s KD-SHG data for molecule 3 was taken in a doubly resonant region between the two photon resonances of the B and A-type states, which are at \( 2 \times 860 = 1720 \text{ nm} \) and \( 2 \times 660 = 1320 \text{ nm} \) respectively. The response is
dominated by the three-level term. A 20-level calculation was done at each of the four data points for the 1ss and 2mm components, and the change between the 3-level and 20-level calculation at these points is rather moderate, especially for the 2mm term. We note that for both the 1ss and 2mm components the data point at 1680nm seems to be an outlier. The SOS model does not account for this behavior, and it seems possible that competing resonant two-photon induced fluorescence may be present since excitation at 1680nm is very near the two photon-absorption resonance at 1720nm. At any rate, the semi-quantitative agreement between the first three points in each case and the multi-level model is encouraging, as again no adjustable parameters have been used.

KD-HRS measurements at 795nm are reported for carbocations 2, 5, and 6. This is a particularly difficult region to model because all three of these molecules have nearly degenerate A and B-type excited states in the 600-675nm range. Inability to determine the individual resonance frequencies of these two overlapping states can lead to rather large errors. For example, errors in determining the resonant wavelengths of 5-10% can propagate to 40-80% errors in the hyperpolarizability at $\omega/\omega_0 = 0.85$, according to eq. (5.6). Thus it is unsurprising that we have varying degrees of success applying multi-level calculations to 5 and 6 data (see fig. 5.22). Data for cyanines 28 and 29 is also included in this figure. These results show agreement with experiment to within a factor of ~2, except for the 1ss component of cyanines 28 and 29. Thus, the origin of the large vector response in 29 remains particularly puzzling.
In general, the multi-level SOS calculations suggest ways to creatively use level-spacing and resonance enhancement to circumvent some of the problem associated with reduced $R$ values in two dimensions, at least in the context of SHG. For example, fig 5.20 shows an enhancement factor of $\sim 3$ when comparing the two-level and three-level model of molecule $1$. The enhancement is even more pronounced in figure 5.21, where the three-level model gives order of magnitude increases over the two-level results for $3$. As another similar example, we compare three-state calculations of the KD-component for $4$
and 5 in figure 5.23. These molecules (see table 5.1) have similar lowest-lying B-type states (similar $R$ values, energies) but they differ significantly in their A-type states. The two lowest-lying states in 5 are nearly degenerate (~680 nm), yet highly separated in 4 (700nm and 490nm). As a result the KD-SHG dispersion differs significantly for these molecules over the Vis/near-IR region.

![Figure 5.23](image)

**Figure 5.23** Comparison of three-level dispersion of the 2mm component for 4 and 5.

Furthermore, this suggests that the geometry changes in going from 6/7 to 10/11, while having slightly negative impact on the $R$ value, may create a much more favorable energy level spacing, since the calculations suggest that the A and B-type states are more separated in 10/11. As a final note, we comment that such details concerning resonance and level spacing are less likely to make such large differences for electro-optic hyperpolarizabilities.
5.1.7 Conclusion

A series of Λ-shaped molecules has been examined for Kleinman-disallowed NLO properties. It was shown that for “large” two-dimensional molecules moderately coupled at an apex the charge transfer properties are dominated by geometric factors. This leads to a reduction of the B-type $R$ values by a factor of ~1/2 as compared to analogous one-dimensional molecules. Even strongly coupled Λ-shaped molecules seem to have reduced $R$ values, and this may be a somewhat intrinsic property of two-dimensional charge transfer molecules, based on the variety of molecules considered in this report. Nevertheless, higher order parameters in nonpolar media are expected to overcome this factor. Furthermore, it was shown that two-dimensional molecules are not easily characterized by their charge transfer properties alone. It is more likely in two-dimensions to have two moderately strong low-lying transitions of B and A symmetry, respectively. For SHG, when these states are moderately separated in energy it is more feasible to utilize the double resonant region in between the one-photon resonance of the low-energy state and the two-photon resonance of the high(er) energy state.

Acknowledgements

Measurements of the linear optical spectra in Table 1 by Guilin Mao and Lionel Sanguinet are gratefully acknowledged. Thanks also to Lionel Sanguinet for preparation of carbocations 1-7.
5.2 References


(48) Mao, Guilin, PhD. Dissertation, Case Western Reserve University, 2007.


Chapter 6: “Modulated conjugation” as a means to maximizing the hyperpolarizability?

6.1 Introduction

In this chapter approaches to maximizing the 1-dimensional off-resonant hyperpolarizability are described. Ultimately we will discuss a new concept termed “modulated conjugation” and argue that while this design principle for organics has potential, the interpretation of the underlying theory as presented in the literature is not as clear. The main tool in evaluating/screening molecules for optimal hyperpolarizability is the quantum sum-over-states model, first published by Orr and Ward\(^1\). The truncated “two level model” has been used as a good first-order indicator of molecular hyperpolarizabilities for decades.\(^2\) In this model the non-resonant hyperpolarizability for one-dimension molecules is proportional to \(\mu_{01}^2 \Delta \mu / E_{01}^2\), where \(\mu_{01}\) is the transition dipole moment between the ground and first excited state, \(E_{01}\) is the energy difference between the ground and first excited state, and \(\Delta \mu\) is the change in dipole moment between these states. Various chemical and geometrical approaches have been attempted to control this two-level term for quasi one-dimensional molecules, with “wave-function optimization” as the end goal.\(^3\) Modifying electron donor/acceptor groups at opposite ends of a molecule allow for simultaneous tuning of all three parameters in the two-level expression, though eventually the transition moment will decrease as charge transfer
increases, and all three parameters cannot be increased monotonically through increasing the electron donating/withdrawing strengths of the substituents. Another strategy for increasing the two-level term is to modify the conjugation bridge (either the length, or the type) between opposing donor/acceptor groups. Approaches at modifying the type of conjugation bridge include using auxiliary donors/acceptors, as well as using solvent polarity to tune bond-length alternation in structures with charge-separated resonance forms (see Ref. 5 and references therein). Simple scaling arguments in one-dimension would suggest that within the two-level model, increasing the length of the molecule should increase the density of the nonlinear response without limit. In the crudest approximation we might expect the transition moment and change in dipole each to scale as $\sim L$, and the energy to scale as $\sim 1/L^2$, which suggests that the hyperpolarizability per unit length should scale as $\sim L^6$. In reality the exponent is usually somewhere in the range of 1-3 for polyene/yne extensions of mid-sized molecules. This is not because of any major failure in the two-level approximation, but rather due to the poor scaling assumptions mentioned above for the parameters in that model. It is not the goal to discuss this in detail, but molecules similar to those of reference 6 (NH$_2$-polyene-NO$_2$) were characterized with ZINDO and the two-level model and the calculations supported the experimental range for the scaling exponent. This range of exponents is also consistent with more detailed calculations in the literature on polyenes (including 100 states in the SOS). This provides motivation for designing longer and longer molecules to increase the density of hyperpolarizability response. However, there are difficulties with this approach to maximizing hyperpolarizability densities. It is sometimes chemically more difficult to make larger molecules, and solubility can be an issue. Also,
longer molecules will generally have a larger dipole moment, which can limit macroscopic chromophore loading densities. Furthermore, lengthening molecules lowers their absorption energy, and in practical electro-optic devices this can lead to reduced transparency in the near-IR region (the well-known transparency/nonlinearity tradeoff). In addition, the length effect will saturate at some point, as longer molecules tend to lose planarity/rigidity and are therefore not able to support electron delocalization over their entire length, giving them a shorter effective length and reduced hyperpolarizability density (e.g. see ref 7, fig. 3). All these issues aside, the goal of creating the highest density molecular response still remains.

Instead of approaching the problem of maximizing the hyperpolarizability from a chemical or geometric viewpoint, Kuzyk addressed the question from the standpoint of fundamental physics. Using the Thomas-Kuhn sum-rule and a three-level ansatz a quantum mechanical limit on the non-resonant hyperpolarizability of a system of \( N \) electrons in one dimension was established to be

\[
\beta_{\text{MAX}} = 3^{1/4} \left( e \hbar / \sqrt{m} \right)^3 N^{3/2} / E_{10}^{7/2}
\]

where \( E_{10} \) is the energy difference between the ground state and lowest-lying excited state. In applying this limit to organic molecules the number of electrons in the system is limited to \( \pi \)-electrons of unsaturated chemical bonds (i.e. twice the number of double/triple bonds). The upper limit derived in this way was shown to be much larger, by roughly a factor of 30, than all of the known “good” molecules reported in the literature. This naturally leads to the question of how to design molecules that come closer to approaching this fundamental limit.
To begin to answer that question, Zhou et al\textsuperscript{12} considered the case of a single electron in one dimension and numerically searched for a potential function that would give optimum quadratic NLO response. They reported that in many cases the converged potential function that maximized the response contained a series of large spatial undulations. It is claimed that the role of these undulations is to spatially separate the ground state wavefunction from all but two of the excited state wavefunctions, leaving effectively/approximately a three-level system. The maximum hyperpolarizability attained in their calculations is roughly 71\% of the theoretical maximum, which is much higher than the $<5\%$ achieved by real molecules. As a result, Zhou et al have proposed a new molecular design paradigm based on “modulated conjugation”. The following article (section 6.2) describes some initial comments and possible objections to this idea. This comment has been published in \textit{Optics Letters}. Following this article an updated discussion of this topic is presented (section 6.3), along with some general observations about maximizing the hyperpolarizability in one-dimension.

\section*{6.2 Comment on “Pushing the hyperpolarizability to the limit”}

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\textbf{Abstract:} It is shown that energy / length scaling complicates maximizing the first hyperpolarizability of a single electron as a function of the potential. A more transparent formula for this hyperpolarizability is given. Examining this formula demonstrates that
Zhou et al.\textsuperscript{12} have not proven that modulated conjugation results in large hyperpolarizability.

A recent paper\textsuperscript{12} examines the hyperpolarizability of a single electron moving according to Schrodinger’s equation in one dimension in a potential $V(x)$ and a small electric field $\varepsilon x$. e.g. (in atomic units) 

$$
-(\partial_x^n + (V(x) + \varepsilon x)\psi = E\psi .
$$

The electron moves on a finite line, $0 < x < L$. Parameters specifying $V(x)$ are varied to maximize $\beta_s = E_{10}^{7/2}\beta$ where $\beta = \partial^2 \langle x \rangle / \partial \varepsilon^2$ is the second derivative of the average of the particle position with respect to the applied electric field and $E_{nm} = E_n - E_m$, where $E_n$ is the $n+1^{\text{st}}$ lowest eigenvalue in zero field ($\varepsilon = 0$). Two methods are used to calculate $\beta_s$, the usual sum-over-states (SOS) formula\textsuperscript{1} and a dipole free (DF) sum-over-states\textsuperscript{13}. The infinite sums over energy states in these formulae are approximated by summing over the lowest lying 15 states. This scaled hyperpolarizability $\beta_s$ is invariant under translation and changes in an energy or length scale. A potential maximizing $\beta_s$ can therefore be characterized by an otherwise arbitrary energy difference, such as $E_{10}$, or a length scale such as $r^2 = \langle (x - \langle x \rangle)^2 \rangle$, related through $E_{10} \propto r^{-2}$ as in atomic units $[\Delta E] = [L^{-2}]$.

This scale is not explicitly controlled in Ref. 12, which finds an optimized potential in which either or both of the ground and first excited state wave function are large only in about 10% of the region $0 < x < L$. It is physically implausible that $\beta_s$ should depend on the potential where both these wavefunctions are small. Elementary formulae make this clear for $E_0$ and $E_1$, hence for $E_{10}$. In this one-dimensional problem it is possible to verify directly that $\beta$ depends on $V(x)$ only in regions between points
where \( \psi_{0,0} \) is not small - for \( \mid x - x > / r \) not too large - by expanding the ground state wavefunction in the electric field \( \mathcal{E} \), \( \psi_0(x, \mathcal{E}) = \psi_{0,0}(x) + \mathcal{E} \psi_{0,1}(x) + \mathcal{E}^2 \psi_{0,2}(x) + O(\mathcal{E}^3) \), so that

\[
\beta = \int dx \left( 2\psi_{0,2} \psi_{0,0} + \psi_{0,1}^2 \right) x. \tag{6.2}
\]

With the boundary condition \( \psi(0) = \psi(L) = 0 \) elementary mathematics yields

\[
\psi_{0,1}(x) = \psi_{0,0}(x)(v_1(x) - \langle v_1 \rangle) \tag{6.3},
\]

where

\[
v_1(x) = \int_0^x dx' \psi_{0,0}^{-2}(x') \left[ \int_0^x dx''(x'' - \langle x'' \rangle) \psi_{0,0}^2(x'') \right] \tag{6.4}.
\]

Similarly,

\[
\psi_{0,2} = \psi_{0,0} \left( u_2 - \frac{1}{2} \int dx \psi_{0,1}^2 - \langle u_2 \rangle \right) \tag{6.5}
\]

where

\[
u_2(x) = \int_0^x dx' \psi_{0,0}^{-2}(x') \left[ \int_0^x dx'' \left( r(x'') - \psi_{0,0}^2(x'') \right) \int dx''' r(x''') \right] \tag{6.6},
\]

\[
r(x) = (x - \langle x \rangle) \psi_{0,0}(x) \psi_{0,1}(x) \quad \text{and} \quad \langle f(x) \rangle = \int dx f(x) \psi_{0,0}^2(x). \quad \text{As the potential is related to} \quad \psi_{0,0} \quad \text{locally}^{14} \quad \text{through Schrodinger’s equation} \quad V(x) - E_0 = \psi_{0,0}^n / \psi_{0,0}, \quad \text{it is clear that} \quad \beta \quad \text{depends on the potential substantially only between points where} \quad \psi_{0,0} \quad \text{is not small, although this is not immediate from the SOS or DF.}
\]

A precise representation of the potential where \( \psi_{0,0} \) is not small must be important so that if \( \Delta x \) is the distance between points where \( V(x) \) is parameterized
\( r / \Delta x \) should be large: in fact ref. 12 finds \( r / \Delta x \sim 1 \), much smaller than \( L / r \sim 10 \). To understand why the minimization in ref. 12 has sacrificed precision in \( V(x) \) where it matters to \( \beta_s \), with no apparent cost in confinement effects, we examine other dimensionless ratios.

If \( E_{M0} \) is the difference between the energies of the highest and lowest states included in the SOS or DF, then \( g = r^{-1} E_{M0}^{-1/2} \) is the ratio of the minimum distance over which the electric field can change the wavefunction to \( r \). Large \( g \) results in inaccurate \( \beta \). As \( g \) is not constrained, supposing \( \beta \) can be unphysically large for any \( V(x) \) and moderate \( g \), it is likely that the minimization will find potentials close to a scaled best potential, where the ground state wave function is large, but adjust \( g \) so that \( V(x) \) can be perturbed to make \( \beta \) unphysically large. If a fixed number of states are included in a DF or SOS this is plausibly achieved by choosing \( r \) (or \( E_{10} \)) so as to localize the ground state in a deep, narrow well and localize many of the other wavefunctions included in the sum elsewhere. This adjusts \( g \), yielding apparently advantageous results. In fact, ref 12 finds a quite large final value for \( g \), and a solution qualitatively consistent with the above scenario. The hypothesis that the final value for \( g \) is large enough to result in substantial error is supported by the fact that the SOS and DF, which are equal for small \( g \), have significantly different values. Moreover, the lack of saturation in the ground state dipole matrix element sum rule \( r_{00} \), is significant. Both the SOS and DF involve higher lying states than the ground state so the fractional error in their predicted \( \beta_s \) likely exceeds \( r_{00} \), particularly for the DF, because the unconstrained optimization of the DF
approximation to $\beta$ will also maximize any positive error therein. Near the maximum of $\beta$, the error in $\beta$ is proportional to the square of the error in $V(x)$. Thus the error in $V(x)$, particularly where the ground and excited state wavefunctions are small and $\beta$ is not sensitive to $V(x)$, is likely significantly larger than the error in $\beta$.

### 6.3 Further Discussion on Modulated Conjugation

In their reply to the above comment (section 6.2), Zhou et al\textsuperscript{15} make the following assertions: (i) the numerical errors and approximations mentioned in our comment, especially those related to truncation of SOS or DF expressions, are not significant enough to invalidate their original conclusions; (ii) therefore, the idea that “large” wiggles in the potential function (in regions where the ground state wavefunction is negligible) are not only meaningful but also a possible means of attaining high intrinsic hyperpolarizabilities; (iii) and finally, there is experimental evidence that supports the theoretical claims of their study.\textsuperscript{16} Based on their response, we agree that truncation of the SOS/DF seems to be less important than we initially hypothesized, but on points (ii) and (iii) we still disagree with Zhou et al. In our comment we may have tied a few independent factors together too strongly, which gave the impression that small errors in the relative hyperpolarizability values between the traditional SOS and DF (as reported in their response\textsuperscript{15}) invalidates our arguments. We maintain that the hyperpolarizability is changed very little by changes in the potential function in regions where a ground state wavefunction with a single maximum is negligible. We will argue that it is quite possible that an optimization scheme over a length $L$ could effectively shorten this length by
developing a very large potential barrier somewhere on the interval $[0,L]$. Such a barrier
closes off the ground state well from the rest of the system. Since the intrinsic
hyperpolarizability (which is determined by the ground state well) is invariant to such a
change in length scale, there is nothing in the optimization scheme to prevent this from
happening. However, as this occurs, the part of the potential outside of the ground state
well is basically free to alter its form (i.e. to oscillate erratically) without significant
consequence to the hyperpolarizability. At the same time, the ground state well is
changing shape to create an optimized hyperpolarizability. Since this seems to be the
case, we do not believe that a part of the potential function that has little to no effect on
determining the intrinsic hyperpolarizability should be considered as theoretical
motivation for a design strategy based on modulated conjugation.

Moreover, we remark and will argue in more detail below, the scaled
hyperpolarizability can be derived in terms of *solely* the ground and excited state
wavefunctions, without any reference to the potential. On one hand this is a simple
corollary of the Hellman-Feynman theorem. However, it is also true that our formula for
the hyperpolarizability does not seem to depend directly on the potential and although the
optimum potentials found in references 12 and 15 are very strikingly different, for
different starting potentials, the ground and relevant first excited state wavefunction are
strikingly similar. For even more examples of this, see ref 17. *This clearly demonstrates
that only those aspects of the potential required to reproduce the ground and excited
state wavefunctions are germane to the scaled hyperpolarizability*. As the relationship
between the relatively important wavefunction and the relatively unimportant potential
involves a second derivative of the former, it is unsurprising that there are modulations in
the latter. To demonstrate convincingly that there are modulations in an optimized potential requires some assessment of their importance. This can (in principle) be done numerically. Below we argue that the first derivative and \textit{a fortiori} the second derivative of $\beta_i$ with respect to modulations in the potential are small. This implies that demonstrating that such modulations are real, rather than a consequence of approximate minimization, would require very careful study. In the following discussion we will assume truncation errors are not critically important, and instead focus on reformulating what we believe to be the greatest difficulty with the results of Zhou et al and more importantly their interpretation of these results.

As mentioned previously, the quantum limit for the hyperpolarizability is derived by using the sum rules and assuming that only two excited states overlap with the ground state. Therefore, it seems reasonable that creating a system in which only two ground-to-excited state transition moments are nonzero may be a good first step towards optimization. The second step would be to optimize the two free parameters in the 3-level sum-rule restricted SOS expression ($E = E_{10}/E_{20}$ and $x_{10}$, the first transition moment). This amounts to having a large separation in energies between the two important excited states (i.e. $E \rightarrow 0$), and also tuning the first transition moment to $(1/3)^{1/4} = 0.7598$ of the possible maximum value (suggested in prior work by Kuzyk\textsuperscript{9}) to result in maximum scaled hyperpolarizability. The above scenario seems to be what Zhou et al. claim is happening during optimizations that result in potentials with “modulated conjugation”. In essence a two-part process takes place simultaneously, whereby the potential function forms deep oscillating wells in order to trap all except two of the excited states away from the ground state well, and at the same time the ground
state well optimizes its shape to tune the ratio of excited state energies and the first important transition moment towards their optimal values. It is of course possible for each of these steps to take place separately, and we believe that in order to evaluate the efficacy of modulated conjugation we must think about these two steps separately. For example, we know that it is possible to attain a record intrinsic hyperpolarizability \((\beta / \beta_{\text{MAX}} \sim 0.71)\) without modulated conjugation.\(^{17}\) In fact, a near record could be attained (0.705) by the simple two-parameter potential shown in figure 6.1, which was obtained by simple “trial and error” optimization of the parameters and calculation of the scaled hyperpolarizability using the equations from section 6.2.

![Figure 6.1](image)

**Figure 6.1:** This potential function results in an intrinsic hyperpolarizability of \(\beta_s = \beta / \beta_{\text{MAX}} = 0.705\). The calculation used the equations from section 6.2.

The existence of such optimized potentials as seen in figure 6.1 have led Zhou et al\(^{17}\) to classify two types of potentials: those that are relatively “smooth” and those that have...
“modulated conjugation”. The question to be answered is whether “modulated conjugation” plays any role in optimizing the hyperpolarizability for the subset of numerically optimized potentials that do have such large oscillations. More precisely, we want to consider whether the functional derivative \( \frac{\delta \beta_s}{\delta V(x)} \) is much different from zero as the wiggly part of the potential is changed.

To suggest an answer to this question we first consider a simple example. Figure 6.2 shows two potential functions to be compared, one with a large “wiggle” and one where the wiggle is replaced by a flat line. In the region \( 0 < x < 5 \) both potentials are the same. The slope of the initial linear part of each potential is 5, and this serves to localize the ground state wavefunction in the region \( 0 < x < 3 \) and the first excited state wavefunction in the region \( 0 < x < 4 \). The value of the slope is not important, except that it is chosen large enough so as to avoid interaction between the low-lying excited states and the confining wall at \( x=6.5 \).

\[ V(x) \]

(a) 

(b)

\[ V(x) \]

Figure 6.2: Shown are two potential functions with the same “ground state well” \( 0 < x < 5 \) but very different shapes in the region \( 5 < x < 6.5 \) for comparison. The large well near \( x=5.5 \) in (a) localizes an excited state away from the ground state.

A semi-infinite linear potential has an intrinsic hyperpolarizability of roughly 0.658 (see appendix for solution). A confined linear potential in a box produces an intrinsic
hyperpolarizability dependent upon the ratio of the slope \((a)\) to the size of the box \((L)\), but for a ratio \(a/L\) greater than about 1, the confined and unconfined linear potential produce an intrinsic hyperpolarizability that agree to at least 3 decimal places. The first few wavefunctions for the potentials in 6.2(a) and (b) are shown in figure 6.3.

Figure 6.3 Lowest-lying eigenfunctions for the potential functions 6.2(a) and (b).
The deep and narrow well in 6.2(a) localizes an excited state away from the ground state well. Otherwise, the wavefunctions between the two systems are nearly identical, especially the ground and first two excited states.

Using the SOS and the first two excited states (i.e. the “three level model”), the intrinsic hyperpolarizability is calculated to be 0.7173 in both cases, showing the degree to which the lowest-lying excited states are identical. Calculating more terms in the SOS, the 7-level model gives intrinsic hyperpolarizabilities of 0.6610 and 0.6603 for 6.2(a) and (b) respectively. Clearly both of the potentials are converging towards some value for the intrinsic hyperpolarizability that is very similar to the analytical result of 0.658 for a semi-infinite line. Comparing these two potentials illustrates the argument that wiggles “outside” of the ground state well have little to no effect on the wavefunctions in the ground state well. We could imagine adding more large “wiggles” to fig. 6.2(a) in the region \(5 < x < 6.5\), and this could potentially create more localized states away from the ground state well. However, we emphasize that such states are created, not at the expense of any of the important states in the ground state well. In our example this would merely insert more localized excited states between \(\psi_2\) and the next excited state in the ground state well. In their original work which used truncated SOS/DF models, Zhou et al recognize this when they say “One might argue that our results are artificial because we are using only 15 states and because our space is bounded by an infinite potential. These two issues go hand in hand…” They then proceed to explain how optimization using a finite number of levels in the SOS results in the wiggles. Their conclusion was that the more levels in the SOS used, the more wiggles result, and this should proceed ad infinitum. It is plausible that maximization using a truncated SOS could result in wiggles
that localize/isolate multiple excited states, but the only cases we can think of require that the sum rules be violated. In the most extreme case, imagine a potential that could localize all excited states but one from the ground state well. Then using only a finite number of states in the SOS one would calculate the two level result. For the potentials in fig 6.2 this happens to be $\beta_{s}^{2L} = 0.928$. This of course is an artificially high value (the real value is ~0.66) and the ground to excited state sum rule would not be well-saturated. So then more states would need to be considered, and eventually enough states in the ground state well would be considered to satisfy the sum rule well, and the resulting intrinsic hyperpolarizability would be the same as if the wiggles were never introduced in the first place. However, since the extra states were introduced via the wiggles, the SOS had to count more states in order to get to the important ones in the ground state well. The same reasoning would apply to using the truncated DF, except that the extreme 2-level case mentioned above could not happen. At any rate, the point of making these arguments is to suggest that the only reasonable way that the types of wiggles described by Zhou et al can make improvements to the intrinsic hyperpolarizability is if they lead to an artificial situation where the sum rules are violated. In the results of Zhou et al this is not the case, and therefore the wiggles cannot in any way improve the hyperpolarizability. An even stronger objection can be made when Zhou et al\textsuperscript{15} abandon the SOS/DF and use the more exact finite-difference evaluation for the hyperpolarizability. The more exact solution is equivalent to doing an infinite sum over states. While it might make sense (as mentioned above) that a finite state optimization would make large wiggles, an infinite state optimization does not have similar motivation to make wiggles. This would impart some sort of intelligence/extrapolation ability to the
computer performing the optimization, because the potentials being optimized by necessity occur on a finite line. As implied in the above arguments, in a real calculation one cannot avoid the higher energy states in the ground state well forever, and doing an infinite SOS would require infinite wiggles. To imagine that the computer is trying to make infinitely many wiggles to localize all the excited states is unreasonable. The reasoning is straightforward: while there might be some benefit to having infinitely many wiggles (this is even debatable/confusing), along the way to achieving an infinite number of wiggles there is no incremental benefit to having the wiggles, and since the computer doesn’t know the “end goal” it can’t be incrementally moving towards it during an optimization procedure. We prefer to interpret such large oscillations in the potential function in regions where the ground state and important excited state wavefunction(s) are small as having minimal effect on the hyperpolarizability. The fact that chaotic large oscillations form in some cases is the result of the freedom of regions of the potential to change without much consequence to the hyperpolarizability. Since this is a functional optimization, it is not the whole functional form that matters, but only a part of it. By comparing 6.2(a) and (b) we have shown that the change in hyperpolarizability as a function of the deep narrow well is less than 0.1%, even though we made large changes to roughly 20% of the potential function. We believe similar results would obtain for Zhou et al’s optimized potentials if the amplitude of the oscillations far away from the ground state well were reduced to zero. Because of this, we again struggle to find the benefit of such wiggles in the potential.
To examine this more precisely, we give an “analytic” equation for the variation in $\beta$, with a change in the potential in terms of the ground and first excited state wavefunctions, which are assumed to be known. We find

$$
\delta \beta = \beta \left( \beta^{-1} \delta \beta - \frac{7}{2} (E_1 - E_0)^{-1} \int dx \delta V(x) \left( |\psi_{1,0}|^2 - |\psi_{0,0}|^2 \right) \right) \quad (6.7),
$$

where

$$
\delta \beta = 2 \int dx \left( \delta \psi_{0,2} \psi_{0,0} + \psi_{0,2} \delta \psi_{0,0} + \psi_{0,1} \delta \psi_{0,1} \right) x \quad (6.8).
$$

The wavefunctions $\psi_{0,1}$, $\psi_{0,2}$ have been defined above, and $\delta \psi_{0,n}(x)$ is the change in each of these wavefunctions resulting from a change $\delta V$ in the potential. These functions can all be derived analytically as integrals, or solved for numerically using numerical differential equation solvers. In what follows we give somewhat more detail concerning the analytic solution, so as to be able to discuss the likely “best” potentials $V$.

Use of these formulae in numeric solutions could also result in more reliable solutions.

We consider the equation

$$
-\psi'' + \left[ V(x) + \delta V(x) + \epsilon x - E(\delta V, \epsilon) \right] \psi = 0 \quad (6.9),
$$

and expand the wavefunction and energy in powers of $\epsilon, \delta$ as

$$
\psi_0 = \sum_m \epsilon^m \left( \psi_{(0,m)} + \delta \psi_{(0,m)} \right), \quad E_0 = \sum_m \epsilon^m \left( E_{(0,m)} + \delta E_{(0,m)} \right). \quad \text{It is then possible to find higher order functions from any function that is “one lower” in either direction. We will use the equations}
$$

$$
-\psi''_{(0,m+1)} + \left[ V(x) - E_0 \right] \psi_{(0,m+1)} = -x \psi_{(0,m)} + p_m \quad (6.10),
$$

and
where \( p_m(x) = \sum_{n=0}^{m} \psi_{(0,n)} E_{(0,m-n)} \) is a known function, except that in (6.10) \( E_{(0,m)} \) is unknown, as is \( \delta E_{(0,m)} \) in (6.11). Writing \( \psi_{(0,n)} = v_{(0,n)} \psi_0 \) results in two first order differential equations, that have the solution

\[
\psi_{(0,m+1)}(x) = \int_{X}^{x} dx' \psi_0^{-2} \int_{X}^{x'} dx'' \psi_0 \left( p_m(x) - x \psi_{(0,m)} \right) \tag{6.12}
\]

\[
\delta \psi_{(0,m)}(x) = \int_{X}^{x} dx' \psi_0^{-2} \int_{X}^{x'} dx'' \psi_0 \left( p_{m+1}(x) - \delta V \psi_{(0,m)} \right) \tag{6.13}
\]

where \( X \) can be either end of the interval and we require for consistency that

\[
E_{(0,m+1)} = \int dx \left[ \sum_{n=1}^{m} \psi_{(0,n)} E_{(0,m-n)} - x \psi_{(0,m)} \right] \psi_0 \tag{6.14}
\]

\[
\delta E_{(0,m)} = \int dx \left[ \sum_{n=1}^{m} \psi_{(0,n)} E_{(0,m-n)} - \delta V(x) \psi_{(0,m)} \right] \psi_0 \tag{6.15}
\]

These formulae are actually quite difficult to evaluate numerically: the formulae (6.12) and (6.13) tend \textit{analytically} to zero at the end of the interval other than \( X \), because of eqns, however this requires good numerical precision, or, it requires exchanging “ends” in doing the integral somewhere in the middle, or similar. Substituting (6.2), (6.8), (6.12)-(6.15) into, (6.7) we find

\[
\delta \beta_s = \int dx g(x) \delta V(x) \tag{6.16}
\]

where \( g \) is sums and differences of (multiple) integrals of the ground and excited state wavefunctions. This formula (which is quite complex) will not be reproduced in its
entirety here. However, it does, in principle give the derivative of $\beta_x$ with respect to the potential. This would (therefore) allow the use of far better and more accurate numerical routines in determining the best potential. Moreover, it allows qualitative discussion of the “best” potential. Specifically, all examples of potentials / wavefunctions we know of that well approximate “best” wavefunctions for $\beta_x$, including those published in refs 12, 15, and 17 are smooth rather featureless wavefunctions, with a single smooth maximum in the ground state wavefunction. The integrand in these integrals is never terribly large, and integration is a smoothing operation. Moreover, the integrand is always small when the ground state wavefunction is small, unless the wavefunction is small between two maxima of the wavefunction. This never happens in hypothesized wavefunctions. Thus, it is expected that the function $g(x)$ is the sum or difference of a number of quite smooth functions. Unless the smooth parts of these functions effectively cancel, it is also expected that $g(x)$ is smooth. Moreover, in the absence of hard “walls” or “ends”, the three parameter change $V(x) \rightarrow V_0 + \lambda V \left( \lambda^{-1/2} (x - x_0) \right)$ does not result in any change in $\beta_x$. Taking derivatives with respect to these parameters we find that

$$\int dx \left( \delta V_0 \delta x_0 V'(x) + \delta \lambda \left( -\frac{1}{2} V' + x V''(x) \right) \right) = 0 \text{ for any } V, \delta, \delta x_0, \lambda.$$ 

Thus the fact that there are multiple differences in $g$ - a possible source of modulation – is (in part) simply a consequence of this required relationship of $g$. Hence, is our expectation that the derivative of $\beta_x$ with respect to modulated potentials $\delta V$ is very small – this is clearly true of simple model potentials that can be easily checked: we believe (but see below) that this is also true of the potentials calculated by Zhou et al. “Modulated” $\delta V$
are effectively irrelevant to $\beta$, particularly in regions where the wavefunctions are small. Given this irrelevance, and the nature of the minimization algorithm used by Zhou et al., we find it quite natural that their minimizations result in such a wide variety of noisy, modulated potentials: all that really matters to the calculation of the hyperpolarizability is the wavefunction: the potential is the second derivative thereof. Of course, without a clear calculation of the actual “best” wavefunctions, it is impossible to demonstrate that $g(x)$ can not be modulated – in fact it is clear that if the exact solution for $V(x)$ were to be found, then addition of a small modulation would result in a $g(x)$ proportional to some (very small) constant times this modulated potential. However, given that derivatives are known to be “noisy”, that the minimization routine used by Zhou et al. effectively “guesses” potentials without regard for their smoothness, and that the modulated parts of the potential both logically and through an explicit derivation of the variational form for change in the scaled hyperpolarizibility have been shown to be largely irrelevant to the function that is to be maximized, it seems very clearly that the actual “best” potential is smooth, but that modulation in the potential maybe a valuable way to change the effective average potential in such a way as to optimize the hyperpolarizability.

These techniques can be extended to finding the second derivative of $\beta$ with respect to a variation in the potential. Such a formula is clearly a very complicated double integral, and will not be constructed herein, even at the level at which we have constructed the first derivative. However, it is clear that this double integral,

$$\delta^2 \beta = \int dx dx' K(x, x') \delta V(x) \delta V(x')$$

with the above assumptions about the
wavefunctions, has a kernel \( K(x,x') \) which is a smooth function of its arguments, and which is small when both wavefunctions are small. Hence, we expect that both the first and second derivatives of \( \beta \) with respect to modulations in the potential are very small.

A consequence is that any inexact minimization technique, which allows the formation of modulated potentials, is likely to result in modulated potentials. The above formulae would (in principle) allow clear assessment of the importance of such modulations, e.g. by comparing the size of the modulation to \( \delta \beta / \delta^2 \beta \), where \( \delta \beta, \delta^2 \beta \) have been evaluated for a specific chosen change in the potential, which change has arbitrarily been assigned a unit size, in the same way that the size of the modulated potential is calculated. Equally, if \( (\Delta \beta)^2 \) is the square of the expected precision with which \( \beta \) has been calculated, then we should compare the size of a modulation to \( (\Delta \beta) (\delta^2 \beta)^{-1/2} \). In both these formulae a small value of \( (\delta^2 \beta) \), expected from both our analytic and numerical work, for modulations in the potential, make the clear assessment of the importance of modulations in the potential difficult.

At this point we would like to discuss the experimental results that suggest modulated conjugation leads to higher intrinsic hyperpolarizabilities.\(^{16}\) Perhaps surprisingly, we agree that designing molecules with modulated conjugation between donor and acceptors is a reasonable idea. Our main disagreement is with the underlying interpretation/motivation of the idea. Modulating conjugation along a path between donors and acceptors will modify the potential in the region between the ground and important excited state wavefunction(s). Thus, such modulation has a direct effect on the ground state and important excited state(s). This is a completely different effect than
what happens in the theoretical optimization that led to the idea of modulated
conjugation. In the toy model the modulated conjugation must occur outside the well
containing the ground and important excited state, in order to localize many other excited
states away from this well. We realize that the model is simply providing an analogy, but
there is such a strong disagreement between what happens in the model and what is being
done experimentally that calling it by the same name is confusing. The two ideas are
completely incompatible. We agree that the experimental implementation of modulated
conjugation\textsuperscript{16} does have a direct effect on improving the intrinsic hyperpolarizability, but
not because it is in any way isolating certain excited states away from the important
one(s). Thus, we believe it is more appropriate to consider this first experimental
implementation of modulated conjugation as an extension of the “auxiliary
donors/acceptors” idea proposed by Albert et al.\textsuperscript{4} In that paper it was shown that
modifying the aromaticity of the conjugation bridge between donors and acceptors can
enhance the hyperpolarizability, presumably because the bridge itself becomes an
auxiliary donor or acceptor group which enhances the effect of the end donor or acceptor
group, depending on whether the bridge is electron rich or electron poor.

In summary, to apply the principle of modulated conjugation as described by
Zhou et al in their theoretical work would require modulating conjugation away from the
region where the ground state and important excited state(s) overlap. We would caution
against trying to mimic such a situation in real molecules (or perhaps via a quantum well
structure), as the results based on such reasoning will not move one closer to a record
intrinsic hyperpolarizability.
Appendix: Intrinsic Hyperpolarizability of a Semi-Infinite Line

Consider a potential on the semi-infinite line given by $V(x) = ax$. The ground state is an Airy function, $\psi_0 = Ai(a^{1/3}x - Ea^{-2/3})$. We can get the energies of the excited states in terms of the zeros of the Airy function, vis $E_n = a^{2/3}x_{-n}$, which allows us to find

$$\beta = \frac{1}{2} \frac{\partial^3 E_0}{\partial a^3} = \frac{1 2 1 4}{2 3 3 3} a^{-7/3} x_0.$$  
Finally, we find (with $x_0 = -2.338$ and $x_{-1} = -4.088$) that

$$\frac{\beta}{\beta_{\text{MAX}}} = \frac{1 2 1 4}{2 3 3 3} a^{-7/3} x_0 a^{7/3} (x_{-1} - x_0)^{7/2} \frac{3^{1/4} 2^{3/2}}{3^{1/4} 2^{3/2}} = 0.658...$$
6.4 References


(14) Of course, global properties of the potential determine global properties of the wavefunction such as which state is the ground state.


Chapter 7: Conclusion

7.1 Summary of Thesis

This thesis has explored a variety of molecules from a semi-quantitative quantum chemical viewpoint, with the goal of understanding the structure/property relationships of various molecules suitable for Kleinman-Disallowed (KD) quadratic response, and also specifically analyzing KD HyperRayleighScattering (HRS) data recorded at Case Western Reserve University (CWRU) over the past several years. Quantum chemical calculations have provided a means to characterize a rational figure of merit for the density of KD-NLO response in these systems, but we have also shown that more accurate understanding of the KD-NLO mechanism, especially for SHG, requires a more complicated/careful multi-level SOS approach.

At the molecular level we have focused on propeller and Λ-shaped molecules. Chapter 2 described conjugated propeller shaped molecules which were less successful than we had hoped because of the large twist angle requirement for good KD-hyperpolarizabilities, which is difficult to achieve in strongly conjugated propellers. Furthermore, even the moderately twisted cyano-substituted truxenone derivatives investigated had planar distortions that were too large to accommodate discotic liquid crystalline phases.

In chapters 3-5 a variety of Λ-shaped molecules were described and characterized using quantum chemical calculations. The phenanthrenequinone derivatives (chapter 4) studied displayed lowest-lying B-type transitions. Calculations
showed very weak oscillator strengths and surprisingly small changes in the ground to excited state dipole moment for this lowest-lying B-type state. Dibenzophenazine derivatives showed larger charge transfers for the lowest-lying B-type state, but similarly had very weak oscillator strength. Higher-lying B-type states in these (rather large) molecules seem moderately good for KD hyperpolarizabilities, but experimental KD-HRS results could not be attained due to high levels of background multi-photon induced fluorescence.

Chapter 5 presented two-level figure of merit calculations on about 30 \( \Lambda \)-shaped molecules. Also in chapter 5, results of previous KD-HRS measurements undertaken at CWRU were discussed and rationalized through careful examination of excited state properties and use of the SOS model. Analysis of KD hyperpolarizabilities proved to be challenging due to multiple resonance effects. However, it appears that many \( \Lambda \)-shaped molecules may have largely increased resonance enhancement over their one-dimensional counterparts. Such resonant enhancements, coupled with thermodynamically more stable macroscopic alignment schemes theoretically suggests competitive advantages to materials based on the KD response, especially materials designed for SHG.

Chapter 6 is outside this general development of KD NLO. It rather discusses a more fundamental problem: what is the nature of the potential that results in the largest hyperpolarizability. Here we find clear evidence that the hyperpolarizability is rather insensitive to the potential, allowing for easy confusion that modulation in the potential is important to the hyperpolarizability.
7.2 Future Work

Continued computational work and comparison to (new) KD-HRS data is needed in order to gain an even greater regular predictive methodology for molecular KD-NLO properties. While the rationalization of HRS data has proven difficult in highly resonant regions, combined efforts involving careful SOS computations and measurement of molecular KD-HRS dispersions will build upon the foundation laid in this thesis. There are several molecules in chapter 5 whose synthesis is known (or at least plausible) and could be investigated experimentally. The “X” shaped chromophore (molecule 25) of chapter 5 showed a particularly large figure of merit and is worth investigating further, as is the extended TAMC (molecule 12). These hints suggest both synthesizing and measuring such molecules and suggest the further quantum chemical analysis of similar molecules.

In addition the chiral-axial (chiraxial) NLO project could benefit from some controlled, small-scale macromolecular studies that quantitatively investigate the hypothesized non-coupled orientational effects in chiraxial materials. Changes in HRS when molecules associate with each other is one possible avenue of research, as these require only the relative orientation of chromophores and not the orientation of all molecules in the system. This latter was tried without much success by orienting dyes with liquid crystal DNA. The former would require only liquid DNA. Such systems could fail to be realistic building blocks of macroscopic chiraxial materials, but would bolster the fundamental understanding of the KD-NLO response of oriented molecular systems.
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