DEVELOPMENT OF PHOTOREACTIVE ORGANIC COMPOUNDS WITH LARGE TWO-PHOTON ABSORPTION CROSS SECTIONS

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ABSTRACT

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The natural enediynes are the most potent antitumor-pharmacophores ever discovered. The high biological activity of these antineoplastic agents is due to a (Z)-3-ene-1,5-diyne moiety that undergoes Bergman cycloaromatization when activated chemically or photochemically. The clinical application of enediynes is limited because of their modest selectivity for cancer cells. Numerous approaches have been developed to increase selectivity and to control reactivity of enediyne antibiotics. However, in spite of intensive research over the past decade, a safe enediyne-based drug has yet to be developed. To address the issue of selectivity we have explored the approach of controlling reactivity of natural enediynes using methods of photodynamic therapy.

There are several ways of generating reactive 9- or 10-membered cyclic enediynes. One is to start with a stable 11-membered enediyne and photochemically initiate ring contraction. This can be achieved via photo-Wolff reaction of α-diazocarbonyl-incorporated cyclic enediynes. Another method is to generate one or both triple bonds of the enediyne framework in situ. Photodecarbonylation of a cyclopropenone-incorporated 10-membered cyclic enediyne-precursor is a suitable reaction for this approach.

In photo-triggering of either of these photoreactions one must consider the depth or light penetration into mammalian tissues and the cytotoxic effects of UV-Vis light. The greatest depth of light penetration into human soft tissues is achieved in the region of the so called “phototherapeutic window” extending between 650 and 950 nm. Luckily this range corresponds to the region of lowest light cytotoxicity. However, there is no spectral overlap between linear absorption of photoreactive substrate and NIR light. In order to photolytically trigger photoreaction one must use NIR light of high flux.

The feasibility of two-photon induced photo-Wolff reaction was proven using 800 nm light of a Ti:sapphire laser reacting with diazonaphthoquinone 2.14.
It is known that alkyl- or aryl-substituted cyclopropenones are thermally stable photoreactive compounds that undergo decarbonylation upon excitation with UV light. The feasibility of two-photon induced photodecarbonylation was demonstrated using cyclopropenone 3.23.

Two-photon absorption properties of previously studied model α-diazocarbonyl- and cyclopropenone containing chromophores were relatively low. To determine the feasibility of two-photon absorption cross section enhancement of such chromophores we synthesized a series of symmetrical aryl-cyclopropenones 4.1-4.3 and 2-diazo-1,3-diketones 4.4 and 4.5 designed based on Donor-π-Acceptor-π-Donor structure. Two-photon absorption cross sections of 4.1-4.5 were determined using photochemical and white-light continuum probe methods. Experimental values of two-photon absorption cross sections of 4.1-4.5, although somewhat variable depending on the method employed, were generally in good agreement with one another. There was no direct correlation between two-photon absorption cross-section and the total area of a π-conjugated system of photoreactive substrates we studied. A better correlation was observed between two-photon absorption cross-section and the extinction coefficient at 400 nm. 2-diazo-1,3-diketone 4.5 possesses one of the highest reported two-photon absorption cross section, i.e. 440 GM, among photoreactive compounds. In summary, enhanced of two-photon absorption cross sections were achieved using photoreactive organic molecules 4.1-4.5.
DEDICATION

To my parents, who supported me throughout this entire venture.
I appreciate the time that a number of individuals took to share ideas, discuss their own experiences, and review many drafts of this document.

My advisor, Dr. Vladimir V. Popik, provided me with his considerate guidance, valuable advice and wholesome insights throughout my graduate studies at BGSU. I owe much to his motivating encouragement and constructive criticism in my formation as an independent researcher. I want to express my cordial gratitude to Dr. Douglas C. Neckers for reviewing the manuscript in a draft form and offering his suggestions. My special thanks to my ever favorite teacher Dr. Thomas H. Kinstle for his useful discussions and inestimable contributions to my research. I owe a word of thanks to my Graduate Faculty Representative committee member, Dr. Julie Barnes for her thorough reading of the manuscript.

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CHAPTER 1. INTRODUCTION

1.1. Two-photon absorption

1.1.1. Historical overview

Two-photon absorption is a non-linear optical process in which simultaneous absorption of two photons promotes a molecule to the excited state. The energy of the excited state corresponds to the sum of the energy of absorbed photons. Theoretical possibility of two-photon absorption was predicted by Göppert-Mayer in 1929.\(^1\) The first experimental evidence of nonresonant absorption of electromagnetic waves of radiofrequency was reported by Hughes and Grabner in 1950.\(^2\) While acquiring the radiofrequency spectrum of Rb\(^{85}\)F they observed an unpredicted absorption line at exactly one-half the frequency of a line group in the weak field spectrum. Hughes and Grabner explained this phenomenon as two-photon absorption by Rb\(^{85}\)F.

Two-photon absorption is an intrinsically inefficient process caused by somewhat low probability of two photons “hitting” the same molecule at the same time. Therefore the experimental observation of two-photon absorption of light was delayed until the 1960s, when lasers became available that could emit light of high flux. Two-photon absorption of visible light was reported for the first time in 1961 by Kaiser and Garret.\(^3\) They observed the generation of blue fluorescence emission (425 nm) from CaF\(_2\)Eu\(^{2+}\) when it was irradiated with red light (694 nm) of ruby laser. Two years later, Peticolas and Goldsborogh reported\(^4\) the first experimental observation of two-photon absorption by organic matter. They detected two-photon excitation in a number polycyclic aromatic compounds. When anthracene (1.1), phenanthrene (1.2), pyrene (1.3) and benzo[a]pyrene (1.4) were irradiated using a ruby laser (694 nm), they observed blue-green fluorescence (400-500 nm) emission from organic crystals (Figure 1.1).
In 1966 Schlossberg and Javan reported the first experimental evidence of two-photon absorption of infrared light. This evidence was obtained while exploring hyperfine structure and paramagnetic properties of Xe excited states using polarized IR laser light. The golden era of two-photon absorption is associated with invention of high-resolution multiphoton spectroscopy by arguably Pritchard et al. or Popescu et al. in 1974. Utilizing continuous-wave (CW) laser Pritchard et al. measured the fine-structure splitting of the $4d^2D$ state of sodium using simultaneous two-photon excitation from the $3s^2S$ ground state. Popescu et al. used a pulsed laser to explore two-photon excitation of atomic cesium. These successful experiments initiated the growth of the field of laser spectroscopy - excited-state spectroscopy, Rydberg spectroscopy, two-photon doppler-free spectroscopy, multiphoton ionization spectroscopy and photolytic spectroscopy in 1975-1980s. Commercialization of high-intensity lasers of broad range of wavelengths and realization of the advantages of two-photon absorption expanded the applications two-photon absorption spectroscopy tremendously. In the 1990s, extensive theoretical and laboratory research led to awareness of potential applications of two-photon spectroscopy in optical power limiting, two-photon upconversion lasing, two-photon fluorescence excitation microscopy, three-dimensional optical data storage and photodynamic therapy. Nowadays the field of two-photon absorption research is still extremely dynamic and is believed to have enormous potential.
1.1.2. Theory of two-photon absorption

The promotion of molecules from the ground state to an excited state normally occurs through resonant single-photon absorption. However, under appropriate conditions the same excitation can be achieved by absorption of two or more photons of longer wavelength.

There are four models or multiphoton absorption, three of which are - (a) Excited-State Absorption, (b) Two-Photon Absorption, (c) Two-Photon Assisted Excited-State Absorption

(Figure 1.2). The first is (a) Excited-State Absorption (ESA), sometimes also called reverse saturable absorption. In this model absorption of the first photon promotes an electron from the ground state to a higher singlet state, which then vibrationally relaxes to the $S_1$ level. The second photon is then absorbed either by the $S_1$ state ($S_1 \rightarrow S_n$) or by the $T_1$ state ($T_1 \rightarrow T_n$) following intersystem crossing ($S_1 \rightarrow T_1$). The second model is (b) Two-Photon Absorption (TPA), in which absorption of the first photon promotes the molecule to a "virtual state," wherefrom...
absorption of the second photon takes place. The combined energy of two photons stimulates a molecule to the same excited state that could otherwise be achieved through absorption of a single photon of twice-the energy. If the absorbed photons are identical in energy (wavelength) the process is called degenerate TPA. Contrarily, if the photons are of different energy (wavelength) the two-photon absorption process is nondegenerate. Finally, the third model is (c) Two-Photon Assisted Excited-State Absorption (TPA-ESA), which could be considered as a superposition of the first two models. Two-photons are needed to promote the $S_0 \rightarrow S_1$ electronic transition. Absorption of the third photon occurs from the excited state of either singlet ($S_1$) or triplet ($T_1$) manifold following intersystem crossing. In the former case excited-state absorption results in population of a $S_n$ state, and in the latter – a $T_n$ state. The fourth model (d) of multiphoton absorption is based on Sequential Two-Step Resonant Single Photon Absorption process (STS-SPA). In this model the first photon absorbed by a chromophore promotes the HOMO electron to the excited state. The photoexcited chromophore undergoes rearrangement or photoreaction that forms a new ground-state short-lived intermediate. The second photon is then absorbed by the ground-state intermediate that eventually affords the final stable photoproduct. Although studying models (a), (c) and (d) certainly presents scientific challenge, they are beyond the scope of our research interests and goals. Thus, hereafter we will focus on exploring and describing only the two-photon absorption (b) model.

When a chromophore is exposed to nonresonant light, a virtual state may form that lasts for a very short duration (on the order of a few femtoseconds). Since the “virtual state” is very short-lived, two-photon absorption occurs only if the second photon arrives before the decay of the virtual state. Thus, TPA is a nearly concerted process that demands a high density (flux) of incident photons.

The detailed information on quantum mechanical description of the theory of TPA can be found elsewhere, thus will not be discussed here. Alternatively, TPA can be described in terms of two mechanistic models. The first model considers two-photon absorption of nonpolar
molecules with a low energy and strongly absorbing virtual state. According to Birge et al., for these molecules only excited states that are forbidden by single-photon selection dipole rules can be populated via two-photon absorption. The probability of a low energy state contributing to the virtual state is predicted by Heisenberg’s uncertainty principle. The virtual state lifetime is approximated as \( h/(4\pi\Delta E) \), where \( h \) is Planck’s constant and \( \Delta E \) is the difference in energy of the virtual and actual states. Using this equation, it is estimated that an allowed state can contribute to the formation of the virtual state for time \( t_{\text{virtual}} \) that is roughly equal to \( h/(4\pi\Delta E) \) with the transition probability proportional to the squared transition dipole moment change, \( \Delta \mu^2 \). The second mechanistic model considers TPA of polar molecules. For these species strong TPA occurs by a different mechanistic pathway in which a large change in dipole moment (\( \Delta \mu > 10 \) D) occurs upon electronic transition from the ground state to an excited state. In contrast to the previous case, single photon allowed states can then be achieved via TPA. Both the virtual state lifetime and the transition probability are proportional to \( \Delta \mu^2 \). Also, in this model both the ground and excited states can participate in the formation of the virtual state, which enhances TPA.

1.1.3. Two-photon absorption advantages

One of the major advantages that distinguish TPA from single photon absorption (SPA), is the difference in the rate of energy (light) absorption as a function of the incident light intensity. In the linear absorption process, the rate of light absorption is directly proportional to the incident light intensity (\( dw/dt \propto I \)), and is independent of the rate of photons passing through the molecule. In contrast, the TPA process depends on both spatial and temporal overlap of the incident photons. Therefore the rate of light absorption is proportional to the square of the incident light intensity (\( dw/dt \propto I^2 \)). This difference between SPA and PTA has significant implications. Since the probability of a TPA depends linearly on the square of the incident light intensity, photoexcitation is spatially confined to the focal volume and negligible absorption occurs in any out-of-focus volume. Such precise control of photoexcitation is fascinating, and is
leading to the development of new technologies, processes, and materials that require 3-D spatial resolution of physical properties, both static (permanent) and dynamic (reversible). Exceptionally high spatial resolution is not the only advantage of TPA. The other advantages of TPA for particular systems and conditions are discussed in introductory sections of later chapters.

1.2. Two-photon photochemistry

In spite of extensive two-photon absorption research the field of two-photon photochemistry remains relatively unexplored. There are a few examples of two-photon induced cycloaddition/cycloreversion reactions, photopolymerization, photochromism and the uncaging of bioactive molecules all of which will be briefly discussed here. All two-photon induced photoreactions can be classified by their reversibility. Photodimerization and photochromism are reversible photoreactions whereas photopolymerization and two-photon uncaging are irreversible photoreactions. Another way of classifying two-photon photoreactions is by the chemical class of the reactions such as cycloaddition/cycloreversion ([2+2] and [4+4]), radical reactions, and so on.

1.2.1. Two-photon cycloaddition and cycloreversion reactions

1.2.1.1. Two-photon [2πs+ 2πs] cycloaddition/cycloreversion reactions

The photochemical [2πs+ 2πs] cycloaddition reaction has become an important synthetic method for forming two new carbon-carbon bonds with a maximum of four new stereogenic centers. The first photochemical [2+2] cycloaddition reaction was reported by Ciamician and Silber in 1908. It was the photoinduced cyclodimerization of carvone (1.5) into carvone camphor 1.6 (Scheme 1.1).

Two-photon induced cycloreversion of coumarin dimer was reported by Kim et al. When coumarin (1.8) is irradiated with UV light of > 300 nm [2+2] cycloaddition takes place that
Scheme 1.1. First example of [2+2] photocycloaddition reaction

Scheme 1.2. Reversible photodimerization of coumarin

Scheme 1.3. Photocycloaddition of 5,7-dimethoxycoumarin
results in coumarin dimer \textbf{1.7} (Scheme 1.2). Cycloreversion of the dimer normally requires irradiation with < 280 nm light, but was also accomplished by irradiation with 532 nm light of mode-locked Nd:YAG laser. Similarly, Belfield \textit{et al.}\textsuperscript{39} studied two-photon induced photodimerization of 5,7-dimethoxycoumarin \textbf{1.9} (Scheme 1.3). When \textbf{1.9} was irradiated either with UV light (355 nm) or visible light (650 nm) four photoproducts were obtained (\textbf{1.10}, \textbf{1.11}, \textbf{1.12} and \textbf{1.13}). In both cases \textit{syn}-head-to-head (\textbf{1.10}) and \textit{syn}-head-to-tail (\textbf{1.11}) cycloaddition dimers were formed in ca 1:3 ratio. Both \textit{anti}-dimers - head-to-head (\textbf{1.12}) and head-to-tail (\textbf{1.13}) were minor photoproducts.

\textbf{1.2.1.2. Two-photon \([4\pi_s+4\pi_s]\) cycloaddition/cycloreversion reactions}

When irradiated, anthracene (\textbf{1.1}) undergoes a photochemically allowed \([4\pi_s+4\pi_s]\) cycloaddition to form compound \textbf{1.14} (Scheme 1.4).\textsuperscript{40}

\begin{center}
\centering
\begin{tikzpicture}
\node [shape=rectangle,draw] (a) at (0,0) {\includegraphics[width=0.4\textwidth]{anthracene.png}};
\node [shape=rectangle,draw] (b) at (0,2) {\includegraphics[width=0.4\textwidth]{dimer.png}};
\draw [->] (a) to node [midway] {$h\nu$} (b);
\draw [-] (a) to node [midway] {$\Delta$} (b);
\end{tikzpicture}
\end{center}

\textbf{Scheme 1.4.} Photodimerization of anthracene

The dimerization occurs upon exposure of a saturated benzene solution of anthracene to UV light of ca. 250 nm.\textsuperscript{41} Cycloreversion of the anthracene dimer is carried out thermally at temperature of ca. 280\degree C. Dvornikov \textit{et al.} reported\textsuperscript{42} on two-photon induced photodimerization of 9-\textit{n}-decylanthracene \textbf{1.15} (Scheme 1.5). The long alkyl chain at 9-position was added to increase the solubility of anthracene in polymer matrices for practical purposes. The head-to-tail photodimer was the only product formed in the photoreaction.
1.2.2. Two-photon photoisomerization

The most common type of two-photon induced photoisomerization is photochromism, which is defined as a reversible transformation of a chemical species between two isomers that have different optical properties upon photoirradiation.\(^{43}\) There are several molecular systems that have been reported to undergo two-photon induced photochromic transformations including spiropyranes,\(^ {44}\) fulgides,\(^ {45}\) azobenzenes,\(^ {46,47}\) and diarylenes.\(^ {48}\)

1.2.2.1. Spiropyranes

The first example of two-photon induced photochromism of spirobenzopyranes was reported by Parthenopulos and Rentzepis in 1989 (Scheme 1.6).\(^ {44a}\)
To convert the closed “spiro-form” (1.17) into open zwitterionic form (1.18) the authors used two-photon absorption of either a 1064 nm photon and a 532 nm photon (achieving 355 nm excitation) or two 532 nm photons (corresponding to 266 nm excitation). To reverse the process two-photon absorption of IR light (1064 nm) was employed.

1.2.2.2. Fulgides

Belfield and co-workers reported on two-photon induced photoisomerization of indolyfulgide 1.19. Upon irradiation with 350 nm UV or 775 nm visible light indolyfulgide 1.19 undergoes reversible electrocyclic ring closure to the isomer 1.20 (Scheme 1.7).

\[
\text{Scheme 1.7. Photoisomerization of indolyfulgide 1.19}
\]

Absorption maxima of 1.19 and 1.20 are 385 nm and 590 nm respectively. When the ring-closed isomer was irradiated with white light continuum (400-800 nm) a rise of the absorption band at 385 nm was observed indicating reverse photoreaction.

1.2.2.3. Azobenzenes

The first example of two-photon induced photoisomerization of azobenzenes was reported by Zhao et al. in 1995. These authors studied the dynamic behavior of laser induced gratings through TPA in an azobenzene-doped poly(methyl methacrylate) film. In more recent studies Magennis et al. used azo dye 1.21 to investigate the kinetics of azo-group cis-trans photoisomerization (Scheme 1.8). Compound 1.21 exhibits a major absorption band with $\lambda_{\text{max}}$
approximately 370 nm and weak absorption in 440-520 nm range. Laser light of 457 nm and 740 nm were employed for single- and two-photon excitation respectively.

**1.2.2.4. Diarylethenes**

Sekkat *et al.* reported\textsuperscript{48} on two-photon induced photoisomerization of diarylethene-doped poly(methyl methacrylate) film (Scheme 1.9). Similar to fulgides, photoisomerization of diarylethenes is an electrocyclic ring opening/closure reaction.

The open-form isomer 1.23 has significant absorption at 380-400 nm suitable for two-photon excitation using a Ti:sapphire laser. Transformation of 1.23 to 1.24 was accompanied by rise of a new absorption band with $\lambda_{\text{max}}$ approximately 520 nm. The reverse reaction is accomplished using second harmonics of Nd:YVO\textsubscript{4} laser (532 nm).
1.2.3. Two-photon polymerization

The first reports on two- or multiphoton induced photopolymerization appeared in the literature in the early 1970s.\textsuperscript{49} Most of these involve sequential two- or multistep, resonant single photon absorption processes at single or multiple wavelengths.\textsuperscript{50-52}

1.2.3.1. Two-photon radical polymerization

Morita and Sadakiyo reported\textsuperscript{53} on gaseous phase two-photon radical polymerization of methyl acrylate \textsuperscript{1.25} at pressures of 10-65 Torr.

\[
\text{O} \quad \text{O}
\]

\textsuperscript{1.25}

Upon exposure to N\textsubscript{2} laser light (337 nm) gaseous methyl acrylate produced polymeric thin film on the surface of the optical quartz window. The yield of poly(methyl acrylate) was “roughly” proportional to the square of the laser light power.

Morita and colleagues reported\textsuperscript{54} on a gas-phase two-photon radical polymerization reaction between trimethyl(2-propynoxy)silane \textsuperscript{1.26} and 2-propenal \textsuperscript{1.27}.

\[
\text{Si} \quad \text{O} \quad \text{O}
\]

\textsuperscript{1.26} \quad \textsuperscript{1.27}

Irradiation of a gaseous mixture of \textsuperscript{1.26} and \textsuperscript{1.27} with a N\textsubscript{2} laser provided aerosol particles of trimethyl(2-propynoxy)silane-incorporated polyacrolein.

Belfeld \textit{et al.} reported\textsuperscript{55} on two-photon radical polymerization of (meth)acrylate monomers using a fluorone/amine initiating system. Two-photon initiated polymerization was accomplished at 775 nm via direct excitation of the visible light absorbing fluorone dye (5,7-diiodo-3-butoxy-6-luorone \textsuperscript{1.28}) in the presence of arylamine (\textit{N},\textit{N}-dimethyl-2,6-diisopropylamine, \textsuperscript{1.29}) and (meth)acrylate monomer (Scheme 1.10).
As shown in Scheme 1.10 the process of polymerization initiation involves intermolecular electron transfer from aromatic amine 1.29 to the fluorine derivative 1.28, followed by proton transfer from amine to the fluorone dye.\textsuperscript{56} This results in formation of an arylamine bearing a free radical at the $\alpha$-methylene carbon that initiates the polymerization of (meth)acrylate derivatives. A mechanistically similar two-photon induced polymerization reaction was reported by Cumpston \textit{et al.}\textsuperscript{26} This research group developed a series of new arylamine based photoinitiators (1.30-1.38 see Figure 1.3) and tested their performance on acrylate monomers as well as their two-photon absorption properties.
The authors reasoned that the radical ions formed by electron transfer from photoexcited arylamine 1.30 to an acrylate, or subsequent radical products, could initiate polymerization of acrylates. Indeed, arylamine 1.30 initiated polymerization with all examined acrylates.
(methacrylate 1.25, methyl methacrylate 1.39 and various tri- and penta-acrylates) via a radical mechanism following both single- and two-photon excitation of 1.30.

Joshi et al. reported⁵⁷ a two-photon induced polymerization mediated by radiative energy transfer. The two-photon fluorophore 6-benzothiazol-2-yl(2-naphthyl) diphenylamine 1.40 (AF183, Air Force Research Laboratory) exhibits very strong two-photon absorption at near-IR wavelengths.⁵⁸

Photoexcited fluorophore 1.40 decays via radiative pathway producing a strong up-converted blue fluorescence ($\lambda_{\text{max}} \sim 465$ nm). The photocurable epoxide (NOA 72, Norland Products Inc.) containing urethane acrylate type oligomers absorbs the emission produced by the fluorophore. Upon photocuring, the oligomers undergo polymerization in the regions exposed to the fluorescence.

### 1.2.3.2. Two-photon cationic polymerization

Photoinitiated cationic polymerization has received increasing attention in the last few years due to the oxygen insensitivity of the process.⁵⁹

Belfield and co-workers reported⁴⁵ on cationic two-photon polymerization of multifunctional epoxide and vinyl ether monomers using diaryliodonium (1.41, CD-1012, Sartomer) and triarylsulfonium (1.42, CD-1010, Sartomer) salts as photoinitiators (Figure 1.4).
Studied two-photon cationic photoinitiators.

Typical multifunctional epoxide monomers studied were a mixture of poly(bisphenol A-co-epichlorohydrin, glycidyl endcapped and 3,4-epoxycyclohexanecarboxylate (K126, Sartomer) or Epon SU-8 (Shell) and K126 in 1:4 weight ratios, respectively, with 1 wt.% of either the sulfonium or iodonium salt photoinitiators. Feasibility of the two-photon polymerization with these materials was demonstrated via polymeric microstructures.

Boiko et al. reported on two-photon induced cationic polymerization of epoxides using isopropylthioxanthone/diaryliodonium salt initiator system. Upon irradiation of the mixture of the cycloaliphatic epoxide (K126, Sartomer), diaryl iodonium salt (1.41, CD-1012, Sartomer) and isopropylthioxanthone, (1.43, ITX) at 710 nm the formation of polymer was detected using interferometry.

Based on work by Manivannan et al. and own experimental data the authors proposed the following mechanism for photopolymerization. Isopropylthioxanthone, 1.43 absorbs two photons of 710 nm and forms a singlet excited state, which rapidly undergoes intersystem crossing to produce triplet excited state (Scheme 1.11). Electron transfer from triplet ITX to diaryl iodonium
salt \textbf{1.41} \((\text{Ph}_2\text{I}^+)\) yields an exciplex. The exciplex dissociates into ITX radical-cation and diaryliodyl radical. The latter decomposes into aryl iodide and aryl radical that initiates the polymerization.

\[
\text{ITX} + 2h\nu \rightarrow \text{ITX} \rightarrow 3\text{ITX}
\]

\[
3\text{ITX} + \text{Ph}_2\text{I}^+ \rightarrow \text{Exciplex (ITX...Ph}_2\text{I}^+))
\]

\[
\text{(ITX...Ph}_2\text{I}^+) \rightarrow \text{ITX}^+ + \text{Ph}_2\text{I}^-
\]

\[
\text{Ph}_2\text{I}^- \rightarrow \text{PhI} + \text{Ph}^-
\]

**Scheme 1.11.** Mechanism of photoinitiated cationic polymerization using \textbf{1.43} as photosensitizer.\textsuperscript{60}

Zhou \textit{et al.} reported\textsuperscript{62} on two-photon induced cationic polymerization of epoxides using two-photon-activatable photoacid generator based on the bis[(diarylamino)styryl]benzene core with covalently attached sulfonium salt. The process of polymerization initiation involves intramolecular electron transfer from aromatic amine to sulfonium moiety resulting in photoacid generation (PAG). The model compound \textbf{1.44} used in these studies is shown in Figure 1.5.

\[ \text{Figure 1.5. Structure of model compound 1.44} \]
The photochemically generated acid yield increased quadratically with excitation power, thus, proving the TPA nature of the process.

### 1.2.4. Two-photon uncaging of bioactive molecules

Over the past several years, the use of photolabile protecting groups to control the release of bioactive compounds has been established as a promising technique in biological and biochemical sciences.\(^\text{63-66}\)

Nikolenko et al. reported\(^\text{63}\) on designing phototriggers based on transition-metal complexes. The irradiation of ruthenium bispyridyl 4-aminopyridine complex \([\text{Ru(bpy)}_2(4\text{AP})_2]\text{Cl}_2\) (bpy = 2,2’-bipyridine, 4AP = 4-aminopyridine), \(1.45\) with 725 nm light leads to photocleavage of Ru-N bond resulting in free 4-aminopyridine \(1.46\) and the complex \([\text{Ru(bpy)}_2(\text{H}_2\text{O})(4\text{AP})]\text{Cl}_2^{2+}\) (Scheme 1.12). Thus, two-photon induced photoreaction results in uncaging the neuroactive compound \(1.46\) that serves as \(K^+\) channel blocker in physiological systems.

Fedoryak et al. reported\(^\text{64}\) on synthesis and single- and two-photon photochemistry of 4-methoxy-5,7-dinitroindolinyl-glutamate, \(1.47\) (Scheme 1.13). Upon exposure to 730 nm light of high power (900 mW), compound \(1.47\) undergoes rearrangement resulting in release of
Scheme 1.13. Photorelease of glutamate from 1.47

L-glutamate, 1.48. The latter causes rapid increase in intracellular Ca\(^{2+}\) concentration in astrocytes.

Zhao et al. reported\(^{66}\) on two-photon induced uncaging of coumarin fluorophores that

Scheme 1.14. Photorelease of coumarin fluorophore from 1.49

can be used for tracking molecular dynamics with high spatiotemporal resolution in biological environment. The irradiation of 1-(2-nitrophenyl)ethyl-caged coumarin 1.49 at 740 nm evokes the photorearrangement of 1.49 that results in release of 2-nitrosoacetophenone 1.50 (Scheme 1.14). The uncapped parent coumarin 1.51 exhibits 200-fold fluorescence enhancement
compared to the caged counterpart making it an attractive substrate for biological imaging applications.

Kiskin et al. reported on similar two-photon induced uncaging from 1-(2-nitrophenyl)ethyl-caged chromophore. The illumination of sodium 8-(1-(2-nitrophenyl)ethyl)pyrene-1,3,6-trisulfonate 1.52 with 640 nm pulsed light leads to photodecomposition of 1.52 providing 2-nitrosoacetophenone 1.50 and sodium 8-hydroxypyrene-1,3,6-trisulfonate 1.53 (Scheme 1.15). The fluorescence intensity of uncaged pyranine 1.53 was plotted against irradiation power and quadratic dependence was obtained.

Scheme 1.15. Photorelease of pyranine fluorophore from 1.52

Thus, the authors presented a technique for two-photon induced photorelease of neurotransmitter 1.53 in biological systems.

1.3. Conclusions

In spite of the vast number of advantages associated with two-photon induced photochemistry is still a relatively unexplored field of photoscience. Considering the diversity of
potential applications of two-photon induced processes and photochemical transformations we believe that development of photoreactive organic molecules with large two-photon cross sections is a promising research investment. Such molecules may potentially be utilized in 3-D volumetric optical recording, 3-D imaging, optical sensor protection, photodynamic therapy, and 3-D microfabrication. In the years to come, we can anticipate witnessing technological breakthroughs, due to harnessing spatially-resolved two-photon induced photochemical reactions in organic materials and biological matter.

1.4. References


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(55) Belfield, K. D.; Ren, X.; Van Stryland, E. W.; Hagan, D. J.; Dubikovski, V.; Meisak, E. J. 


2.1. Introduction

2.1.1. Discovery

The reaction of α-diazocarbonyl compounds into ketenes, and the products derived therefrom was discovered by Wolff in 1902. When heating 2-diazo-3-oxobutyrate (2.1) with water Wolff obtained ethane-1,1-dicarboxylic acid (2.3) by way of ethyl ester 2.2 (Scheme 2.1).

\[ \text{OEt} \quad \text{O} \quad \text{N}_2 \quad \text{HO} \quad \text{OEt} \quad \text{HO} \quad \text{OH} \]

\[ \text{H}_2\text{O} \quad 110 \degree \text{C} \quad \text{2.1} \quad \text{2.2} \quad \text{2.3} \]

Scheme 2.1. The first examples of Wolff rearrangement (1)

Under similar conditions, 2-diazo-1-phenylbutane-1,3-dione (2.4) provided 1-phenylpropan-2-one 2.6 (Scheme 2.2). These examples indicated that a 1,2-shift took place and that the migratory aptitudes are Ph > Me > OEt. However, it was unclear how water was incorporated \textit{en route} to the carboxylic acids 2.2 and 2.5, respectively. To explain this...
phenomenon Wolff used chemistry of ketenes developed by Staudinger and Schröter’s studies on 2-diazo-1,2-diphenylethanone (2.7).

\[
\begin{align*}
\text{Ph} & \text{O} \\
& \text{\text{Ph}} \\
\end{align*}
\]

The first example of light-induced Wolff rearrangement was reported on ring contraction of 2-diazocyclohexa-3,5-dienones (o-quinone diazides).

The first example of light-induced Wolff rearrangement was reported on ring contraction of 2-diazocyclohexa-3,5-dienones (o-quinone diazides).

Scheme 2.3. Ring contraction by light-induced Wolff rearrangement

In general, photolysis was proven to be an efficient procedure for the Wolff rearrangement of acyclic and alicyclic diazo ketones.

2.1.2. Mechanism

The most important mechanistic question in the Wolff rearrangement is whether nitrogen expulsion and 1,2-shift proceed concomitantly (in a concerted manner) or stepwise, involving a carbene intermediate.

2.1.2.1. Concerted pathway

The concerted mechanism can be viewed as displacement of nitrogen by the migrating group. In this pathway, ketene (2.11) is formed directly from \( \alpha \)-diazocarbonyl compound (Scheme 2.4). Ketene (2.11) is then trapped by a nucleophile - usually water or methanol to yield the corresponding acid (2.12) or ester.
2.1.2.2. Stepwise pathway

In contrast to concerted photo-Wolff reaction pathway, the stepwise mechanism involves another short lived intermediate – carbene, 2.13 (Scheme 2.5). In this mechanism carbene 2.13 is a product of nitrogen expulsion from starting α-diazocarbonyl compound 2.10 and the precursor of ketene 2.11. The rest of the pathway is identical to the concerted mechanism.

2.2. Project goals

The most important industrial application of the Wolff rearrangement is found in photolithography, a process used in the production of electronic microchips and integrated circuit boards. The photoactive components of common Novolac-based positive photoresists
are derivatives of 2-diazo-1(2H)-naphthalenone (2-diazo-1,2-naphthoquinone, 2.14).\textsuperscript{25} The
photodecomposition of 2.14 in the presence of water ultimately results in the formation of 1H-
indene-3-carboxylic acid,\textsuperscript{25,26} which makes exposed areas of the resist soluble in the aqueous
base.

The Wolff rearrangement of α-diazocarbonyl compounds is usually induced by UV
irradiation. So far, there has been no report on two-photon induced Wolff rearrangement.
Considering the industrial importance of Wolff rearrangement and advantages offered by two-
photon induced processes we set the goal to investigate the possibility and efficiency (if any) of
two-photon induced Wolff rearrangement.

2.3. Selection of the model 2-diazocarbonyl compound

2-Diazo-1(2H)-naphthalenone (DNQ, 2.14) was selected as a model 2-diazocarbonyl
compound (Figure 2.1).

\textbf{Figure 2.1.} 2-Diazo-1(2H)-naphthalenone (DNQ)

DNQ is a photoactive compound that undergoes photo-Wolff rearrangement upon
irradiation with UV-Vis light. The main reason for us to select this substance as a model
compound was its suitable absorption spectrum (Figure 2.2).
Figure 2.2. Absorption spectrum of 2-diazo-1(2H)-naphthalenone; C(DNQ) = $3 \times 10^{-6}$ M in MeOH.

The ultrafast Ti:sapphire lasers have an output wavelength of 800 nm (Figure 2.3), whereas DNQ has an absorption band maximum at about 400 nm allowing the probability of two-photon photoreaction. Evidently, there is no spectral overlap between the irradiation source and the substrate 2.14, which is required for single-photon excitation.

Figure 2.3. The spectral width of Ti:sapphire laser output beam
2.4. Photochemistry of 2-diazo-1(2H)-naphthalenone

2.4.1. Single-photon photochemistry

2.4.1.1. Steady state photochemistry

Irradiation of 2.14 in methanol at 254, 300, and 350 nm affords methyl 1H-indene-1-carboxylate (2.15), which then rearranges into thermodynamically more stable methyl 1H-indene-3-carboxylate (2.16, M13C) through keto-enol tautomerization (Scheme 2.6). In our studies we observed formation of only isomer 2.16.

![Scheme 2.6. Photochemistry of 2-diazo-1(2H)-naphthalenone](image)

The steady state absorption spectra are shown in Figure 2.4. As seen from the graph the

![Figure 2.4. Steady state absorption spectra (DNQ). Irradiation with one 350 nm UV lamp C0(DNQ) = 3 x 10^-6 M in MeOH.](image)
The UV spectrum of DNQ in methanol (violet line) shows a strong absorbance at 263 nm (log \( \varepsilon \) = 4.56) and a weaker band at 398 nm (log \( \varepsilon \) = 3.92), while the longest wavelength absorbance of methyl MI3C is at 265 nm (brown line). Since the photoproduct 2.16 does not absorb above 350 nm, the absorption band with the \( \lambda_{\text{max}} \) at 398 nm was chosen for monitoring the reaction progress.

Absorbance change at 410, 440 and 450 nm was followed to determine single-photon absorption quantum yields at 254, 300 and 350 nm respectively, using potassium ferrioxalate actinometry. The concentration of DNQ was maintained to achieve an optical density of ca. 2 at the wavelength of irradiation. The photodecomposition of the diazo compound 2.14 was followed by UV spectroscopy. Quantum yields of the photodecomposition of DNQ show good linear correlation with the wavelength of irradiation (Figure 2.5). A similar trend was reported for the photolysis of 2.14 in different solvents.

\[
\Phi_\lambda = 0.744 - 0.00166 \times \lambda
\]

**Figure 2.5.** The wavelength dependence of the quantum yield of the photo-Wolff reaction of DNQ.

HPLC analysis of the DNQ decomposition at 254 and 300 nm irradiation confirm 2.16 to be the major product at these wavelengths.
The summary of results on single-photon photochemistry is shown in Table 2.1.

**Table 2.1.** Summary of results on single-photon photochemistry of 2-diazo-1(2H)-naphthalenone.

<table>
<thead>
<tr>
<th>Irradiation (Monitoring) Wavelength, nm</th>
<th>ε, L mol⁻¹ cm⁻¹</th>
<th>ΔA/t</th>
<th>ΔA/t</th>
<th>Iₜ</th>
<th>ΔA/t</th>
<th>φₜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>254 (410)</td>
<td>6640 ± 30</td>
<td>(7.5 ± 0.3) × 10⁻⁴</td>
<td>(4.8 ± 0.3) × 10⁻⁴</td>
<td>(1.0 ± 0.1) × 10⁻⁹</td>
<td>0.33 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>300 (440)</td>
<td>1240 ± 10</td>
<td>(1.4 ± 0.1) × 10⁻³</td>
<td>(6.6 ± 0.4) × 10⁻³</td>
<td>(1.4 ± 0.1) × 10⁻⁶</td>
<td>0.23 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>350 (450)</td>
<td>425 ± 2</td>
<td>(5.1 ± 0.3) × 10⁻⁴</td>
<td>(9.4 ± 0.5) × 10⁻³</td>
<td>(2.1 ± 0.1) × 10⁻⁸</td>
<td>0.17 ± 0.02</td>
<td></td>
</tr>
</tbody>
</table>

ε – extinction coefficient at monitoring wavelength (λ); ΔA – absorbance change at monitoring wavelength; t – time, min; Iₜ – intensity of the lamp at irradiation wavelength λ; φₜ – quantum yield of photoreaction at irradiation wavelength λ.

### 2.4.1.2. Time-resolved photochemistry

The mechanism of photo-Wolff rearrangement was investigated using time-resolved spectroscopy. The goal was to observe carbene 2.17 and/or ketene 2.18 using femtosecond time-resolved IR spectroscopy (fs TRIR) and study kinetics of ketene 2.18
methanolysis using nanosecond time-resolved IR spectroscopy (ns TRIR). Femtosecond time-resolved UV-visible (fs TRUV-Vis) spectroscopy experiments were also conducted to elucidate the kinetics of DNQ excited state(s) decay.

*Nanosecond time-resolved IR spectroscopy*

500 ml of 1 mM or 2 mM DNQ solution was prepared in neat MeOH and MeOH:CH$_2$Cl$_2$ binary solvent mixtures of 95, 80 and 50 vol.% methanol content. The sample solutions were degassed with Ar for about half an hour before irradiation as well as during the experiment. The test solution was arranged to circulate through 1 mm quartz flow cell using variable rate chemical pump. The sample was irradiated with Nd:YAG laser operating at 10 Hz repetition rate and 355 nm excitation wavelength of variable intensity (4-15 mJ/pulse).

It was known from steady state IR experiments that diazo- group of DNQ exhibits rather strong absorption signal at 2116 cm$^{-1}$. Therefore it was expected to observe the ground state bleaching at this wavelength. That was in fact the case. In addition to the ground state absorption, a signal was detected at 2126 cm$^{-1}$ (Figure 2.6). This transient was assigned to

![Figure 2.6. Nanosecond time-resolved IR spectrum of DNQ.](image)
The kinetics of ketene decay is shown in Figure 2.7. The lifetime of 2.18 in neat MeOH (231 ± 10 ns) was in good agreement with the literature data (220 ns). As expected, ketene 2.18 had a significantly longer lifetime in non-nucleophilic media (ca 4 ms in dichloromethane, not shown). In all experiments % decomposition of DNQ measured after the irradiation was below 23%.

![Figure 2.7. Nanosecond time-resolved IR kinetics of DNQ (1)](image)

As seen from the graph the lifetime of ketene depends on the concentration of MeOH. This dependence turned out to be linear (Figure 2.8), which was extrapolated to the low methanol content to estimate the lifetime of 2.18 at low methanol concentration. In accordance with the extrapolation the lifetime of about 750 ns is expected at very low (1-2 %) methanol content. This speculation was addressed and tested in further experiments.

500 ml of 1 mM DNQ solution was prepared in MeOH:CH$_2$Cl$_2$ binary solvent mixtures of 1, 1.5, 2, 2.5, 3, 4 and 5 vol.% methanol content. The sample solutions were degassed with Ar for about half an hour before irradiation as well as during the experiment. The absorbance of the sample measured in 1 mm quartz cuvette was ca. 0.88 at 400 nm. The test solution was
Figure 2.8. Dependence of ketene lifetime on methanol concentration

arranged to circulate through 1 mm quartz flow cell using variable rate chemical pump. The sample was irradiated with Nd:YAG laser operating at 10 Hz repetition rate and 355 nm excitation wavelength of variable intensity (6-8 mJ/pulse).

Figure 2.9. Nanosecond time-resolved IR kinetics of DNQ (2)
As expected, the lifetime of ketene 2.18 decreased with increase of methanol concentration. The kinetic traces of 2.18 decay are shown in Figure 2.9.

The summary of results on ns TRIR studies of ketene 2.18 methanolysis is shown in Table 2.2.

**Table 2.2. Summary of results on ns TRIR studies of ketene methanolysis**

<table>
<thead>
<tr>
<th>Vol.% MeOH in CH₂Cl₂</th>
<th>Molarity of MeOH</th>
<th>Energy of the 355 nm pulse, mJ</th>
<th>Concentration of the DNQ solution, mM</th>
<th>Ketene 2.18 lifetime, ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>4</td>
<td>1</td>
<td>ca. 4 ×10⁶</td>
</tr>
<tr>
<td>1</td>
<td>0.247</td>
<td>6</td>
<td>1</td>
<td>(544 ± 5) ×10³</td>
</tr>
<tr>
<td>1.5</td>
<td>0.371</td>
<td>6</td>
<td>1</td>
<td>(182 ± 1) ×10³</td>
</tr>
<tr>
<td>2</td>
<td>0.494</td>
<td>6</td>
<td>1</td>
<td>(87.9 ± 0.3) ×10³</td>
</tr>
<tr>
<td>2.5</td>
<td>0.618</td>
<td>6</td>
<td>1</td>
<td>(50.7 ± 0.2) ×10³</td>
</tr>
<tr>
<td>3</td>
<td>0.741</td>
<td>8</td>
<td>1</td>
<td>(33.4 ± 0.1) ×10³</td>
</tr>
<tr>
<td>4</td>
<td>0.988</td>
<td>5.5</td>
<td>1</td>
<td>(20.2 ± 0.1) ×10³</td>
</tr>
<tr>
<td>5</td>
<td>1.235</td>
<td>8</td>
<td>1</td>
<td>(12.0 ± 0.1) ×10³</td>
</tr>
<tr>
<td>50</td>
<td>12.4</td>
<td>15</td>
<td>2</td>
<td>503 ± 8</td>
</tr>
<tr>
<td>80</td>
<td>19.8</td>
<td>7</td>
<td>2</td>
<td>336 ± 19</td>
</tr>
<tr>
<td>95</td>
<td>23.5</td>
<td>10</td>
<td>1.9</td>
<td>288 ± 12</td>
</tr>
<tr>
<td>100</td>
<td>24.7</td>
<td>15</td>
<td>1</td>
<td>231 ± 10</td>
</tr>
</tbody>
</table>

The observed rate constants, \( K_{obs} \) for 1-5 vol.% MeOH solutions were calculated using ketene lifetimes and eq. 2.1

\[
K_{obs} = \frac{1}{\tau_{ket}}, \tag{2.1}
\]

where \( \tau_{ket} \) is ketene lifetime, in s (Table 2.3).
Table 2.3. Dependence of observed rate constant of ketene methanolysis on concentration of methanol

<table>
<thead>
<tr>
<th>Concentration of MeOH, M</th>
<th>Observed rate constant, $K_{\text{obs}}$, s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.247</td>
<td>1844</td>
</tr>
<tr>
<td>0.371</td>
<td>5499</td>
</tr>
<tr>
<td>0.494</td>
<td>11381</td>
</tr>
<tr>
<td>0.618</td>
<td>19706</td>
</tr>
<tr>
<td>0.741</td>
<td>29967</td>
</tr>
<tr>
<td>0.988</td>
<td>49619</td>
</tr>
<tr>
<td>1.235</td>
<td>83237</td>
</tr>
</tbody>
</table>

In general,

$$K_{\text{obs}} = K_0 + K_q [\text{MeOH}]$$

(2.2),

where $K_0$ is the rate constant for ketene decay in the absence of a quencher (methanol); $K_q$ is quenching rate constant, and $[\text{MeOH}]$ is the molar concentration of methanol.

$K_{\text{obs}}$ was plotted vs. molar concentration of the quencher (Figure 2.10).

![Diagram](image)

Figure 2.10. Dependence of observed rate constant of ketene methanolysis on concentration of methanol
At low content of quencher the plot of \( K_{\text{obs}} \) vs. \([\text{MeOH}]\) showed nonlinear dependence.

**Femtosecond time-resolved IR spectroscopy**

It was known from the literature\(^{31}\) that the carbene signal is usually found at around 1640-1680 cm\(^{-1}\) (C=O stretch). It was also known from nanosecond IR experiments that the ketene \(2.18\) exhibits rather strong absorption signal at 2126 cm\(^{-1}\). These wavelengths were monitored in fs TRIR experiments that were performed as follows.

500 ml 1mM DNQ solution was prepared in MeOH. The sample solution was degassed with Ar for about half an hour before the experiment. The absorbance of the sample was measured in 1 mm quartz cuvette (A ca. 0.88 at 400 nm). The sample solution was arranged to circulate through 1 mm quartz flow cell. The solution was irradiated with the ultrafast Ti:sapphire laser operating at 1 kHz repetition rate and 400 nm excitation wavelength (10 mJ s\(^{-1}\)). The signal associated with carbene \(2.17\) was searched setting the probe IR pulse (8 mJ s\(^{-1}\)) in the range of 1640-1680 cm\(^{-1}\). Since no signal was observed the probe IR light was set to 2126 cm\(^{-1}\) to monitor formation of ketene \(2.18\). No signal corresponding to ketene \(2.18\) was detected. It was known from steady state as well as nanosecond IR experiments that diazo- group of DNQ.

![Graph](image)

**Figure 2.11.** Femtosecond UV-visible kinetics of DNQ.
exhibits strong absorption signal at 2116 cm\(^{-1}\). Therefore probe IR pulse was set to 2114 cm\(^{-1}\) to behold the ground state bleaching. As seen from the kinetic trace (Figure 2.11) the transient species decay with the lifetime of 13.5 ± 0.9 ps. This signal was assigned to S\(_1\) singlet excited state of DNQ (\(^1\)DNQ). The lifetime of \(^1\)DNQ is in reasonable agreement with value obtained by Landing and Wirtz (7 ps).  

*Femtosecond time-resolved UV-visible spectroscopy*

500 ml 1mM DNQ solution was prepared in MeOH. The sample solution was degassed with Ar for about half an hour before the experiment. The absorbance of the sample was measured in 1 mm quartz cuvette (A ca. 0.88 at 400 nm). The test solution was arranged to circulate through 1 mm quartz flow cell. The sample was irradiated with the ultrafast Ti:sapphire laser operating at 1 kHz repetition rate and 400 nm excitation wavelength (5 mW) and probed with wide-spectral (360-750 nm) probe light generated on CaF\(_2\) crystal. The obtained spectrum and kinetics are shown in Figure 2.12 and Figure 2.13 respectively. The observed transient with the lifetime of 5.59 ± 0.06 ps was assigned to S\(_1\) singlet excited state of DNQ (\(^1\)DNQ).

![Femtosecond transient absorption spectrum of DNQ at 2.55 ps](image-url)

*Figure 2.12. Femtosecond transient absorption spectrum of DNQ at 2.55 ps*
The lifetime of $^1$DNQ is in good agreement with value obtained by Landing and Wirtz (7 ps).$^{32}$ Percent decomposition of DNQ after irradiation determined by UV-Vis spectroscopy was 19.5%.

![Graph of Δ OD at 460 nm vs. Time / ps](image)

**Figure 2.13.** Femtosecond UV-visible kinetics of DNQ.

### 2.4.2. Two-photon photochemistry

As said earlier, photoproduct 2.16 does not have a linear absorption above 350 nm (Figure 2.4, brown line). Thus, we anticipated negligible two-photon absorption by the MI3C even if its two-photon absorption properties would turn out to be greater than those of DNQ.

The irradiation of DNQ in methanol with 800 nm pulses from a Ti:sapphire laser results in the same process as the UV photolysis, i.e., Wolff rearrangement.$^{33}$ The possibility of two-photon photoreaction was confirmed by irradiation of 1 mM methanol solution of DNQ in a 1×1 cm quartz cuvette at 800 nm with the amplified Ti:sapphire laser light of 0.9 W (see Table 2.4 for laser parameters).

Dependence of MI3C yield on irradiation pulse energy was studied as follows. The laser beam was attenuated by a diaphragm with a 6.15 mm opening. The power output of the laser after the diaphragm is 0.90 W, which is reduced to 0.81 W after passing through the sample. At
the concentration of the substrate used in these experiments (ca. 1 mM) the loss of energy after
the sample is mostly due to the losses on the phase boundaries, which allows us to evaluate the
laser power within the sample as 0.855 W or 855 μJ pulse⁻¹.

The degassed 1.1 ml of ca. 10⁻³ M methanolic solutions of DNQ were irradiated in 1×1
cm quartz cell. The cross-section of the solution in the cell is 1.1 cm², while the cross-section of
the beam is 0.297 cm². Thus, the irradiated volume was 27% of the total volume. Duration of
irradiation experiments required to achieve certain conversion were therefore scaled down by
the factor of 0.27.

48% conversion was achieved in about 1 hours of irradiation (Figure 2.14, Table A.1 in
Appendix A).

![Figure 2.14. Two-photon Wolff reaction of DNQ – plot of product yield vs. irradiation
time](image)

Two-photon photoreaction dynamics was monitored by raise of MI3C signal in HPLC
chromatograms. A sample of MI3C prepared independently (see sections 2.6.2 and 2.8.3) found
to be identical to the photolysis product 2.16. Yield of the product formation was determined
using HPLC calibration plot (Figure 2.15, Table A.2 in Appendix A) that shows correlation
between integration areas of the photoproduct 2.16 signal and its concentration.

To verify that a two-photon reaction is observed, the expected quadratic dependence of the rate of MI3C formation on the irradiation power was analyzed. The yield of ester 2.16 formed

Figure 2.15. MI3C HPLC calibration plot

Figure 2.16. Two-photon Wolff reaction of DNQ – plot of product yield vs. pulse energy
in 970 s irradiation of DNQ with laser pulses of variable energy is displayed in Figure 2.16 (Table A.3 in Appendix A). The laser power output was attenuated using glass filters to achieve the intensity of the laser pulses in the range from 245 to 939 μJ pulse⁻¹. Figure 2.16 illustrates the observed nonlinear dependence of the rate of photo-Wolff reaction on the pulse energy.

The logarithmic representation of this dependence has a slope of 1.98 (Figure 2.17, Table A.4 in Appendix A) confirming the two-photon nature of the observed photochemistry.

![Graph showing the logarithmic dependence of the rate of photo-Wolff reaction on pulse energy]

**Figure 2.17.** Two-photon Wolff reaction of DNQ – plot of ln(product yield) vs. ln (pulse energy).

We have not observed two-photon absorption and/or decomposition of the ester under the 800 nm irradiation.

### 2.4.3. Two-photon photolithography

To test the feasibility of two-photon photolithography we conducted 800 nm pulsed irradiation (400 mW) of the integrated circuit board laminated with a DNQ-based (10-15 wt.% loading) photoresist through a chromium-coated glass mask for 4 hours. The board was developed in 0.1 M NaOH solution for 2 min and then rinsed with distilled water. The photoresist came off the irradiated areas, which allowed us to pattern the image shown in Figure 2.18.
2.5. Two-photon absorption cross section

2.5.1. Photochemical method

The conversion of the starting material under two-photon-induced photoreaction can be discussed in terms of Beer’s law for the two-photon absorption, the differential form of which is represented by eq. 2.3.

\[-dI = 2\sigma I_0^2 N dx\]  \hspace{1cm} (2.3)

\(I\) in eq. 2.3 is the light flux (photons cm\(^{-2}\) s\(^{-1}\)), \(\sigma\) is a two-photon absorption cross-section (cm\(^4\) s photon\(^{-1}\) molecule\(^{-1}\)), \(N\) is the concentration of the substrate (molecules cm\(^{-3}\)), and \(x\) is the thickness of the sample (in cm). As light intensity virtually does not change when passing through the sample due to the very low probability of two-photon absorption, we can rewrite eq. 2.3 in a simplified form (eq. 2.4),

\[-\Delta I = 2\sigma I_0^2 N x\]  \hspace{1cm} (2.4)

where \(\Delta I\) represents the light flux absorbed by the sample. The rate of photoreaction is equal to the absorbed light flux abated by the quantum yield of the reaction under two-photon excitation (2PE) conditions (\(\Phi_{2PE}\)). The former is proportional to the squared light intensity \(I_0^2\) (eq. 2.5).

\[-\frac{dN}{dt} = \frac{1}{2} \frac{\Delta I}{x} = \Phi_{2PE} I_0^2 N\]  \hspace{1cm} (2.5)
The coefficient $\frac{1}{2}$ in equation 2.5 reflects the two-photon nature of the process. The pulsed source of irradiation should be taken into account and equation 2.5 is converted into eq. 2.6,

$$-\frac{dN}{dt} = \sum_{\nu=N}^{\infty} \int_{\text{pulse}} P \, d\nu : \nu : N$$

(2.6)

where squared light intensity $I_0^2$ is integrated for the duration of the laser pulse and $\nu$ represents repetition rate. For the integration of the squared light intensity we have selected the integration limits of ± 100 fs from the center of the pulse, as the value $I^2$ at these extremes drops to less than 0.2% of the maximum.

The shape of the laser pulse was determined to be close to Gaussian (Figure 2.19) with the width at half-height of 94 fs.

![Figure 2.19. The temporal shape of the laser pulse (X axis – time; Y axis – light intensity)](image)

Using these parameters we have calculated the temporal distribution of light intensity and squared light intensity within the pulse assuming ideal Gaussian shape of the pulse. The spatial distribution (cross section) of light intensity of the laser beam (Figure 2.20) is also close to Gaussian.
Integration of eq. 2.6 and the application of the 94 fs laser pulse width results in kinetic eq. 2.7, 

\[
\frac{N}{N_0} = \exp^{-\frac{\omega_{WR}^2}{(\sigma_{WR}I_0^2)}}
\]

where \( \sigma_{WR} \) is a two-photon absorption cross section for the induction of the Wolff reaction and is a product of quantum efficiency and the cross-section for the two-photon absorption by the substrate, \( \sigma_{WR} = \Phi_{2PE} \cdot \sigma \). Least-squares fitting of the experimental data represented in Figure 2.14 (see Table A.1 in Appendix A) to eq. 2.7 gives \( \sigma_{WR} = (1.73 \pm 0.02) \times 10^{-52} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1} \) or 0.0173 ± 0.0002 GM.\(^{33,35}\)

Least-squares fitting of the variable-power experimental data (Figure 2.16, Table A.3 in Appendix A) to eq. 2.7 gives \( \sigma_{WR} = (1.67 \pm 0.01) \times 10^{-52} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1} \), which is very close to the value obtained in variable time of irradiation experiment.
The cross-section for the two-photon photo-Wolff reaction of 2-diazo-1(2H)-naphthalenone is a product of the two-photon absorption cross-section of DNQ at 800 nm and the quantum yield of the photoreaction, \( \sigma_{WR} = \sigma_{800} \Phi_{2PE} \).

Photochemical reactions generally occur from the lowest singlet or triplet excited states regardless of the excitation wavelength. Thus, we can assume that \( \Phi_{800} = \Phi_{400} \). The latter can be extrapolated from the single-photon excitation wavelength-quantum yield dependence (Figure 2.5) to give \( \Phi_{400} = 0.080 \). The two-photon absorption cross-section of DNQ at 800 nm is calculated to be \( \sigma = (2.16 \pm 0.03) \times 10^{-51} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1} \).

2.5.2. Z-scan method

Two-photon absorption cross section (TPACS) was determined using nonlinear transmission technique. The differential form of Beer’s law for two-photon absorption (eq. 2.8),

\[
- \frac{dl}{dz} = -a I - b I^2 \tag{2.8}
\]

where \( I \) is the light intensity, \( z \) is propagation distance in the absorbing medium, \( a \) and \( b \) single- and two-photon absorption coefficients respectively. The relationship between \( \sigma \) (TPACS) and \( b \) is expressed in eq. 2.9.

\[
y^2 = \frac{h \cdot b}{N} = \frac{10^3 h \cdot b}{C \cdot N_i} \tag{2.9}
\]

The pictorial representation of Z-scan setup is shown in Figure 2.21. The output light from Ti:sapphire laser (800 nm) or Optical Parametric Amplifier (OPA; variable wavelength) was passed through the set of neutral density filters, focused (\( f = 250 \text{ mm} \)) into quartz sample cell (2 cm), and transmitted beam was refocused again (\( f = 100 \text{ mm} \)) into detector photodiode. The sample was installed on a computer controlled motorized linear stage and shifted along the laser beam axis. The diode was coupled with gated integrator and boxcar averager (BCI), and signal was integrated over the pulse duration. In order to avoid the detector saturation the output from the diode was kept below 60 mV, which was monitored by digital oscilloscope.
The analog signal from the integrator was digitized using data acquisition board (DAQ) and recorded by LabView™ software. The data was acquired with 0.5 mm step size on stage ruler (of 250 mm total length) and 250 pulses averaging. The laser output beam energy was optimized to avoid artifacts associated with non-linear absorption of solvent and caused by cell surface at high irradiation power, and to get detectable two-photon absorption signal at low irradiation power. The control Z-scan traces were recorded using neat solvent prior to testing the samples. The experiment time was optimized to get maximum number or average points at minimum percent decomposition of the light-sensitive substrate. Each sample was run three times to get a reproducible Z-scan trace.

The equation 2.10 was used to fit experimentally measured transmission curves,

$$ T_{nc}(x) = \frac{1}{1 + 0.5 \cdot Q \cdot [a \tan(x + l) - a \tan(x)]} $$

(2.10)

where: $Q = \beta \cdot I_0 \cdot z_R$; $I_0$ is light intensity,
\[ l_0 = \frac{2F}{r \, w_0^2 \, x} \]  \hspace{1cm} (2.11)

and \( z_R \) is Rayleigh length,

\[ z_R = \frac{r \, w_0^2}{m} \]  \hspace{1cm} (2.12)

\( x \) is dimensionless coordinate,

\[ x = \frac{z}{z_R} \]  \hspace{1cm} (2.14)

\( l \) is dimensionless thickness of the sample,

\[ l = \frac{L}{z_R} \]  \hspace{1cm} (2.15)

\[ \nu^2 = \frac{10^3 \, h \, : \, b}{C : N_A} = \frac{b}{C : m} : 3.2 \times 10^7 \]  \hspace{1cm} (2.9a)

\( \sigma^2 \) – is two-photon absorption cross section in GM (cm⁴ s photons⁻¹ molecule⁻¹); \( \beta \) – in cm/GW; 

\( C \) – in mM; \( \lambda \) – in nm.

The TPACS of DNQ was measured using open aperture Z-scan technique.\(^{37} \)

---

**Figure 2.22.** Z-scan trace of 50 mM methanol solution of DNQ. – Experimental data; ····· Theoretical fit using eq. 2.10. Experimental details: 250 mm lens; light power 62 mW; attenuation 2.602; AlSi diode; \( \beta = 5.3 \times 10^{-4} \);
The methanol solution of Rhodamine 6G was used as a calibration standard, as its TPACS (has been reported.\textsuperscript{38} The Z-scan trace of 50 mM methanol solution of DNQ is shown in Figure 2.22. As seen from Figure 2.22 the theoretical fitting of the experimental trace is good. TPACS of DNQ measured using Z-scan method is \(0.42 \pm 0.01\) GM.

2.5.3. White light continuum pump-probe method

Although Z-scan method provides a simple and fast way of determining TPACS, the experiment is limited to measurement of a cross section at single wavelength at a time. Thus, acquisition of two-photon absorption spectrum (TPACS vs. wavelength) of a chromophore becomes tedious and cumbersome. The recent attempts to overcome such a limitation led to development of two new TPACS measurement techniques – white light Z-scan\textsuperscript{39} and white light continuum (WLC) pump-probe method (WLCPPM).\textsuperscript{40} The latter was used in our work since minor modifications to existing ultrafast pump-probe setup\textsuperscript{41} were required. The detailed experimental setup and mathematical processing of data were adopted from literature,\textsuperscript{40} and will not be discussed here.

The attenuated output from Ti:sapphire laser or OPA was used as a pump, whereas white light continuum generated in CaF\(_2\) crystal was used as a probe. The relative polarizations of both pump and probe lights were maintained parallel. The pump and probe beams were focused so that they spatially overlapped within 2 mm thick quartz cell containing sample solution. The power of the pump pulse was significantly higher than that of probe pulse (\(P_{\text{pump pulse}} = 10-15\) \(\mu\)J; \(P_{\text{probe pulse}} < 0.5\) \(\mu\)J). Absorbance of the sample measured vs. delay time was converted to transmittance, and obtained curve was fitted using eq. 2.16.

\[
Q(v, x, d, W, t, C) = \frac{\exp(-2v)}{W} \sum_{n=1}^{3} \frac{x + x_d - t}{W} \sqrt{\frac{W}{t}} \text{erf}(x) - \text{erf}(x - t) \Delta t
\] (2.16)
where parameters are:

\[
C = L \frac{n}{n_p} I_p^0 b \quad (2.17)
\]

\[
W = \frac{\sim}{\sim_p} \quad (2.18)
\]

\[
t = L \frac{c}{\sim p} Dn_g \quad (2.19)
\]

\[
v = \frac{\alpha L}{2} \quad (2.20)
\]

\[
a(z,x) = \frac{E(z,x)}{E(0,x)} \quad (2.21)
\]

The index \( p \) refers to “pump” pulse parameters. In the proceeding equations (2.17-2.21) \( L \) is the sample thickness, \( n \)'s are refractive indices, and \( \omega \)'s are temporal widths of pulses. The other parameters: \( \Delta n_g \) is the difference for group indices for pump and probe beams, \( \alpha \) is the linear absorption coefficient, \( c \) is the speed of light in vacuum, and \( \beta \) is two-photon absorption coefficient.

The kinetic trace of DNQ obtained using WLCPPM is shown in figure 2.23. TPACS of DNQ at 800 nm determined using WLCPPM was 0.44, which is in excellent agreement with Z-scan value and in good agreement with photochemical method value.

![Figure 2.23.](image)

**Figure 2.23.** Kinetic trace of DNQ obtained using WLCPPM; e-e-e - Experimental data, — Theoretical fit using eq. 2.16.
2.6. Synthesis

2.6.1. Synthesis of 2-diazo-1(2H)-naphthalenone

The 2-diazo-1,2-naphthoquinone (2.14) was prepared following the published procedure\(^{42}\) (Scheme 2.8; see section 2.8.3 for detailed procedure) and purified by recrystallization from hexane. 2-Amino-1-naphthalene sulfonic acid (2.17) was used as a starting material. Amino-group in starting compound was diazotized with sodium nitrite. The sulfo- group was removed, and the compound was oxidized under mild conditions. The product 2-diazo-1(2H)-naphthalenone (2.14) was extracted from aqueous media by dichloromethane. Overall yield of the reaction is 75%.

\[
\begin{align*}
\text{SO}_3\text{H} & \quad \text{NaNO}_2, \text{NaOH} \\
\text{NH}_2 & \quad \text{HCl}, 5^\circ\text{C} \\
\text{O} & \quad \text{KI}; 4) \text{NaOCl}, \text{NaOH} \\
\text{N}_2 & \quad \text{HCl}; 6) \text{Na}_2\text{S}_2\text{O}_3
\end{align*}
\]

\text{2.17} \quad \text{1) NaNO}_2, \text{NaOH} \quad \text{2) HCl, 5}^\circ\text{C} \quad \text{3) KI; 4) NaOCl, NaOH} \quad \text{5) HCl; 6) Na}_2\text{S}_2\text{O}_3 \quad \text{2.14}

\text{Scheme 2.8. Synthesis of 2-diazo-1(2H)-naphthalenone}

2.6.2. Synthesis of methyl 1H-indene-3-carboxylate

The preparative 350 nm irradiation of DNQ in methanol allowed us to isolate methyl 1H-indene-3-carboxylate (2.16), which was found to be identical to the sample prepared independently (see section 2.8.3).

Methyl 1H-indene-3-carboxylate (2.16) was prepared (Scheme 2.9) in accordance with the published procedure.\(^{43}\)
Scheme 2.9. Synthesis of methyl 1H-indene-3-carboxylate

Indene was carboxylated with carbon dioxide and thus obtained acid 2.19 was treated with thionyl chloride to produce corresponding acid chloride, 2.20.

The latter was converted to the target methyl ester of 1H-indene-3-carboxylic acid (2.16) in the presence of excess methanol and trimethyl amine.

2.7. Conclusions

Single- as well as two-photon photochemistry of 2-diazo-1(2H)-naphthalenone (2.14) was studied. Time-resolved spectroscopy studies of DNQ allowed determining rate constants of ketene methanolysis at different methanol concentrations. Two-photon induced Wolff rearrangement of DNQ was reported for the first time. The feasibility of this process was demonstrated using two-photon photolithography imaging. Two-photon absorption cross sections of DNQ were determined using three methods and obtained values are in good agreement.
2.8. Experimental

2.8.1. Materials

Moisture- and oxygen-sensitive reactions were carried out in flame-dried glassware under argon atmosphere. Dichloromethane was distilled from phosphorus pentoxide, and hexane and diethyl ether were distilled from sodium under argon immediately before use. All other reagents were used as purchased. A copper clad laminated board precoated with a DNQ-based photoresist was purchased from Injectorall Electronic Corp. A glass mask (1.5 mm soda lime glass coated with chromium, NBS1963A resolution target) was purchased from Edmund Scientific.

2.8.2. Instruments

Melting points were measured on Fisher-Johns melting point apparatus. Nuclear magnetic resonance (NMR) spectra were acquired with Varian Gemini 200 MHz, Varian Unity Plus 400 MHz and/or Bruker Avance System 300 MHz. $^1$H NMR and $^{13}$C NMR spectra were recorded using tetramethylsilane (TMS) as an internal standard, and chemical shifts are reported in parts per million (ppm) relative to TMS. UV-visible spectra were obtained using either Varian Cary 50 Bio or Varian Cary 300 UV-Visible spectrometer. IR spectra were acquired on Mattson Galaxy 6020 FT-IR instrument. GC/MS analysis was conducted using either HP 5987 A or Shimadzu QP5050A GC spectrometers equipped with ZB5MS 30 m x 0.25 mm x 0.25 μm columns. High-resolution mass spectra (HRMS) were collected by the Mass Spectrometry Laboratory, University of Illinois at Urbana-Champaign, IL. The preparative and analytical photolysis of DNQ was conducted in methanol solution using RMR-600 Rayonet™ photochemical reactor equipped with carousel sampleholder. The variable rate chemical pump for transient absorption experiments was purchased from Fisher Scientific. The methodology and instrumentation of Q-switched Nd:YAG laser based ns step-scan TRIR, and Ti:sapphire laser based fs TRUV-Vis setups are described in literature.⁴⁴,⁴⁵

TPA experiments were conducted using 800 nm pulses generated by an amplified Ti:sapphire laser (Hurricane by Spectra Physics) operating at 1 kHz.

**Table 2.4.** “Hurricane” Ti:sapphire laser parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum output power, W</td>
<td>1.15</td>
</tr>
<tr>
<td>Irradiation wavelength, nm</td>
<td>800</td>
</tr>
<tr>
<td>Pulse duration, fs</td>
<td>94</td>
</tr>
<tr>
<td>Repetition rate, Hz</td>
<td>1000</td>
</tr>
</tbody>
</table>

**2.8.3. Synthetic procedures**

**2-Diazo-1(2\(H\))-naphthalenone (2.14).** Diluted hydrochloric acid (50 ml 0.2 M) was cooled to 5°C. Separately, sodium hydroxide (4.4 ml, 1 M), 1.00 g solid 2-amino-1-naphthalene sulfonic acid, and 3.09 g sodium nitrite were dissolved sequentially in the 10 ml water, and the solution was cooled to 5°C. This solution was added to the aforementioned diluted HCl in a short time under vigorous agitation, followed by continuous agitation for 30 min. The resultant crude solution of 2-diazo-1(2\(H\))-naphthalenone was neutralized (initially pH of the solution was ca. 4.5-5) by dropwise addition of 1 M NaOH, and potassium iodide (0.044 g) was added thereto and dissolved. A mixture containing 1.9 ml an aqueous solution of sodium hypochlorite (available chlorine 10-13%) and 0.65 ml 35% aqueous solution of sodium hydroxide was added dropwise at 20-25°C over 2-3 hours. After completion of the reaction (controlled by TLC) , the reaction mixture was neutralized by dropwise addition of 0.2 M hydrochloric acid, and free iodine was removed therefrom by addition of 0.066 g Na\(_2\)S\(_2\)O\(_3\)
·5H\(_2\)O. The obtained 2-diazo-1(2\(H\))-naphthalenone, was extracted by means of 2.5 ml methylene chloride, and recrystallized from hexane; mp = 74.5-75°C (75°C Lit.\(^46\)). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 6.58 (d, 1H), 6.89 (d,
H), 7.49 (m, 2H), 7.62 (t, 1H), 8.33 (d, 1H); $^{13}$C NMR (CDCl$_3$) δ 116.2, 117.4, 125.4, 127.2, 128.2, 132.7, 137.5; IR 2941, 2831, 1833, 1609, 1588, 1506, 1150, 1087, 810, 748; (see $^1$H NMR and $^{13}$C NMR spectra titled B2MNCP in Appendix D).

**1H-Indene-3-carboxylic acid (2.19).** 2 ml 1H-indene (17 mmol) was added to 17 ml (0.17 mol) anhydrous diethyl ether in a 50 ml round bottom flask (RBF) equipped with a condenser. Through a top mouth of the condenser the solution was purged with argon. After about 15 min of agitation with a magnetic stirrer, and Ar saturation, 6.9 ml of 2.5 M hexane solution of 1-butyl lithium (17 mmol) was added through septa at a rate sufficiently low that gentle refluxing was maintained. After the base addition, the yellow-orange solution was refluxed for 1 h and then poured onto 400 ml crushed dry ice. The mixture was allowed to warm to r.t., and then to resultant light magenta colored solution 10 ml water was added with stirring. The aqueous layer was separated from ether on a separatory funnel, warmed to the temperature of ca. 40°C to remove dissolved ether, cooled and acidified to pH < 2 by concentrated hydrochloric acid. The resulting yellow solid was collected on a filter, washed with cold water and dried overnight at ca. 50°C to give a yellow solid: 2.245 g (81.4%). The ether layer was extracted two times with 10 ml water and the aqueous extracts were treated as above giving more yellow solid: 0.148 g (5.4%; 86.8% total); mp = 154-155°C (158-160°C Lit.47). $^1$H NMR (300 MHz, CDCl$_3$) δ 3.59 (d, 2H), 7.27 (t, 1H), 7.29 (dt, 1H), 7.38 (t, 1H), 7.50 (d, 1H), 7.65 (t, 1H), 8.09 (d 1H); $^{13}$C NMR (CDCl$_3$) δ 38.7, 122.5, 123.8, 125.8, 126.8, 135.7, 140.4, 143.3, 147.1, 169.1 (see $^1$H NMR and $^{13}$C NMR spectra titled ICA in Appendix D).

**1H-Indene-3-carbonyl chloride (2.20).** 1 g of 1H-indene-3-carboxylic acid 2.19 (6.3 mmol) from the first extraction was dissolved in 25 ml of freshly distilled CH$_2$Cl$_2$ in a 50 ml RBF. The RBF was equipped with a condenser. A CaCl$_2$ drying tube was connected to an upper mouth of the condenser. 0.54 ml thionyl chloride (7.4 mmol; 18% excess) was added to the solution with agitation. In about 5 min 4 drops of distilled DMF were added to the reaction mixture. Upon DMF addition formation of white fog was observed. The reaction mixture was
agitated at r.t. overnight. The brownish dark gray colored product mixture of gel consistency was obtained. TLC with 1:5 EtOAc:hexane elution showed absence of the starting acid. The resultant acid chloride 2.20 was used in the next step without purification.

**Methyl 1H-indene-3-carboxylate (2.16).** All the calculations of reagent amounts were made assuming that 1H-indene-3-carbonyl chloride was formed quantitatively (6.3 mmol). 20 ml anhydrous CH$_2$Cl$_2$ was added to the reaction products mixture of 2.20. The solution was cooled to 0 - +2°C by ice bath. To the cooled solution the mixture of 1.3 ml MeOH (3.1 mmol; 5 times excess with respect to the theoretical amount of the acid chloride) and 1.1 ml Et$_3$N (7.5 mmol, 20% excess) was added. The reaction mixture was agitated at r.t. overnight. The dark brown colored reaction mixture was analyzed by GC/MS. The gas chromatogram showed that methyl 1H-indene-3-carboxylate 2.16 was one of the two major products formed in approximately equal amounts (49.5:50 ratio in GC). The weight of the resultant mixture was 1.47 g. MI3C was purified by vacuum distillation (bp = 76°C at 0.1 Torr). The weight of collected yellow distillate was 0.3678 g (33.8% yield). $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 3.53 (d, 2H), 3.91 (s, 3H), 7.1-7.5 (m, 4H), 8.05 (d 1H); see $^1$H NMR spectrum in Appendix D.

### 2.9. References


C.; Licha, K.; Ebert, B.; Sukowski, U.; Semmler, W.; Wiedenmann, B.; Grötzinger, C.


CHAPTER 3. TWO-PHOTON INDUCED PHOTODECARBONYLATION OF CYCLOPROPENONES

3.1 Introduction

3.1.1. Background

Since the first preparation in 1959 cyclopropenones attracted considerable attention owing to their possible classification as aromatic compounds. The discovery of natural cyclopropenone-containing antibiotic peritricin and cyclopropenone-based protease inhibitors caused amplification of interest in this class of cyclic ketones.

The first example of photochemical decarbonylation of cyclopropenones to the corresponding acetylenes was reported in 1969. Studying photochemistry of \( \alpha,\alpha' \)-bisdiazoketone Whitman and Trost observed photolytical formation of diphenylacetylene, Scheme 3.1 from diphenylcyclopropenone, 3.1 (Scheme 3.1).

\[
\text{hv}
\]

![Scheme 3.1. First evidence of photodecarbonylation of cyclopropenones](image)

Photodecarbonylation of cyclopropenones to produce corresponding acetylenes was utilized in the synthesis of strained ring incorporated acetylenes, such as cyclopentyne, 3.6 and acenaphthyne, 3.10 (Schemes 3.2 and 3.3). Upon UV irradiation of 2,6-bisdiazocyclohexanone, 3.3 at 8 K Trost and Williams obtained 2-diazoketene, 3.4 that transformed into cyclopropenone, 3.5 (Scheme 3.2). Further irradiation of 3.5 leads to photodecarbonylation of the latter to form cyclopentyne, 3.6. Unstable acetylene, 3.6 underwent [1,3s]-sigmatropic shift to ultimately yield allene 3.7.
Scheme 3.2. Photodecomposition of 2,6-bisdiazocyclohexanone.

Similar photochemistry was reported by Chapman et al.\textsuperscript{7} UV irradiation of 1,3-bisdiazo-1\textsubscript{H},3\textsubscript{H}-phenalen-2-one, 3.8 at 15 K resulted in 3.9 that was identified via IR spectroscopy. Continued irradiation with UV light led to photodecomposition of 3.9 into carbon monoxide and acenaphthyne, 3.10. Subsequent warming of acetylene, 3.10 resulted in its trimerization producing decacylene, 3.11.

Scheme 3.3. Photodecomposition of 1,3-bisdiazo-1\textsubscript{H},3\textsubscript{H}-phenalen-2-one.

In recent studies by Kresge and co-workers\textsuperscript{8} photodecarbonylation of amino-, 3.12, methoxy-, 3.13, and hydroxyphenyl, 3.14 cyclopropenones was utilized in synthesis of ynamines, 3.15, ynols, 3.16, and methoxyacetylenes, 3.17, respectively (Scheme 3.4).
Scheme 3.4. Photodecarbonylation of amino-, methoxy- and hydroxyphenyl cyclopropenones.

Thus, irradiation of various cyclopropenones results in the formation of respective acetylenes.

3.1.2. Mechanism

The triangular molecular framework of cyclopropenone is formed of formally $sp^2$ hybridized carbon atoms. Despite the angular strain cyclopropenones feature high thermal stability.\textsuperscript{2,9} The chemical reactivity of cyclopropenone is characterized by two major processes\textsuperscript{2}: the nucleophilic ring opening that results in the formation of acrylic acid derivatives,\textsuperscript{10} and decarbonylation under high-temperature pyrolysis or in the presence of various catalysts.\textsuperscript{11}

Irradiation with UV light also results in loss of carbon monoxide and formation of respective acetylenes.\textsuperscript{8,10,12} The acetylenic photoproduct is often produced quantitatively with high quantum yield.\textsuperscript{9,13}

Photodecarbonylation of diphenylcyclopropenone, 3.1 is very fast, and is complete within 20 ps after excitation.\textsuperscript{14} Recent femtosecond time-resolved UV spectroscopy studies by Takeuchi and Tahara\textsuperscript{15} revealed that 266 nm excitation of 3.1 results in the formation of $S_2$ state of the chromophore. The loss of CO from the latter proceeds on the electronically excited state surface.

Thermal as well as photochemical decarbonylation of cyclopropenones is stepwise process (Scheme 3.5).\textsuperscript{9} The initial cleavage of one of the bonds in the cyclopropenone ring
produces an intermediate \(3.20a,b\) (hereafter \(3.20\)). The electronic structure of the intermediate can be viewed as a resonance hybrid of ketenylcarbene \(3.20a\) and zwitterion \(3.20b\). The quantum-mechanical calculations and experimental evidence\(^9\) indicates that there is a substantial charge separation in \(3.20\). Hence, the actual distribution of electronic density in the intermediate is dominated by zwitterionic structure, \(3.20b\). Upon UV irradiation, the zwitterionic intermediate \(3.20b\) is formed directly from the singlet excited state of the cyclopropenone chromophore. The scission of the first carbon-carbon bond in the cyclopropenone ring requires 32 kcal/mol, whereas the energy barrier for cleavage of the second C-C bond is substantially lower.\(^9\)

### 3.2. Project goals

The development of novel photonucleases prepared by cyclopropenone photodecarbonylation for the \textit{in situ} generation of reactive cyclic enediyne compounds\(^{16}\) utilizes UV irradiation, a procedure that is not compatible with biomedical applications. These applications require use of light in the so called “phototherapeutic window”, a region of relative tissue transparency between 650 and 950 nm. One of the approaches allowing for the alleviation of this problem is to employ nonresonant two-photon excitation (2PE). At high light fluxes chromophores might simultaneously absorb two red/NIR photons producing excited
states the same as or similar to ones accessible by excitation with UV light of twice the frequency. So far, there has been no report on two-photon induced photodecarbonylation of cyclopropenones. Considering the potential biomedical significance of cyclopropenone photodecarbonylation and advantages offered by two-photon induced processes we set the goal to investigate the possibility and efficiency (if any) of two-photon induced photodecarbonylation of cyclopropenones.

### 3.3. Selection of the model cyclopropenone compound

Bis-(2-methoxy-1-naphthyl)cyclopropenone (BMNCP, 3.23) was selected as a model cyclopropenone (Figure 3.1).

![Figure 3.1. Bis-(2-methoxy-1-naphthyl)cyclopropenone (BMNCP)](image)

BMNCP is a photoactive compound that undergoes photodecarbonylation upon irradiation with UV-Vis light. The main reason for us to select this substance as a model compound was its suitable absorption spectrum (Figure 3.2). As seen from the graph, BMNCP features an absorption band with $\lambda_{\text{max}} = 390$ nm ($\log \epsilon = 4.24$).

The ultrafast Ti:sapphire lasers have the output wavelength of 800 nm (Figure 2.3, Chapter 2), whereas BMNCP has a substantial absorption at 400 nm allowing to anticipate the possibility of two-photon photoreaction. Evidently, there is no spectral overlap between the irradiation source and the substrate 3.23, which is required for single-photon excitation.
3.4. Photochemistry of BMNCP

3.4.1. Single-photon photochemistry

Irradiation of 3.23 in methanol at 254, 300, and 350 nm results in efficient photodecarbonylation of BMNCP leading to formation of bis-(2-methoxy-1-naphthyl)acetylene (BMNA, 3.24, Scheme 3.6).

Scheme 3.6. Photochemistry of bis-(2-methoxy-1-naphthyl)cyclopropenone
The steady state absorption spectra are shown in Figure 3.3. As seen from the graph the absorbance of the photoproduct 3.24 (brown line) at 400 nm is substantially lower than that of cyclopropenone 3.23 (dark blue line). Thus, at low degrees of 3.23 photodecomposition any two-photon absorption would be considered due to cyclopropenone 3.23.

![Figure 3.3](image)

**Figure 3.3.** Steady state absorption spectra (BMNCP). Irradiation with one 350 nm UV lamp $C_0$(BMNCP) = 1.1 × 10$^{-5}$ M in MeOH.

Absorbance change at 415 and 425 nm was followed to determine single-photon absorption quantum yields at 254, 300 and 350 nm (Table 3.1) using potassium ferrioxalate actinometry.$^{18}$ The concentration of BMNCP was maintained to achieve an optical density of ca. 2 at the wavelength of irradiation. The photodecomposition of the cyclopropenone 3.23 was followed by UV spectroscopy.

The summary of results on single-photon photochemistry is shown in Table 3.1.
Table 3.1. Summary of results on single-photon photochemistry of bis-(2-methoxy-1-naphthyl)cyclopropenone

<table>
<thead>
<tr>
<th>Irradiation (Monitoring) Wavelength, nm</th>
<th>ε, L mol⁻¹ cm⁻¹</th>
<th>ΔA/t</th>
<th>ΔA/t</th>
<th>Iλ, Einstein/min</th>
<th>Φλ</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMNCP</td>
<td>254 (415)</td>
<td>(7.7 ± 0.4)×10⁻⁴</td>
<td>(5.9 ± 0.2)×10⁻⁴</td>
<td>(1.27 ± 0.04)×10⁻⁹</td>
<td><strong>0.31 ± 0.04</strong></td>
</tr>
<tr>
<td>BMNCP</td>
<td>300 (425)</td>
<td>(4.6 ± 0.2)×10⁻³</td>
<td>(8.5 ± 0.3)×10⁻⁴</td>
<td>(1.8 ± 0.1)×10⁻⁹</td>
<td><strong>0.46 ± 0.06</strong></td>
</tr>
<tr>
<td>BMNCP</td>
<td>350 (425)</td>
<td>(3.9 ± 0.2)×10⁻⁴</td>
<td>(6.9 ± 0.3)×10⁻⁴</td>
<td>(1.5 ± 0.1)×10⁻⁹</td>
<td><strong>0.47 ± 0.06</strong></td>
</tr>
</tbody>
</table>

ε – extinction coefficient at monitoring wavelength (λ); ΔA – absorbance change at monitoring wavelength; t – time, min; Iλ – intensity of the lamp at irradiation wavelength λ; Φλ – quantum yield of photoreaction at irradiation wavelength λ.

### 3.4.2. Two-photon photochemistry

The irradiation of BMNCP in methanol with 800 nm ultrashort (ca. 95 fs) pulses from a Ti:sapphire laser results in the same process as the UV photolysis, i.e., the loss of carbon monoxide and the formation of the corresponding acetylene 3.24 via nonresonant two-photon absorption of light.¹⁹ The possibility of two-photon photoreaction was confirmed by irradiation of 1.5 mM methanol solution of BMNCP in a 1×1 cm quartz cuvette at 800 nm with the amplified Ti:sapphire laser light of 0.85 W (see Table 2.4 for laser parameters, Chapter 2).

Dependence of BMNA yield on irradiation pulse energy was studied as follows. The degassed 1.35 ml of ca. 10⁻³ M methanolic solution of 3.23 was irradiated in 1×1 cm quartz cell. The laser beam was attenuated by a diaphragm with a 6.15 mm opening. At the concentration of the substrate used in these experiments (ca. 1 mM) the loss of energy (ca. 7%) after the sample is mostly due to the losses on the phase boundaries. The laser power was measured before and after the cell and the average of these two values was used as laser power within the sample (0.91 W or 910 μJ pulse⁻¹).
The cross-section of the solution in the cell is 1.35 cm$^2$, while the cross-section of the beam is 0.297 cm$^2$. Thus, the irradiated volume was 22% of the total volume. Duration of irradiation experiments required to achieve certain conversion was therefore scaled down by the factor of 0.22.

During the 800 nm irradiation experiments up-converted blue emission from the sample was observed (Figure 3.4).

![Up-converted emission of 1 mM BMNCP sample irradiated at 800 nm](image)

**Figure 3.4.** Up-converted emission of 1 mM BMNCP sample irradiated at 800 nm

Later, it was found that observed luminescence was due to acetylene 3.24 (Figure 3.5).

We have not observed decomposition of diarylacetylene, 3.24 under the 800 nm irradiation.

The two-photon induced decarbonylation of bis(2-methoxy-1-naphthyl)cyclopropenone (3.23) was quite efficient and allowed us to calculate $\sigma_R$ not only from the rate of photoproduct 3.24 formation (blue line) but also from the kinetic data on the consumption of 3.23 (orange line; Figure 3.6, Table B.1 in Appendix B).
Figure 3.5. Normalized absorption and emission spectra of BMNA

Figure 3.6. Two-photon induced photodecarbonylation of BMNCP – plot of product yield vs. irradiation time; – formation of 3.24; – decomposition of 3.23.

Two-photon photoreaction dynamics was monitored by raise of BMNA signal in HPLC chromatograms. A sample of BMNA was prepared photochemically and characterized
spectroscopically (see sections 3.6.2 and 3.8.3). Yield of the product formation was determined using HPLC calibration plot (Figure 3.7, Table B.2 in Appendix B) that shows correlation between integration areas of the photoproduct 3.24 signal and its concentration.

![Figure 3.7. BMNA HPLC calibration plot.](image)

To verify that a two-photon reaction is observed, the expected quadratic dependence of the rate of BMNA formation on the irradiation power was analyzed. The yield of acetylene 3.24 formed in 486 s irradiation of BMNCP with laser pulses of variable energy is displayed in Figure 3.8 (Table B.3 in Appendix B). This dependence was also analyzed in terms of consumption vs. pulse energy (Figure 3.9; Table B.4 in Appendix B). The laser power output was attenuated using glass filters to achieve the intensity of the laser pulses in the range from 125 to 835 μJ pulse⁻¹. Figures 3.8 and 3.9 illustrate the observed nonlinear dependence of the rate of photodecarbonylation reaction on the pulse energy.
Figure 3.8. Two-photon induced photodecarbonylation of BMNCP – plot of product yield vs. pulse energy.

Figure 3.9. Two-photon induced photodecarbonylation of BMNCP – plot of consumption vs. pulse energy.

The logarithmic representation of these dependences has slopes of 2.02 (Figure 3.10, Table B.5 in Appendix B) and 2.11 (Figure 3.11, Table B.6 in Appendix B) confirming the two-photon nature of the observed photochemistry.
Figure 3.10. Two-photon induced photodecarbonylation of BMNCP – plot of \( \log(\text{product yield}) \) vs. \( \log(\text{pulse energy}) \).

\[ \text{Slope} = 2.02 \pm 0.02 \]

Figure 3.11. Two-photon induced photodecarbonylation of BMNCP – plot of \( \log(\text{consumption of 3.23}) \) vs. \( \log(\text{pulse energy}) \).

\[ \text{Slope} = 2.11 \pm 0.03 \]
3.5. Two-photon absorption cross section

3.5.1. Photochemical method

The theoretical bases for two-photon absorption cross section (TPACS) calculation using photochemical method are given in Chapter 2 (see section 2.5.1.) Here we present only critical equations used in calculations:

\[ C = C_0 \cdot \exp \left( -v_R \int_{100\%}^{100\%} \frac{d\alpha}{v \cdot t} \right) \]  
\[ \sigma_R = (0.20 \pm 0.04) \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1} \text{ or } 0.20 \pm 0.02 \text{ GM}. \]

In addition to the use of the exponential equation (eq. 3.1), we have applied a zero-order kinetic equation (eq. 3.2) to calculate TPACS\(_R\) (\(\sigma_R\)) for the induction of the decarbonylation reaction using data in the region of low conversion as well as calculated the cross section from the consumption of 3.23 (Table 3.2).

**Table 3.2.** Two-photon absorption cross sections of BMNCP, 3.23.

<table>
<thead>
<tr>
<th>(\sigma_R), GM</th>
<th>(\sigma), GM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated from eq. 3.1</td>
<td>Calculated from eq. 3.2</td>
</tr>
<tr>
<td>0.20 ± 0.04</td>
<td>0.18 ± 0.04</td>
</tr>
</tbody>
</table>
Values produced by all three calculations are in very good agreement with one another.

To convert experimentally-determined two-photon cross sections for the induction of the photodecarbonylation reactions, $\sigma_{R}$, into the two-photon absorption cross-sections of cyclopropenone 3.23 ($\sigma$), we need to know the fraction of two-photon excited molecules that undergo decarbonylation, $\Phi_{2PE}$. The excited state initially populated upon two-photon excitation might be different from that initially populated upon single-photon excitation. However, according to Kasha’s rule, photochemical reactions generally occur from the lowest singlet or triplet excited states regardless of the excitation method and the initial exited state.\textsuperscript{21} Thus, we can assume that the quantum yield of the two-photon initiated process is equal to its single-photon counterpart, $\Phi_{800} = \Phi_{400}$.

The latter values were determined by chemical actinometry\textsuperscript{18} at 350 nm (Table 3.1). To check the validity of Kasha’s rule for excitation of cyclopropenones, we also measured the quantum yield for the decarbonylation reaction of 3.23 at 254 nm and 300 nm, which showed little variation from the 350 nm values (Table 3.1). The two-photon absorption cross-sections (TPACS) of cyclopropenone 3.23 at 800 nm were calculated using single-photon quantum yield at 350 nm, $\sigma = \sigma_{R} / \Phi_{SPE}$, and are shown in Table 3.2.

### 3.5.2. Z-scan method

Two-photon absorption cross section (TPACS) of BMNCP was determined using nonlinear transmission technique.\textsuperscript{22} The theory, detailed experimental setup and mathematical expressions for data processing were adopted from literature (see Chapter 2, section 2.5.2), and will not be discussed here. The pictorial representation of Z-scan setup is shown in Figure 2.21 (Chapter 2).

The TPACS of BMNCP was measured using open aperture Z-scan technique.\textsuperscript{23} The methanol solution of Rhodamine 6G was used as a calibration standard as its TPACS has been reported.\textsuperscript{24} The Z-scan trace of 20 mM methanol solution of BMNCP is shown in Figure 3.12.
As seen from Figure 3.12 theoretical fitting of the experimental trace is good. TPACS of BMNCP measured using Z-scan method is $0.62 \pm 0.03$ GM.

### 3.5.3. White light continuum pump-probe method

Comparison of white light continuum (WLC) pump-probe method (WLCPPM) with photochemical and Z-scan methods is given in Chapter 2 (section 2.5.3). The detailed experimental setup and mathematical processing of data were adopted from literature\textsuperscript{25} and will not be discussed here. The attenuated output from Ti:sapphire laser (800 nm) was used as a pump, whereas white light continuum generated in CaF$_2$ crystal was used as a probe. The relative polarizations of both pump and probe lights were maintained parallel. The pump and probe beams were focused so that they spatially overlapped within 2 mm thick quartz cell containing sample solution. The power of the pump pulse was significantly higher than that of probe pulse ($P_{\text{pump pulse}}=10-15$ μJ; $P_{\text{probe pulse}}<0.5$ μJ). Absorbance of BMNCP sample (20 mM in CH$_2$Cl$_2$) measured vs. delay time was converted into transmittance, and obtained curve was fitted using eq. 2.16 (Chapter 2).
The kinetic trace of BMNCP obtained using WLCPPM is shown in Figure 3.13. TPACS of BMNCP at 790 nm determined using WLCPPM was 1.4 GM, which is in reasonable agreement with Z-scan and photochemical method 800 nm values.

**Figure 3.13.** Kinetic trace of BMNCP obtained using WLCPPM; e-e-e - Experimental data, −− Theoretical fit using eq. 2.16 (Chapter 2).

**Figure 3.14.** Kinetic trace of BMNCP and CH$_2$Cl$_2$ obtained using WLCPPM;
To insure that the kinetic trace was due to BMNCP (Figure 3.14; black trace) the control experiment was run using neat solvent (green trace).

Two-photon absorption spectrum of BMNCP was acquired using WLCPPM method (Figure 3.15). As seen from the graph, the two-photon absorption spectrum of BMNCP resembles that of single-photon absorption. However, the maximum of nonlinear absorption is not twice that of linear absorption. Similar two-photon properties have been observed for other two-photon absorbing chromophores.23

![Graph showing two-photon absorption spectrum of BMNCP](image)

**Figure 3.15.** TPA spectrum of BMNCP obtained using WLCPPM.

### 3.6. Synthesis

#### 3.6.1. Synthesis of BMNCP

Bis-(2-methoxy-1-naphthyl)cyclopropenone (3.23) was prepared by Friedel-Crafts alkylation of the 2-methoxynaphthalene with trichlorocyclopropenium cation followed by hydrolysis of the resulting 1,1-dichlorocyclopropene (Scheme 3.7).9
3.6.2. Synthesis of BMNA

Bis-(2-methoxy-1-naphthyl)acetylene (3.24) was prepared by 350 nm irradiation of 10 mg sample of cyclopropenone 3.23 in methanol (Scheme 3.6).

3.7. Conclusions

In summary, we have shown the feasibility of the two-photon induced decarbonylation of cyclopropenones, which produces quantitative yields of the corresponding acetylenes. The two-photon absorption cross-sections of cyclopropenone 3.23 were determined by three methods – photochemical, Z-scan and WLCPPM, and the values obtained are in reasonable agreement.

3.8. Experimental

3.8.1. Materials

Friedel-Crafts alkylation reactions were carried out in flame-dried glassware under argon atmosphere. Dichloromethane was distilled from phosphorus pentoxide, and hexane was distilled from sodium under argon immediately before use. All other reagents were used as purchased.

3.8.2. Instruments

Melting points were measured on Fisher-Johns melting point apparatus. Nuclear magnetic resonance (NMR) spectra were acquired with Bruker Avance System 300 MHz. $^1$H
NMR and $^{13}$C NMR spectra were recorded using tetramethylsilane (TMS) as an internal standard, and chemical shifts are reported in parts per million (ppm) relative to TMS. UV-visible spectra were obtained using either Varian Cary 50 Bio or Varian Cary 300 UV-Visible spectrometer. IR spectra were acquired on Mattson Galaxy 6020 FT-IR instrument. GC/MS analysis was conducted using either HP 5987 A or Shimadzu QP5050A GC spectrometers equipped with ZB5MS 30 m x 0.25 mm x 0.25 μm columns. High-resolution mass spectra (HRMS) were collected by the Mass Spectrometry Laboratory, University of Illinois at Urbana-Champaign, IL. The preparative and analytical photolysis of 3.23 was conducted in methanol solution using RMR-600 Rayonet™ photochemical reactor equipped with a carousel sampleholder. TPA experiments were conducted using 800 nm pulses generated by an amplified Ti:sapphire laser (Hurricane by Spectra Physics) operating at 1 kHz.


### 3.8.3. Synthetic procedures

**Bis-(2-methoxy-1-naphthyl)cyclopropenone (3.23).** A solution of 2-methoxynaphthalene (3.00 g, 19 mmol) in 3.5 ml of dichloromethane was added dropwise to a stirred suspension of tetrachlorocyclopropene (1.69 g, 9.5 mmol) and anhydrous aluminum chloride (1.33 g, 10 mmol) in 18 ml of dichloromethane at -78°C. The mixture was stirred for 2 h and cooling bath was removed. Reaction mixture was stirred at room temperature for 6 h (until TLC showed complete consumption of the 2-methoxynaphthalene). The reaction mixture was poured onto 40 ml of water, organic layer was separated, aqueous layer was extracted with two 30 ml portions of dichloromethane, combined organic layers were washed with 50 ml of brine, and dried with anhydrous sodium sulfate. Solvent was removed in vacuum, crude cyclopropenone (3.38 g) was recrystallized from hexanes-dichloromethane mixture to give 2.67
g (7.3 mmol, 77%) 3.23; mp = 162.0 C (162.0 C Lit.). $^1$H NMR (300 MHz, CDCl$_3$) δ 3.65 (s, 6H), 7.26 (dd, 2H), 7.42 (t, 2H), 7.58 (t, 2H), 7.83 (d, 2H), 8.04 (d, 2H), 8.29 (d, 2H); $^{13}$C NMR (CDCl$_3$) δ 55.8, 109.5, 112.2, 124.4, 125.5, 125.8, 128.0, 128.2, 128.4, 133.6, 134.3, 145.7, 157.3, 158.0 (see $^1$H NMR and $^{13}$C NMR spectra titled B2MNCP in Appendix D); IR 2941, 2831, 1833, 1609, 1589, 1506, 1408, 1150, 1087, 810, 748; HRMS calc for C$_{25}$H$_{18}$O$_3$ (M$^+$-H) 366.1256, found 366.1254;

Bis-(2-methoxy-1-naphthyl)acetylene (3.24). The solution of ca 10 mg of bis-(2-methoxy-1-naphthyl)cyclopropenone in methanol was irradiated in a quartz vessel equipped with an immersible cooling finger with 16 lamp ($\lambda_{\text{emission}}$ = 254 or 350 nm) in a Rayonet™ photochemical reactor. After complete decomposition of starting material (controlled by TLC) removal of solvent resulted in formation of an essentially pure photoproduct; mp = 180.0 C (177-180.0 C Lit.). $^1$H NMR (300 MHz, CDCl$_3$) δ 4.14 (s, 6H), 7.30 (dd, 2H), 7.41 (t, 2H), 7.61 (t, 2H), 7.83 (t, 4H), 8.62 (d, 2H); $^{13}$C NMR (CDCl$_3$) δ 56.9, 93.8, 107.5, 113.0, 124.2, 125.8, 127.3, 128.0, 128.7, 129.9, 134.5, 158.8 (see $^1$H NMR and $^{13}$C NMR spectra titled 3.24 in Appendix D); IR 2934, 2838, 1618, 1587, 1460, 1408, 1333, 1259, 1104, 1054, 803, 745; MS calc for C$_{24}$H$_{18}$O$_2$ (M$^+$) 338, found 338;

3.9. References


CHAPTER 4. DEVELOPMENT OF PHOTOREACTIVE ORGANIC COMPOUNDS WITH LARGE TWO-PHOTON ABSORPTION CROSS SECTIONS

4.1. Introduction

The two-photon absorption cross section, $\sigma_{2PA}$ (TPACS) represents the efficiency of two-photon absorption by a chromophore. Recognition of advantages of TPA (see Chapter 1, section 1.1.3) initiated efforts on design and synthesis of efficient two-photon absorbing compounds. Unfortunately, the strict criteria to predict if a molecule would efficiently absorb two photons simultaneously have not been developed yet. However, vast theoretical and laboratory research conducted in the recent years elucidated the matter to some extent and allowed for developing several general principles. A variety of compounds including donor-bridge acceptor (D-\(\pi\)-A) dipoles,\(^1\) donor-bridge-donor (D-\(\pi\)-D) quadrupoles,\(^2-4\) multibranched compounds,\(^5\) dendrimers,\(^6\) and octupoles\(^7\) have been synthesized and their structure-property relationships established.\(^1\)-\(^8\) The results of these studies revealed that increasing the effective conjugation (coplanarity of linked \(\pi\)-systems) length, molecular symmetry (especially D-\(\pi\)-A-\(\pi\)-D arrangement), presence of strong electron-donor substituents (especially aromatic amino-groups), polarizability of \(\pi\)-centers, and extended \(\pi\)-electron delocalization (charge transfer) results in increase of TPACS of organic compounds.\(^1a,3,7a,b\)

A number of compounds with different structures exhibit large ($\sigma_{2PA}>10^3$ GM)\(^9-11\) and very large ($\sigma_{2PA}>10^4$ GM)\(^12-14\) experimental TPACS. The largest theoretically calculated TPACS values are in the order of $10^5$.\(^15\) The experimental two-photon absorption cross section values depend on many factors including laser pulse duration - nanosecond TPACS are 2-3 orders of magnitude higher than those determined using femtosecond pulses.\(^3\) This is because in TPACS ascertained utilizing nanosecond lasers there is a significant contribution of excited state two-
photon absorption (see Chapter 1, section 1.1.2. for detailed explanation). Thus, in our opinion, only the TPACS values calculated using femtosecond pulses should be considered reliable.

4.2. Project goals

Most of the chromophores that exhibit large TPACS are highly fluorescent and photochemically inactive. Our research interests are focused on organic molecules that have large two-photon absorption cross sections and undergo efficient two-photon induced photoreactions. In spite of vast advantages and great promising potential of two-photon induced photochemistry from the literature review (see Chapter 1) it is apparent that this area of organic photochemistry remains relatively unexplored. Therefore, this research project grapples with the problem of developing a new series of α-diazocarbonyl- and cyclopropenone-containing photoreactive organic compounds based on the preceded TPACS enhancement principles.

4.3. Design strategies and developed photoreactive organic compounds

As said earlier, molecular symmetry (especially D-π-A-π-D arrangement), presence of strong electron-donor substituents, and extended π-electron delocalization results in enhancements of TPACS of organic chromophores. Based on these factors we have developed a series of cyclopropenone-containing and two α-diazocarbonyl-incorporated photoreactive organic compounds (Figure 4.1). Cyclopropenones 4.1-4.3 and 2-diazo-1,3-diketone 4.5 feature D-π-A-π-D arrangement. Two-photon absorption cross sections of cyclopropenones 4.1-4.3 will be compared to that of 3.23 studied earlier (Chapter 3). 2-diazo-1,3-diketone 4.4 was included in order to evaluate the contribution of dialkylamino- substituent into TPACS (based on comparison of 4.4 and 4.5 cross sections.)
Figure 4.1. Developed photoreactive organic compounds
4.4. Photochemistry of photoreactive organic compounds 4.1-4.5

4.4.1. Single-photon photochemistry

Cyclopropenones 4.1-4.3 are photoactive compound that undergo photodecarbonylation upon irradiation with UV-Vis light.

\[
\text{hv} - \text{CO} \\
\]

\[
\text{R} \quad \text{R} \\
\]

\[
\text{R} = \text{OMe} \\
\text{R} = \text{p-methoxyphenyl} \\
\text{R} = \text{p-methoxystyryl} \\
\]

Scheme 4.1. Photochemistry of cyclopropenones 4.1-4.3.

Irradiation of bis-\(p\)-anisylcyclopropenone, 4.1 (BMPCP), bis-\(p\)-(\(p\)-anisyl)phenylcyclopropenone, 4.2 (BAPCP), and bis-\(p\)-(\(p\)-methoxystyryl)phenylcyclopropenone, 4.3 (BASCP) in methanol at 254, 300, and 350 nm results in efficient photodecarbonylation of cyclopropenone.

**Figure 4.2.** Absorption spectra of cyclopropenones 4.1-4.3. 
\[ 
\text{C}(4.1) = 2.04 \times 10^{-5} \text{ M in MeOH}; \text{C}(4.2) = 6.8 \times 10^{-5} \text{ M in CH}_2\text{Cl}_2; \\
\text{C}(4.3) = 3.8 \times 10^{-4} \text{ M in CH}_2\text{Cl}_2; 
\]
leading to formation of bis-\(p\)-anisylacetylene, 4.6 (BMPA), bis-\(p\)-(\(p\)-anisyl)phenylacetylene, 4.7 (BAPA), and bis-\(p\)-(\(p\)-methoxystyryl)phenylacetylene, 4.3 (BASA; Scheme 4.1). The normalized absorption spectra of cyclopropenones 4.1-4.3 are shown in Figure 4.2. We have not observed any absorption bands with \(\lambda_{\text{max}} > 400 \text{ nm}\) even at very high substrate concentrations (up to 0.01 M; Figure 4.3).

![Absorption Spectra](image)

**Figure 4.3.** Absorption spectra of cyclopropenones 4.1-4.3 at high concentration of substrate.

2-Diazo-1,3-bis-(4-phenylethynylphenyl)propane-1,3-dione, 4.4 (DDK1) and 2-diazo-1,3-bis-[4-(4-\(N,N\)-dimethylaminophenylethynyl)phenyl]propane-1,3-dione, 4.5 (DDK2) undergo Wolff rearrangement upon UV-Vis irradiation (Scheme 4.2). Illumination of DDK1 and DDK2 in presence of methanol results in formation of methyl 3-oxo-2,3-bis-(4-phenylethynylphenyl)propionate, 4.9 (MKE1) and methyl 2,3-bis-[4-(4-dimethylaminophenylethynyl)phenyl]-3-oxo-propionate, 4.10 (MKE2) respectively.
Scheme 4.2. Photochemistry of 2-diazo-1,3-diketones 4.4 and 4.5.

The normalized absorption spectra of 2-diazo-1,3-diketones 4.4 and 4.5 are shown in Figure 4.4.

Figure 4.4. Absorption spectra of 2-diazo-1,3-diketones 4.4 and 4.5.

The ultrafast Ti:sapphire lasers have the output wavelength of 800 nm (Figure 2.3, Chapter 2). Evidently, there is no spectral overlap between the irradiation source and linear
absorption of cyclopropenones 4.1-4.3 and diazodiketones 4.4 and 4.5, which is required for single-photon excitation.

The steady state absorption spectra of 4.1-4.5 are shown in Figures 4.5-4.9.

**Figure 4.5.** Steady state absorption spectra of BMPCP, 4.1. Irradiation with one 350 nm UV lamp; \( C_0(\text{BMPCP}) = 2 \times 10^{-5} \text{ M in MeOH} \).

**Figure 4.6.** Steady state absorption spectra of BAPCP, 4.2. Irradiation with one 350 nm UV lamp; \( C_0(\text{BAPCP}) = 3 \times 10^{-5} \text{ M in MeOH} \).
As seen from the graphs in Figures 4.5-4.7 the acetylenic photoproducts 4.6-4.8 feature absorption maxima at shorter wavelengths in comparison with the corresponding cyclopropenones 4.1-4.3. In case of 4.4 and 4.5 \( \lambda_{\text{max}} \) of photoproducts 4.9 and 4.10 are...
Figure 4.9. Steady state absorption spectra of DDK2, 4.5. Irradiation with one 350 nm UV lamp; $C_0$(DDK2) = $1.7 \times 10^{-5}$ M in dichloromethane.

also blue-shifted compared to respective 2-diazo-1,3-diketones. However, photoproduct 4.9 has a higher extinction coefficient at 400 nm than its photoprecursor diazodiketone 4.4. Hence, when studying the two-photon photochemistry of DDK1 it is essential to keep the percent decomposition of DDK1 as low as possible (preferably <10%). Thus, at low degrees of photodecomposition of 4.1-4.5 any two-photon absorption would be considered due to starting photoreactive substrate.

Absorbance change at 355, 388 and 425 nm was followed in order to determine 350 nm single-photon absorption quantum yields of 4.1, 4.2 and 4.3 respectively (Table 4.1) using potassium ferrioxalate actinometry.\textsuperscript{16} Single-photon quantum yields of 4.4 and 4.5 were determined following the photoreaction progress at 390 and 460 nm respectively. The concentration of cyclopropenones and diazodiketones was maintained to achieve an optical density of ca. 2 at the wavelength of irradiation. The photodecomposition of the cyclopropenones 4.1-4.3 and diazodiketones 4.4 and 4.5 was followed by UV spectroscopy.
The summary of results on single-photon photochemistry of photoreactive substrates 4.1-4.5 at 350 nm is shown in Table 4.1.

**Table 4.1.** Summary of results on single-photon photochemistry of photoreactive organic compounds 4.1-4.5 at 350 nm

<table>
<thead>
<tr>
<th>Substrate (Monitoring Wavelength), nm</th>
<th>ε, L mol⁻¹ cm⁻¹</th>
<th>ΔA/t 4.1-4.5</th>
<th>ΔA/t K₃Fe(C₂O₄)₃</th>
<th>I₃₅₀, Einstein/min</th>
<th>Φ₃₅₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 (355)</td>
<td>3770 ± 20</td>
<td>(4.97 ± 0.11)×10⁻⁴</td>
<td>(6.9 ± 0.3)×10⁻⁴</td>
<td>(1.5 ± 0.1)×10⁻⁹</td>
<td>0.26 ± 0.04</td>
</tr>
<tr>
<td>4.2 (388)</td>
<td>3290 ± 30</td>
<td>(8.47 ± 0.21)×10⁻⁴</td>
<td>(6.9 ± 0.3)×10⁻⁴</td>
<td>(1.5 ± 0.1)×10⁻⁹</td>
<td>0.50 ± 0.01</td>
</tr>
<tr>
<td>4.3 (425)</td>
<td>1390 ± 15</td>
<td>(3.41 ± 0.19)×10⁻⁴</td>
<td>(6.9 ± 0.3)×10⁻⁴</td>
<td>(1.5 ± 0.1)×10⁻⁹</td>
<td>0.49 ± 0.05</td>
</tr>
<tr>
<td>4.4 (390)</td>
<td>981 ± 3</td>
<td>(6.95 ± 0.16)×10⁻⁴</td>
<td>(6.9 ± 0.3)×10⁻⁴</td>
<td>(1.6 ± 0.2)×10⁻⁶</td>
<td>0.13 ± 0.01</td>
</tr>
<tr>
<td>4.5 (460)</td>
<td>3680 ± 25</td>
<td>(7.24 ± 0.28)×10⁻⁵</td>
<td>(6.9 ± 0.3)×10⁻⁴</td>
<td>(1.6 ± 0.2)×10⁻⁶</td>
<td>0.004 ± 0.0002</td>
</tr>
</tbody>
</table>

ε – extinction coefficient at monitoring wavelength λ; ΔA – absorbance change at monitoring wavelength; t – time, min; I₃₅₀ – intensity of the lamp at 350 nm; Φ₃₅₀ - quantum yield of photoreaction at 350 nm.

### 4.4.2. Two-photon photochemistry

The irradiation of cyclopropenones 4.1-4.3 in methanol and/or dichloromethane with 800 nm ultrashort (ca. 95 fs) pulses from a Ti:sapphire laser results in the same process as the UV photolysis, i.e., the loss of carbon monoxide and the formation of the corresponding acetylenes 4.6-4.8 via nonresonant two-photon absorption of light.¹⁷ The possibility of two-photon induced photodecarbonylation of 4.1-4.5 was confirmed by irradiation of 1.35 ml solutions of these cyclopropenones in a 1×1 cm quartz cuvette at 800 nm with the amplified Ti:sapphire laser light (Table 4.2).
Table 4.2. Two-photon induced photodecarbonylation of 4.1-4.3.

<table>
<thead>
<tr>
<th>Cyclopropenone</th>
<th>Concentration, mM</th>
<th>Solvent</th>
<th>Irradiation time, min</th>
<th>Pulse energy, μJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>1</td>
<td>MeOH</td>
<td>360</td>
<td>630</td>
</tr>
<tr>
<td>4.2</td>
<td>1</td>
<td>1:1 MeOH:CH₂Cl₂</td>
<td>240</td>
<td>630</td>
</tr>
<tr>
<td>4.3</td>
<td>0.6</td>
<td>CH₂Cl₂</td>
<td>60</td>
<td>550</td>
</tr>
</tbody>
</table>

The irradiation of 2-diazo-1,3-diketones 4.4 and 4.5 in presence of methanol with 800 nm pulses from a Ti:sapphire laser results in the same process as the UV photolysis, i.e., Wolff rearrangement. The possibility of two-photon induced Wolff rearrangement was corroborated by irradiation of 1.33 ml solutions of these diazodiketones in a 1×1 cm quartz cuvette at 800 nm with the amplified Ti:sapphire laser light (Table 4.3).

Table 4.3. Two-photon induced Wolff rearrangement of 4.4 and 4.5.

<table>
<thead>
<tr>
<th>Diazoketone</th>
<th>Concentration, mM</th>
<th>Solvent</th>
<th>Irradiation time, min</th>
<th>Pulse energy, μJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4</td>
<td>0.7</td>
<td>1:9 MeOH: CH₂Cl₂</td>
<td>90</td>
<td>685</td>
</tr>
<tr>
<td>4.5</td>
<td>0.45</td>
<td>1:9 MeOH: CH₂Cl₂</td>
<td>5</td>
<td>685</td>
</tr>
</tbody>
</table>

Dependence of acetylene (4.6-4.8) and ester (4.9 and 4.10) yield on irradiation pulse energy was studied as follows. The degassed 1.35 ml solutions of 4.1-4.5 were irradiated in 1×1 cm quartz cell. The laser beam was attenuated by a diaphragm with a 6.15 mm opening. At the concentration of the substrate used in these experiments (0.5-1 mM) the loss of energy (6-9%) after the sample is mostly due to the losses on the phase boundaries. The laser power was
measured before and after the cell and the average of these two values was used as laser power within the sample.

The cross-section of the solution in the cell is 1.35 cm$^2$, while the cross-section of the beam is 0.297 cm$^2$. Thus, the irradiated volume was 22% of the total volume. Duration of irradiation experiments required to achieve certain conversion was therefore scaled down by the factor of 0.22.

During the 800 nm irradiation experiments up-converted blue emission from the sample of 4.5 was observed.

The plots of photoproduct yield vs. irradiation time are shown in Figures 4.10-4.14.

![Figure 4.10. Two-photon induced photodecarbonylation of 4.1 – plot of product (4.6) yield vs. irradiation time (Table C.1 in Appendix C).](image)

We have not observed decomposition of diarylacetylenes, 4.6-4.8 and/or ketoesters 4.9 and 4.10 under the 800 nm irradiation.

The two-photon induced decarbonylation of BMPCP (4.1) was quite inefficient. Therefore the photoproduct yield vs. pulse energy dependence was not studied. It was shown earlier
(Chapter 3) that two-photon absorption cross sections \( (\sigma_R) \) calculated from the rate of photoproduct formation and from the kinetic data on the photoreactive starting compound consumption are in excellent agreement. Thus, two-photon photoreaction dynamics of

**Figure 4.11.** Two-photon induced photodecarbonylation of 4.2 – plot of product (4.7) yield vs. irradiation time (Table C.2 in Appendix C).

**Figure 4.12.** Two-photon induced photodecarbonylation of 4.3 – plot of product (4.8) yield vs. irradiation time (Table C.3 in Appendix C).
4.3-4.5 was monitored by bleaching of photoreactive substrate signal in HPLC chromatograms. Yield of the photoproduct formation was determined using HPLC calibration plots (Figures 4.15-4.20).

Figure 4.13. Two-photon induced Wolff rearrangement of 4.4 – plot of product (4.9) yield vs. irradiation time (Table C.4 in Appendix C).

Figure 4.14. Two-photon induced Wolff rearrangement of 4.5 – plot of product (4.10) yield vs. irradiation time (Table C.5 in Appendix C).
Figure 4.15. BMPA (4.6) HPLC calibration plot (Table C.6 in Appendix C).

Figure 4.16. BAPA (4.7) HPLC calibration plot (Table C.7 in Appendix C).
Figure 4.17. BASCP (4.3) HPLC calibration plot (Table C.8 in Appendix C).

For diazodiketone 4.4 HPLC calibration plot was compiled at two wavelengths – 310 and 345 nm.

Figure 4.18. DDK1 (4.4) HPLC calibration plot at 310 nm (Table C.9 in Appendix C).
To verify that, in fact, two-photon reaction is observed, the expected quadratic dependence of the rate of photoproduct (4.6-4.10) formation, or alternatively substrate (4.1-4.5) consumption on the irradiation power was analyzed. The laser power output was attenuated
using glass filters to achieve the energy of the laser pulses in the range from 50 to 720 μJ/pulse.

The yield of acetylene (4.6-4.8) and ketoester (4.9 and 4.10) formed upon irradiation of 4.1-4.5 with laser pulses of variable energy are displayed in Figures 4.21-4.24.

**Figure 4.21.** Two-photon induced photodecarbonylation of 4.2 – plot of product (4.7) yield vs. pulse energy (Table C.12 in Appendix C).

**Figure 4.22.** Two-photon induced photodecarbonylation of 4.3 – plot of product (4.8) yield vs. pulse energy (Table C.13 in Appendix C).
Figures 4.21-4.24 illustrate the observed nonlinear dependence of the rate of two-photon induced photodecarbonylation (4.1-4.3) and photo-Wolff reaction (4.4 and 4.5) on the pulse energy.
The logarithmic representations of these dependence have a slopes of ca. 2 (Figures 4.25-4.28) confirming the two-photon nature of the observed photochemistry.

**Figure 4.25.** Two-photon induced photodecarbonylation of 4.2 – plot of ln(product (4.7) yield) vs. ln(pulse energy); Table C.16 in Appendix C.

**Figure 4.26.** Two-photon induced photodecarbonylation of 4.3 – plot of ln(product (4.8) yield) vs. ln(pulse energy); Table C.17 in Appendix C.
Figure 4.27. Two-photon induced Wolff rearrangement of 4.4 – plot of ln(product (4.9) yield) vs. ln(pulse energy); Table C.18 in Appendix C.

Figure 4.28. Two-photon induced Wolff rearrangement of 4.5 – plot of ln(product (4.10) yield) vs. ln(pulse energy); Table C.19 in Appendix C.
4.5. Two-photon absorption cross section

4.5.1. Photochemical method

The theoretical bases for two-photon absorption cross section (TPACS) calculation using photochemical method is given in Chapter 2 (see section 2.5.1.) Here we present only the essential equations used in calculations:

\[ C = C_0 \exp \int_{-100\text{fs}}^{100\text{fs}} \frac{v R I_0^2 dt}{100\text{fs}} \cdot t \]  
(4.1)

where \( C \) the concentration of the substrate.

The averaged least-squares fitting of the experimental data represented in Figure 4.10 (see Table C.1 in Appendix C) to eq. 4.1 gives \( \sigma_R = (2.0 \pm 0.5) \times 10^{-53} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1} \) or 0.0020 ± 0.0005 GM.\(^{17,18}\) \( \sigma_R \) is the two-photon absorption cross section for the induction of the photoreaction and is a product of quantum efficiency and the two-photon absorption cross-section of the substrate, \( \sigma_R = \Phi_{2PE} \cdot \sigma \).

In addition to the use of the exponential equation (eq. 4.1), we have applied a zero-order kinetic equation (eq. 4.2) to calculate \( \text{TPACS}_R (\sigma_R) \) for the induction of the photoreaction using data in the region of low conversion (Table 4.4).

\[ \frac{DC}{C_0} = -v R \int_{-100\text{fs}}^{100\text{fs}} \frac{\Phi_{2PE} \cdot t \cdot \sigma}{100\text{fs}} dt \]  
(4.2)

To convert experimentally-determined two-photon absorption cross sections for the induction of the photoreactions, \( \sigma_R \), into the two-photon absorption cross-sections of the substrates 4.1-4.5 (\( \sigma \)), we need to know the fraction of two-photon excited molecules that undergo photoreaction, \( \Phi_{2PE} \). The excited state initially populated upon two-photon excitation might be different from that initially populated upon single-photon excitation. However, according to Kasha’s rule, photochemical reactions generally occur from the lowest singlet or triplet excited states regardless of the excitation method and the initial exited state.\(^{19}\) Thus, we can assume that the quantum yield of the two-photon initiated process is equal to its single-
photon counterpart, $\Phi_{800} = \Phi_{400}$. The two-photon absorption cross-sections (TPACS) of substrates 4.1-4.5 at 800 nm were calculated using single-photon quantum yield at 350 nm, $\sigma = \sigma_R / \Phi_{SPE}$, and are shown in Table 4.4. As seen from Table 4.4 TPACS values produced by eq. 4.1 and 4.2 are in an excellent agreement.

**Table 4.4.** Two-photon absorption cross sections of 4.1-4.5 (photochemical method).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$\sigma_R$, GM Calculated from eq. 4.1</th>
<th>$\sigma_R$, GM Calculated from eq. 4.2</th>
<th>$\sigma$, GM</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>0.0020 ± 0.0005</td>
<td>0.0019 ± 0.0004</td>
<td>0.0077</td>
</tr>
<tr>
<td>4.2</td>
<td>0.0080 ± 0.0001</td>
<td>0.0078 ± 0.0001</td>
<td>0.016</td>
</tr>
<tr>
<td>4.3</td>
<td>0.3259</td>
<td></td>
<td>0.665</td>
</tr>
<tr>
<td>4.4</td>
<td>0.0122</td>
<td>0.0122</td>
<td>0.094</td>
</tr>
<tr>
<td>4.5</td>
<td>1.768</td>
<td></td>
<td>442</td>
</tr>
</tbody>
</table>

**4.5.2. White light continuum pump-probe method**

Comparison of white light continuum (WLC) pump-probe method (WLCPPM) with photochemical method is given in Chapter 2 (section 2.5.3). The detailed experimental setup and mathematical processing of data were adopted from literature\textsuperscript{20,21} and will not be discussed here. The attenuated output from Ti:sapphire laser or OPA was used as a pump, whereas white light continuum generated in CaF\textsubscript{2} crystal was used as a probe. The relative polarizations of both pump and probe lights were maintained parallel. The pump and probe beams were focused so that they spatially overlapped within 2 mm thick quartz cell containing sample solution. The power of the probe pulse was significantly lower than that of pump pulse ($P_{\text{pump pulse}} = 10-15 \, \mu J; P_{\text{probe pulse}} < 0.5 \, \mu J$). Absorbance of the sample measured vs. delay time was converted into transmittance, and obtained curve was fitted using eq. 2.16 (Chapter 2).
The kinetic traces of 4.3, 4.4 and 4.5 obtained using WLCPPM are shown in Figures 4.29, 4.30 and 4.31 respectively.

**Figure 4.29.** Kinetic trace of 4.3 obtained using WLCPPM; e-e-e - Experimental data, — Theoretical fit using eq. 2.16 (Chapter 2).

**Figure 4.30.** Kinetic trace of 4.4 obtained using WLCPPM; e-e-e - Experimental data, — Theoretical fit using eq. 2.16 (Chapter 2).

TPACS of 4.3, 4.4 and 4.5 at 800 nm determined using WLCPPM are shown in Table 4.5, and are in good agreement with photochemical method values.
Figure 4.31. Kinetic trace of 4.5 obtained using WLCPPM; e-e-e - Experimental data, – Theoretical fit using eq. 2.16 (Chapter 2).

Table 4.5. Two-photon absorption cross sections of 4.1-4.5 (WLCPPM).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>( \sigma, \text{GM} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3</td>
<td>1.096</td>
</tr>
<tr>
<td>4.4</td>
<td>0.172</td>
</tr>
<tr>
<td>4.5</td>
<td>460</td>
</tr>
</tbody>
</table>

4.6. Conclusions

The design of symmetric two-photon absorbing chromophores is usually based on the Donor–π–Acceptor–π–Donor motif, where –π– is an extended conjugated π-system.\(^{3b,c}\) The very small two-photon absorption cross-section of bis-\(p\)-anisylcyclopropenone (4.1) is, therefore, not surprising since the π-system of this molecule is rather small (total area of a π-conjugated system is \(305 \text{ Å}^2\)). However, extension of the conjugation by the \(p\)-phenylene unit on both sides of the cyclopropenone in 4.2 (area \(463 \text{ Å}^2\)) does not bring much gain in the two-photon
absorption cross-section. The somewhat smaller bis-(2-methoxy-1-naphthyl)cyclopropenone 3.23 (area 390 Å²), on the other hand, shows a twenty six times larger two-photon absorption cross-section than 4.2. A much better correlation is observed between the two-photon absorption cross sections and the extinction coefficients at 400 nm for 4.1-4.5 (Table 4.6).

Table 4.6. Two-photon absorption cross sections and 400 nm extinction coefficients of 4.1-4.5.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>(\sigma_{PCM}), GM</th>
<th>(\sigma_{WLC}), GM</th>
<th>(\varepsilon_{400}) M⁻¹ cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>0.0077</td>
<td></td>
<td>4.6</td>
</tr>
<tr>
<td>4.2</td>
<td>0.016</td>
<td></td>
<td>292</td>
</tr>
<tr>
<td>4.4</td>
<td>0.094</td>
<td>0.172</td>
<td>940</td>
</tr>
<tr>
<td>4.3</td>
<td>0.665</td>
<td>1.096</td>
<td>2550</td>
</tr>
<tr>
<td>4.5</td>
<td>442</td>
<td>480</td>
<td>46800</td>
</tr>
</tbody>
</table>

However, compounds studied earlier (2.14 and 3.23) do not fit into this correlation (Table 4.7).

Table 4.7. Two-photon absorption cross sections and 400 nm extinction coefficients of 2.14 and 3.23.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>(\sigma_{PCM}), GM</th>
<th>(\sigma_{Z}), GM</th>
<th>(\sigma_{WLC}), GM</th>
<th>(\varepsilon_{400}) M⁻¹ cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.14</td>
<td>0.22</td>
<td>0.42</td>
<td>0.44</td>
<td>73900</td>
</tr>
<tr>
<td>3.23</td>
<td>0.42</td>
<td>0.62</td>
<td>1.4</td>
<td>14550</td>
</tr>
</tbody>
</table>

The fact that cyclopropenones 4.1 and 4.2 have very low absorption at 400 nm indicates that the energy of two 800 nm photons is insufficient to achieve excitation to the lowest SPE-
accessible excited state. Apparently, there are no other lower lying states, which can be populated by 800 nm two-photon excitation.

In summary, we have achieved an enhancement of two-photon absorption cross section for series of symmetrical cyclopropenones 4.1-4.3 and 2-diazo-1,3-diketones 4.4 and 4.5. The presence of electron-donor substituents (-N(CH$_3$)$_2$) in two-photon absorbing chromophores increases TPACS substantially (4.4 vs. 4.5). The two-photon absorption cross sections of 4.5 is one of the highest among photoreactive organic compounds, and certainly the highest reported so far for photoreactive 2-diazo-1,3-diketones.

4.7. Synthesis

4.7.1. Synthesis of cyclopropenones 4.1-4.3

Bis-p-anisylcyclopropenone, 4.1 (BMPCP), bis-p-(p-anisyl)phenylcyclopropenone, 4.2 (BAPCP), and bis-p-(p-methoxystyril)phenylcyclopropenone, 4.3 (BASCP) were prepared by Friedel-Crafts alkylation of anosile, 4.11, 4-methoxybiphenyl, 4.12 and 4-styrylanisole, 4.13, respectively with trichlorocyclopropenium cation followed by hydrolysis of the resulting 1,1-dichlorocyclopropene (Schemes 4.3-4.5).$^{22}$

Scheme 4.3. Synthesis of bis-p-anisylcyclopropenone, 4.1 (BMPCP)
Compounds 4.12 and 4.13 were synthesized using reported\textsuperscript{23} efficient hydroxyapatite-supported Pd catalyst \((\text{Ca}_{9}\text{HPO}_4\text{(PO}_4)_5\text{(OH)}\text{PdCl}_2\text{(PhCN)}_2\text{ or PdHAP-1})\) that was prepared from ammonium phosphate and calcium nitrate tetrahydrate (Scheme 4.6).
\[
6 \text{ (NH}_4\text{)}_2\text{HPO}_4 + 9 \text{ Ca(NO}_3\text{)}_2\cdot4\text{H}_2\text{O} \rightarrow \text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH})
\]
\[
\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH}) + \text{PdCl}_2(\text{PhCN})_2 \rightarrow \text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH})\cdot\text{PdCl}_2(\text{PhCN})_2
\]

**Scheme 4.6.** Synthesis of PdHAP-1

4-methoxybiphenyl, 4.12 was synthesized from 4-bromoanisole, 4.15 and phenylboronic acid, 4.16 using Suzuki coupling (Scheme 4.7). \(^{23}\)

![Scheme 4.7. Synthesis of 4-methoxybiphenyl, 4.12](image)

4-styrylanisole, 4.13 was synthesized from 4-bromoanisole, 4.15 and styrene, 4.17 using Heck coupling (Scheme 4.8). \(^{23}\)

![Scheme 4.8. Synthesis of 4-styrylanisole, 4.13](image)

**4.7.2. Synthesis of acetylenes 4.6-4.8**

Bis-\(p\)-anisylacetylene, 4.6 (BMPA), bis-\(p\)-(\(p\)-anisyl)phenylacetylene, 4.7 (BAPA), and bis-\(p\)-(\(p\)-methoxystyryl)phenylacetylene, 4.8 (BASA) were prepared by 350 nm irradiation of 30 mg samples of corresponding cyclopropenones in methanol or dichloromethane (Scheme 4.1)
4.7.3. Synthesis of 2-diazo-1,3-diketones 4.4 and 4.5

2-Diazo-1,3-bis-(4-phenylethynylphenyl)propane-1,3-dione, 4.4 (DDK1) and 2-diazo-1,3-bis-[4-(4-N,N-dimethylaminophenylethynyl)phenyl]propane-1,3-dione, 4.5 (DDK2) were synthesized in three steps. In the first step 4-bromoacetophenone 4.18 and methyl 4-bromobenzoate 4.19 were coupled using Claisen condensation (Scheme 4.9).

\[
\begin{align*}
\text{Br} & \quad \text{O} \\
\text{O} & \quad \text{Br} \\
\end{align*}
\]

Scheme 4.9. Synthesis of diketone, 4.20

In the second step 1,3-bis-(4-bromophenyl)propane-1,3-dione 4.20 underwent Sonogashira coupling with phenylacetylene, 4.21 or 4-ethyl-N,N-dimethylaniline 4.23 (Schemes 4.10 and 4.11).
Finally, in the third step diketones 4.22 and 4.24 were diazotated with tosyl azide\textsuperscript{26} using standard procedure\textsuperscript{27} to yield synthetic targets 4.4 and 4.5 (,).

Scheme 4.12. Synthesis of 2-diazo-1,3-diketones 4.4 and 4.5
4.8. Experimental

4.8.1. Materials

Moisture- and oxygen-sensitive reactions were carried out in flame-dried glassware under argon atmosphere. Dichloromethane was distilled from phosphorus pentoxide, and hexane, benzene and THF were distilled from sodium under argon immediately before use. All other reagents were used as purchased.

4.8.2. Instruments

Melting points were measured on Fisher-Johns melting point apparatus. Nuclear magnetic resonance (NMR) spectra were acquired with Bruker Avance System 300 MHz. $^1$H NMR and $^{13}$C NMR spectra were recorded using tetramethylsilane (TMS) as an internal standard, and chemical shifts are reported in parts per million (ppm) relative to TMS. UV-visible spectra were obtained using either Varian Cary 50 Bio or Varian Cary 300 UV-Visible spectrometer. IR spectra were acquired on Mattson Galaxy 6020 FT-IR instrument. GC/MS analysis was conducted using either HP 5987 A or Shimadzu QP5050A GC spectrometers equipped with ZB5MS 30 m x 0.25 mm x 0.25 μm columns. High-resolution mass spectra (HRMS) were collected by the Mass Spectrometry Laboratory, University of Illinois at Urbana-Champaign, IL. The preparative and analytical photolysis of 4.1-4.5 was conducted in methanol and/or dichloromethane solution using RMR-600 Rayonet™ photochemical reactor equipped with a carousel sampleholder.


Two-photon experiments were conducted using 800 nm pulses generated by an amplified Ti:sapphire laser (Hurricane by Spectra Physics) operating at 1 kHz.
4.8.3. Synthetic procedures

Bis-\textit{p}-anisylcyclopropenone (4.1).\textsuperscript{22} A solution of anisole (5.77 g, 53.4 mmol) in 10 ml of dichloromethane was added dropwise to a stirred suspension of tetrachlorocyclopropene (5.77 g, 26.7 mmol) and anhydrous aluminum chloride (3.7 g, 28 mmol) in 50 ml of dichloromethane at -78^\circ C. The mixture was stirred for 2 h and cooling bath was removed. Reaction mixture was stirred at room temperature for 24 h (until TLC showed complete consumption of the anisole). The reaction mixture was poured onto 100 ml of water, organic layer was separated, aqueous layer was extracted with two 75 ml portions of dichloromethane, combined organic layers were washed with 100 ml of brine, and dried with anhydrous sodium sulfate. Solvent was removed in vacuum. Crude cyclopropenone (6.4 g) was purified by recrystallization from hexane-dichloromethane mixture to give 5.97 g of 4.1 (22.4 mmol, 84%) as a white solid; mp = 176-178^\circ C (172-182^\circ C \text{Lit.}\textsuperscript{28}). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 3.91 (s, 3H), 7.05 (d, 2H), 7.92 (d, 2H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \(\delta\) 55.6, 114.7, 117.2, 133.5, 144.2, 155.3, 162.7 (see \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra titled 4.1 in Appendix D); IR 1842, 1597, 1570, 1302, 1255, 1163, 1011, 823, 802; HRMS calc for C\textsubscript{17}H\textsubscript{14}O\textsubscript{3} (M\textsuperscript{+}-H) 266.0943, found 266.0943;

Bis-\textit{p}-(\textit{p}-anisyl)phenylcyclopropenone (4.2).\textsuperscript{22} A solution of 4-methoxybiphenyl 4.12 (2.4 g, 13 mmol) in 2.5 ml of dichloromethane was added dropwise to a stirred suspension of tetrachlorocyclopropene (1.16 g, 2.67 mmol) and anhydrous aluminum chloride (0.91 g, 6.8 mmol) in 12 ml of dichloromethane at -78^\circ C. The mixture was stirred for 2 h and cooling bath was removed. Reaction mixture was stirred at room temperature for 21 h (until TLC showed complete consumption of the 4-methoxybiphenyl). The reaction mixture was poured onto 25 ml of water, organic layer was separated, aqueous layer was extracted with two 25 ml portions of dichloromethane, combined organic layers were washed with 40 ml of brine, and dried with anhydrous sodium sulfate. Solvent was removed in vacuum. Crude cyclopropenone was
purified by the chromatography on silica gel (1:20 methanol:dichloromethane) to give 1.14 g of 4.2 (2.7 mmol, 42%) as a white crystalline solid. Rf = 0.35 in 1:20 methanol:dichloromethane; mp = 177.5-179.5°C (recrystallized from methanol). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 3.98 (s, 3H), 7.10 (d, 1H), 7.37 (t, 1H), 7.44 (t, 2H), 7.61 (dd, 2H), 7.76 (dd, 1H), 8.22 (d, 2H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 55.5, 55.6, 111.4, 114.5, 114.8, 117.0, 121.0, 133.5, 133.9, 134.1, 134.2, 144.0, 155.4, 162.8 (see \(^1\)H NMR and \(^{13}\)C NMR spectra titled 4.3 in Appendix D); IR 3046, 2939, 1856, 1617, 1478, 1454, 1273, 1247, 1006, 813, 755, 694; MS calc for C\(_{29}\)H\(_{22}\)O\(_3\) (M\(^+\)) 418, found 418; HRMS calc for C\(_{29}\)H\(_{22}\)O\(_3\) (M\(^+\)-H) 418.1569, found 418.1559;

**Bis-p-(p-methoxystyryl)phenylcyclopropenone (4.3).** A solution of 4-styrylanisole 4.13 (2.0 g, 9.5 mmol) in 2 ml of dichloromethane was added dropwise to a stirred suspension of tetrachlorocyclopropene (0.85 g, 4.76 mmol) and anhydrous aluminum chloride (0.67 g, 5.0 mmol) in 8 ml of dichloromethane at -78°C. The mixture was stirred for 2 h and cooling bath was removed. Reaction mixture was stirred at room temperature for 20 h (until TLC showed complete consumption of the 4-styrylanisole). The reaction mixture was poured onto 10 ml of water, organic layer was separated, aqueous layer was extracted with two 10 ml portions of dichloromethane, combined organic layers were washed with 30 ml of brine, and dried with anhydrous sodium sulfate. Solvent was removed in vacuum. Crude cyclopropenone was purified by recrystallization from hexanes-dichloromethane mixture to give 0.29 g of 4.2 (0.62 mmol, 13%) as a yellow solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 3.80 (s, 3H), 6.65 (d, 2H), 6.93 (d, 2H), 7.21 (d, 1H), 7.31 (m, 5H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 55.2, 55.3, 113.7, 113.8 (2), 114.3, 124.2, 127.3, 127.4, 128.0, 128.2, 128.3 (2), 128.4 (2), 128.5, 128.6, 128.7 (3), 128.8, 128.9, 129.2, 131.7, 132.1, 132.3, 137.2, 144.4, 147.0, 156.8, 160.7 (see \(^1\)H NMR and \(^{13}\)C NMR spectra titled 4.2 in Appendix D); IR 1833, 1609, 1588, 1506, 1465, 1257, 1217, 1150, 1087, 1069, 810, 748; MS calc for C\(_{33}\)H\(_{26}\)O\(_3\) (M\(^+\)) 470, found 470; HRMS calc for C\(_{33}\)H\(_{26}\)O\(_3\) (M\(^+\)-H) 470.1882, found 470.1889;
**Bis-p-anisylacetylene (4.6).** The solution of 30 mg of bis-p-anisylcyclopropenone (4.1) in 5 ml methanol was irradiated in a quartz vessel equipped with an immersible cooling finger with 16 lamp ($\lambda_{\text{emission}} = 350$ nm) in a Rayonet™ photochemical reactor. After complete decomposition of starting material (controlled by TLC) removal of solvent resulted in formation of 27 mg of essentially pure photoproduct 4.6 (0.1 mmol); mp = 145-146°C (141.5-143°C Lit.29). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 3.82 (s, 6H), 6.86 (d, 4H), 7.45 (d, 4H); $^{13}$C NMR (CDCl$_3$) $\delta$ 55.3, 87.9, 114.0, 115.8, 132.9, 159.4; (see $^1$H NMR and $^{13}$C NMR spectra titled B4MPA in Appendix D); IR 2966, 2840, 1903, 1457, 1284, 1242, 1169, 1105, 1024, 836, 816, 747; MS calc for C$_{16}$H$_{14}$O$_2$ (M$^+$) 238, found 238.

**Bis-p-(p-anisyl)phenylacetylene (4.7).** The solution of 30 mg of bis-p-(p-anisyl)phenylcyclopropenone (4.2) in 5 ml dichloromethane was irradiated in a quartz vessel equipped with an immersible cooling finger with 16 lamp ($\lambda_{\text{emission}} = 350$ nm) in a Rayonet™ photochemical reactor. After complete decomposition of starting material (controlled by TLC) removal of solvent resulted in formation of 28 mg of essentially pure photoproduct 4.7 (0.1 mmol); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 3.98 (s, 3H), 6.98 (d, 1H), 7.32 (t, 1H), 7.43 (t, 2H), 7.56 (m, 3H), 7.80 (d, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ 56.1, 89.9, 111.1, 113.1, 126.7, 126.9, 128.3, 128.8, 132.2, 133.6, 140.1, 159.5 (see $^1$H NMR and $^{13}$C NMR spectra titled 4.7 in Appendix D); IR 3018, 2943, 2840, 1872, 1598, 1486, 1278, 1150, 1116, 760, 690; MS calc for C$_{28}$H$_{22}$O$_2$ (M$^+$) 390, found 390; HRMS calc for C$_{28}$H$_{22}$O$_2$ (M$^+$) 390.1620, found 390.1619.

**Hydroxyapatite-supported Pd catalyst (PdHAP-1).** 5.28 g of (NH$_4$)$_2$HPO$_4$ (40 mmol) was dissolved in deionized water (150 ml) and pH was adjusted to 11 aqueous NH$_3$ solution. To a solution of Ca(NO$_3$)$_2$ (14.17 g, 60 mmol) in deionized water (120 ml) adjusted to pH 11 with aqueous NH$_3$ solution was added dropwise over 30 min into the above solution with vigorous stirring at room temperature, and then obtained milky solution was heated to at 90°C for 10 min. The precipitate was filtered, washed with deionized water, and dried at 110°C overnight, giving 6.13 g (97%) of Ca$_9$(HPO$_4$)(PO$_4$)$_5$(OH) (HAP-1). 1 g of HAP-1 (1 mmol) was stirred at 25°C for 3
h in 75 ml of 2.67 × 10^{-4} M acetone solution of PdCl2(PhCN)2 (0.0077 g, 0.02 mmol). The obtained slurry was filtered, washed with acetone and dried under vacuum, yielding 0.72 g (71%) of Ca9(HPO4)(PO4)5(OH)-PdCl2(PhCN)2 (PdHAP-1; Pd content: 0.015 mmol·g^{-1}).

4-Methoxybiphenyl (4.12).

PdHAP-1 (0.108 g, Pd: 1.62 μmol), K2CO3 (4.44 g, 32 mmol), and phenylboronic acid, 4.16 (3.92 g, 32 mmol) were placed into a 100 ml round bottom flask with a reflux condenser. Under Ar atmosphere, o-xylene (36 ml) and 4-bromoanisole, 4.15 (5.00 g, 27 mmol) were added, and the resulting mixture was stirred at 120°C for 10 h. The progress of reaction was monitored by GC/MS. Crude product (4.16 g) was purified by the chromatography on silica gel (1:2 dichloromethane:hexanes) to give 2.02-2.61 g (41-53%) of 4-methoxybiphenyl, 4.12. Rf=0.45 in 1:1.5 dichloromethane:hexanes; mp = 88-89°C (89-91°C Lit.30); 1H NMR (300 MHz, CDCl3) δ 3.85 (s, 3H), 6.97 (dt, 2H), 7.30 (tt, 1H), 7.42 (t, 2H), 7.53 (m, 4H); 13C NMR (CDCl3) δ 55.4, 114.2, 126.7 (2), 128.2, 128.7, 133.8, 140.9; (see 1H NMR and 13C NMR spectra titled 4.12 in Appendix D); MS calc for C13H12O (M^+) 184, found 184.

4-Styrylanisole (4.13).

PdHAP-1 (0.108 g, Pd: 1.62 μmol) and K2CO3 (4.44 g, 32 mmol) were placed into a 100 ml round bottom flask with a reflux condenser. Under Ar atmosphere, N-methylpyrrolidone (NMP; 36 ml), 4-bromoanisole, 4.15 (5.00 g, 27 mmol), and styrene, 4.17 (3.35 g, 32 mmol) were added, and the resulting mixture was stirred at 130°C for 30 h. The progress of reaction was monitored by GC/MS. Crude product mixture was poured onto 100 ml benzene. NMP was extracted with water (3 × 50 ml). Crude product (5.37 g) was purified by the chromatography on silica gel (1:1.5 dichloromethane:hexanes) to give 3.88-4.16 g (69-74%) of 4-styrylanisole, 4.13 (E:Z = 15:1). Rf=0.5 in 1:1.5 hexanes:dichloromethane; mp = 135-136°C (135-140°C Lit.31); 1H NMR (300 MHz, CDCl3) δ 3.83 (s, 3H), 6.90 (d, 2H), 7.02 (q, 2H), 7.23 (t, 1H), 7.35 (t, 2H), 7.48 (t, 4H); 13C NMR (CDCl3) δ 55.3, 114.2, 126.3, 126.6, 127.2, 127.7, 128.2, 128.6 (see 1H NMR and 13C NMR spectra titled 4.13 in Appendix D); MS calc for C15H14O (M^+) 210, found 210.
1,3-Bis-(4-bromophenyl)propane-1,3-dione (4.20).\textsuperscript{24} To a stirred mixture of 1.4 g of ca. 60% sodium hydride in oil dispersion (34.9 mmol) and 3.23 g (15 mmol) of methyl 4-bromobenzoate, 4.19 in 25 ml of dry benzene, maintained at 60\(^\circ\)C, was added, from a dropping funnel, a solution of 2.99 g (15 mmol) of 4-bromoacetophenone 4.18 made up to 5 ml in dry benzene. 0.5 ml of 4.18 solution was added, and stirred for 5 h. The remainder of the solution was then added dropwise over a period of 2 h, and stirring and heating was continued for another 14 h. The cooled mixture was treated with 1 ml of methanol, then with a mixture of concentrated sulfuric acid and ice. Precipitated material was separated, washed with deionized water and dried at 40\(^\circ\)C. The crude diketone (4.20) was recrystallized from benzene to give 0.225 g (0.59 mmol, 39%) pure product (mp = 198\(^\circ\)C; 197-198.5\(^\circ\)C Lit.\textsuperscript{24}). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 6.77 (s, 1H), 7.64 (dt, 4H), 7.84 (dt, 4H); \(^13\)C NMR (CDCl\(_3\)) \(\delta\) 93.4, 128.7, 132.0, 184.8 (see \(^1\)H NMR and \(^13\)C NMR spectra titled 4.20 in Appendix D); MS calc for C\(_{15}\)H\(_{10}\)Br\(_2\)O\(_2\) (M\(^+\)) 382, found 382.

1,3-Bis-(4-phenylethynylphenyl)propane-1,3-dione (4.22).\textsuperscript{25} Pd(PhCN)\(_2\)Cl\(_2\) (90 mg, 0.24 mmol), 1,3-bis-(4-bromophenyl)propane-1,3-dione, 4.20 (3.00 g, 7.9 mmol), and CuI (30 mg, 0.16 mmol) were added to a dry, 50-ml septum-capped round bottom flask, which was then purged with argon and charged with anhydrous dioxane (15 ml). P(t-Bu)\(_3\) (0.2 ml of a 0.25 M solution in dioxane; 0.47 mmol), HN(i-Pr)\(_2\) (2.7 ml, 18.8 mmol), and phenylacetylene, 4.21 (2.1 ml, 18.8 mmol) were added via syringe to the stirred reaction mixture. During the reaction, precipitation of [H\(_2\)N(i-Pr)\(_2\)]Br was observed. After 3 h of agitation at r.t., the reaction mixture is diluted with THF (50 ml), filtered through a small pad of silica gel (with THF rinsing), concentrated, and purified by recrystallization from EtOAc:THF, which yielded the desired product, 4.22 (2.11 g, 5 mmol, 63%); mp = 157-158\(^\circ\)C (melts with decomposition); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 6.88 (s, 1H), 7.37 (m, 6H), 7.56 (m, 4H), 7.64 (d, 4H), 7.98 (d, 4H); MS (DIP) calc for C\(_{31}\)H\(_{20}\)O\(_2\) (M\(^+\)) 424, found 424; HRMS calc for C\(_{31}\)H\(_{20}\)O\(_2\) (M\(^+\)) 424.1463, found 424.1458;
1,3-Bis-[4-(4-dimethylaminophenylethynyl)phenyl]propane-1,3-dione (4.24).\textsuperscript{25}

Pd(PhCN)\textsubscript{2}Cl\textsubscript{2} (90 mg, 0.24 mmol), 1,3-bis-(4-bromophenyl)propane-1,3-dione, 4.20 (3.00 g, 7.9 mmol), 4-(N,N-dimethylamino) phenylacetylene, 4.23 (2.74 g, 18.8 mmol), and Cul (30 mg, 0.16 mmol) were added to a dry, 50-ml septum-capped round bottom flask, which was then purged with argon and charged with anhydrous dioxane (15 ml). P(t-Bu)\textsubscript{3} (0.2 ml of a 0.25 M solution in dioxane; 0.47 mmol), and HN(i-Pr)\textsubscript{2} (2.7 ml, 18.8 mmol) were added via syringe to the stirred reaction mixture. During the reaction, precipitation of [H\textsubscript{2}N(i-Pr)\textsubscript{2}]Br was observed. After 3 h of agitation at r.t., the reaction mixture is diluted with THF (50 ml), filtered through a small pad of silica gel (with THF rinsing), concentrated, and purified by recrystallization from EtOAc:THF, which yielded the desired product, 4.24 (2.24 g, 56%); mp = 242\textdegree C (melts with decomposition); \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) δ 2.99 (s, 12H), 6.67 (d, 4H), 6.86 (s, 1H), 7.43 (dd, 4H), 7.59 (d, 4H), 7.97 (d, 4H) – see \textsuperscript{1}H NMR spectrum titled 4.24 in Appendix D); MS calc for C\textsubscript{35}H\textsubscript{30}N\textsubscript{2}O\textsubscript{2} (M\textsuperscript{+}) 510, found 510; HRMS calc for C\textsubscript{35}H\textsubscript{30}N\textsubscript{2}O\textsubscript{2} (M\textsuperscript{+}) 510.2307, found 510.2315.

\textsuperscript{p}-Toluenesulfonyl azide.\textsuperscript{26} To distilled 1.91 g (10 mmol) of \textsuperscript{p}-toluenesulfonyl chloride in 11 ml of 96% ethanol was added with swirling 0.79 g (12.1 mmol) of sodium azide in 2.5 ml of deionized water. After agitation 1 h the mixture was poured into 40 ml of water. The separated oily crude product was washed with water and dried over sodium sulfate. The crude \textsuperscript{p}-toluenesulfonyl azide (1.92 g, 97%) was used without further purification.

2-Diazo-1,3-bis-(4-phenylethynylphenyl)propane-1,3-dione (4.4).\textsuperscript{27} A mixture of 2.97 g (7 mmol) of 1,3-bis-(4-phenylethynylphenyl)propane-1,3-dione (4.22) and 1.38 g (7 mmol) of \textsuperscript{p}-toluenesulfonyl azide was stirred in THF (10 ml) with KF on alumina (3.00 g) at 0\textdegree C during 24 h. The precipitated solid was filtered, and washed with ethyl ether (2 × 5 ml). 100 ml of dichloromethane was added to the filtrate and the crude product was washed with potassium hydroxide (2.27 g of KOH in 100 ml water). The crude product was dried over magnesium sulfate. Solvent was removed in vacuum. The crude 4.4 was recrystallized from THF:EtOAc to
give 1.20 g (2.66 mmol, 38%) of pure product; mp = 137-138°C (melts with effervescence); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.35 (m, 6H), 7.49 (m, 8H), 7.52 (m, 4H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 128.4, 128.5, 131.5, 131.8, 136.2 (see \(^1\)H NMR and \(^{13}\)C NMR spectra titled DDK1 in Appendix D); IR 3125, 2207, 2115, 1695, 1597, 1547, 1487, 1443, 1349, 1242, 1166, 1076, 814, 755, 662;

**2-Diazo-1,3-bis-[4-(4-N,N-dimethylaminophenylethynyl]phenyl)propane-1,3-dione (4.5).**\(^{27}\) A mixture of 3.57 g (7 mmol) of 1,3-bis-[4-(4-dimethylaminophenylethynyl]phenyl]-propane-1,3-dione (4.24) and 1.38 g (7 mmol) of \(p\)-toluenesulfonyl azide was stirred in THF (10 ml) with KF on alumina (3.00 g) at 0°C during 24 h. The precipitated solid was filtered, and washed with ethyl ether (2 × 5 ml). 100 ml of dichloromethane was added to the filtrate and the crude product was washed with potassium hydroxide (2.27 g of KOH in 100 ml water). The crude product was dried over magnesium sulfate. Solvent was removed in vacuum. The crude 4.5 was recrystallized from THF:EtOAc to give 0.92 g (1.71 mmol, 29%) of pure product. mp = 212°C (melts with decomposition); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 3.00 (s, 12H), 6.64 (d, 4H), 7.41 (dd, 8H), 7.55 (d, 4H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 40.1, 84.2, 87.0, 94.7, 109.2, 111.8, 128.5, 129.1, 131.0, 133.0, 135.2, 150.5, 185.5 (see \(^1\)H NMR and \(^{13}\)C NMR spectra titled DDK2 in Appendix D); IR 2797, 2208, 2118, 1633, 1593, 1522, 1310, 1258, 1123, 943, 860, 821, 750, 656;

**Methyl 3-oxo-2,3-bis-(4-phenylethynylphenyl)propionate (4.9).** The solution of 100 mg (0.22 mmol) of 2-diazo-1,3-bis-(4-phenylethynylphenyl)propane-1,3-dione (4.4) in 10 ml 1:4 methanol: dichloromethane was irradiated in a Pyrex test-tube with 16 lamp (\(\lambda_{\text{emission}}\) = 350 nm) in a Rayonet™ photochemical reactor. Decomposition of the starting material was controlled by TLC. Crude photoproduct (98 mg) was purified by the chromatography on silica gel (neat dichloromethane; \(R_f= 0.71\)) to give 58 mg (0.13 mmol; 58%) of MKE1, 4.9; mp = 165-167°C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 3.28 (s, 3H), 7.35 (m, 6H), 7.62 (m, 8H), 7.97 (dd, 2H), 8.14 (d, 2H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 51.7, 60.5, 87.7, 108.0, 121.8, 125.8, 126.3, 127.3, 127.4, 127.7, 128.2, 128.6, 130.6 (2), 130.5, 130.7, 130.8, 132.8, 133.3, 136.4, 170.1, 195.2 (see \(^1\)H NMR and \(^{13}\)C...
NMR spectra titled MKE1 in Appendix D); IR 2924, 2215, 1675, 1598, 1488, 1440, 1261, 1233, 1178, 1105, 1070, 823, 751, 686; MS (DIP) calc for C_{32}H_{22}O_{3} (M^+) 454, found 454.

Methyl 2,3-bis-[4-(4-dimethylaminophenylethynyl)phenyl]-3-oxo-propionate (4.10).
The solution of 100 mg (0.19 mmol) of 2-diazo-1,3-bis-[4-(4-N,N-dimethylaminophenylethynyl)phenyl]pro-pane-1,3-dione (4.5) in 10 ml 1:4 methanol:dichloromethane was irradiated in a Pyrex test-tube with 16 lamp (λ_{emission} = 350 nm) in a Rayonet™ photochemical reactor. Decomposition of the starting material was controlled by TLC. Crude photoproduct (97 mg) was purified by the chromatography on silica gel (neat dichloromethane; R_f = 0.45) to give 63 mg (0.12 mmol; 63%) of MKE2, 4.10: mp = 174-176°C. ^1H NMR (300 MHz, CDCl_3) δ 2.99 (s, 12H), 3.93 (s, 3H), 6.67 (d, 4H), 7.42 (m, 6H), 7.55 (m, 4H), 7.98 (s, 1H; d, 2H); ^13C NMR (CDCl_3) δ 40.2 (2), 52.1, 58.9, 94.2, 109.3, 111.8 (2), 128.6, 129.1, 129.2, 129.5, 130.0, 131.0, 131.4, 131.5, 132.7, 133.0, 133.2, 150.4, 166.7, 191.3 (see ^1H NMR and ^13C NMR spectra titled MKE1 in Appendix D); IR 2895, 2208, 1705, 1592, 1524, 1436, 1357, 1273, 1132, 1104, 1064, 1009, 967, 855, 814, 768, 696; MS (DIP) calc for C_{36}H_{32}O_{3} (M^+) 540, found 540.

4.9. References


Appendix A

Table A.1. Formation of methyl 1H-indene-3-carboxylate in two-photon induced Wolff rearrangement of DNQ at 855 μJ/pulse (Figure 2.14)

<table>
<thead>
<tr>
<th>Time of Irradiation, s</th>
<th>Yield of MI3C</th>
</tr>
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<tr>
<td>0</td>
<td>0</td>
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<tr>
<td>729</td>
<td>0.108</td>
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<tr>
<td>1458</td>
<td>0.217</td>
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<tr>
<td>2269</td>
<td>0.325</td>
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<td>2998</td>
<td>0.403</td>
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<tr>
<td>3727</td>
<td>0.481</td>
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</tbody>
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Table A.2. MI3C HPLC calibration plot (Figure 2.15)

<table>
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<th>Concentration, mM</th>
<th>Integration area, mAU</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>96885</td>
</tr>
<tr>
<td>0.01</td>
<td>93101</td>
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<tr>
<td>0.1</td>
<td>930798</td>
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<tr>
<td>0.1</td>
<td>967094</td>
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<tr>
<td>0.2</td>
<td>1967673</td>
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<tr>
<td>0.2</td>
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<td>0.3</td>
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Linear Regression for data in Table A.2:

\[ Y = A + B \times X \]

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<thead>
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<th>Parameter</th>
<th>Value</th>
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<tr>
<td>A</td>
<td>-41971</td>
<td>41339</td>
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<td>B</td>
<td>1.01259 \times 10^7</td>
<td>1.36526 \times 10^5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>R</th>
<th>SD</th>
<th>N</th>
<th>P</th>
</tr>
</thead>
</table>
Table A.3. Formation of methyl 1H-indene-3-carboxylate in two-photon induced Wolff rearrangement of DNQ (Time of irradiation 970 s, variable pulse energy; Figure 2.16)

<table>
<thead>
<tr>
<th>Pulse energy, μJ</th>
<th>Yield of MI3C</th>
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<tbody>
<tr>
<td>245</td>
<td>0.012</td>
</tr>
<tr>
<td>249</td>
<td>0.014</td>
</tr>
<tr>
<td>298</td>
<td>0.014</td>
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<tr>
<td>300</td>
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</tr>
<tr>
<td>347</td>
<td>0.028</td>
</tr>
<tr>
<td>350</td>
<td>0.021</td>
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<td>698</td>
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<td>698</td>
<td>0.094</td>
</tr>
<tr>
<td>783</td>
<td>0.122</td>
</tr>
<tr>
<td>783</td>
<td>0.122</td>
</tr>
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<td>783</td>
<td>0.124</td>
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<tr>
<td>859</td>
<td>0.145</td>
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<tr>
<td>859</td>
<td>0.141</td>
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<tr>
<td>859</td>
<td>0.143</td>
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<td>939</td>
<td>0.172</td>
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<td>939</td>
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Table A.4. Logarithmic plot of methyl 1H-indene-3-carboxylate formation in two-photon induced Wolff rearrangement of DNQ (Time of irradiation 970 s, variable pulse energy; Figure 2.17)

<table>
<thead>
<tr>
<th>Ln(Pulse energy, μJ)</th>
<th>Ln(Yield of MI3C)</th>
</tr>
</thead>
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<tr>
<td>5.501</td>
<td>-4.423</td>
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<tr>
<td>5.517</td>
<td>-4.269</td>
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</tbody>
</table>
Slope = 1.98 ± 0.04
Linear Regression for data in Table A.4:
Y = A + B × X

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<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-15.30936</td>
<td>0.27481</td>
</tr>
<tr>
<td>B</td>
<td>1.97915</td>
<td>0.04305</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>R</th>
<th>SD</th>
<th>N</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.99624</td>
<td>0.09016</td>
<td>18</td>
<td>&lt;0.0001</td>
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|          |           |    |         |
| 5.697    | -4.269    |    |         |
| 5.704    | -3.963    |    |         |
| 5.849    | -3.576    |    |         |
| 5.858    | -3.863    |    |         |
| 6.548    | -2.303    |    |         |
| 6.548    | -2.303    |    |         |
| 6.548    | -2.364    |    |         |
| 6.663    | -2.104    |    |         |
| 6.663    | -2.104    |    |         |
| 6.663    | -2.087    |    |         |
| 6.756    | -1.931    |    |         |
| 6.756    | -1.959    |    |         |
| 6.756    | -1.945    |    |         |
| 6.845    | -1.76     |    |         |
| 6.845    | -1.802    |    |         |
| 6.845    | -1.808    |    |         |
Appendix B

Table B.1. Formation of bis-(2-methoxy-1-naphthyl)acetylene in two-photon induced photodecarbonylation of BMNC at 910 μJ/pulse (Figure 3.6)

<table>
<thead>
<tr>
<th>Time of Irradiation, s</th>
<th>Concentration of 3.23, M</th>
<th>Concentration of 3.24, M</th>
<th>Yield of BMNA</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>9.83E-04</td>
<td>5.46E-06</td>
<td>0.000</td>
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<td>69</td>
<td>7.57E-04</td>
<td>1.23E-04</td>
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<td>140</td>
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<td>206</td>
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Table B.2. BMNA HPLC calibration plot (Figure 3.7)

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<tr>
<td>0.1</td>
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<td>0.2</td>
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<tr>
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Linear Regression through origin for data in Table B.2:
Y = B × X

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<tr>
<th>Parameter</th>
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<th>Error</th>
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<td>B</td>
<td>7.63506 ×10^7</td>
<td>7.19075 ×10^5</td>
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Table B.3. Formation of bis-(2-methoxy-1-naphthyl)acetylene in two-photon induced photodecarbonylation of BMNCP (Time of irradiation 486 s, variable pulse energy; Figure 3.8)

<table>
<thead>
<tr>
<th>Pulse energy, μJ</th>
<th>Yield of BMNA</th>
</tr>
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<tbody>
<tr>
<td>125</td>
<td>0.0165</td>
</tr>
<tr>
<td>130</td>
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<tr>
<td>260</td>
<td>0.0712</td>
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<td>380</td>
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<td>390</td>
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Table B.4 Consumption of bis-(2-methoxy-1-naphthyl)cyclopropenone in two-photon induced photodecarbonylation of BMNCP (Time of irradiation 486 s, variable pulse energy; Figure 3.9)

<table>
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<th>Pulse energy, μJ</th>
<th>Consumption of BMNCP</th>
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<tr>
<td>125</td>
<td>0.0185</td>
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<tr>
<td>130</td>
<td>0.0152</td>
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<tr>
<td>260</td>
<td>0.0648</td>
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<td>265</td>
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<td>390</td>
<td>0.154</td>
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Table B.5. Logarithmic plot of formation in bis-(2-methoxy-1-naphthyl)acetylene two-photon induced photodecarbonylation of BMNCP (Time of irradiation 486 s, variable pulse energy; Figure 3.10)

<table>
<thead>
<tr>
<th>Log(pulse energy, μJ)</th>
<th>Log(yield of BMNA)</th>
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<tr>
<td>-3.90309</td>
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<tr>
<td>-3.88606</td>
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<td>-3.58503</td>
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<td>-3.57675</td>
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<tr>
<td>-3.42022</td>
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<tr>
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Slope = 2.02 ± 0.02
Linear Regression for data in Table B.5:

\[ Y = A + B \times X \]

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<td>B</td>
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<td>0.01684</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>R</th>
<th>SD</th>
<th>N</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.99965</td>
<td>0.01617</td>
<td>12</td>
<td>&lt;0.0001</td>
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</tbody>
</table>
**Table B.6.** Logarithmic plot of consumption of bis-(2-methoxy-1-naphthyl) cyclopropenone in two-photon induced photodecarbonylation of BMNCP (Time of irradiation 486 s, variable pulse energy; Figure 3.11)

<table>
<thead>
<tr>
<th>Log(pulse energy, μJ)</th>
<th>Log(consumption of BMNCP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3.82681</td>
<td>-1.64782</td>
</tr>
<tr>
<td>-3.81248</td>
<td>-1.7167</td>
</tr>
<tr>
<td>-3.55596</td>
<td>-1.16558</td>
</tr>
<tr>
<td>-3.54821</td>
<td>-1.11238</td>
</tr>
<tr>
<td>-3.4045</td>
<td>-0.84164</td>
</tr>
<tr>
<td>-3.39469</td>
<td>-0.80688</td>
</tr>
<tr>
<td>-3.266</td>
<td>-0.51713</td>
</tr>
<tr>
<td>-3.25806</td>
<td>-0.51145</td>
</tr>
<tr>
<td>-3.14874</td>
<td>-0.25571</td>
</tr>
<tr>
<td>-3.14569</td>
<td>-0.26281</td>
</tr>
<tr>
<td>-3.08566</td>
<td>-0.14388</td>
</tr>
<tr>
<td>-3.08092</td>
<td>-0.134</td>
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Slope = 2.11 ± 0.03

Linear Regression for data in Table B.6:
Y = A + B × X

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6.37477</td>
<td>0.10548</td>
</tr>
<tr>
<td>B</td>
<td>2.11247</td>
<td>0.03115</td>
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</tbody>
</table>

<table>
<thead>
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<th>R</th>
<th>SD</th>
<th>N</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.99891</td>
<td>0.02714</td>
<td>12</td>
<td>&lt;0.0001</td>
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</tbody>
</table>
Appendix C

Table C.1. Formation of 4.6 in two-photon induced photodecarbonylation of 4.1 at 630 μJ/pulse (Figure 4.10)

<table>
<thead>
<tr>
<th>Time of Irradiation, min</th>
<th>Yield of 4.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>24.3</td>
<td>0.011</td>
</tr>
<tr>
<td>48.6</td>
<td>0.024</td>
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<tr>
<td>72.9</td>
<td>0.0365</td>
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<tr>
<td>97.2</td>
<td>0.0498</td>
</tr>
<tr>
<td>121.5</td>
<td>0.0655</td>
</tr>
<tr>
<td>145.8</td>
<td>0.0828</td>
</tr>
<tr>
<td>170.1</td>
<td>0.097</td>
</tr>
<tr>
<td>194.5</td>
<td>0.111</td>
</tr>
</tbody>
</table>

Table C.2. Formation of 4.7 in two-photon induced photodecarbonylation of 4.2 at 630 μJ/pulse (Figure 4.11)

<table>
<thead>
<tr>
<th>Time of Irradiation, min</th>
<th>Yield of 4.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>16.2</td>
<td>0.0459</td>
</tr>
<tr>
<td>32.4</td>
<td>0.0834</td>
</tr>
<tr>
<td>48.6</td>
<td>0.118</td>
</tr>
<tr>
<td>64.8</td>
<td>0.153</td>
</tr>
<tr>
<td>81</td>
<td>0.186</td>
</tr>
<tr>
<td>97.2</td>
<td>0.228</td>
</tr>
<tr>
<td>113.4</td>
<td>0.25</td>
</tr>
<tr>
<td>129.6</td>
<td>0.281</td>
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</table>

Table C.3. Formation of 4.8 in two-photon induced photodecarbonylation of 4.3 at 550 μJ/pulse (Figure 4.12)

<table>
<thead>
<tr>
<th>Time of Irradiation, s</th>
<th>Yield of 4.8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Time of Irradiation, s</td>
<td>Yield of 4.9</td>
</tr>
<tr>
<td>-----------------------</td>
<td>--------------</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>487</td>
<td>0.0685</td>
</tr>
<tr>
<td>973</td>
<td>0.108</td>
</tr>
<tr>
<td>1459</td>
<td>0.147</td>
</tr>
<tr>
<td>1945</td>
<td>0.162</td>
</tr>
<tr>
<td>2917</td>
<td>0.215</td>
</tr>
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</table>

**Table C.4.** Formation of 4.9 in two-photon induced photodecarbonylation of 4.4 at 685 μJ/pulse (Figure 4.13)

<table>
<thead>
<tr>
<th>Time of Irradiation, s</th>
<th>Yield of 4.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Table C.5.** Formation of 4.10 in two-photon induced photodecarbonylation of 4.5 at 685 μJ/pulse (Figure 4.14)
Table C.6. BMPA (4.6) HPLC calibration plot (Figure 4.15)

<table>
<thead>
<tr>
<th>Concentration of 4.6, mM</th>
<th>Integration area, mAU</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.075</td>
<td>3431490</td>
</tr>
<tr>
<td>0.075</td>
<td>3445130</td>
</tr>
<tr>
<td>0.15</td>
<td>6763920</td>
</tr>
<tr>
<td>0.15</td>
<td>6747150</td>
</tr>
<tr>
<td>0.225</td>
<td>10151800</td>
</tr>
<tr>
<td>0.225</td>
<td>10180400</td>
</tr>
<tr>
<td>0.3</td>
<td>13266000</td>
</tr>
<tr>
<td>0.3</td>
<td>13312600</td>
</tr>
<tr>
<td>0.375</td>
<td>16920400</td>
</tr>
<tr>
<td>0.375</td>
<td>17109400</td>
</tr>
<tr>
<td>0.45</td>
<td>20413600</td>
</tr>
<tr>
<td>0.45</td>
<td>20510200</td>
</tr>
</tbody>
</table>

Linear Regression through origin for data in Table C.6:

\[ Y = B \times X \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>4.51942 \times 10^7</td>
<td>1.32251 \times 10^5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>R</th>
<th>SD</th>
<th>N</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9998</td>
<td>1.33812 \times 10^5</td>
<td>13</td>
<td>&lt;0.0001</td>
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</table>

Table C.7. BAPA (4.7) HPLC calibration plot (Figure 4.16)

<table>
<thead>
<tr>
<th>Concentration of 4.7, mM</th>
<th>Integration area, mAU</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
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</table>
Linear Regression through origin for data in Table C.7:
\[ Y = B \times X \]
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>1.11434 \times 10^8</td>
<td>1.909 \times 10^6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>R</th>
<th>SD</th>
<th>N</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.99474</td>
<td>4.01343 \times 10^5</td>
<td>13</td>
<td>&lt;0.0001</td>
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</table>

**Table C.8.** BASCP (4.3) HPLC calibration plot (Figure 4.17)

<table>
<thead>
<tr>
<th>Concentration of 4.3, mM</th>
<th>Integration area, mAU</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.4</td>
<td>9993130</td>
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<tr>
<td>0.6</td>
<td>13574000</td>
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<tr>
<td>0.8</td>
<td>18192400</td>
</tr>
<tr>
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Linear Regression through origin for data in Table C.8:
\[ Y = B \times X \]
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>2.27338 \times 10^7</td>
<td>3.26137 \times 10^5</td>
</tr>
</tbody>
</table>
Table C.9. DDK1 (4.4) HPLC calibration plot at 310 nm (Figure 4.18)

<table>
<thead>
<tr>
<th>Concentration of 4.4, mM</th>
<th>Integration area, mAU</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.1</td>
<td>14131100</td>
</tr>
<tr>
<td>0.2</td>
<td>31477700</td>
</tr>
<tr>
<td>0.3</td>
<td>42374200</td>
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<tr>
<td>0.4</td>
<td>58222600</td>
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<td>0.5</td>
<td>77919600</td>
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</tbody>
</table>

Linear Regression through origin for data in Table C.9:

\[ Y = B \times X \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>1.50309 \times 10^6</td>
<td>2.79378 \times 10^6</td>
</tr>
</tbody>
</table>

Table C.10. DDK1 (4.4) HPLC calibration plot at 345 nm (Figure 4.19)

<table>
<thead>
<tr>
<th>Concentration of 4.4, mM</th>
<th>Integration area, mAU</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.1</td>
<td>6856040</td>
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<tr>
<td>0.2</td>
<td>14647400</td>
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<tr>
<td>0.3</td>
<td>20327800</td>
</tr>
<tr>
<td>0.4</td>
<td>27748400</td>
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<tr>
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<td>36230600</td>
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</table>

Linear Regression through origin for data in Table C.10:

\[ Y = B \times X \]

<table>
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<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>1.50309 \times 10^6</td>
<td>2.79378 \times 10^6</td>
</tr>
</tbody>
</table>
Table C.11. DDK2 (4.5) HPLC calibration plot (Figure 4.20)

<table>
<thead>
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<th>Concentration of 4.5, mM</th>
<th>Integration area, mAU</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.1</td>
<td>20327600</td>
</tr>
<tr>
<td>0.2</td>
<td>39124600</td>
</tr>
<tr>
<td>0.3</td>
<td>60056100</td>
</tr>
<tr>
<td>0.4</td>
<td>83840500</td>
</tr>
<tr>
<td>0.5</td>
<td>102948000</td>
</tr>
</tbody>
</table>

Linear Regression through origin for data in Table C.11: 

\[ Y = B \times X \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
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<tr>
<td>B</td>
<td>2.05245 \times 10^8</td>
<td>1.82775 \times 10^6</td>
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</tbody>
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<table>
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<th>SD</th>
<th>N</th>
<th>P</th>
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</thead>
<tbody>
<tr>
<td>0.99948</td>
<td>1.3555 \times 10^6</td>
<td>6</td>
<td>&lt;0.0001</td>
</tr>
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</table>

Table C.12. Formation of 4.7 in two-photon induced photodecarbonylation of 4.2 
(time of irradiation 1460 s, variable pulse energy; Figure 4.21)

<table>
<thead>
<tr>
<th>Pulse energy, µJ</th>
<th>Yield of 4.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>200</td>
<td>0.0152</td>
</tr>
<tr>
<td>200</td>
<td>0.0161</td>
</tr>
<tr>
<td>300</td>
<td>0.0337</td>
</tr>
<tr>
<td>300</td>
<td>0.035</td>
</tr>
<tr>
<td>400</td>
<td>0.0599</td>
</tr>
<tr>
<td>400</td>
<td>0.0586</td>
</tr>
<tr>
<td>500</td>
<td>0.103</td>
</tr>
</tbody>
</table>
Table C.13. Formation of 4.8 in two-photon induced photodecarbonylation of 4.3 (time of irradiation 600 s, variable pulse energy; Figure 4.22)

<table>
<thead>
<tr>
<th>Pulse energy, µJ</th>
<th>Yield of 4.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>150</td>
<td>0.0453</td>
</tr>
<tr>
<td>150</td>
<td>0.051</td>
</tr>
<tr>
<td>250</td>
<td>0.119</td>
</tr>
<tr>
<td>250</td>
<td>0.165</td>
</tr>
<tr>
<td>350</td>
<td>0.282</td>
</tr>
<tr>
<td>350</td>
<td>0.283</td>
</tr>
<tr>
<td>450</td>
<td>0.476</td>
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<tr>
<td>550</td>
<td>0.693</td>
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Table C.14. Formation of 4.9 in two-photon induced Wolff reaction of 4.4 (time of irradiation 486 s, variable pulse energy; Figure 4.23)

<table>
<thead>
<tr>
<th>Pulse energy, µJ</th>
<th>Yield of 4.9</th>
</tr>
</thead>
<tbody>
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<td>0</td>
</tr>
<tr>
<td>110</td>
<td>0.000701</td>
</tr>
<tr>
<td>270</td>
<td>0.00421</td>
</tr>
<tr>
<td>425</td>
<td>0.0103</td>
</tr>
<tr>
<td>425</td>
<td>0.0107</td>
</tr>
<tr>
<td>565</td>
<td>0.0181</td>
</tr>
<tr>
<td>565</td>
<td>0.0186</td>
</tr>
</tbody>
</table>
Table C.15. Formation of 4.10 in two-photon induced Wolff reaction of 4.5 (time of irradiation 162 s, variable pulse energy; Figure 4.24)

<table>
<thead>
<tr>
<th>Pulse energy, µJ</th>
<th>Yield of 4.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.007</td>
</tr>
<tr>
<td>285</td>
<td>0.261</td>
</tr>
<tr>
<td>365</td>
<td>0.434</td>
</tr>
<tr>
<td>470</td>
<td>0.695</td>
</tr>
<tr>
<td>500</td>
<td>0.797</td>
</tr>
<tr>
<td>520</td>
<td>0.863</td>
</tr>
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</table>

Table C.16. Logarithmic plot of formation of 4.7 in two-photon induced photodecarbonylation of 4.2 (Time of irradiation 1460 s, variable pulse energy; Figure 4.25)

<table>
<thead>
<tr>
<th>Ln(pulse energy, µJ)</th>
<th>Ln(yield of 4.7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.57925</td>
<td>-1.55117</td>
</tr>
<tr>
<td>6.57925</td>
<td>-1.52326</td>
</tr>
<tr>
<td>6.39693</td>
<td>-1.91732</td>
</tr>
<tr>
<td>6.39693</td>
<td>-1.91732</td>
</tr>
<tr>
<td>6.21461</td>
<td>-2.27303</td>
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<tr>
<td>6.21461</td>
<td>-2.27303</td>
</tr>
<tr>
<td>5.99146</td>
<td>-2.81508</td>
</tr>
<tr>
<td>5.99146</td>
<td>-2.83702</td>
</tr>
<tr>
<td>5.70378</td>
<td>-3.39026</td>
</tr>
<tr>
<td>5.70378</td>
<td>-3.35241</td>
</tr>
<tr>
<td>5.29832</td>
<td>-4.18646</td>
</tr>
<tr>
<td>5.29832</td>
<td>-4.12894</td>
</tr>
</tbody>
</table>

Slope = 2.06 ± 0.03
Linear Regression for data in Table C.16:
Y = A + B * X

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-15.10856</td>
<td>0.16261</td>
</tr>
<tr>
<td>B</td>
<td>2.0608</td>
<td>0.0269</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>R</th>
<th>SD</th>
<th>N</th>
<th>P</th>
</tr>
</thead>
</table>
Table C.17. Logarithmic plot of formation of 4.8 in two-photon induced photodecarbonylation of 4.3 (Time of irradiation 600 s, variable pulse energy; Figure 4.26)

<table>
<thead>
<tr>
<th>Ln(pulse energy, μJ)</th>
<th>Ln(yield of 4.8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.30992</td>
<td>-0.362</td>
</tr>
<tr>
<td>6.30992</td>
<td>-0.367</td>
</tr>
<tr>
<td>6.10925</td>
<td>-0.742</td>
</tr>
<tr>
<td>6.10925</td>
<td>-0.811</td>
</tr>
<tr>
<td>5.85793</td>
<td>-1.27</td>
</tr>
<tr>
<td>5.85793</td>
<td>-1.26</td>
</tr>
<tr>
<td>5.52146</td>
<td>-2.13</td>
</tr>
<tr>
<td>5.52146</td>
<td>-1.8</td>
</tr>
<tr>
<td>5.01064</td>
<td>-3.1</td>
</tr>
<tr>
<td>5.01064</td>
<td>-2.98</td>
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</tbody>
</table>

Slope = 2.05 ± 0.06
Linear Regression for data in Table C.17:
Y = A + B * X

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-13.33488</td>
<td>0.3613</td>
</tr>
<tr>
<td>B</td>
<td>2.0571</td>
<td>0.06251</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>R</th>
<th>SD</th>
<th>N</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.99633</td>
<td>0.09069</td>
<td>10</td>
<td>&lt;0.0001</td>
</tr>
</tbody>
</table>

Table C.18. Logarithmic plot of formation of 4.9 in two-photon induced Wolff reaction of 4.4 (Time of irradiation 486 s, variable pulse energy; Figure 4.27)

<table>
<thead>
<tr>
<th>Ln(pulse energy, μJ)</th>
<th>Ln(yield of 4.9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.33683</td>
<td>-3.98</td>
</tr>
<tr>
<td>6.33683</td>
<td>-4.01</td>
</tr>
<tr>
<td>6.05209</td>
<td>-4.53</td>
</tr>
</tbody>
</table>
Slope = 1.998 ± 0.014
Linear Regression for data in Table C18:
\[ Y = A + B \times X \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-16.65231</td>
<td>0.0811</td>
</tr>
<tr>
<td>B</td>
<td>1.9983</td>
<td>0.01381</td>
</tr>
</tbody>
</table>

\[ R = 0.9999, \quad SD = 0.01923, \quad N = 6, \quad P < 0.0001 \]

**Table C.19.** Logarithmic plot of formation of **4.10** in two-photon induced Wolff reaction of **4.5** (Time of irradiation 162 s, variable pulse energy; Figure 4.28)

<table>
<thead>
<tr>
<th>Ln(pulse energy, μJ)</th>
<th>Ln(yield of <strong>4.10</strong>)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.147</td>
<td>6.25383</td>
</tr>
<tr>
<td>-0.227</td>
<td>6.21461</td>
</tr>
<tr>
<td>-0.363</td>
<td>6.15273</td>
</tr>
<tr>
<td>-0.835</td>
<td>5.8999</td>
</tr>
<tr>
<td>-1.34</td>
<td>5.65249</td>
</tr>
</tbody>
</table>

Slope = 1.97 ± 0.02
Linear Regression for data in Table C.19:
\[ Y = A + B \times X \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-12.45841</td>
<td>0.13287</td>
</tr>
<tr>
<td>B</td>
<td>1.96795</td>
<td>0.022</td>
</tr>
</tbody>
</table>

\[ R = 0.99981, \quad SD = 0.01119, \quad N = 5, \quad P < 0.0001 \]
Appendix D

$^1$H NMR and $^{13}$C NMR Spectra of Compounds
4.3 HNMR
CHCl₃