

Adiabatic ring opening in tethered naphthalene and anthracene cycloadducts†

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The cycloadducts of tethered naphthalene and anthracene derivatives undergo photochemical ring opening to an electronically excited product with adiabatic yields up to 90%.

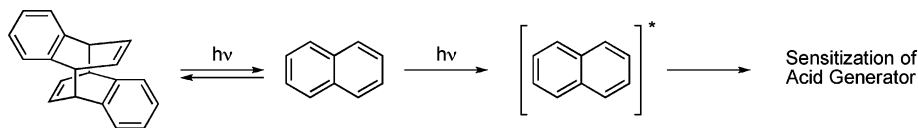
In an adiabatic photoreaction an electronically excited state, *R , is transformed to an electronically excited product, *P . The overall $^*R \rightarrow ^*P$ chemical process occurs entirely on the same excited electronic energy surface.¹ Most photochemical reactions are not adiabatic, that is, the excited state *R reverts to the ground state potential energy surface of R during the course of the reaction so that the photoproduct, P , is formed in its ground state. In an adiabatic photoreaction the photoproduct is formed in its excited state *P . The product *P can then relax to the ground state by radiative and/or non-radiative pathways. Adiabatic photochemical reactions in which substantial bond breaking and bond making occur are relatively rare, presumably because surface crossings of *R allow facile deactivation to the ground state and because the energy of *P is often higher than that of *R . However, adiabatic cycloreversion has been reported for anthracene cycloadducts,^{2,3} and anthracene or naphthalene cycloadducts with benzene^{4,5} and furan.⁴ This report qualitatively and quantitatively examines the adiabatic contribution to ring opening for the cycloadducts of tethered naphthalene–naphthalene (**c1**–**c3**), naphthalene–anthracene (**c4**) and anthracene–anthracene (**c5**) compounds shown in Fig. 1.

The primary motivation for examining the chemistry of naphthalene cycloadducts was to use them as photosensitizers for acid generation, a critical part of current 193 nm photolithography technology.⁶ Our research objective was to use a two-step photochemical (double exposure) process, which would improve the resolution of conventional (one step, single exposure) techniques (see Scheme 1) using a naphthalene-based cycloadduct as a sensitizer. In this scheme, ring opening of the cycloadduct is the first step, forming a stable intermediate (naphthalene).⁷ In a second photochemical event, the intermediate yields a naphthalene chromophore in its excited state that undergoes

competing recyclization or quenching by an accessible transparent acid generator (Scheme 1). A study with 2-methoxynaphthalene demonstrated the feasibility of the process using the corresponding cycloadduct.^{7,8} Although 2-methoxynaphthalene is one of the few naphthalenes that undergoes [4 + 4] cycloaddition, low quantum yields of this reaction necessitated the use of tethered naphthalenes which cyclize efficiently. Structures of the selected tethered naphthalenes and their corresponding cycloadducts discussed in this report are shown in Fig. 1. Although the photochemistry of each tethered naphthalene/anthracene shown in Fig. 1 has been reported, the properties of the cycloadducts are not well established. During the course of our investigations, we discovered that the cycloreversion pathways were to some extent adiabatic. This report compares the extent of adiabatic cycloreversion occurring among the cycloadducts shown in Fig. 1.

Fluorescence spectroscopy is a convenient method to study adiabatic photoreactions. Fig. 2 (left) shows the fluorescence spectrum of **1**, where the structured features between 310 and 360 nm are assigned to naphthalene fluorescence^{9–11} and the broad band between 370 and 520 nm is assigned to intramolecular excimer fluorescence. Photoexcitation of the cycloadduct **c1** generates a nearly identical fluorescence spectrum to the ring-opened form **1**. This is a strong indication of the adiabatic nature of the ring opening reaction. To compare the extent of the adiabatic process with the diabatic process, the fluorescence experiments shown in Fig. 2 (left) were performed with identical absorbance values at the excitation wavelength to ensure that equal amounts of photons were absorbed. Comparison of the integrated fluorescence intensities (monomer + excimer) of **1** and **c1** indicate that the relative adiabatic contribution in the ring-opening process is approximately 80%. Particular care was taken to ensure that the amount of **1** formed *in situ* during the fluorescence measurements of **c1** was negligible and the absence of a significantly absorbing amount of **1** was confirmed by comparing the UV absorption spectra before and after recording the fluorescence.

Fig. 3 shows schematically the general decay pathways for the excited state of any of the cycloadducts studied using **c1** as an example. From the excited cycloadduct, *c1 , the primary photoreaction is the ring opening reaction to produce *1 . Analysis of the emission resulting from the photoexcitation of the cycloadducts of compounds **1**–**5** showed an interesting trend. Based on analysis of the emission data, *1 and *2 were formed from **c1**



Scheme 1 Schematic representation of the sequential two-photon initiated lithography process.

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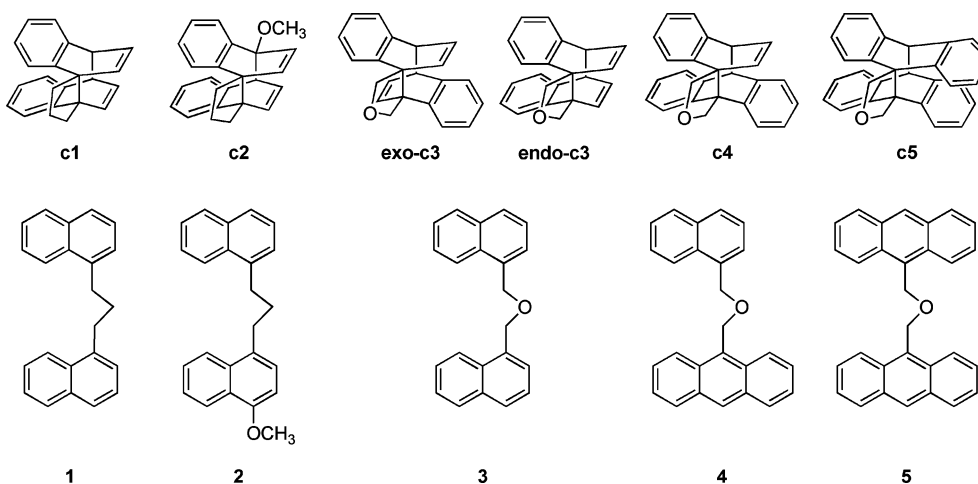


Fig. 1 Structures of the cycloadducts (**c1** to **c5**, top) and the corresponding ring-opened compounds (**1** to **5**, bottom) discussed in this study. (Photocyclization of **3** gave two isomers, *endo*- and *exo*-, whereas only the *endo*-isomers were observed for **1** and **2**.)

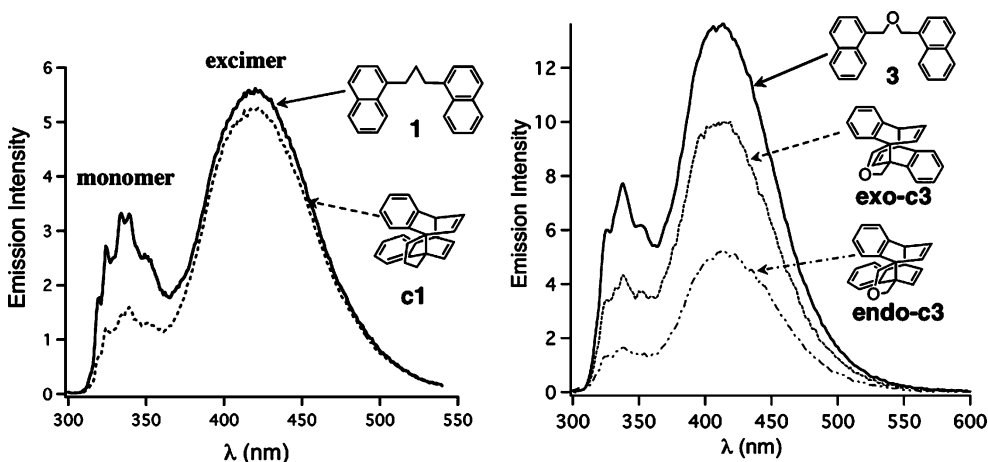


Fig. 2 Left: Emission spectra of **1** (solid line) and **c1** (dotted line) recorded in Ar saturated acetonitrile at room temperature. $\lambda_{\text{exc}} = 273$ nm. The absorbance of **1** and **c1** at λ_{exc} (273 nm) was 0.18. Right: Emission spectra of **3** (solid line), *exo-c3* (dotted line) and *endo-c3* (dash-dotted line) recorded in Ar saturated acetonitrile at room temperature. $\lambda_{\text{exc}} = 265$ nm; absorbance of **3**, *exo-c3* and *endo-c3* at λ_{exc} (265 nm) was 0.20.

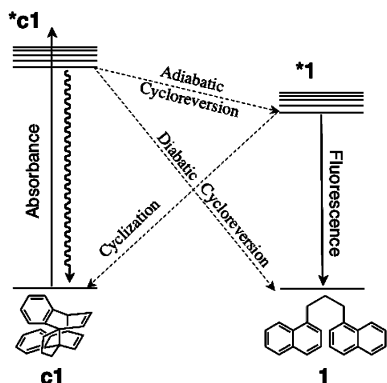


Fig. 3 Schematic representation of the photoreaction of the excited state cycloadduct $*\text{c1}$. Solid lines represent absorption or emission; dashed lines represent reaction.

and **c2** in about 80% yield, respectively (Table 1). Furthermore, the fraction of adiabatic reaction was larger (90%) with the anthracene cycloadducts **c4** and **c5** (for emission spectra, see

ESI†). Although a higher ratio of adiabatic cycloreversion is reported in anthracene adducts (up to 91%),^{15–17} similar trends for naphthalene-cycloadducts have not been reported, probably due to poor yield of cycloaddition of naphthalenes. Cycloadducts of naphthalene-furan,⁴ naphthalene-benzene,^{4,5} and naphthalene-phthalic anhydride¹⁸ exhibit adiabatic ring opening, to varying degrees (0% for 1-cyanonaphthalene-furan adduct to 63% for naphthalene-benzene adduct). This study showed that a large fraction of ring opening occurs adiabatically in both naphthalene-naphthalene adducts **c1** and **c2**, and naphthalene-anthracene adduct **c4**.

Unlike the methylene bridged tethered naphthalenes **1** and **2**, which photochemically form only the *endo*-cycloadduct, the ether bridged **3** formed two cycloadducts, *exo-c3* and *endo-c3*.¹² Although the *endo*-adduct thermally isomerizes to a stable Cope-rearrangement product, the photochemistry of both compounds is identical. The arrangement of the benzene rings is significantly different in these two isomers; the two rings are almost overlapped in *endo-c3* and are farther apart in *exo-c3*. Contrary to our initial expectations, among all compounds studied, adiabatic

Table 1 Relative adiabatic contribution during the ring opening of the cycloadducts and fluorescence quantum yields of the corresponding photoproducts

Compound	c1	c2	exo-c3	endo-c3	c4	c5
Relative adiabatic contribution	80%	80%	65%	32%	90%	90%
$\Phi_{\text{fluorescence}}/\text{open form}^a$	0.1 ^b	0.27 ^b	0.033 ^c	0.09 ^d	0.03 ^e	0.03 ^e

^a Sum of monomer and excimer fluorescence for **1**, **2** and **3**; compounds **4** and **5** do not show excimer fluorescence in the conditions used for this experiment. ^b Determined using 1-methylnaphthalene as standard in argon saturated acetonitrile at room temperature. ^c Ref. 12. ^d Ref. 13. ^e Ref. 14.

ring opening was least efficient for *endo*-**c3** (32%), while the fraction for *exo*-**c3** was 65% (Fig. 2, right), marginally lower than **c1** and **c2**. Since the cycloreversion can occur with minimum distortion of the overall structure in any one of the six adducts discussed here, a major deviation from the trend of highly adiabatic ring opening observed with *endo*-**c3** and to certain extent with *exo*-**c3** is intriguing. Further analysis of similar cycloadducts is being pursued to better understand the role of structure and substitutions in adiabatic ring opening processes.

In conclusion, as demonstrated by quantitative emission spectroscopy, and in contrast to most photochemical reactions, cycloadducts in Fig. 1 undergo photoinduced [4 + 4] retrocycloaddition in an adiabatic manner, that is, the electronically excited state of the cycloadduct, *R, undergoes a ring opening to an electronically excited product, *P, with adiabatic yields of up to 90%. Two general features of the adiabaticity of these reactions for the systems studied are (1) the more or less concerted nature of the reaction which avoids surface crossings and conical intersections along the reaction path to *P and (2) the exothermicity of the *R → *P process, which avoids a significant barrier to *P along the reaction pathway.

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