Adiabatic Photocycloreversion of Bridged Benzene-Anthracene Biplanemers: Controlling of the Efficiency of the Excited Product Formation by Auxiliary Substituents on the Side-Chains

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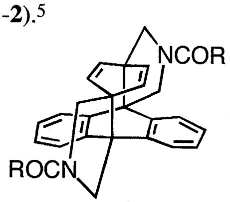
The efficiency for excited product formation in the adiabatic photocycloreversion of bridged biplanemer **1** was controlled by the size of its side-chain substituents which changed the interchromophore distance in the photoproduct **2**.

Adiabatic photocycloreversion of biplanemers (4π+4π cycloadducts of aromatic compounds) is an useful probe to investigate reaction pathways in an excited state because the efficiency of the reaction can be monitored by the emission from the photoproduct (photo-chemiluminescence, PCL), and factors controlling the efficiency for excited product formation and shapes of potential surface of an excited state have been discussed.[1-4] Anthracene-benzene biplanemers undergo adiabatic photodissociation providing a benzene and an electronically excited singlet anthracene.[2] A naphthalene-benzene biplanemer derivative also gave both excited singlet and triplet naphthalene to give off both fluorescence and phosphorescence from the excited naphthalene.[3] The efficiency of excited product formation in the PCL is primarily controlled by both slopes of correlation lines connecting a starting biplanemer and product aromatic and relative pericyclic minimum which are determined by combination of component aromatics.[1,3] We have shown that bridgehead substituents on biplanemers also affected the efficiency of the PCL of biplanemers without changing parent aromatics.[4] It has not been noted that controlling of the efficiency for excited product formation in the PCL of biplanemers without electronic perturbation on the component aromatics. Herein we wish to report that the efficiency is also controlled by a steric effect of substituents, which gave no electronic conjugation into parent aromatic nuclei, using a bridged biplanemer-cyclophane system (**1**-**2**).[5]



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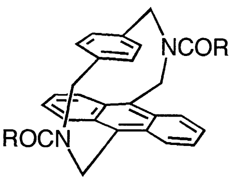


2

a R = Me
b R = CF_3
c R = ^{i}Pr
d R = ^{t}Bu

The cyclophane **2** was developed by Usui et al. as a photochromic device on the basis of photointerconversion with the biplanemer form **1**.[6] Although the biplanemer **1** has been reported as non-fluorescent, we interested in its photocycloreversion in relation to that of non-bridged biplanemers. Concerning the photoproperties of **2**, both the quantum yields of fluorescence (Φ_f) and photocycloaddition providing **1** (Φ_{add}) were sensitive to the size of the side-chain substituents, that was, as the size of the substituents increased, Φ_f decreased and Φ_{add} increased.[6] These promoted us to examine whether the photolysis of **1** is chemiluminescent and to study the steric effects of side-chain substituents on the photoproperties of **1**.

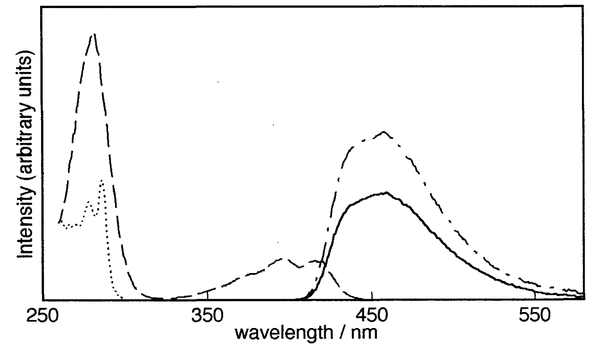


Figure 1. The emission spectra of **1a** and **2a**. The photo-chemiluminescence (————) and the excitation spectra (············) of **1a**; fluorescence emission (—·—·—) and the excitation spectra (— — — —) of **2a** in $CHCl_3$.

Figure 1 shows the fluorescence emission and the excitation spectra of **1a** and **2a**. On irradiation at 286 nm, **1a** gave off luminescence which was same in profile as the fluorescence of **2a**. The peaks of the corrected excitation spectrum were identical with those of absorption of **1a**.[7] These observations indicate that excited singlet **1a*** reverted into **2a*** through an adiabatic pathway and the PCL was observed. Excited **1b-d*** also gave off PCL attributable to the formation of the corresponding **2*** and cyclophane **2** was detected as a sole product. The lifetimes of the PCL of **1** and fluorescence of **2** are summarized in Table 1. Both the emissions are analyzed to have two components. The τ_1 and τ_2 values of the PCL of **1** are almost same as those of the fluorescence of the corresponding **2**. There may be an equilibrium between **2*** and an non-emitting species, e.g. an intramolecular exciplex, in excited singlet state,[8] and details of the dynamic behavior are under investigation. Considering the emission region of the PCL and the lifetimes it is indicated that the photoexcited **1*** relaxed rapidly into **2***

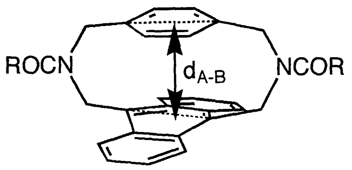
Table 1. Quantum Yields and Lifetimes of Photo-chemiluminescence of **1** and Fluorescence of **2** [a]

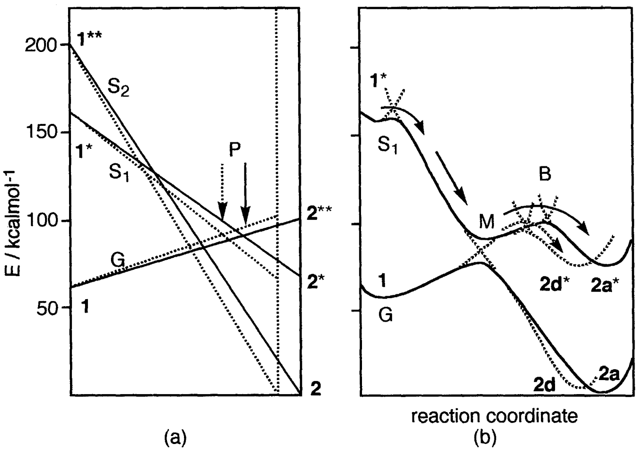
Compd	Φ_{PCL} [b]	Φ_f [b]	Φ_{ex*}	lifetimes / ns τ_1	lifetimes / ns τ_2
1a	0.34	—	0.61 ± 0.02	10.7	21.2
2a	—	0.56	—	14.4	23.2
1b	0.25	—	0.67 ± 0.03	3.5	14.6
2b	—	0.37	—	5.5	14.9
1c	0.31	—	0.71 ± 0.03	5.3	15.5
2c	—	0.44	—	5.8	15.5
1d	0.083	—	0.89 ± 0.08	1.4	3.9
2d	—	0.093	—	1.5	3.9

[a] The quantum yields and lifetimes were measured in Ar purged $CHCl_3$ at 25 °C. Φ_{PCL} : Quantum yield of the photo-chemiluminescence of **1**; Φ_f : Fluorescence Quantum yield of **2**; Φ_{ex*} : Quantum yield for formation of **2***. [b] Standard deviations for 3-5 independent runs were within 0.02.

which is the same state as that generated by excitation of **2**. Thus the quantum yield of the excited product formation (Φ_{ex^*}) is estimated by the equation of $\Phi_{PCL} = \Phi_{ex^*} \times \Phi_f$, where Φ_{PCL} is the quantum yield of the PCL and Φ_f is the fluorescence of **2**, and the values are listed in Table 1.[9] The efficiency of excited product formation tends to increase as the size of the side-chain substituents becomes larger.

Determining factors for Φ_{ex^*} was considered on the basis of electronic and steric features of **1** and **2**. The electronic spectra of **1** were not affected by the side-chain substituents R and λ_{max} of **2** appeared at almost same wavelength independent of R although a slight red-shift of absorption edge for **2d** was observed.[7] So the electronic properties of both **1** and **2** seem to vary little by change of R. An alternative factor(s) determining Φ_{ex^*} may be operative in the PCL of **1**. Then steric features of **1** and **2** were analyzed by empirical force field (MM2) method.[10] The geometry of the bridged biplanemer skeleton of **1a**-**d** is almost same each other reflecting the characteristics of their electronic spectra. While, in the case of **2**, the nearest separation between the benzene and the anthracene chromophores ($d_{A\text{-}B}$) reduces systematically as the size of the R increases; **2a** (2.93 Å) > **2b** (2.92 Å) > **2c** (2.89 Å) > **2d** (2.85 Å). As it has been pointed that photoproperties of [3.3](9,10)anthracenoparacyclophane and [3.3](1,4)naphthaleno(9,10)anthracenophane derivatives were sensitively affected by the interchromophore distance,[11] the steric effect on the PCL of **1** may reflect the difference in $d_{A\text{-}B}$ of the photoproduct **2**.





(a) (b)

Figure 2. Schematic state correlation diagram (a), and image of the reaction coordinate (b) of the chemiluminescent photo-cycloreversion of **1**: for **1a**-**2a** (————); for **1d**-**2d** (············).
G: ground state; S_1: singly excited state; S_2: doubly excited state; M: pericyclic minimum; B: barrier.

From the present observations, we draw schematically a description of the PCL behavior of **1** (Figure 2).[1a,c,12] The barrier starting from **1*** to the pericyclic minimum (M) is independent of the side-chain substituents R. On the other hand, the height of the barrier between M and **2*** may vary with change in $d_{A\text{-}B}$ as follows. When $d_{A\text{-}B}$ becomes shorter, a crossing point P between singly excited surface (S_1) and a ground state (G) occurs earlier [Figure 2(a)]. So the barrier between the minimum M and **2*** (B) is lower for shorter $d_{A\text{-}B}$ [Figure 2(b)]. Consequently, it may easier for **1** having shorter $d_{A\text{-}B}$ to go over the barrier to give **2*** [Figure 2(b), dotted arrow], and thus the order of Φ_{ex^*} is **1d** > **1c** > **1b** > **1a**.

Although there is a problem whether the relatively small change in $d_{A\text{-}B}$ is significant to control the height of the barrier B, the present model is consistent with the PCL behavior of **1** and also applicable to explain the reported efficiency of photocyclization of **2**.[6] Such a steric factor has not been noted in the PCL of non-bridged biplanemers.

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9 The quantum yields of the PCL of **1** were determined as reported before.[3] The absorbance of the solutions at excitation wavelength (286 nm) were set to 0.05 and the obtained spectra were corrected against the response of fluorescence spectrophotometer.

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