Circular polarization of photochemiluminescence from the photoisomer of a conformationally fixed 2,11-diaza[3.3](9,10)anthracenoparacyclophane derivative‡

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The conformation of 2,11-diaza[3.3](9,10)anthracenoparacyclophane 1, which underwent photointerconversion with isomer 2, was fixed with the aid of a chiral camphanic auxiliary to have molecular chirality, and the photochemiluminescence from the modified 2a was circularly polarized reflecting the chirality of the emitting state.

2,11-Diaza[3.3](9,10)anthracenoparacyclophane **1** has been developed as a photochromic material which undergoes photointerconversion with isomer **2**.[1] In the photochromic reaction, we recently found that photocycloreversion of **2** to **1** was chemiluminescent, attributable to the formation of excited **1*** as in the case of non-bridged cycloadducts between benzene and anthracene (Scheme 1).[2,3] Such chemiluminescent photoreactions are attractive as a probe to analyze the potential surface of excited states and as an optical data storage system of read-out by fluorescence.[2–4] We have attempted to introduce a chiral source into the cyclophane system since the chirality may cause circular polarization of both the fluorescence of **1** and the photochemiluminescence of **2** as well as photocontrol of chiroptical properties. Circular polarization of luminescence (CPL) is a useful probe to obtain structural and electronic information in an excited state,[5] and steric and electronic features of the emitting state of the photochemiluminescence may be analyzed by CPL. Here, we report a simple method to introduce molecular chirality into the cyclophane system **1** by modification with a chiral auxiliary, and CPL from the modified **1a** and **2a**.

The cyclophanes **1a** and **1b** were prepared by acylation of the amino derivative **1d** with commercially available (1*S*)-(−)-camphanic chloride and (1*S*)-(+)-10-camphorsulfonyl chloride, respectively. The modified cyclophane **1a** showed circular dichromism (CD) in its absorption bands suggesting the side-chains were fixed in a special conformation inducing molecular chirality (Fig. 1) while **1b** indicated CD only arising from the carbonyl chromophore in the auxiliary camphorsulfonyl groups. As the chiral center in **1b** was separated by one extra methylene group than in **1a**, the camphorsulfonyl group may not restrict the side-chain conformation in **1b**. The conformation of **1a** was analyzed by NOESY spectroscopy. Fig. 2 shows the NOESY spectrum of **1a** in which four cross-peaks important in determining the conformation of **1a** appeared and are correlated by dotted lines. From the spectrum, it is evident that the 7′-Me^1 proton was located close to aromatic protons H$_e$, H$_g$ and H$_j$, and

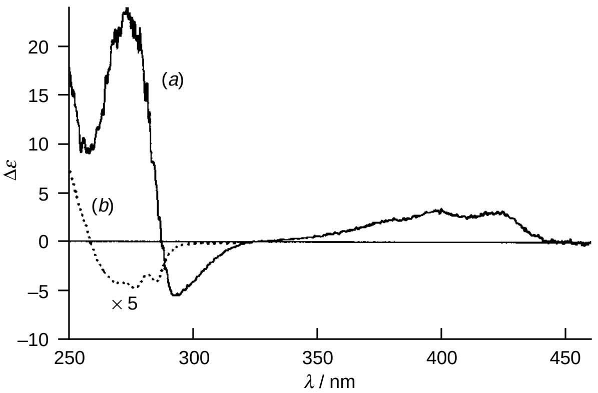


Fig. 1 CD spectra of (*a*) **1a** and (*b*) **2a** in CH$_2$Cl$_2$

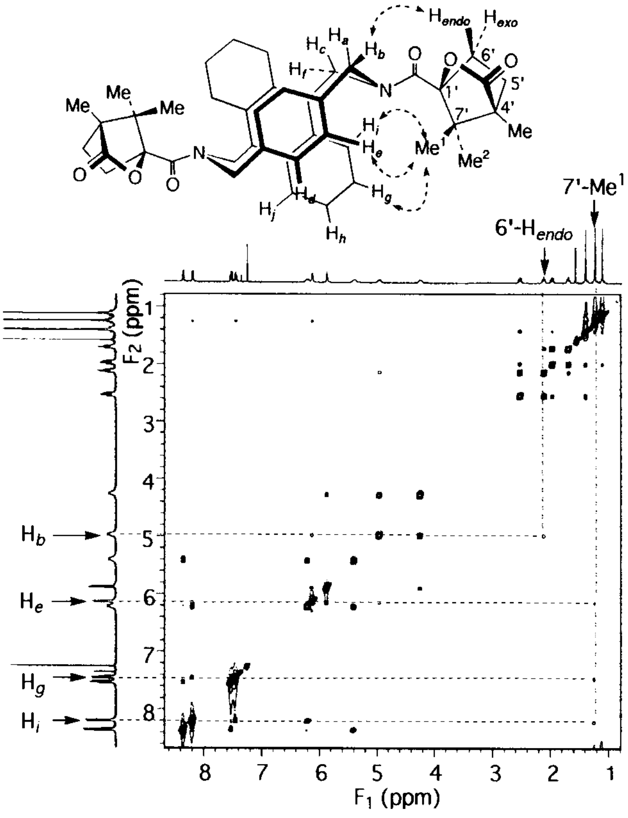
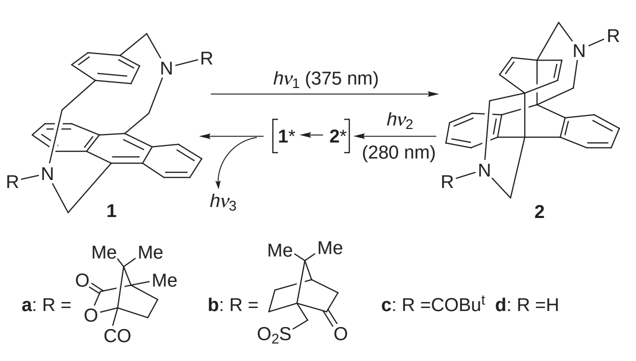


Fig. 2 NOESY spectrum of **1a** in CDCl$_3$ (500 MHz)



Scheme 1

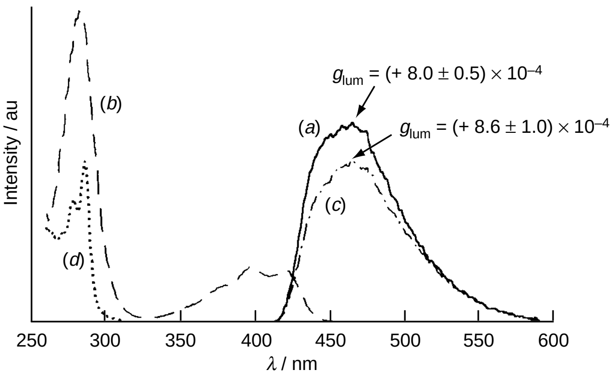


Fig. 3. Fluorescence spectra of **1a** and **2a** (in CH_2Cl_2); (*a*) Emission and (*b*) the excitation spectra of **1a**; (*c*) Photochemiluminescence and (*d*) the action spectra of **2a**. The observed g_{lum} values are shown at the detection wavelength (460 nm).

that 6′-H$_{endo}$ was fixed near by one of the bridge methylene protons H$_b$. Empirical force field (MM2)[6] calculation showed that **1a** adopted the most stable C_2-symmetrical conformer consistent with the NOESY results .

The cyclophane **1a** underwent photointerconversion with **2a** and a change in CD was detected (Fig. 1). Cyclophane **1a** showed a positive Cotton effect in the longer wavelength absorption band, while **2a** showed a negative Cotton effect in its absorption band centered at 280 nm. The specific rotation of **1a** was $[\alpha]_D^{23}$ ($CHCl_3$) +192° and that of **2a** was $[\alpha]_D^{23}$ ($CHCl_3$) $-1.4°$.

Compound **2a** underwent chemiluminescent photocycloreversion providing excited **1a*** as in the case of **2** which underwent no conformational restriction such as **2c**.[2] The photochemiluminescence spectrum was the same in profile with that of fluorescence of **1a** (Fig. 3). Fluorescence assignable to **2a** itself was not detected.[3] The action spectrum for the emission of **2a** was identical with the absorption of **2a** showing no contamination with **1a** during the measurement. The quantum yields of fluorescence of **1a** and the photochemiluminescence of **2a** were 0.33 and 0.23, respectively. The decay of both emissions was analyzed as a dual exponential curve and the lifetimes were 7.8 ns (26%) and 18.4 ns (74%) for **1a**, and 6.9 ns (28%) and 16.6 ns (72%) for **2a**.

The fluorescence of **1a** was circular polarized as expected from its structural features. The dissymmetry factor for the fluorescence [$g_{lum} = 2(I_L - I_R)/(I_L + I_R)$; I_L and I_R are intensity of left and right circularly polarized emission, respectively] of **1a** was g_{lum} $(+8.0 \pm 0.5) \times 10^{-4}$ (λ_{em} = 460 nm, λ_{ex} = 375 nm, in CH_2Cl_2). The CPL for the photochemiluminescence of **2a** was also detected and its g_{lum} value was the same as that of fluorescence of **1a** within experimental error, g_{lum} = $(+8.6 \pm 1.0) \times 10^{-4}$($\lambda_{em}$ = 460 nm, λ_{ex} = 280 nm in CH_2Cl_2).§ This is the first observation of circular polarization of photochemiluminescence which may enable examination of structural change in an excited state during an adiabatic reaction. The dissymmetry factor for the absorption [$g_{abs} = 2(\varepsilon_L - \varepsilon_R)/(\varepsilon_L + \varepsilon_R)$; ε_L and ε_R are molar absorptivity for left and right circular polarized light, respectively] of **1a** was $+6.4\times 10^{-4}$ at 375 nm (in CH_2Cl_2). In the case of **1a**, overlap between fluorescence and long wavelength absorption bands suggested that the fluorescent process was the reverse transition of the absorption [*cf.* Fig. 3, curves (a) and (b)], and the g_{abs} was almost same as g_{lum}. These suggest that the structure of **1a** did not differ largely between the ground and the emitting states. Differently, for **2a**, g_{abs} was -6.3×10^{-4} at 280 nm (in CH_2Cl_2) showing opposite sign compared with the g_{lum} of the photochemiluminescence. In the case of **2a**, as the structures of the light absorbing and the emitting species were quite different from each other, the changes of electronic and steric properties during the photoreaction caused inversion of sign between g_{abs} and g_{lum}.

In summary, modification with a chiral camphanic auxiliary induced molecular chirality of the cyclophane **1a** and the photoisomer **2a**. The photoexcited **2a*** rapidly reverted to **1a*** and recalled the electronic and steric features of **1a*** which was the same as those generated on excitation of **1a**.

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Notes and References

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‡ Here photochemiluminescence denotes luminescence which is emitted from an electronically excited product formed by an adiabatic reaction of an excited starting molecule ($h\nu_3$ in Scheme 1).

§ In the CPL measurement on **2a**, both the starting **2a** and the photoproduct **1a** were capable of absorbing the excitation light (280 nm), however after the measurement only **2a** was detected in the sample. Thus in the photostationary state **2a** existed preferentially to **1a** and the present CPL observed in photochemiluminescence of **2a** was regarded as that responsible mainly to **2a**.

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