

## Orientation of Rotational Isomers of 1,2-Bis(2-anthryl)ethene in Liquid Crystals

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The fluorescence spectra of three rotational isomers of *E*-1,2-bis(2-anthryl)ethene (**1**) were obtained by the principal component analysis-self modeling (PCA-SM) method in solution. Based on the resolved spectra, the orientation of the rotational isomers in nematic and cholesteric liquid crystals (LC) were investigated. **1** mainly exists as the (*s*-trans, *s*-trans) conformer in these LC phases.

Rotational isomerization of *E*-2-anthrylethenes in the ground and excited states are of current interest in photochemistry. The *E*-isomer is useful since the 2-anthrylethenes undergo a *Z*→*E* one-way isomerization.<sup>1</sup> The 2-anthrylethenes have two rotational isomers concerning the single bond between the anthryl and ethenyl groups, *s*-trans and *s*-cis rotamers. In the *s*-trans and *s*-cis rotamers, an ethenyl group is aligned along the long and short axes of the anthryl moiety, respectively. Ethene with two 2-anthryl groups, **1**, has three rotamers, (*s*-trans, *s*-trans), (*s*-trans, *s*-cis), and (*s*-cis, *s*-cis), because two 2-anthryl groups are attached to the ethene (Figure 1). The fluorescence spectra observed by excitation at various wavelengths reflect the equilibrium of rotational isomers in the ground state, since it is known that no isomerization takes place during their short lifetime in the singlet excited state.<sup>2</sup> The three rotamers of **1** show larger shifts in  $\lambda_{\max}$  than the rotamers of other mono(2-anthryl)ethenes,<sup>3</sup> and they are useful for studying the molecular alignment in the orientation field of LC.

**1** was prepared by the Wittig reaction of 2-anthryltriphosphonium bromide<sup>4</sup> and 2-anthracenecarbaldehyde using *n*-butyllithium as a base. 2-Anthracenecarbaldehyde was prepared from 2-cyanoanthracene by hydrolysis after reduction by LiAlH(OCOCH<sub>3</sub>)<sub>3</sub>. The products were identified using a JEOL JMS-HX110 mass-spectrometer and a JEOL LA-400 <sup>1</sup>H-NMR spectrometer in CDCl<sub>3</sub>. The absorption and fluorescence spectra were measured by a Hitachi U-3000 and an F-4010 spectrometers, respectively, in spectroscopic grade benzene (Dotite). The PCA-SM program was home-made based on the

literature,<sup>2a,5</sup> and checked by comparing the spectra of the 2-anthrylethenes with those already reported.<sup>2b</sup> The LCs, 4-methoxyphenyl *trans*-4-butylcyclohexanecarboxylate (**2**), and cholesteryl oleate (**3**) (Figure 1) were purchased from the Kanto Chemical Co. The LC samples were prepared in a cell (E.H.C. Co.) with a 6 μm spacer, and sandwiched by copper plates (which have an observing hole) to change the temperature. The copper plates were heated using a plate-type heater by thermal conduction, and the temperature was measured by a thermocouple. The LCs were observed using a polarized microscope (Olympus BX50).

Figure 2a shows the fluorescence spectra of **1** in argon-purged benzene. The spectrum was unchanged when the excitation was performed below 390 nm. However, the  $\lambda_{\max}$  of the spectra shifted to longer wavelengths when the excitation wavelength was moved to longer wavelengths (> 390 nm). The fluorescence apparent rise up observed by the excitation at 450 nm was shifted almost 50 nm from that observed by excitation at 400 nm.

Since PCA-SM method is well described in the literature,<sup>2a,5</sup> only brief summary is given here. Thirtysix spectra ( $Y_i$ ) were measured by excitation at every 2 nm between 390 and 460 nm to make a matrix of excitation wavelengths and spectral data  $Y_i$  (intensities are digitized every 1 nm between 350 and 700 nm).  $Y_i$  is the essentially the sum of the fluorescence spectra of three principal components to be solved ( $S_n$ ,  $n = 1-3$ ), therefore,  $Y_i$  is a linear combination of the three-component spectra,  $Y_i = \zeta_1 S_1 + \zeta_2 S_2 + \zeta_3 S_3$ . The sum of elements of rows of the input spectral matrix is normalized. Diagonalization of matrix  $M$  ( $M = Y^T Y$ ) by using transpose of  $Y$  ( $Y^T$ ) gives eigenvalues and their corresponding eigenvectors ( $V_m$ ).  $S_n$  is a linear combination of  $V_m$ , ( $m = 1-3$ ),  $S_n = x_{1n} V_1 + x_{2n} V_2 + x_{3n} V_3$ , where  $x_{mn}$  is a combination coefficients. The three ( $x_{1n}$ ,  $x_{2n}$ ,  $x_{3n}$ ) coordinates are converted to polar coordinates, then  $S_n$  is expressed as the following equation,  $S_n = V_1 \cos \theta + V_2 \sin \theta \cos \phi + V_3 \sin \theta \sin \phi$ . This equation is simplified as follows,  $S_n = V_1 \cos \theta + \sin \theta (V_2 \cos \phi + V_3 \sin \phi) = V_1 \cos \theta + V_4 \sin \theta$ , ( $V_4 =$

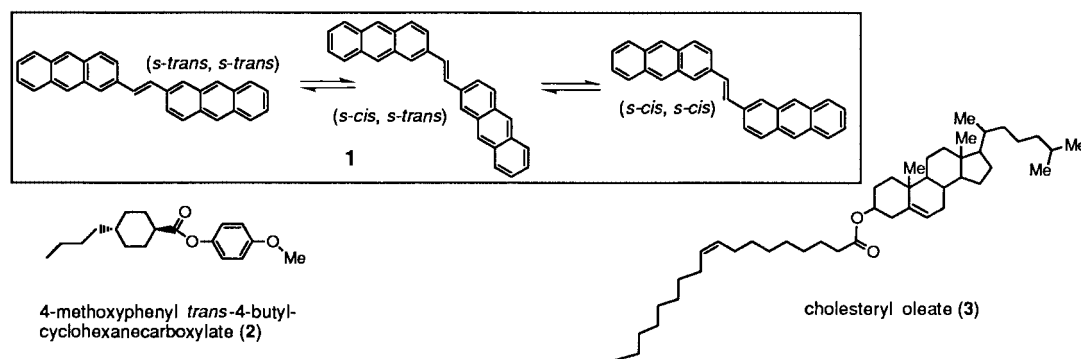
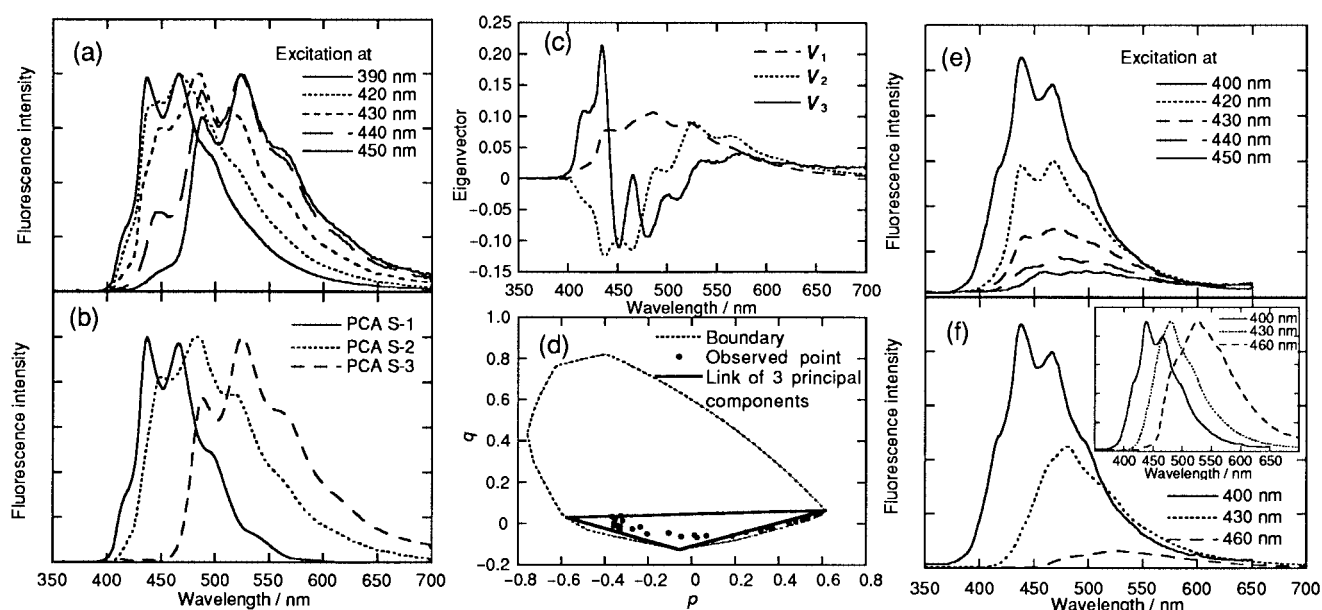


Figure 1. Three rotational isomers of **1** in equilibrium and the structures of LC molecules.



**Figure 2.** Excitation wavelength effects on the fluorescence spectra of **1** in benzene (a), and resolved three-component spectra (b). Eigenvectors (c) and projection diagram of parameters  $q$  vs  $p$  (d). Excitation wavelength effects on the fluorescence spectra of **1** in cholesteric phase (e) and isotropic phase (f) of **3** (inset spectra in f are normalized at the maxima).

$V_2\cos\phi + V_3\sin\phi$ ), and it makes possible to reduce the dimension. Then, introducing parameters,  $p = \theta\cos\phi$  and  $q = \theta\sin\phi$ , for arbitrary  $\phi$  ( $\phi = 1-360^\circ$ , calculated for every  $1^\circ$ ), it become possible to project  $p$  and  $q$  on the single planar surface with suitable boundary conditions ( $S_n \geq 0$ , spectra do not have negative elements) (Figure 2d). The task of SM procedure is the determination of the combination of  $x_{m,n}$ . In the  $p$ - $q$  plot, the experimentally observed spectra are plotted as dots, and eigenvectors are estimated from the corners of the boundary near the dots. Figure 2c shows the obtained eigenvectors, and Figure 2b shows the three principal component spectra (PCA S1-3).

It has been reported that the s-trans isomer is more stable than the s-cis isomer in the ground state, having a shorter wavelength fluorescence 0-0 band than that of the s-cis isomer in other 2-anthrylethenes.<sup>6</sup> By analogy, the spectra of PCA S1-3, which have a 0-0 band  $\lambda_{\max}$  from shorter to longer wavelengths in this order, are (s-trans, s-trans), (s-cis, s-trans), and (s-cis, s-cis) rotamers, respectively.

Next, the orientations of **1** in the LCs were examined. In a typical run, 2% **1** was dissolved in LC. The fluorescence was measured at 50 and 45 °C for nematic LC **2** ( $T_{CN}42$ ,  $T_{NI}59$  °C)<sup>7</sup> and cholesteric LC **3**, respectively. **3** shows monotropic transition, therefore, after reaching 60 °C, the temperature was reduced to 45 °C ( $T_{CI}50.5$ ,  $T_{Ch}47.5$ ,  $T_{ChSmA}42$  °C).<sup>7</sup> The polarized microscope images, before and after dissolving **1** in LC, were identical and showed typical textures. Figure 2e shows the fluorescence spectra of **1** in **3** using a 6  $\mu\text{m}$  thick LC cell. The spectra were almost independent of the excitation wavelengths. This means that the equilibrium among the three conformers was shifted to the state for nearly the 100% (s-trans, s-trans) population. This phenomenon is similar when LC was **2**, but it contained a minor contribution of the (s-cis, s-trans) conformer. **1** is considered to be aligned along the molecular ordering in **3** without changing LC pitch of **3**, since no significant change of LC mosaic texture was observed in the presence or absence of **1**.

Further study is needed how **1** is aligned along **3**.

If the temperature of **2** or **3** is increased to be isotropic phase (70 and 60 °C for **2** and **3**, respectively), the fluorescence spectra of **1** are excitation wavelength dependent (Figure 2f) as seen in benzene.

In conclusion, **1** has three rotational isomers in equilibrium in solution, however, it aligns as a (s-trans, s-trans) rotamer along the liquid crystal molecules.

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