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Synthesis and Properties of [2.2](3,3')Biphenylo(3,6)phenanthrenophane

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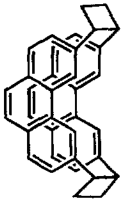
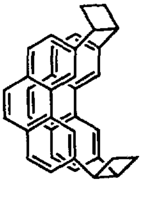
Abstract: The intermolecular [2 + 2] photocycloaddition between 3,6-divinylphenanthrene and 4,4'-dimethoxy-3,3'-divinylbiphenyl successfully afforded a [2.2](3,3')biphenylo(3,6)phenanthrenophane possessing a phenanthrene and biphenyl unit. In this compound, the emission from the biphenyl moiety was quenched due to the intramolecular energy transfer to the phenanthrene moiety.

[2.2]Cyclophanes have been of much interest in their structure, reactivities, and physical properties.[1] Among them, unsymmetrical cyclophanes containing two different aromatic nuclei are attractive compounds from the viewpoint of their intramolecular transannular interaction between the two π-electron systems. Especially, syn-conformers, in which two aromatic rings are aligned face-to-face, are expected to bring about larger electronic interaction than the corresponding anti-conformers. Although some unsymmetrical cyclophanes have been so far synthesized,[1] they usually required long and troublesome synthetic processes, and the selective synthesis of syn-conformers was not necessarily easy.


exo,exo-**1**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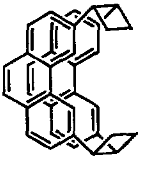
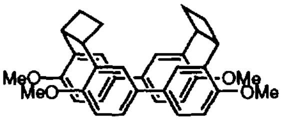
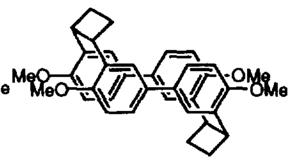

endo,endo-**1**

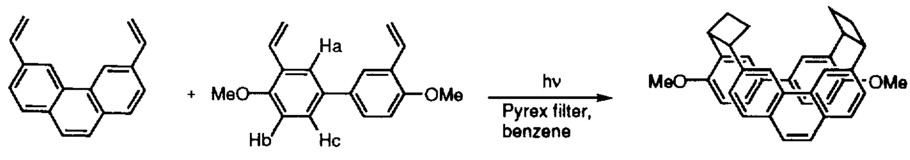


2a



2b

We have successfully synthesized [2.2]cyclophanes by means of intermolecular [2 + 2] photocycloaddition of divinylarenes.[2] This reaction enabled the selective synthesis of various symmetrical *syn*-[2.2]cyclophanes, such as phenanthrenophanes **1**[3] and biphenylophanes **2**.[4] The photocycloaddition between the precursors of **1** and **2**, 3,6-divinylphenanthrene (**3**) and 4,4'-dimethoxy-3,3'-divinylbiphenyl (**4**), is worthy of examination, since they are expected to afford a novel unsymmetrical cyclophane possessing a phenanthrene and biphenyl moiety due to the common structural unit of **3** and **4**. Actually, we have succeeded in the synthesis of [2.2](3,3')biphenylo(3,6)phenanthrenophane **5**, as shown in Eq. 1. In 1973, Staab and Haenel reported the synthesis of a similar cyclophane, [2.2](4,4')biphenylo(2,7)phenanthrenophane.[5] They obtained the compound by the pyrolysis of the corresponding disulfone and subsequent DDQ oxidation of the aromatic moiety, while we readily prepared **5** by a simple photocycloaddition. In this communication, the synthesis and electronic properties of **5** are described in detail.



3 4 5 (1)

Divinylarenes **3** and **4** were prepared by the methods reported previously.[3,4] The benzene solution containing **3** (1 eq.) and **4** (5 eq.) was irradiated with a 400-W high-pressure mercury lamp through a Pyrex-filter under a nitrogen atmosphere at room temperature. Divinylbiphenyl **4** was employed in excess, since the photoreaction between **3** is much faster than that between **4**.[3,4] Nevertheless, only **3** was almost completely consumed within 3 h, and, thus, the irradiation was stopped. The reaction mixture was concentrated, and treated with diborane/THF complex in order to destroy the remaining olefins. The purification of the residue by column-chromatography and preparative TLC (SiO_2, hexane/benzene) gave a desired compound **5** in 3% yield, along with **1** (11%) and a trace amount of **2**, in spite of the use of excessive **4**. Biphenylophenanthrenophane **5** was isolated as a single isomer because of the steric requirements, in contrast with **1** and **2**; three isomers were obtained for **1** due to the conformation of the two cyclobutane rings (exo,exo-, exo,endo-, and endo,endo-isomers)[3] and two isomers for **2** due to the rotation of the biphenyl axis.[4] In **5**, both structural flexibilities are expected to be excluded. The structure of the isolated **5** was determined on the basis of ^{1}H- and ^{13}C NMR and mass spectroscopies.[6]

In the ^{1}H NMR spectrum of **5**, the methine and methylene protons of the cyclobutane rings appeared around 4.6 and 2.5 ppm, respectively, as multiplets. Table 1 summarizes the chemical shifts for the aromatic protons of **5**, along with those of *endo,endo*-**1**, **2a**, **3**, and **4** for the comparison. On the whole, the aromatic protons of **5** resonate at higher fields than those of **3** and **4**, because of the shielding effect of the aromatic nuclei. Therefore, **5** was concluded to have a syn-conformation. Exceptionally, the H4 and H5 protons of the phenanthrene moiety and the Ha protons of the biphenyl moiety in **5** showed lower-field shifts, compared with the corresponding protons of the starting olefins **3** and **4** (0.22 and 0.30 ppm, respectively). This is mainly due to the steric repulsion between these four protons and the protons of the cyclobutane rings, as in the case of **2a**.[4] The Hb and Hc protons of biphenyl moiety in **5** showed larger high-field shifts than those in **2a**. This is apparently derived from the larger shielding effect by the phenanthrene moiety in **5** than that by the biphenyl moiety in **2a**.

Table 1. Chemical Shifts of Aromatic Protons of *endo,endo*-**1**, **2a**, **3**, **4**, and **5**

Position	Chemical Shifts/δ				
	5	*endo,endo*-**1**[a]	**2a**[b]	**3**[a]	**4**[b]
Ha	7.95	–	7.51	–	7.65
Hb	6.32	–	6.56	–	6.94
Hc	6.80	–	6.97	–	7.43
H1 and H8	7.46	7.40	–	7.82	–
H2 and H7	7.10	7.06	–	7.73	–
H4 and H5	8.82	9.11	–	8.60	–
H9 and H10	7.36	7.36	–	7.67	–

a. Ref. 3. b. Ref. 4.

The absorption spectrum of **5** measured in cyclohexane at room temperature is shown in Fig. 1, along with those of phenanthrene and 4,4'-dimethoxybiphenyl. The spectrum is similar to that of phenanthrene rather than that of 4,4'-dimethoxybiphenyl, as expected from the fact that the absorption bands of the former are stronger than those of the latter; the molar extinction coefficient (ε) at the absorption maximum (λ_{max}) is about 67,000 (250 nm) for phenanthrene, while about 22,000 (263 nm) for 4,4'-dimethoxybiphenyl.[7] The band around 260 nm in **5** is broadened and red-shifted (ca. 10 nm), and that in the region of 270–300 nm is enhanced, compared to those in phenanthrene. These observations are apparently derived from the overlap of the absorption band of the biphenyl moiety. The position of 0-0 transition (355 nm) in the $S_1 \leftarrow S_0$ band of **5**, slightly red-shifted relative to phenanthrene (346 nm), is almost the same as that of *endo,endo*-**1**.[3] The absorption spectrum of **5** is essentially interpreted by the sum of the bands of the two aromatic moieties, suggesting weak intramolecular electronic interaction between the two aromatic nuclei in **5**, as in the case of **1**. This result appears to be brought about by the structure of **5**; the two aromatic rings are probably arranged not in parallel, but considerably tilted, since they are fixed by the two cyclobutane rings on the same side.

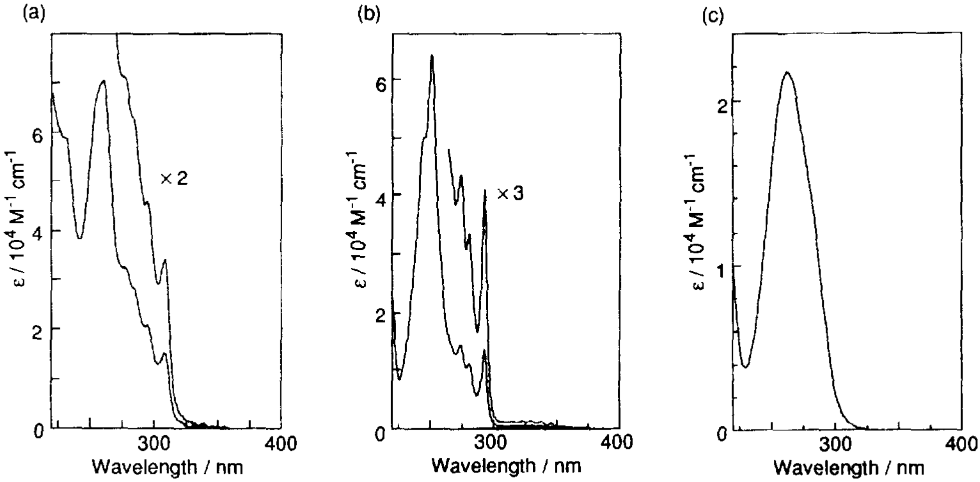


Fig. 1. Absorption spectra of (a) **5**, (b) phenanthrene, and (c) 4,4'-dimethoxybiphenyl in cyclohexane at room temperature.

The fluorescence spectrum of **5** was measured upon 280-nm excitation in cyclohexane at room temperature. Both aromatic moieties of **5** can be excited at this wavelength. Figure 2 illustrates the spectrum of **5** along with those of phenanthrene and 4,4'-dimethoxybiphenyl. The spectrum of **5**, exhibiting sharp vibrational structures, is similar to those of phenanthrene and *endo,endo*-**1**.[3] The peak positions are also comparable to those in **1**. The fluorescence intensity is extremely low in the region of shorter than 350 nm. Since 4,4'-dimethoxybiphenyl afford emission at such wavelengths with a sufficient intensity, the emission from the biphenyl moiety appears to be not involved in the spectrum of **5**. Thus, the observed emission is concluded to be substantially derived from the phenanthrene moiety of **5**. The fluorescence excitation spectra of **5**, monitored at the peak maxima, were in good agreement with the absorption spectrum. Since the energy level of the S_1 state of the biphenyl moiety is higher than that of the phenanthrene moiety, the quenching of the fluorescence from the biphenyl moiety is obviously ascribable to the intramolecular energy transfer from S_1(biphenyl) to S_0(phenanthrene). Such observation has not been so far reported for unsymmetrical cyclophanes. The result in the fluorescence spectrum is in contrast with that in the absorption spectrum; there is little interaction between the two aromatic moieties in the ground state, whereas a distinct interaction in the singlet excited state.

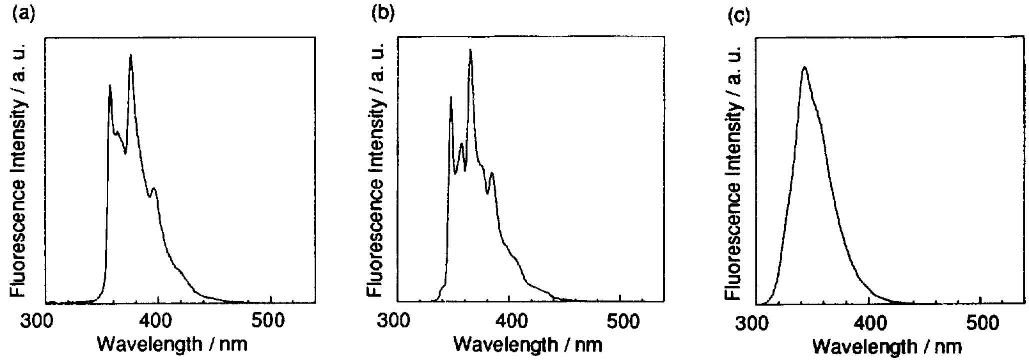


Fig. 2. Fluorescence spectra of (a) **5**, (b) phenanthrene, and (c) 4,4'-dimethoxybiphenyl in cyclohexane at room temperature.

In summary, we have succeeded in the synthesis of an unsymmetrical cyclophane, [2.2](3,3')biphenylo(3,6)phenanthrenophane **5**, by the [2 + 2] photocycloaddition between two different divinylarenes for the first time. This method seems to be applicable to the synthesis of other unsymmetrical cyclophanes.

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5. Staab, H. A.; Haenel, M. W. *Chem. Ber.* **1973**, 106, 2190–2202.
6. The spectral data of **5** are as follows. mp> 300 °C; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.82 (2H, s), 7.95 (2H, d, J = 2.1 Hz), 7.46 (2H, d, J = 7.9 Hz), 7.36 (2H, s), 7.10 (2H, d, J = 7.9 Hz), 6.80 (2H, dd, J = 8.2 & 2.1 Hz), 6.35 (2H, d, J = 8.2 Hz), 4.68 (2H, m), 4.35 (2H, m), 3.64 (6H, s), 2.80 (6H, m), 2.69 (2H, m); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 155.41, 140.07, 131.41, 130.06, 129.78, 129.27, 128.20, 127.27, 126.53, 125.47, 123.71, 121.25, 109.89, 55.42, 45.92, 38.15, 24.79, 24.19; LRMS m/z 496 (M$^+$), 266, 230; HRMS m/z 496.2416, calcd for $C_{36}H_{32}O_2$ 496.2402.
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