Synthesis and Fluorescence Emission Behavior of *anti*-[2.3](3,10)Phenanthrenophane: Overlap between Phenanthrene Rings Required for Excimer Formation

Yosuke Nakamura, Takahiro Fujii, and Jun Nishimura*
Department of Chemistry, Gunma University, Tenjin-cho, Kiryu, Gunma 376-8515

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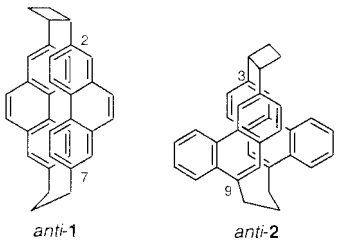
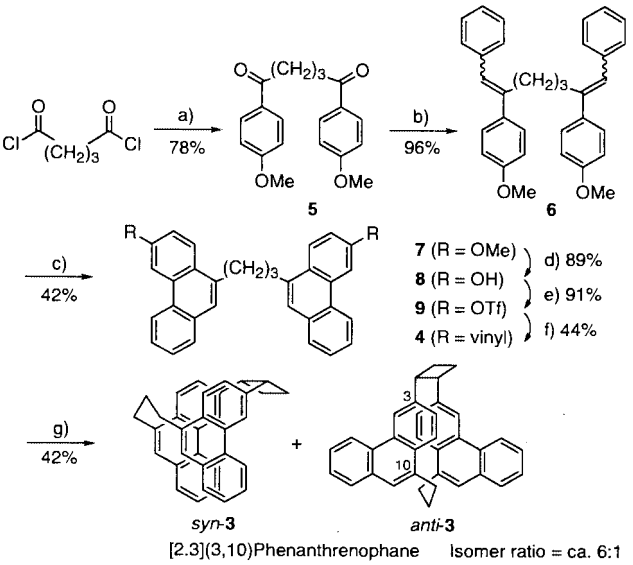
Novel *anti*-[2.3](3,10)phenanthrenophane **3**, prepared by the intramolecular [2 + 2] photocycloaddition of 1,3-bis(3-vinyl-10-phenanthryl)propane, exhibited monomer fluorescence. This is in a remarkable contrast with the excimer fluorescence emission from *anti*-[2.3](3,9)phenanthrenophane **2** with slightly larger overlap between phenanthrene rings than in *anti*-**3**.

Among a series of aromatic hydrocarbons, phenanthrene is unique in its failure to give excimer fluorescence in solution at room temperature.[1] Even 1,3-diphenanthrylpropanes mainly afford monomer fluorescence,[2] on the contrary to Hirayama's rule.[3] We have succeeded in the first observation of excimer fluorescence almost free from monomer fluorescence at room temperature for *syn*-[2.2](1,6)phenanthrenophanes whose phenanthrene rings are held almost in parallel.[4] For phenanthrene, however, the relationship between the arrangement of aromatic nuclei and fluorescence behavior has been hardly clarified, mainly due to the difficulty in the synthesis and separation of appropriate model compounds. The fluorescence for *anti*-phenanthrenophanes with partially overlapped phenanthrene rings had been unknown before our recent research on *anti*-[2.3](2,7)phenanthrenophane **1**[5] and *anti*-[2.3](3,9)phenanthrenophane **2**,[6] although Staab et al. observed excimer fluorescence from a mixture of *syn*- and *anti*-[2.2](2,7)phenanthrenophanes in a fluorene host crystal at 4.2 K.[7,8] Intriguingly, even *anti*-**2** where the two phenanthrene rings overlap mainly at the single six-membered ring afforded broad and structureless excimer fluorescence blue-shifted relative to that of the *syn*-isomer.[6] This result raised a question what degree of overlap is essential or sufficient for the excimer formation of phenanthrene. In order to answer the question, we have designed *anti*-[2.3](3,10)phenanthrenophane **3**, which is expected to have further small overlap than *anti*-**2**, according to MM2 calculation. Here, we report the preparation and fluorescence behavior of *anti*-**3**.



anti-**1** *anti*-**2**

1,3-Bis(3-vinyl-10-phenanthryl)propane **4**, precursor of **3**, was prepared as shown in Scheme 1. The oxidative photocyclization of stilbene derivative **6** toward **7** was employed as a key step. The photoreaction of **4** was carried out in benzene (2 mM) using a 400-W high-pressure mercury lamp through a Pyrex filter under a nitrogen atmosphere in the manner reported in the literature,[5,6,9] to afford a mixture of *syn*- and *anti*-**3** in 42% yield. The *syn*:*anti*-isomer ratio was determined as ca. 6:1 on the basis of the peak areas of ^{1}H NMR spectra. Both isomers were successfully separated by repeated GPC (polystyrene column, chloroform), and no interconversion between them was observed at room temperature for at least several months.



a) $AlCl_3$, anisole. b) Benzyltriphenylphosphonium bromide, *n*-BuLi, THF. c) *hν*, I_2, propylene oxide, toluene. d) BBr_3, CH_2Cl_2. e) $(CF_3SO_2)_2O$, pyridine. f) $(n\text{-Bu})_3SnCH{=}CH_2$, $(Ph_3P)_4Pd$, LiCl, dioxane. g) *hν* (Pyrex), benzene.

Scheme 1.

The structures of *syn*- and *anti*-**3** were determined mainly by ^{1}H NMR spectroscopy in a manner similar to **2**.[10] In *syn*-**3**, only eight sets of aromatic proton peaks were observed and generally high-field shifted compared to those of precursor **4**. The two methine protons of the cyclobutane ring appeared as an equivalent peak. These results apparently indicate the *syn*-conformation where the two chromophores are well overlapped. The configuration of cyclobutane ring was determined as depicted in Scheme 1 on the basis of an NOESY experiment;[11] NOE interaction was detected between the cyclobutane methylene protons and H4 protons of the phenanthrene ring.

In the ^{1}H NMR spectrum of *anti*-**3**, sixteen peaks for aromatic protons and two peaks for the methine protons were observed, suggesting a lower symmetrical structure. Among the aromatic protons, H1, H2, and H4 are high-field shifted relative to **4**, while H5–9 are hardly shifted. Especially, the H2 (δ 5.75, 6.13) and H1 protons (δ 6.28, 6.34) in *anti*-**3** resonate at much higher fields than those in *syn*-**3** (H2: δ 6.67; H1: δ 7.42), indicating that these protons are located above the opposite phenanthrene ring. On the contrary, the H4 protons (δ 8.15, 8.48) of *anti*-**3** are resonated at lower fields than those in *syn*-**3**

(δ 7.88), though higher fields than those in **4** (δ 8.67). Thus, the H4 protons of *anti*-**3** suffer from much less shielding effect by the opposite phenanthrene ring than H1 and H2. These observations are rather different from those for *anti*-**2**, where the H4 as well as H1 and H10 resonates at high fields relative to *syn*-**2** and the two phenanthrene rings overlap mainly at the single six-membered ring on the cyclobutane side. These results obviously indicate that *anti*-**3** possesses a less overlapped structure than *anti*-**2**; the overlap in *anti*-**3** is only about half of the six-membered ring on the cyclobutane side. Although single crystals suitable for X-ray crystallographic analysis have not been obtained, MM2 calculations demonstrated such overlap between the two phenanthrene rings, which are arranged almost in parallel with a distance of ca. 3.5 Å.[12]

The absorption spectra of *syn*- and *anti*-**3** in cyclohexane exhibited considerable broadening and a red shift relative to that of phenanthrene, though their shapes were rather different from each other.[13]

The fluorescence spectra of *syn*- and *anti*-**3** were measured upon 280 nm excitation in cyclohexane at room temperature (Figure 1). The spectrum of *syn*-**3** is composed of a broad structureless and red-shifted emission with a maximum at 420 nm similar to *syn*-**2**, though weak emission is also observed around 370 nm. This broad emission is reasonably assignable to the excimer fluorescence, as in the other cases.[4–6] The latter weak emission is probably due to photodecomposition products, since the relative intensity increased with repeated measurements. On the other hand, *anti*-**3** affords vibrational structures characteristic of monomer fluorescence, which shows the mirror image of the longest absorption band. Although the contribution of excimer fluorescence cannot be completely excluded, it is reasonable to assume that the observed emission is derived predominantly from monomer fluorescence. This behavior is in a remarkable contrast with that in *anti*-**2**, which afforded distinct excimer fluorescence without vibrational structures. Such difference is apparently ascribed to the slight difference in the extent of overlap between *anti*-**3** and *anti*-**2**. Therefore, it is definitely concluded that the excimer formation of phenanthrene requires at least the overlap at one six-membered ring of two phenanthrene nuclei, provided that they are arranged almost in parallel with a distance of ca. 3.5 Å.

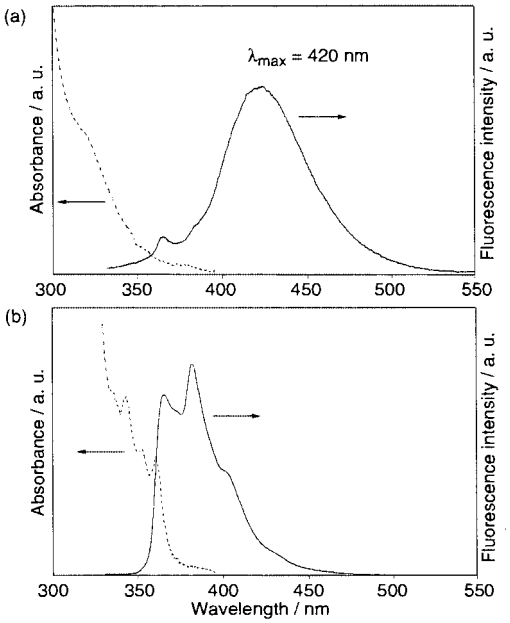


Figure 1. Fluorescence (—; λ_{ex} = 280 nm) and absorption (----) spectra of (a) *syn*-**3** and (b) *anti*-**3** in cyclohexane at room temperature.

In summary, novel *anti*-[2.3](3,10)phenanthrenophane **3** was prepared by the intramolecular [2 + 2] photocycloaddition of **4** and successfully isolated from the *syn*-isomer. Intriguingly, *anti*-**3** exhibited monomer-like emission due to the smaller overlap between phenanthrene rings than in *anti*-**2**.

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Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

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10 The spectral data of *syn*- and *anti*-**3** are as follows. *syn*-**3**: mp 255 °C (dec.); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.03 (2H, dd, *J* = 7.8 and 0.8 Hz, H5), 7.88 (2H, d, *J* = 1.6 Hz, H4), 7.42 (2H, d, *J* = 8.5 Hz, H1), 7.26 (2H, dd, *J* = 7.6 and 1.5 Hz, H8), 7.10 (2H, s, H9), 7.04 (4H, m, H6 and H7), 6.67 (2H, dd, *J* = 8.6 and 2.0 Hz, H2), 4.45 (2H, m, cyclobutane methine), 3.56 (2H, m, one of $ArCH_2CH_2$), 2.94 (3H, m, one of $ArCH_2CH_2$ and one of $ArCH_2CH_2$), 2.16 (1H, m, one of $ArCH_2CH_2$); ^{13}C NMR (125.65 MHz, CD_2Cl_2) δ 131.87, 134.80, 131.78, 131.10, 129.38, 129.14, 128.88, 127.66, 126.81, 126.06, 125.33, 124.60, 122.12, 121.83, 47.44, 35.97, 25.95, 20.84; HRMS (FAB) found: *m/z* 448.2192. Calcd for $C_{35}H_{28}$: M^+, 448.2191. *anti*-**3**: mp 255 °C (dec.); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (1H, dd, *J* = 7.7 and 0.6 Hz, H5), 8.60 (1H, dd, *J* = 7.9 and 1.8 Hz, H5), 8.48 (1H, s, H4), 8.15 (1H, d, *J* = 1.2 Hz, H4), 7.92 (1H, dd, *J* = 8.4 and 1.5 Hz, H8), 7.87 (1H, dd, *J* = 8.2 and 2.1 Hz, H8), 7.71 (1H, s, H9), 7.67 (1H, s, H9), 7.62 (4H, m, H6, H6, H7 and H7), 6.34 (1H, d, *J* = 8.5 Hz, H1), 6.28 (1H, d, *J* = 8.6 Hz, H1), 6.13 (1H, dd, *J* = 8.7 and 1.4 Hz, H2), 5.75 (1H, dd, *J* = 8.6 and 1.5 Hz, H2), 4.51 (1H, m, one of cyclobutane methine), 4.23 (1H, m, one of cyclobutane methine), 2.78 (7H, m), 2.52 (3H, m); ^{13}C NMR (125.65 MHz, $CDCl_3$) δ 139.11, 138.07, 135.99, 135.85, 131.94, 131.91, 130.01, 129.96, 129.83, 129.63, 129.53, 129.50, 128.54, 127.92, 127.86, 126.10, 125.51, 125.47, 124.41, 124.12, 123.80, 123.47, 123.26, 122.88, 122.72, 122.65, 119.56, 47.54, 46.70, 31.69, 24.38, 24.19, 21.48, 19.44; HRMS (FAB) found: *m/z* 448.2174. Calcd for $C_{35}H_{28}$: M^+, 448.2191.
11 The isomer possessing a cyclobutane ring directed to the H2-side seems to be only slightly formed, but its isolation and characterization has been unsuccessful.
12 MM2 calculations were performed by CS Chem 3D Pro Version 4.0 (Cambridge Soft Corporation).
13 Absorption and fluorescence spectra were measured for the solutions in the range of 10^{-5}–10^{-4} M. The fluorescence excitation spectra were in good agreement with the corresponding absorption spectra in all cases.