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Synthesis and Fluorescence Spectra of Oxa[3.*n*]phenanthrenophanes

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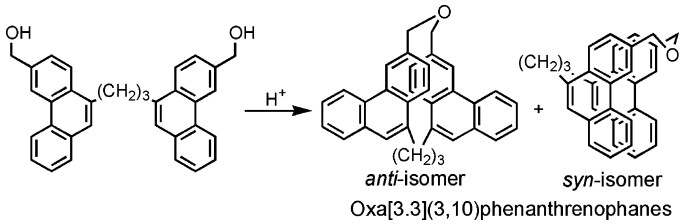
ABSTRACT



Novel photostable oxa[3.*n*](3,9)- and [3.3](3,10)phenanthrenophanes ($n = 3, 4$) bearing trimethylene-type linkage(s) were successfully synthesized by the intramolecular acid-catalyzed etherification of the corresponding precursor diols. *syn*-Oxa[3.3](3,10)phenanthrenophane afforded the most red-shifted excimer fluorescence ($\lambda_{max} = 432$ nm) among the phenanthrenophanes so far prepared.

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 afford mainly monomer fluorescence,[2] contrary to Hirayama's rule.[3] A cyclophane composed of two phenanthrene nuclei, namely phenanthrenophane, in which the relative arrangement of two phenanthrene chromophores is fixed more rigidly, is a desirable compound for the elucidation of the relationship between the chromophore arrangement and fluorescence properties, such as excimer formation. However, the availability of phenanthrenophanes has been quite limited,[4−6] mainly due to the difficulty in their synthesis and isolation.

We have succeeded in the preparation of two [2.2]-phenanthrenophanes **1** and **2** by the intermolecular [2 + 2] photocycloaddition of divinylphenanthrenes (Figure 1).[7] Noticeably, *syn*-**1**, whose phenanthrene rings are held almost in parallel, enabled the first observation of excimer fluorescence almost free from monomer fluorescence at room temperature.[7] The first preparation and isolation of various *anti*-phenanthrenophanes with partially overlapped phenanthrene rings, such as **3**,[8] **4**,[9] and **5**,[10] were also accomplished by the intramolecular [2 + 2] photocycloaddition of vinylphenanthrene derivatives, although Staab et al. had obtained a mixture of *syn*- and *anti*-[2.2](2,7)phenanthrenophane.[4,11]

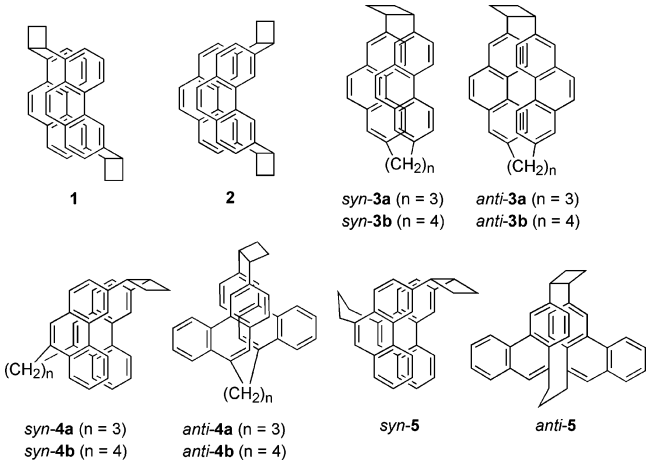


Figure 1. Phenanthrenophanes so far prepared.

(1) Chandross, E. A.; Thomas, H. *J. Am. Chem. Soc.* **1972**, *94*, 2421.
(2) Zachariasse, K. A.; Busse, R.; Schrader, U.; Kühnle, W. *Chem. Phys. Lett.* **1982**, *89*, 303.
(3) Hirayama, F. *J. Chem. Phys.* **1965**, *42*, 3163.
(4) Staab, H. A.; Haenel, M. *Chem. Ber.* **1973**, *106*, 2190.
(5) Thulin B.; Wennerström, O. *Acta Chem. Scand.* **1976**, *B30*, 369.
(6) Aly, A. A.; Hopf, H.; Ernst, L. *Eur. J. Org. Chem.* **2000**, 3021.
(7) Nakamura, Y.; Tsuihiji, T.; Mita, T.; Minowa, T.; Tobita, S.; Shizuka, H.; Nishimura, J. *J. Am. Chem. Soc.* **1996**, *118*, 1006.

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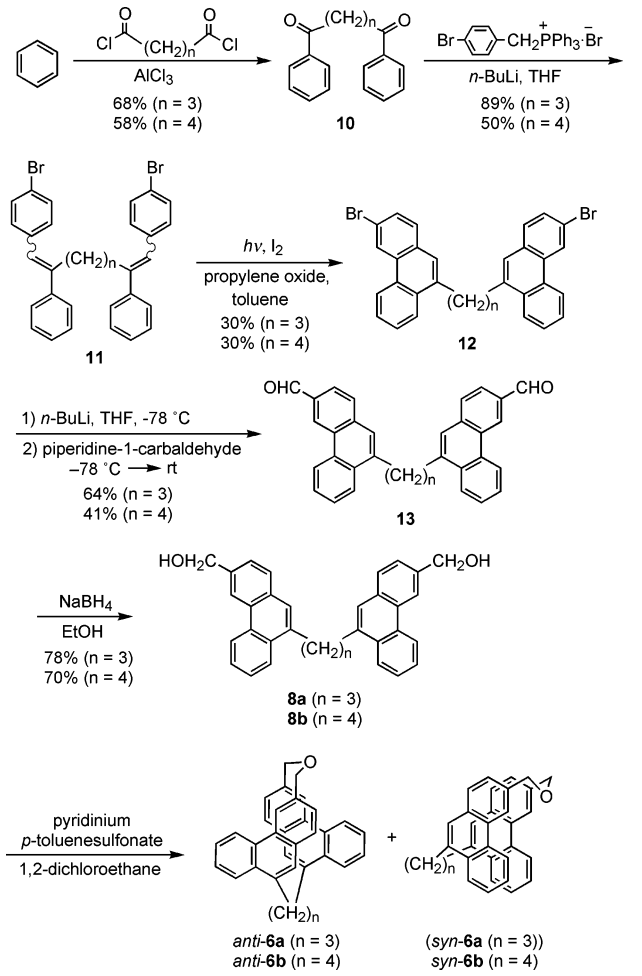
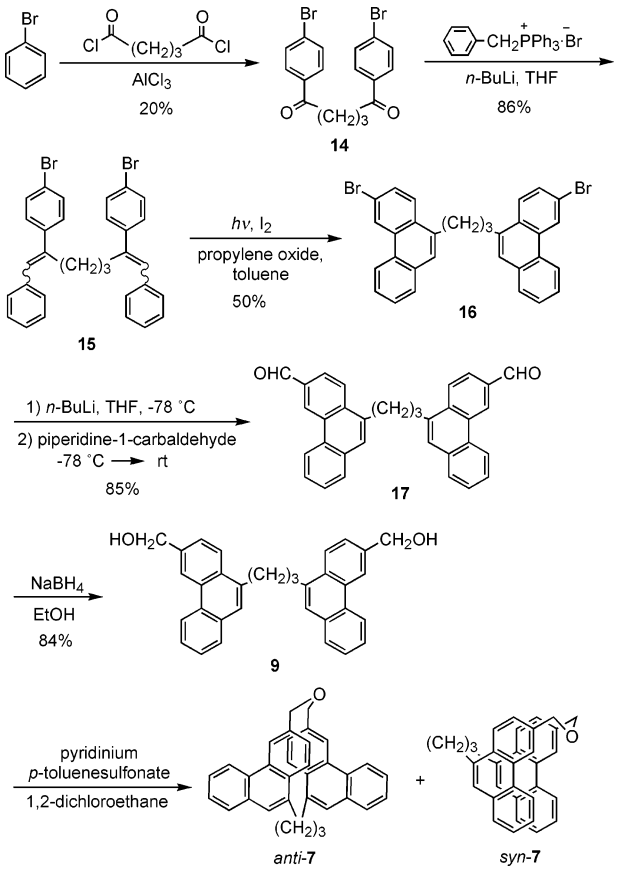
Scheme 1



Scheme 2



These photochemical methods have enabled the systematic synthesis of phenanthrenophanes and other cyclophanes, which would be otherwise difficult to prepare.[12] In addition, the phenanthrenophanes obtained, whose aromatic nuclei are effectively fixed by cyclobutane ring(s) as bridging linkages, are suitable for the clarification of the relationship between the arrangement of aromatic nuclei and photophysical properties. However, this methodology can only afford [2.*n*]-phenanthrenophanes, but no [3.3]phenanthrenophanes, which seem to be more suitable for excimer formation. Furthermore, [2.*n*]phenanthrenophanes carrying cyclobutane ring(s) are generally unstable toward UV light, mainly due to the cleavage of cyclobutane ring(s), to give precursor vinyl compounds. Actually, some phenanthrenophanes, especially *syn*-isomers, undergo partial decomposition even during the measurement of emission spectra.

As an alternative to a cyclobutane ring, we have examined the introduction of a $-CH_2OCH_2-$ linkage, which is expected to be readily prepared by the intramolecular dehydration between two hydroxymethyl groups.[13] Thus, oxa[3.*n*](3,9)-phenanthrenophanes **6** (n = 3, 4) and oxa[3.3](3,10)phenanthrenophane **7** were designed, in which a cyclobutane ring of **4** and **5** is replaced by a $-CH_2OCH_2-$ linkage. Herein, we report the preparation and characterization of **6** and **7** and a preliminary investigation on their photophysical properties.

Schemes 1 and 2 depict the synthetic sequence to **6** and **7**, respectively. In both cases, the oxidative photocyclization of stilbene derivatives **11** and **15** to phenanthrene derivatives **12** and **16**, respectively, was employed as a key step.[14] The intramolecular etherification of diols **8** and **9** to **6** and **7** was carried out in the presence of acid catalyst. The transformation of **8a** into **6a** was investigated first under a variety of conditions. The reflux of **8a** in dichloromethane or 1,2-dichloroethane in the presence of *p*-toluenesulfonic acid monohydrate failed to give desired phenanthrenophane **6a**. Instead, a product carrying a formyl group was obtained, though its mode of formation is obscure. The reaction using pyridinium *p*-toluenesulfonate as milder acid catalyst in

(8) Nakamura, Y.; Fujii, T.; Sugita, S.; Nishimura, J. *Chem. Lett.* **1999**, 1039.
(9) Nakamura, Y.; Fujii, T.; Nishimura, J. *Tetrahedron Lett.* **2000**, *41*, 1419.
(10) Nakamura, Y.; Fujii, T.; Nishimura, J. *Chem. Lett.* **2001**, 970.
(11) Schweitzer, D.; Colpa, J. P.; Behnke, J.; Hausser, K. H.; Haenel, M.; Staab, H. A. *Chem. Phys.* **1975**, *11*, 373.
(12) (a) Nishimura, J.; Okada, Y.; Inokuma, S.; Nakamura, Y.; Gao, S. R. *Synlett* **1994**, 884. (b) Nishimura, J.; Nakamura, Y.; Hayashida, Y.; Kudo, T. *Acc. Chem. Res.* **2000**, *33*, 679 and references therein.
(13) Nakamura, Y.; Yamazaki, T.; Kakinoya, Y.; Shimizu, H.; Nishimura, J. *Synthesis* **2004**, 2743.
(14) (a) Liu, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. *J. Org. Chem.* **1991**, *56*, 3769. (b) Laarhoven, W. H. *Org. Photochem.* **1989**, *10*, 163 1989. (c) Laarhoven, W. H. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 185. (d) Laarhoven, W. H. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 241.

refluxing dichloromethane or THF for several days resulted only in the recovery of **8a** without the formation of **6a**. In contrast, with reflux in 1,2-dichloroethane in the presence of the same acid catalyst for 10 days, desired **6a** was successfully obtained along with recovered **8a**. The purification of the reaction mixture by column chromatography (silica gel) and GPC led to the isolation of **6a** as a single isomer in 13% yield. As described below, isolated **6a** is the *anti*-isomer, and no *syn*-isomer was detected in the reaction mixture.

The intramolecular dehydration of **8b** under similar conditions gave **6b** as a mixture of *syn*- and *anti*-isomers in 5% yield, in contrast with **6a**. The *syn*/*anti*-isomer ratio was determined as 2:5 on the basis of ^{1}H NMR integration. Under the same conditions, diol **9** also produced both *syn*- and *anti*-isomers of **7** in a ratio of 1:4 (total 6% yield). It was quite difficult to separate and isolate each isomer of **6b** and **7**, especially the *syn*-isomers, but a small amount of both isomers was isolated by repeated preparative HPLC (ODS column, methanol).

The structures of oxa[3.*n*]phenanthrenophanes **6a**, **6b**, and **7** obtained were mainly determined by ^{1}H NMR spectroscopy. In both *syn*-isomers with C_s symmetry and *anti*-isomers with C_2 symmetry, eight sets of aromatic proton peaks are observed. However, their spectral patterns are remarkably different from each other.

The aromatic protons of *syn*-**6b** and *syn*-**7** are almost equally high-field shifted compared to those of precursors such as **8b** and **9**, as observed in the *syn*-phenanthrenophanes reported previously.[7−10] This observation demonstrates that the two phenanthrene nuclei are wholly overlapped with each other.

In contrast, the aromatic protons of *anti*-**6a**,**b** and *anti*-**7** range over a wider region. Among the aromatic protons of *anti*-**6a**,**b**, H6−8 are hardly shifted relative to **8a**,**b**, while H1 and H10 are extremely high-field shifted, indicating that these protons are located above the opposite phenanthrene ring. Therefore, *anti*-**6a**,**b** are expected to adopt a conformation where one six-membered ring of one phenanthrene nucleus is mainly overlapped with that of the other phenanthrene nucleus, as similar to *anti*-**4a**,**b** reported previously.[9]

The ^{1}H NMR spectrum of *anti*-**7** exhibits a pattern rather different from *anti*-**6a**,**b**. Among the aromatic protons in *anti*-**7**, H5−9 are hardly shifted relative to precursor **9**, whereas the H1 and H2 protons resonate at much higher fields than those in **9** and *syn*-**7**, indicating that these protons are located above the opposite phenanthrene ring. These observations clearly contrast with those for *anti*-**6a**,**b**, and suggest that *anti*-**7** possesses a less overlapped structure than *anti*-**6a**; similar to *anti*-**5**,[10] the overlap in *anti*-**7** is only about half of the six-membered ring on the C1−C4 side, as also demonstrated by MM2 calculations (see below).

According to the optimized molecular structures of **6a**, **6b**, and **7** by MM2 calculations, the two phenanthrene rings are arranged almost in parallel for all of **6a**,**b** and **7**, though the distance between C9 atoms is relatively long in **6b** carrying a tetramethylene linkage. Apparently, *syn*- and *anti*-isomers differ in the extent of overlap of the phenanthrene rings. They are fully overlapped in the *syn*-isomer, whereas in the *anti*-isomer they are partially overlapped, in the manner suggested by the ^{1}H NMR spectra as mentioned above (Figure 2).

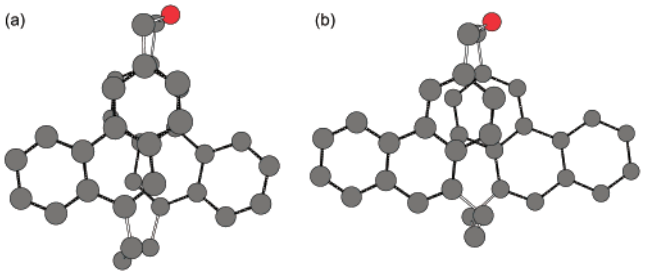


Figure 2. Optimized structures of (a) *anti*-**6b** and (b) *anti*-**7** determined by MM2 calculations.

The absorption spectra of **6a**, **6b**, and **7**, measured in cyclohexane at room temperature, exhibit considerable broadening and shift relative to those of phenanthrene and 3,9-dimethylphenanthrene. These observations indicate that the two phenanthrene nuclei interact electronically with each other in the ground state. Roughly speaking, the spectral features of *syn*-**6b** and *syn*-**7** with full overlap are similar to each other, and those of *anti*-**6a**, *anti*-**6b**, and *anti*-**7** with partial overlap are also similar to one another.

The fluorescence spectra of **6a**, **6b**, and **7** in cyclohexane at room temperature are shown in Figure 3, which also shows the spectrum of 3,9-dimethylphenanthrene as a reference. The fluorescence excitation spectra, on monitoring these emissions, were in good agreement with the absorption spectra, obviously indicating that these emissions originate from the phenanthrenophanes. No decomposition was observed after fluorescence measurements.

The fluorescence spectrum of *anti*-**7** is considerably different from those of the other phenanthrenophanes and relatively similar to that of 3,9-dimethylphenanthrene, indicating monomer-like emission. The quite small overlap between phenanthrene rings in *anti*-**7** cannot be sufficient for the excimer formation, as also demonstrated in *anti*-**5** reported previously.[10]

In contrast, *anti*-**6a**, *syn*- and *anti*-**6b**, and *syn*-**7** exhibit red-shifted broad emission without vibrational structures. Since the large peak shift is characteristic of excimer fluorescence for most aromatic compounds,[15] it is reasonable to assign these broad structureless emissions to intramolecular excimer fluorescence.

The excimer fluorescence of *syn*-**7** is the most red-shifted (λ_{max} = 432 nm) among the excimers of phenanthrenophanes so far observed.[7−10] This large peak shift in *syn*-**7** is ascribed to its arrangement where the distance between the two fully overlapped phenanthrene nuclei is moderately short due to the bridging by two trimethylene-type linkages leading to larger stabilization energy in the excited state and larger repulsion energy in the ground state. The trimethylene-type

(15) Klöpffer, W. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; John Wiley and Sons: New York, 1973; Vol. 1, pp 357−401.

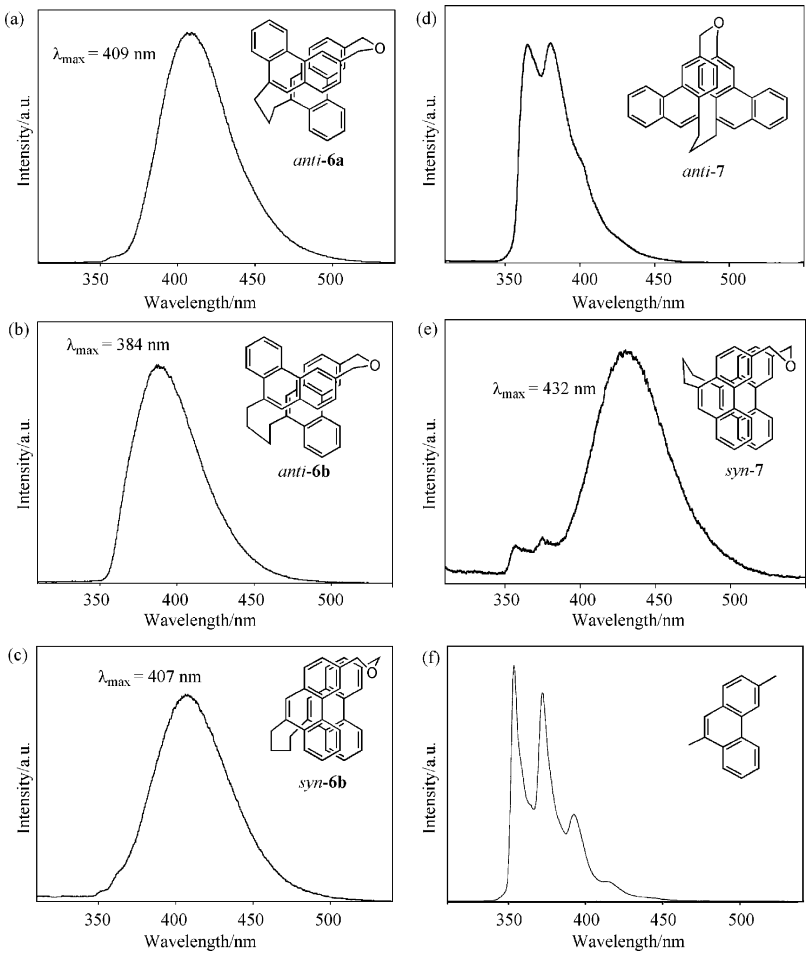


Figure 3. Fluorescence spectra of (a) *anti*-**6a**, (b) *anti*-**6b**, (c) *syn*-**6b**, (d) *anti*-**7**, (e) *syn*-**7**, and (f) 3,9-dimethylphenanthrene on 280-nm excitation in cyclohexane at room temperature.

linkages appear to be more suitable for excimer formation than the others, such as a cyclobutane, in agreement with Hirayama's rule.[3] The increased distance or decreased overlap between chromophores gives rise to the decrease in peak shift. In *syn*-**6b** bearing one tetramethylene linkage, the maximum wavelength is much blue-shifted ($\lambda_{max} = 407$ nm). In *anti*-**6b** with a partial-overlap arrangement, further blue shift is observed ($\lambda_{max} = 384$ nm). It seems only accidental that the quite similar emission maximum was observed for *anti*-**6a** and *syn*-**6b** with different distance and overlap between two chromophores. Thus, the maximum wavelength is sensitively affected by the extent of overlap and separation of phenanthrene rings, but its quantitative estimation is difficult at the present stage.

In summary, novel oxa[3.*n*](3,9)phenanthrenophanes **6a** ($n = 3$), **6b** ($n = 4$), and oxa[3.3](3,10)phenanthrenophane **7** were successfully prepared by the intramolecular acid-catalyzed dehydration of diols **8a**, **8b**, and **9**, respectively. The introduction of a $-CH_2OCH_2-$ linkage instead of cyclobutane ring obviously enhances the photostability of phenanthrenophanes. The phenanthrenophanes other than *anti*-**7** gave red-shifted broad emission, which is assignable to excimer fluorescence. The maximum wavelength is sensitively dependent on the extent of overlap and separation of phenanthrene rings. The excimer fluorescence of *syn*-**7** is the most red-shifted ($\lambda_{max} = 432$ nm) among the excimers of phenanthrenophanes so far observed. The more detailed investigation on photophysical properties such as fluorescence lifetime or initial photophysical processes is now in progress.

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Supporting Information Available: The spectroscopic data including ^{1}H and ^{13}C NMR spectra of *anti*-**6a**, *anti*-**6b**, *syn*-**6b**, *anti*-**7**, and *syn*-**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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