Synthesis, Structure, and Electronic Properties of *syn*-[2.2]Phenanthrenophanes: First Observation of Their Excimer Fluorescence at High Temperature

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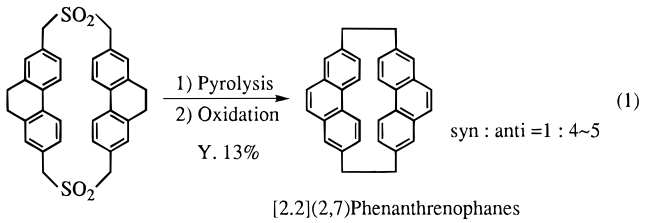
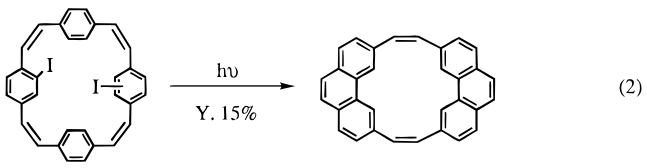
Abstract: Two *syn*-[2.2](1,6)- and -(3,6)phenanthrenophanes, **1a**,**b**, were synthesized for the first time by means of intermolecular [2 + 2] photocycloaddition of the corresponding divinylphenanthrenes. Phenanthrenophanes **1a**,**b** were obtained as mixtures of two (exo,exo and exo,endo) and three (exo,exo, exo,endo, and endo,endo) structural isomers, respectively, which were isolated by reversed-phase HPLC and gel permeation chromatography. All of the isomers, whose structures were characterized mainly on the basis of ^{1}H NMR spectroscopy, were in a syn conformation. X-ray crystallographic analysis of *exo*,*endo*-**1a** was successful, also in agreement with the results of ^{1}H NMR. Birch reduction of **1b**, followed by DDQ oxidation, afforded [4.4](3,6)phenanthrenophane **5b** in an anti conformation, due to opening of the cyclobutane rings. The absorption spectra of **1b** were relatively similar to that of phenanthrene itself, while those of **1a** were rather broadened and red-shifted compared to those of phenanthrene and **1b**. In both cases, the spectra were independent of the configuration of the cyclobutane rings. The fluorescence spectra of **1b** exhibited sharp vibrational structures, as in phenanthrene, suggesting fluorescence from the locally excited state. On the other hand, **1a** afforded a broad and structureless emission due to the excimer fluorescence, even at room temperature. This is the first observation of the excimer emission almost free from the monomer-like emission for phenanthrene derivatives at rather high temperature. Such differences in the absorption and fluorescence spectra between **1a**,**b** can be explained reasonably in terms of differences in the arrangement of the two phenanthrene rings; they are tightly held almost in parallel for **1a**, according to the X-ray structural analysis, while tilted by the dihedral angle of ca. 30° for **1b** on the basis of MM2 calculations.

Introduction

[2.2]Cyclophanes, including [2.2]naphthalenophanes and phenanthrenophanes, have been of much interest from the viewpoints of their synthesis, reactivities, and physical properties resulting from the intramolecular interaction between the π-electron systems of the two aromatic nuclei.[1] Among them, *syn*-cyclophanes, in which the two aromatic rings are aligned face-to-face, are more attractive compounds, since they can bring about larger electronic interaction than the corresponding anti conformers. Various [2.2]naphthalenophanes[2] have been synthesized by various methods since the preparation of [2.2](2,7)-naphthalenophane by Baker et al. in 1951,[2a] but the selective synthesis of *syn*-[2.2]naphthalenophanes had not been attained for a long time. Recently, we have successfully synthesized [2.2]cyclophanes by means of intermolecular [2 + 2] photocycloaddition of divinylarenes.[3] This reaction also enabled the selective and systematic synthesis of several *syn*-[2.2]naphthalenophanes for the first time.[3c]

The synthesis of [2.2]phenanthrenophanes has been much less known because of its great difficulties. Staab and Haenel reported the synthesis of [2.2](2,7)phenanthrenophane by the pyrolysis of the disulfones derived from dithia[3.3]phenanthrenophane (eq 1).[4] The obtained phenanthrenophane, however, was a mixture of the syn and anti isomers, whose separation was not achieved. [2.2](3,6)Phenanthrenophanediene was prepared by a sequence of Wittig reaction and aryl iodide photolysis (eq 2).[5] Its ^{1}H NMR data suggested a relatively





planar structure, while the UV spectrum indicated that the two phenanthrene rings are almost perpendicular without significant electronic interaction.[5] According to the molecular mechanics calculations, the aromatic nuclei were expected to form a V-shape with an angle of 67°.[6] As in the case of naphthale-

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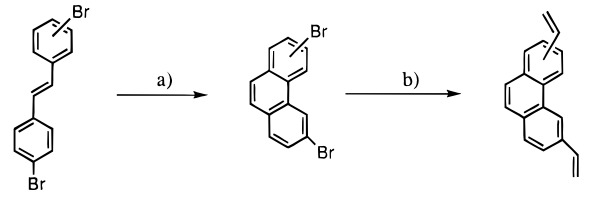
nophanes, *syn*-[2.2]phenanthrenophanes have not been obtained selectively. Therefore, we have been stimulated to apply the intermolecular [2 + 2] photocycloaddition to two divinylphenanthrenes for the synthesis of *syn*-[2.2]phenanthrenophanes. In both cases, desired syn isomers were obtained efficiently and selectively.

The photophysical properties of [2.2]phenanthrenophanes are of great interest from the viewpoint of the intramolecular excimer formation. A large number of aromatic hydrocarbons in the excited states are known to form excimers whose fluorescence has been observed in a concentrated solution or crystalline states.[7] Cyclophanes, including naphthalenophanes, have proved to provide intramolecular excimer fluorescence, even in a dilute solution.[8] In contrast with such aromatic hydrocarbons and cyclophanes, unambiguous excimer fluorescence of phenanthrene has hardly been observed under usual experimental conditions in fluid media. The red-shifted, broad spectra due to the excimer fluorescence were detected for the evaporated films[9] and the phenanthrene adlayers on Al_2O_3.[10] Azumi and McGlynn reported the delayed excimer fluorescence in a hydrocarbon matrix at 77 K.[11] Its intensity increased with increasing temperatures, reached the maximum, and then decreased to zero at room temperature.[11] On the other hand, Chandross and Thomas suggested the failure of excimer formation of phenanthrene, on the basis of the study on the photolytic dissociation of the cis,syn dimer of 9-(hydroxymethyl)phenanthrene and others in a rigid matrix at 77 K.[12] Stevens and Dubois found the extremely low self-quenching constant for the fluorescence of phenanthrene, which was attributed to the rapid excimer dissociation at room temperature.[13] At any rate, the excimer formation of phenanthrene seems to be more difficult than that of other aromatic hydrocarbons such as pyrene. The fluorescence spectrum of a phenanthrene derivative, 9-cyano-10-methoxyphenanthrene, in a benzene solution at room temperature exhibited a red-shifted component with an increase in the concentration, suggesting excimer fluorescence, although the monomer fluorescence considerably remained.[14] Concerned with phenanthrenophanes, Staab et al. could detect the excimer fluorescence of [2.2](2,7)-phenanthrenophane, a mixture of the syn and anti isomers, in a fluorene host crystal at 4.2 K, though no mention was made about the spectrum at room temperature.[15] In contrast to the [2.2]phenanthrenophanes prepared so far,[4,5] the obtained ones in this study are kept exclusively in a syn conformation. Therefore, they are considered to produce the intramolecular excimer efficiently and facilitate the observation of its fluorescence.

In this paper, the synthesis, structure, and electronic properties of the first *syn*-[2.2](1,6)- and -(3,6)phenanthrenophanes, **1a**,**b**, are described in detail.

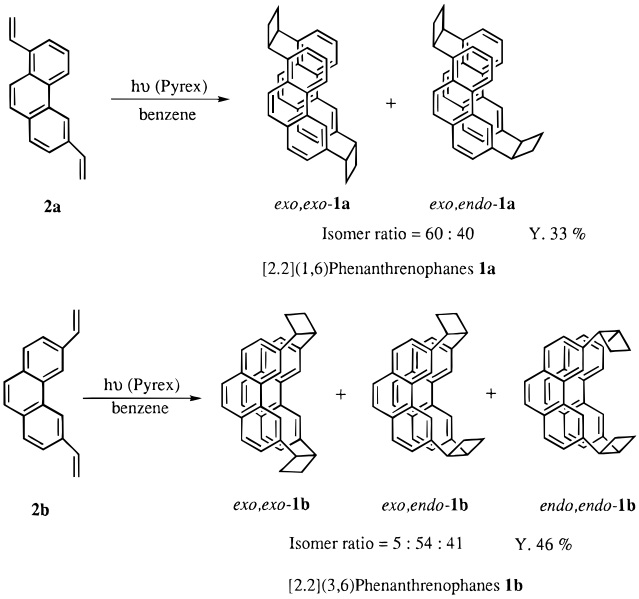
Scheme 1. Preparation of 1,6- and 3,6-Divinylphenanthrene[a]



3a (2,4'-) **4a** (1,6-) **2a** (1,6-)
3b (4,4'-) **4b** (3,6-) **2b** (3,6-)

[a] (a) *hν*, I_2/benzene, (b) $(n\text{-Bu})_3SnCH{=}CH_2$, $(Ph_3P)_4Pd$/toluene.

Scheme 2. Photoreaction of Divinylphenanthrene **2a**,**b**



Results and Discussion

Preparation of Divinylphenanthrenes. The synthesis of divinylphenanthrenes **2a**,**b** is shown in Scheme 1. Vinylarenes are generally prepared either by Stille reaction of the corresponding bromides or triflates[16] or by Wittig reaction of aryl aldehydes. Thus, we synthesized 1,6-dibromophenanthrene (**4a**) from 2,4′-dibromostilbene (**3a**)[17] in a manner similar to that in 3,6-dibromophenanthrene (**4b**),[18] which had been prepared from 4,4′-dibromostilbene (**3b**) by Blackburn et al.[18] Vinylation of dibromides **4a**,**b** was carried out by palladium-catalyzed displacement in good yield.[16a,b]

Preparation and Characterization of [2.2]Phenanthrenophanes. Intermolecular [2 + 2] photocycloaddition of divinylphenanthrenes (**2a**,**b**) was performed with a 400-W high-pressure mercury lamp through a Pyrex filter in dry benzene (100 mmol/L) under a nitrogen atmosphere (Scheme 2). After appropriate periods, the reaction mixture was evaporated and then treated with borane−THF complex in order to react with the remaining olefins. The purification by column chromatography on silica gel gave desired phenanthrenophanes **1a**,**b** as mixtures of structural isomers.

The photocycloaddition of **2a**,**b** afforded **1a** as a mixture of two isomers in 33% yield and **1b** as a mixture of three isomers in 46% yield, respectively. These isomers are derived from the difference in the direction of the cyclobutane rings. The

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Table 1. Comparison of ^{1}H NMR Spectroscopic Data among **1a**, **1b**, **5b**, and Phenanthrene

	chemical shift, δ						
position	$\delta_{exo,endo\text{-}\mathbf{1a}}$	$\delta_{exo,exo\text{-}\mathbf{1a}}$	$\delta_{exo,exo\text{-}\mathbf{1b}}$	$\delta_{exo,endo\text{-}\mathbf{1b}}$	$\delta_{endo,endo\text{-}\mathbf{1b}}$	$\delta_{\mathbf{5b}}$	$\delta_{phenanthrene}$
1			7.49	7.50	7.40	7.76	8.12
2	7.10	7.07	7.28	7.31 (exo side)	7.06	7.41	7.82
3	7.85	7.72					7.88
4	7.10	7.07	8.61	8.72	9.11	8.52	8.93
5	7.67	7.30	8.61	8.99	9.11	8.52	8.93
6							7.88
7	6.52	6.95	7.28	7.03 (endo side)	7.06	7.41	7.82
8	6.99	7.12	7.49	7.38	7.40	7.76	8.12
9	6.99	7.00	7.28	7.26	7.28	7.60	7.71
10	7.46	7.44	7.28	7.27	7.28	7.60	7.71

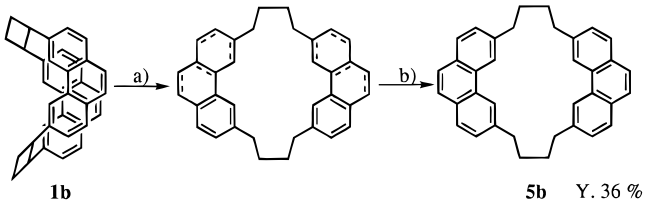
two isomers of **1a** were found to be of exo,exo and exo,endo configurations, and the three of **1b** exo,exo, exo,endo, and endo,endo ones, as described below. The two isomers of **1a** were isolated by the reversed-phase HPLC. The three isomers of **1b** were separated into one (exo,exo) and two isomers (exo,endo and endo,endo) by the reversed-phase HPLC, and the latter two isomers were separated by gel permeation chromatography. The structures of the isolated phenanthrenophanes were mainly determined by NMR spectroscopy including NOESY and COSY experiments. The isomer ratio was determined on the basis of the peak areas of ^{1}H NMR spectra and HPLC charts: *exo,exo*-**1a**:*exo,endo*-**1a** = 60:40; *exo,exo*-**1b**:*exo,endo*-**1b**:*endo,endo*-**1b** = 5:54:41.

The chemical shifts for the aromatic protons of **1a**,**b** and phenanthrene itself are summarized in Table 1 for comparison. The aromatic protons of **1a**,**b** generally resonate at higher fields than those of phenanthrene itself because of the shielding effect of the aromatic nuclei, though the high-field shifts are more remarkable in **1a** than in **1b**. Both **1a** and **1b** are, therefore, concluded to have a syn conformation. The observed syn selectivity is explained as follows. When a cyclobutane ring is formed by the first photocycloaddition, the two phenanthrene rings can be in either syn or anti conformation. In the second cycloaddition, however, the anti intermediate cannot yield desired intramolecular photocycloadducts, but only byproducts such as polymer, since the two vinyl groups are too far apart to react with each other. On the other hand, the intramolecular two vinyl groups in the syn intermediate can easily react within a molecule due to their closeness, leading to the second cycloaddition. The obtained *syn*-[2.2]phenanthrenophanes were never found to bring about the interconversion into anti isomers at room temperature.

The two isomers of **1a** are derived from the difference in the direction of the cyclobutane ring at C6 (exo or endo). The cyclobutane ring on C1 is considered to face only the exo direction because of the steric hindrance with the C10 hydrogen (peri-hydrogen), while that on C6 can be directed to the both sides. The steric effect of the cyclobutane ring at C6 on the C5 and C7 hydrogens is clearly represented by the chemical shift of their ^{1}H NMR signals as shown in Table 1; the C5 proton in the exo,endo isomer whose cyclobutane ring at C6 faces to the C5 side resonates at a lower field than that in the exo,exo-isomer, while the C7 protons are in the reverse relationship. These interactions, however, were not detected clearly by the NOESY experiments.

On the other hand, the two cyclobutane rings in **1b** can be directed to the both sides, giving the three isomers. Their conformation could be determined on the basis of the signals for the protons on C4 and C5 in the ^{1}H NMR spectra. The protons on C4 and C5 in the *exo,endo*-**1b** are not equivalent, in contrast to those in the other two isomers with C_{2v} symmetry. The C4 and C5 protons of the *endo,endo*-**1b** resonate at the lowest field among the three due to the greatest influence of the cyclobutane rings, while those of the *exo,exo*-**1b** resonate at the highest field. Furthermore, NOE interaction was observed between the aromatic protons (C4 and C5 hydrogens) and the methine protons of cyclobutane rings in *exo,exo*-**1b** and between the aromatic protons (C4 and C5 hydrogens) and the methylene protons of the cyclobutane rings in *endo,endo*-**1b**.

Scheme 3. Birch reduction of **1b**[a]



[a] (a) NH_3Na/Bu^{t}OH, −60 °C, 30 min. (b) DDQ/decalin, 170 °C, 1 h.

Birch Reduction of [2.2]Phenanthrenophanes to [4.4]-Phenanthrenophanes. Cyclobutane rings are known to be opened regioselectively by electron-transfer reactions such as Birch reduction.[19] Especially, the cyclobutane rings at the benzyl position are readily opened by this reaction to afford a tetramethylene unit.[20] Several [2.*n*]cyclophanes can be readily converted into the corresponding [4.*n*]cyclophanes by Birch reduction in more than 60% yield.[21] The ring expansion reaction of [2.*n*]-[22] and [2.2]naphthalenophanes[3c] was also carried out by Birch reduction and subsequent DDQ oxidation of the overreduced aromatic rings.

Thus, this method was applied to the transformation of [2.2]-phenanthrenophanes into [4.4]phenanthrenophanes. The two-isomer mixture of **1a** afforded no desired [4.4]phenanthrenophane, probably because of the severe oxidation conditions by DDQ. On the other hand, the three-isomer mixture of **1b** could be successfully converted into the desired [4.4](3,6)-phenanthrenophane **5b** (Scheme 3) in 36% yield.

[4.4](3,6)Phenanthrenophane **5b**, characterized mainly by ^{1}H and ^{13}C NMR spectroscopy, was found to be a single isomer due to the cleavages of the cyclobutane rings, in contrast with the three-isomer mixture of **1b**. As shown in Table 1, the C4 and C5 protons of **5b** resonate at higher fields than the corresponding ones of **1b**, while the other aromatic protons of **5b** resonate at lower fields. These changes in the chemical shifts are considered to be obviously brought about by changes in the conformation of the phenanthrenophanes, probably from syn to anti conformation. By such a change, the shielding effect on the C4 and C5 protons should be increased, in contrast to

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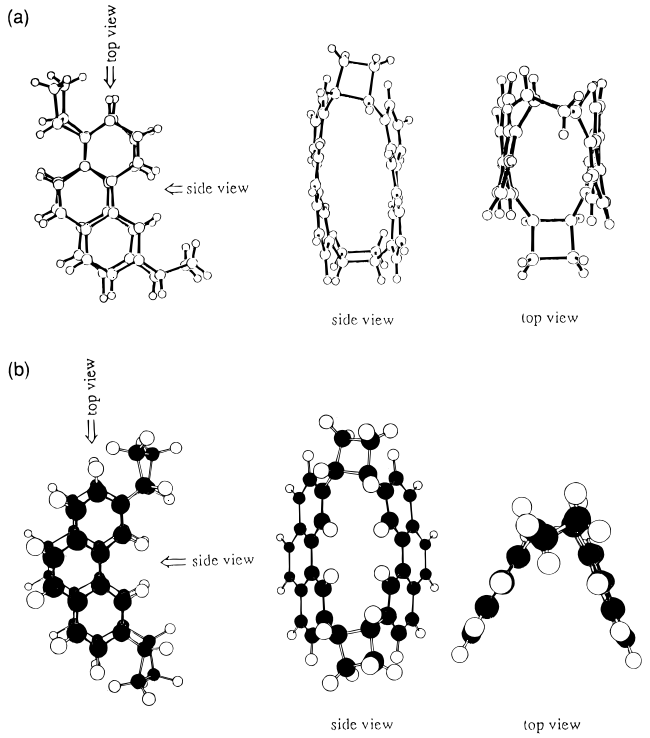

Figure 1. Side and top views of (a) *exo,endo*-**1a** (X-ray crystallographic analysis) and (b) *exo,exo*-**1b** (MM2 calculations).

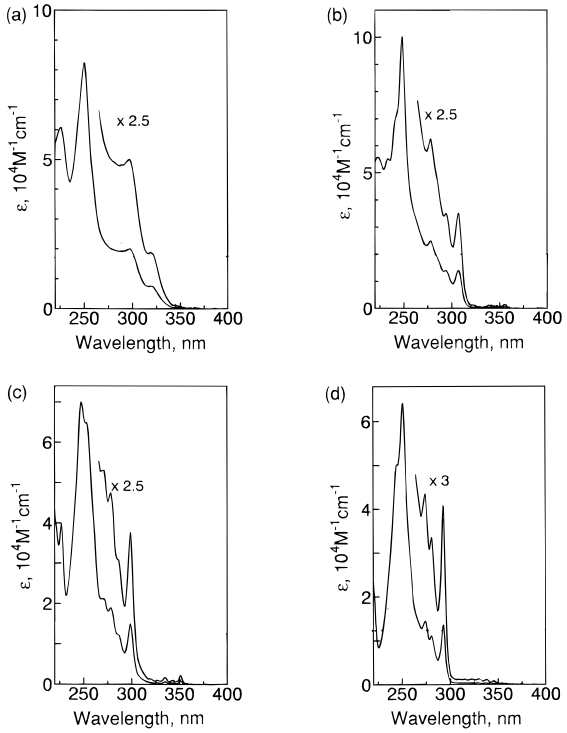

Figure 2. Absorption spectra of (a) *exo,exo*-**1a**, (b) *exo,exo*-**1b**, (c) **5b**, and (d) phenanthrene in cyclohexane at room temperature.

the decrease on the other protons. In the mass spectra, the molecular ion peak of **5b** was observed much more clearly than that of **1b**; the molecular ion peak ($m/z = 464$) was the base peak in **5b**, while that of **1b** ($m/z = 460$) was with an intensity of about 1% of the base ion peak ($m/z = 230$). These results indicate that **5b** is more flexible, more stable, and less strained than **1b**, arising from the loss of the two cyclobutane rings with much strain.

Structures of [2.2]Phenanthrenophanes. It is apparent that both **1a** and **1b** are in a syn conformation, according to the results of ^{1}H NMR. Strictly speaking, however, the arrangement of the two phenanthrene rings is expected to be different between **1a** and **1b**, since the aromatic protons of **1a** resonate at quite higher fields than those of **1b**, as described above, suggesting a larger shielding effect in **1a**. It is necessary and interesting to investigate the structure and electronic properties of **1a**,**b** closely.

X-ray crystallographic analysis of *exo,endo*-**1a** was successful among all the synthesized phenanthrenophanes. The side and top views are shown in Figure 1a. The optimal structures of **1b** and *exo,exo*-**1a**, whose appropriate single crystals have not been obtained, were determined by the MM2 calculations. These calculations are sufficiently reliable because the calculated structure of *exo,endo*-**1a** is in good agreement with that by X-ray analysis. The structure of *exo,exo*-**1b** is shown in Figure 1b as a representative of **1b**.

The two phenanthrene rings in *exo,endo*-**1a** are held almost in parallel by the two cyclobutane rings on the opposite sides and fully overlap with each other. The average interplanar distance is about 3.5 Å (nearest 2.88 Å (C1 position); farthest 4.07 Å (C4 position)). Each phenanthrene ring, however, is slightly distorted for the release of the strain in the molecule. According to the MM2 calculations, the arrangement of the two phenanthrene rings in *exo,exo*-**1a** was virtually the same as that in *exo,endo*-**1a**, in spite of the difference in the direction of the cyclobutane ring at the C6 position.

On the other hand, the two phenanthrene rings in *exo,exo*-**1b**, connected by the two cyclobutane rings on the one side (C3−C6 side), are tilted by the dihedral angle of ca. 30°, as shown in Figure 1b. The interplanar distance is ca. 3.0 Å on the C3−C6 side and ca. 6.0 Å on the C9−C10 side. The planarity of the phenanthrene rings is still maintained because of much less strain than in **1a**. The other isomers, *exo,endo*- and *endo,endo*-**1b**, were found to have structures quite similar to that of *exo,exo*-**1b**.

Thus, the structures of the two phenanthrenophanes **1a**,**b** exhibited a remarkable contrast to each other, though little depending on the direction of their cyclobutane rings. The greater high-field shift of the aromatic protons in **1a** than in **1b** can be explained reasonably in terms of the difference in their structures.

Absorption Spectra. The absorption spectra of [2.2]phenanthrenophanes **1a**,**b** and [4.4]phenanthrenophane **5b** were measured in cyclohexane at room temperature, along with phenanthrene itself as the reference. No distinct difference was observed between the two isomers of **1a** and among the three of **1b**; the absorption spectra were almost independent of the direction of the cyclobutane rings, as expected from their structures. Figures 2 a−d show the spectra of *exo,exo*-**1a**,**b**, **5b**, and phenanthrene.

The absorption bands of phenanthrene itself have been well characterized so far.[23] The extremely weak vibrational structures ($\epsilon \sim 200$) in the region 300−350 nm are the $S_1(^1L_b) \leftarrow S_0(^1A)$ band, and those around 270−300 nm are the $S_2(^1L_a) \leftarrow S_0(^1A)$, whose 0−0 transition is located at 292 nm ($\epsilon \sim 14\,000$). The strong band ($\epsilon \sim 60\,000$) at 250 nm is interpreted by the $S_4(^1B_a) \leftarrow S_0(^1A)$ rather than the $S_3(^1B_b) \leftarrow S_0(^1A)$, which is masked by the much stronger ^1B_a band due to the closeness between the ^1B_a and ^1B_b bands. Phenanthrenophanes **1b** and **5b** also exhibited vibrational structures, as in phenanthrene. It is reasonable to assign the quite weak bands around 320−350 nm and the rather strong ones around 270−310 nm to the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions, respectively, by the comparison of

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Table 2. Position of 0−0 Transition in $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ Absorption Bands and Peak Position of $S_4 \leftarrow S_0$ Band in **1b**, **5b**, and Phenanthrene[a]

	$S_1(^1L_b) \leftarrow S_0(^1A)$	$S_2(^1L_a) \leftarrow S_0(^1A)$	$S_4(^1B_a) \leftarrow S_0(^1A)$
	0−0 transition, nm	0−0 transition, nm (ϵ, 10^4 M^{-1} cm^{-1})	band peak, nm (ϵ, 10^4 M^{-1} cm^{-1})
1b	355	307 (1.4)	249 (10.0)
5b	351	298 (1.5)	248 (7.0)
phenanthrene	346	292 (1.4)	251 (6.4)

[a] The ^1B_b band due to the $S_3 \leftarrow S_0$ transition was probably masked by the strong absorption of the ^1B_a band. For details, see text.

their position, absorbance, and shape with those for phenanthrene. The 0−0 transitions of the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ bands in **1b** and **5b** are summarized in Table 2. These bands are apparently red-shifted and broadened relative to those inphenanthrene. The strong bands around 250 nm in **1b** and **5b** are probably due to the $S_4(^1B_a) \leftarrow S_0(^1A)$ transition, as in phenanthrene. The peak positions of the bands are almost unchanged (Table 2), though the shape appears to depend on the compounds to some extent. The band shape in **1b** is similar to that in phenanthrene, while that in **5b** is relatively broad with a shoulder on the lower wavenumber side. Such difference in the band shape may be correlated with the relative position and/or intensity between the $S_3 \leftarrow S_0$ and $S_4 \leftarrow S_0$ bands. Thus, it is possible that the broadening and shoulder in **5b** suggest the larger contribution of the $S_3 \leftarrow S_0$ band than that in cases of both **1b** and phenanthrene, although the details are unknown at present. The red shift and broadening of the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ bands in **1b** and **5b** are considered to be brought about not only by the presence of the substituent groups at the C3 and C6 positions but also by the intramolecular electronic interaction between the two phenanthrene rings. The red shift in **1b** is more remarkable than in **5b**, obviously indicating the greater intramolecular interaction in **1b** than in **5b**, since the overlap between the two phenanthrene rings of **1b** in a syn conformation is considered to be larger than that of **5b** in an anti conformation, though much smaller compared to that of **1a**.

The absorption spectrum of **1a** exhibited considerable broadening. The $S_1 \leftarrow S_0$ band could be hardly appreciated due to its weakness. The $S_2 \leftarrow S_0$ band is further red-shifted relative to those in **1b** and **5b**; the 0−0 transition seems to be located at 320 nm, though the unambiguous assignment is difficult. Such broadening and the red shift are apparently ascribable to the much greater intramolecular transannular interaction between the two phenanthrene rings tightly held in parallel, in contrast to those of **1b**.

Thus, the difference in the structures among **1a**,**b**, and **5b** was clearly reflected by their absorption spectra. It is surprising that the spectrum of **1b** is similar to that of **5b** in an anti conformation rather than that of **1a** in a syn conformation. In the arrangement of **1b** in Figure 1b, the two phenanthrene rings in a tilted form are not able to interact with each other sufficiently.

Fluorescence Spectra. The fluorescence spectra of **1a**,**b** and **5b** were measured in cyclohexane at room temperature. The spectra were almost independent of the excitation wavelength. The isomers derived from the direction of their cyclobutane rings in **1a**,**b** exhibited the same spectra in each case. Figure 3 a−d illustrates the fluorescence spectra of *exo*,*exo*-**1a**,**b**, **5b**, and phenanthrene upon 250-nm excitation as representatives.

The fluorescence spectra of **1b** and **5b** exhibit sharp vibrational structures, corresponding to the mirror image of the $S_1 \leftarrow S_0$ absorption band, as in the case of phenanthrene. In both **1b** and **5b**, however, all of the peaks are slightly broadened and red-shifted relative to those in phenanthrene, as summarized

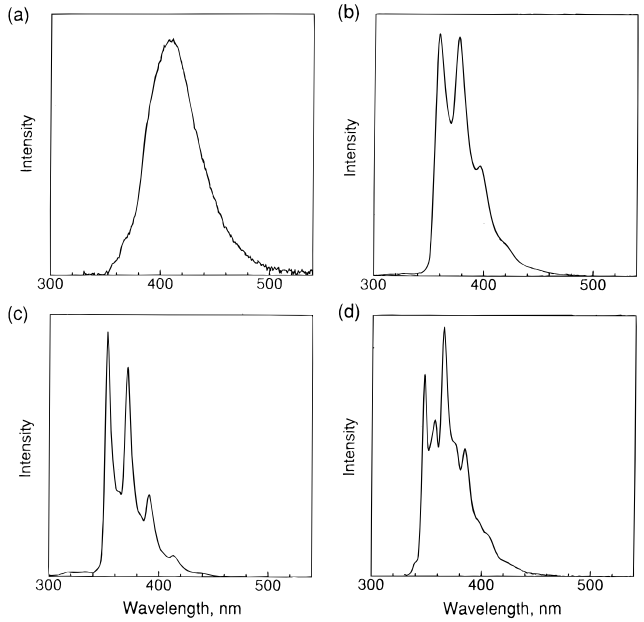

Figure 3. Fluorescence spectra of (a) *exo*,*exo*-**1a**, (b) *exo*,*exo*-**1b**, (c) **5b**, and (d) phenanthrene upon 250-nm excitation in cyclohexane at room temperature.

Table 3. Peak Position of Fluorescence Spectra of **1b**, **5b**, and Phenanthrene

	peak position, nm					
1b	357,		377,		396,	∼420s[a]
5b	352,		371,		390,	414
phenanthrene	347,	357,	365,	375,	384,	∼405s[a]

[a] The suffix "s" denotes a shoulder.

in Table 3, and some peaks observed in phenanthrene are too much weakened to be recognized. The relative intensity of the 0−0 transition in **1b** and **5b** is increased compared to that in phenanthrene. These features in **1b** and **5b** indicate the presence of the intramolecular interaction between the two aromatic nuclei in the excited state, though it is not strong enough to lead to the formation of the excimer, as in the case of the 9-(hydroxymethyl)phenanthrene sandwich pair.[12] The failure to form excimers is obvious from the quite small Stokes shifts (∼100 cm^{-1}) in **1b** and **5b**, which are comparable to that in phenanthrene, as can be seen from a comparison between Tables 2 and 3. Therefore, the fluorescence of **1b** and **5b** is interpreted in terms of that from the locally excited singlet state having a weak intramolecular interaction. The spectrum of **1b** shows a larger red shift and broadening compared with the case of **5b**, probably resulting from the larger interaction than that in **5b**, in agreement with the results of the absorption spectra.

On the other hand, **1a** exhibited an entirely different fluorescence spectrum, as shown in Figure 3a. It is a broad and structureless emission with a peak at 410 nm, much red-shifted in comparison with that of **1b** and phenanthrene; the red shifts are ca. 3600 and 4400 cm^{-1} relative to the emissions of **1b** and phenanthrene, respectively. These shifts are apparently larger than those in the absorption spectrum of **1a** versus **1b** and phenanthrene. In the S_1 state of **1a**, much larger intramolecular interaction between the two phenanthrene rings is established than in the ground state. In other words, the structure in the S_1 state of **1a** is different from that in the ground state; the two aromatic moieties get close to each other in the excited state. Therefore, it is reasonable to assign the fluorescence observed for **1a** to the intramolecular excimer ($^1EX^*$) emission. Excimer fluorescences are usually observed with a red shift of 5000−6000 cm^{-1} relative to the corresponding

monomer fluorescences.[24] The observed red shift in **1a** is slightly smaller, probably because the two aromatic moieties cannot approach to the most stable conformation in the S_1 state, due to its relatively rigid structure. The fluorescence spectrum of **1a** is similar to the delayed excimer fluorescence of phenanthrene at low temperatures reported by Azumi et al.,[11] though the peak is shifted to shorter wavelengths (for phenanthrene, 430 nm). It is also similar to the excimer fluorescence of [2.2](2,7)phenanthrenophanes at 4.2 K by Staab et al., including the position of the maximum.[15] To the best of our knowledge, the excimer fluorescence so far observed for phenanthrene derivatives at room temperature contains vibrational structures suggesting monomer-like components. The emission spectrum of **1a** is the first observation of the excimer fluorescence almost free from the monomer-like fluorescence for phenanthrene derivatives *at room temperature*. This easy detection of the excimer fluorescence in **1a** is apparently derived from the conformation of the two phenanthrene rings which are kept tightly in parallel by the two cyclobutane rings.

The fluorescence excitation spectra of **1a**,**b** and **5b**, monitored at the maximum of each fluorescence spectrum, were in good agreement with the corresponding absorption spectra. It is concluded that the observed fluorescence undoubtedly results from the lowest excited singlet state of each compound.

The emission spectra were also measured at 77 K in MP (methylcyclohexane:isopentane = 3:1 (v/v)). The obtained spectra were almost the same as those at room temperature, though the vibrational structures in **1b** and **5b** became slightly sharper at 77 K. No excimer fluorescence was observed for **1b** at all because this molecule is conformationally hardly changeable to form a suitable excimer structure due to its rigidity.

The fluorescence spectra of **1a**,**b** were considerably different from each other. Although this difference was more remarkable than that in the absorption spectra, the whole tendency for **1a**,**b**, and **5b** resembled that in the absorption spectra; the deviation of their absorption and fluorescence spectra from those of phenanthrene becomes larger in the order **5b** < **1b** ≪ **1a**, reflecting the magnitude of the intramolecular electronic interaction.

Conclusion

We have succeeded in the selective synthesis of *syn*-[2.2]-phenanthrenophanes (**1a**,**b**) for the first time by means of intermolecular [2 + 2] photocycloaddition of the corresponding divinylphenanthrenes. Although both **1a** and **1b** are apparently in a syn conformation, the arrangements of the two phenanthrene rings were found to be quite different from each other. This structural difference had a significant effect on their electronic properties in the ground state as well as the excited state, as revealed by the absorption and fluorescence spectra. Especially, the fluorescence spectra are entirely different from each other: the intramolecular excimer fluorescence was observed for **1a** in a parallel form, whereas the fluorescence from the locally excited state for **1b** was in a tilted form. The former is the first observation of excimer fluorescence almost free from the monomer-like components of phenanthrene derivatives at room temperature. It is enabled by the presence of the two cyclobutane rings; they keep the two phenanthrene rings rigidly in a parallel conformation favorable for the excimer formation and prevent the dissociation which would be extremely rapid without such bridging units. The fact that no excimer fluorescence is detected for **1b** is in contrast to the case of the naphthalenophanes, in which the excimer fluorescence is detected for not only parallel forms but also tilted forms and antiparallel forms.[8d] The excimer formation of phenanthrenes may be influenced by the arrangement much more sensitively.

(24) Klöpffer, W. *Organic Molecular Photophysics*; Birks, J. B., Ed.; John Wiley and Sons: New York, 1973; Vol. 1, p 357.

Experimental Section

General Procedure. NMR spectra were recorded on a JEOL Alpha-500 FT NMR spectrometer. Mass spectra were measured on a JEOL JMS-DX302 mass spectrometer. HPLC analysis was performed with a Shimadzu LC-6A pump, an LC-6A UV detector, and an RC4A data processor. Gel permeation chromatography was performed on a Japan Analytical Industry LC-08 system. Melting points are uncorrected. Absorption spectra were recorded on a JASCO Ubest-50 spectrophotometer. Fluorescence spectra and fluorescence excitation spectra were measured on a Hitachi-4010 spectrofluorimeter. These spectra were obtained in cyclohexane (spectroscopic grade) with a quartz cell of 10-mm optical path. The sample concentration is in the range 10^{-5} -10^{-4} M.

1,6-Dibromophenanthrene (4a). The mixture of *trans*-2,4′-dibromostilbene (**3a**) (3.0 g, 8.9 mmol) and iodine (56.3 mg, 0.44 mmol) was dissolved in benzene (450 mL) in a Pyrex flask and then irradiated by a 400-W high-pressure mercury lamp while being monitored by TLC (SiO_2, hexane). Irradiation was continued until the disappearance of the reactant olefin (after about 20 h). The reaction mixture was evaporated and purified by column chromatography (SiO_2, hexane−benzene) to afford **4a** as a colorless solid (2.4 g, 79.7%): mp 158−159 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.81 (1H, s, C5-H), 8.59 (1H, d, J = 8.5, C4-H), 8.23 (1H, d, J = 9.2, C8-H), 7.92 (1H, d, J = 7.6, C2-H), 7.80 (1H, d, J = 8.9, C10-H), 7.80 (1H, d, J = 8.9, C9-H), 7.73 (1H, d, J = 9.2, C7-H), 7.52 (1H, dd, J = 7.6 and 8.5, C3-H). Anal. Calcd for $C_{14}H_8Br_2$: C, 50.04; H, 2.40. Found: C, 50.05; H, 2.62.

3,6-Dibromophenanthrene (4b). 3,6-Dibromophenanthrene (**4b**) was synthesized in a way similar to that in the literature[18] (yield 77.2%): mp 187−188 °C (lit.[18] 194 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.70 (2H, s, C4- and C5-H), 7.75 (2H, d, J = 8.6, C1- and C8-H), 7.70 (2H, d, J = 8.6, C2- and C7-H), 7.69 (2H, s, C9- and C10-H).

1,6-Divinylphenanthrene (2a).[16a,b] To a solution of 1,6-dibromophenanthrene (**4a**) (3.0 g, 9.0 mmol) in toluene (357 mL) were added tri-*n*-butylvinylstannane (11.4 g, 35.7 mmol), prepared from vinylmagnesium bromide and tri-*n*-butyltin chloride, tetrakis(triphenylphosphine)palladium(0) (443.3 mg, 0.36 mmol), and a few crystals of 4-*tert*-butylcatechol as a polymerization inhibitor. The resulting suspension was heated to reflux for 4 h, cooled to room temperature, filtrated, concentrated, and then diluted with ether. The ether solution was treated with 20% aqueous potassium fluoride solution (70 mL) and stirred vigorously for 30 min. The ether phase was decanted from the aqueous phase containing the solid of tin fluoride polymer and evaporated. The residue was purified by column chromatography (SiO_2, hexane−benzene) to afford **2a** as a colorless solid (1.81 g, 87.6%): mp 79−80 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.68 (1H, d, J = 8.3, C4-H), 8.63 (1H, s, C5-H), 8.03 (1H, d, J = 9.2, C8-H), 7.85 (1H, d, J = 8.2, C10-H), 7.74 (1H, d, J = 8.2, C9-H), 7.73 (1H, d, J = 7.3, C2-H), 7.75 (1H, d, J = 9.2, C7-H), 7.63 (1H, dd, J = 8.3 and 7.3, C3-H), 7.54 (1H, dd, J = 17.4 and 11.0, C1-C*H*=CH_2), 7.00 (1H, dd, J = 17.4 and 11.0, C6-C*H*=CH_2), 5.96 (1H, d, J = 17.4, C6-CH=CH_2 (trans)), 5.81 (1H, dd, J = 17.4 and 1.5, C1-CH=CH_2 (trans)), 5.52 (1H, dd, J = 11.0 and 1.5, C1-CH=CH_2 (cis)), 5.39 (1H, d, J = 11.0, C6-CH=CH_2 (cis)); LRMS *m/z* (relative intensity) 230 (100, M^+), 202 (35). Anal. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.66; H, 6.19.

3,6-Divinylphenanthrene (2b). 3,6-Divinylphenanthrene (**2b**) was synthesized in the same way as **2a** (yield 93.8%): mp 69−70 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.60 (2H, s, C4- and C5-H), 7.82 (2H, d, J = 8.3, C1- and C8-H), 7.73 (2H, d, J = 8.3, C2- and C7-H), 7.67 (2H, s, C9- and C10-H), 7.00 (2H, dd, J = 17.2 and 11.0, Ar-C*H*=CH_2), 5.95 (2H, d, J = 17.2, Ar-CH=CH_2 (trans)), 5.39 (2H, d, J = 11.0, Ar-CH=CH_2 (cis)); LRMS *m/z* (relative intensity) 230 (100, M^+), 202 (20). Anal. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.78; H, 6.12.

Intermolecular [2 + 2] Photocycloaddition toward 1,2-Ethano-*syn*-[2.2](1,6)phenanthrenophane (1a). 1,6-Divinylphenanthrene **2a** (1.0 g, 4.3 mmol) dissolved in dry benzene (40 mL) was placed in a

Pyrex flask equipped with a magnetic stirrer, reflux condenser, and nitrogen inlet. It was irradiated with a 400-W high-pressure mercury lamp under a nitrogen atmosphere while being monitored by TLC (SiO_2, hexane/benzene = 7/3). When polymerization predominated over the formation of the desired cyclophanes after about 5 h, irradiation was ceased. The reaction mixture was evaporated and then purified by column chromatography (SiO_2, hexane−benzene) to afford the mixture of *exo,exo*- and *exo,endo*-**1a** as a colorless solid (total: 0.33 g, 33%). Both isomers were separated by the reversed-phase HPLC (ODS column, methanol).

***exo,exo*-1a**: mp > 250 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.72 (2H, dd, J = 4.9 and 4.6, C3-H), 7.44 (2H, d, J = 9.0, C10-H), 7.30 (2H, s, C5-H), 7.12 (2H, d, J = 8.3, C8-H), 7.07 (2H, d, J = 4.9, C2-H), 7.07 (2H, d, J = 4.6, C4-H), 7.00 (2H, d, J = 9.0, C9-H), 6.95 (2H, d, J = 8.3, C7-H), 5.1 (2H, m, C1-methine), 4.4 (2H, m, C6-methine), 2.9 (8H, m, methylene); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.95, 137.24, 130.25, 129.85, 129.75, 129.28, 126.94, 126.35, 125.08, 125.04, 124.76, 124.52, 121.19, 119.93, 47.20, 42.20, 22.27, 21.37; LRMS *m/z* (relative intensity) 460 (1.3, M^+), 230 (100); HRMS *m/z* 460.2178, calcd for $C_{36}H_{28}$ 460.2192.

***exo,endo*-1a**: mp > 250 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.85 (2H, dd, J = 6.0 and 3.4, C3-H), 7.67 (2H, s, C5-H), 7.46 (2H, d, J = 9.2, C10-H), 7.10 (2H, d, J = 6.0, C2-H), 7.10 (2H, d, J = 3.4, C4-H), 6.99 (2H, d, J = 8.6, C8-H), 6.99 (2H, d, J = 9.2, C9-H), 6.52 (2H, d, J = 8.6, C7-H), 5.1 (2H, m, C1-methine), 4.4 (2H, m, C6-methine), 2.9 (8H, m, methylene); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.74, 137.26, 130.48, 130.21, 129.82, 129.41, 129.16, 126.78, 125.00, 124.75, 124.60, 123.04, 121.22, 119.96, 46.69, 42.56, 22.31, 21.05; LRMS *m/z* (relative intensity) 460 (2.5, M^+), 230 (100); HRMS *m/z* 460.2192, calcd for $C_{36}H_{28}$ 460.2192.

Intermolecular [2 + 2] Photocycloaddition toward 1,2-Ethano-*syn*-[2.2](3,6)phenanthrenophane (1b). 3,6-Divinylphenanthrene **2b** (0.48 g, 2.1 mmol), irradiated in the same way as **2a**, afforded the three-isomer mixture of **1b** as a colorless solid (total: 0.22 g, 46%). From the mixture, only the *exo,exo*-**1b** was isolated by the reversed-phase HPLC (ODS column, methanol). The residual two isomers (*exo,endo*- and *endo,endo*-**1b**) were separated by gel permeation chromatography (polystyrene gel column, chloroform).

***exo,exo*-1b**: mp > 250 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.61 (4H, s, C4- and C5-H), 7.49 (4H, d, J = 8.4, C1- and C8-H), 7.28 (4H, d, J = 8.4, C2- and C7-H), 7.28 (4H, s, C9- and C10-H), 4.59 (4H, m, methine), 2.73 (8H, m, methylene); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.81, 129.81, 128.95, 127.97, 125.51, 124.23, 124.00, 45.50, 23.71; LRMS *m/z* (relative intensity) 460 (1.5, M^+), 230 (100); HRMS *m/z* 460.2211, calcd for $C_{36}H_{28}$ 460.2192.

***exo,endo*-1b**: mp > 250 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.99 (2H, s, C5-H), 8.72 (2H, s, C4-H), 7.50 (2H, d, J = 8.1, C1-H), 7.38 (2H, d, J = 8.1, C8-H), 7.31 (2H, d, J = 8.1, C2-H), 7.27 (2H, s, C10-H), 7.26 (2H, s, C9-H), 7.03 (2H, d, J = 8.1, C7-H), 4.65 (2H, m, exo-methine), 4.43 (2H, m, endo-methine), 2.92 (4H, m, endo-methylene), 2.74 (4H, m, exo-methylene); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 139.32, 138.96, 130.11, 129.84, 129.12, 128.13, 128.04, 128.04, 127.70, 125.65, 125.43, 124.26, 124.01, 121.46, 46.71, 45.57, 24.88, 23.81; LRMS *m/z* (relative intensity) 460 (0.4, M^+), 230 (100); HRMS *m/z* 460.2210, calcd for $C_{36}H_{28}$ 460.2192.

***endo,endo*-1b**: mp > 250 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.11 (4H, s, C4- and C5-H), 7.40 (4H, d, J = 7.9, C1- and C8-H), 7.28 (4H, s, C9- and C10-H), 7.06 (4H, d, J = 7.9, C2- and C7-H), 4.46 (4H, m, methine), 2.96 (8H, m, methylene); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 139.42, 130.17, 129.29, 128.06, 127.74, 125.56, 121.33, 46.64, 25.12; LRMS *m/z* (relative intensity) 460 (0.3, M^+), 230 (100); HRMS *m/z* 460.2169, calcd for $C_{36}H_{28}$ 460.2192.

[4.4](3,6)Phenanthrenophane (5b) (Birch Reduction). A 200-mL three-necked round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet, and gas inlet was cooled to ca. −60 °C over a dry ice−methanol bath. Ammonia gas was introduced into the system. When liquid ammonia (ca. 65 mL) was condensed, the gas inlet tube was replaced with a glass stopper. Sodium (ca. 1.3 g) was added carefully piece by piece into the liquid ammonia, and the mixture was stirred for 10 min. The three-isomer mixture of phenanthrenophanes **1b** (0.30 g, 0.65 mmol) and *tert*-butyl alcohol (2.6 mL) dissolved in dry THF (26 mL) were added slowly, and the mixture was stirred for 30 min. The excess sodium was destroyed by cautious addition of water. The ammonia was allowed to evaporate slowly in a hood. The residue was extracted with benzene (20 mL). The benzene extract was washed with water (20 mL × 3) and dried over anhydrous $MgSO_4$. After filtration and evaporation, the residue was purified by column chromatography (SiO_2, benzene−hexane) to give the Birch reduction product (ca. 250 mg).

In a 50-mL flask equipped with a magnetic stirrer, reflux condenser, and nitrogen inlet were placed the Birch reduction product prepared above and DDQ (980 mg, 5.4 mmol), which were dissolved in decalin (15 mL) under a nitrogen atmosphere. The reaction mixture was heated with stirring at 180 °C for 1 h. After the decalin was removed, the desired product **5b** was isolated by column chromatography (SiO_2, hexane−benzene) as a colorless solid (110 mg, 36.3%): mp 228−229 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.52 (4H, s, C4- and C5-H), 7.76 (4H, d, J = 8.3 Hz, C1- and C8-H), 7.60 (4H, s, C9- and C10-H), 7.41 (4H, d, J = 8.3 Hz, C2- and C7-H), 3.00 (8H, m, ArCH_2CH_2−), 1.92 (8H, m, Ar-CH_2-CH_2-); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.40, 130.38, 129.95, 128.57, 127.45, 125.82, 121.39, 35.81, 29.35; LRMS *m/z* (relative intensity) 464 (100, M^+), 245 (6), 231 (21), 219 (12), 218 (15), 217 (22), 205 (21), 191 (25); HRMS *m/z* 464.2504, calcd for $C_{36}H_{32}$ 464.2499.

X-ray Crystallographic Analysis.[25] A colorless prismatic crystal with approximate dimensions of 0.20 × 0.20 × 0.15 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC7S diffractometer with graphite monochromated Cu Kα radiation. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $55.21 < 2\theta < 56.94°$, corresponded to a primitive monoclinic cell with dimensions: a = 10.79(3) Å, b = 8.44(4) Å, c = 26.01(4) Å, β = 96.0(2)°, V = 2357(11) Å^3. For Z = 4 and fw = 460.62, the calculated density is 1.30 g/cm^3. The space group was determined to be $P2_1/n$ (no. 4). The data were collected at a temperature of 20 ± 1 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 120.3°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.38° with a take-off angle of 6.0°. Scans of (1.73 + 0.30 tan θ)° were made at a speed of 16.0 deg/min (in Ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of three scans), and the counts were accumulated to ensure good counting statistics. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 1.0 mm, the crystal to detector distance was 235 mm, and the computer-controlled detector aperture was set to 9.0 × 13.0 mm (horizontal × vertical). Of the 4001 reflections which were collected, 3774 were unique (R_{int} = 0.107). The intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied. The linear absorption coefficient, μ, for Cu Kα radiation is 5.5 cm^{-1}. The structure was solved by the direct method, SAPI91, and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atom coordinates were refined, but their isotropic B's were held fixed. The final cycle of full-matrix least-squares refinement was based on 2616 observed reflections ($I > 3.00\sigma(I)$) and 410 variable parameters and converged (largest parameter was 0.18 times its esd) with unweighted and weighted agreement factors of R = 0.072 and R_w = 0.050. The standard deviation of an observation of unit weight was 6.34.

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Supporting Information Available: ORTEP drawing, tables listing atomic and thermal parameters and bond lengths and angles for *exo,endo*-**1a**, and ^{1}H NMR spectra of **1a**,**b**, and **5b** (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(25) Available in the supporting information.