

# Stereocontrol in Cyclophane Synthesis: A Photochemical Method To Overlap Aromatic Rings

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## ABSTRACT

To overlap aromatic rings in cyclophanes, the inter- and intramolecular [2 + 2] photocycloaddition of vinylarenes has been developed. It gives cyclophanes, naphthalenophanes, phenanthrenophanes, thiophenophanes, and carbazolophanes in reasonable to excellent yields. The structures and properties of cyclophanes obtained are reviewed; especially the excimer emission of phenanthrenophanes, naphthalenophanes, and carbazolophanes stressed that many intriguing cyclophanes can be obtained through the fine molecular design of precursors.

## Introduction

In 1949, [2.2]paracyclophane **1** was prepared by the pyrolysis of *p*-xylene.<sup>1</sup> This event was most intriguing and was highlighted before the birth of cyclophane chemistry, which was coined and initiated by Cram.<sup>2</sup> With the efforts of many leading and eminent chemists, including Cram himself, the chemistry has attracted many researchers in organic and physical chemistry.

The principal aims of cyclophane chemistry are to determine how much strain can be loaded on a benzene ring, to examine how much aromaticity is changed in strained arenes, and to find the electronic properties of face-to-face arranged arene ring systems.<sup>3</sup> This field has been extended to host–guest chemistry, again coined by Cram, applying the rigidity and planarity of the arene rings in cyclophanes as shaping blocks.<sup>4</sup>

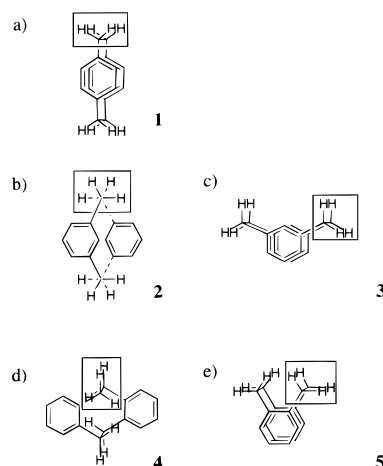
We developed a new synthetic method for cyclophanes having simple cyclobutane rings as tethers, and studied

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**FIGURE 1.** Heat of formation and dihedral angle of [2.2]cyclophane; structures are optimized by PM3. (a) Side view of [2.2]paracyclophane (60.4 kcal/mol; synperiplanar, 0.0°), (b) *anti*-[2.2]metacyclophane (46.3 kcal/mol; synclinal, 58.2°), (c) *syn*-[2.2]metacyclophane (52.5 kcal/mol; synperiplanar, 9.6°), (d) *anti*-[2.2]orthocyclophane (33.8 kcal/mol; anticlinal, 111.3°), and (e) *syn*-[2.2]orthocyclophane (36.8 kcal/mol; synclinal, 40.6°).

the properties of the cyclophanes obtained.<sup>5</sup> The method, namely [2 + 2] photocycloaddition of vinylarenes, has been further extended to calixarene and crown ether chemistry. Many unique, selective-ionophoric calixarenes and crown ethers have been prepared as a result of host–guest chemistry.<sup>5b</sup>

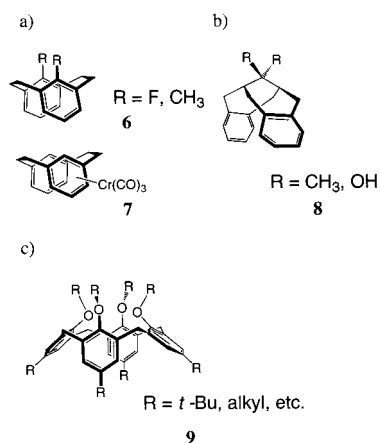
In this Account, we summarize our synthetic approach of inter- and intramolecular photocycloaddition, focusing on the scope and limitations and emphasizing the application to structural chemical studies. The relationship between the structures and the fluorescence emission properties is also discussed.

## Rigidifying Cyclophane Conformation

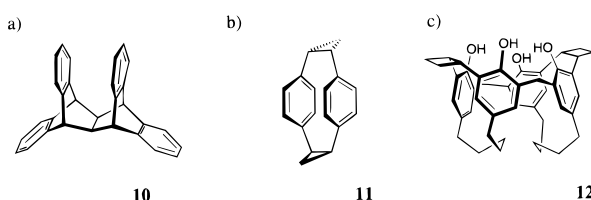
Cyclophane tethers sometimes can be locked into a synperiplanar conformation, because there is no choice of adopting other conformations as recognized in [2.2]-paracyclophane **1**. Yet, if cyclophanes can take a more stable conformation at the tethers than others, they can easily change their conformation to more stable one. For example, [2.2]metacyclophane and [2.2]orthocyclophane have two possible conformations around aromatic nuclei, unstable *syn* (synperiplanar and synclinal around ethano bridges) and stable *anti* (synclinal and anticlinal), the stability differences of which are estimated to be 6 and 3 kcal/mol, respectively (see Figure 1). Therefore, the rotation of aromatic nuclei occurs together with the conformational change of the tethers. Accordingly, it was desired to develop a certain synthetic method in order to maintain the tether at the unstable conformation, in which the aromatic nuclei generally overlap largely.

To keep cyclophanes in the unstable conformation, two methods have been developed: one uses steric hindrance

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**FIGURE 2.** Steric hindrance working against the conformational interconversion. (a) Metacyclophane, syn-conformer; (b) orthocyclophane, syn-conformer; and (c) calix[4]arene, cone-conformer.



**FIGURE 3.** Cyclic systems for rigid arrangements. (a) Janucene, (b) dimethano[2.2]paracyclophane, and (c) calixarene analogue.

of bulky substituents at the aromatic nuclei or tethers; the other uses conformationally stable polycyclic frameworks.

Mitchell and co-workers developed a method to make *syn*-[2.2]metacyclophanes **6** and **7** conformationally stable. They used steric hindrance caused by a fluoro- or methyl-substituent and also coordination by chromium carbonyl on the benzene ring at the final C–C bond-formation step (see Figure 2).<sup>6</sup> Recently, Mataka and co-workers reported another application of steric hindrance to make *syn*-[3.3]-orthocyclophanes **8** conformationally stable.<sup>7</sup> In a popular example, to maintain the conformational stability of calixarene, *tert*-butyl and alkyl groups are attached at the benzene rings and at the phenoxy oxygen atoms, respectively (see structure **9** in Figure 2).<sup>8</sup>

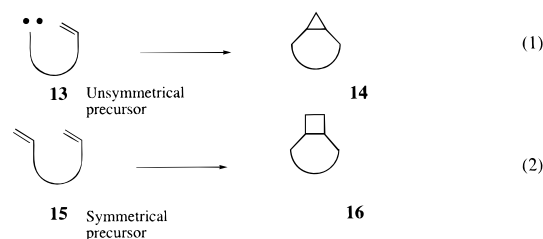
For four decades the importance of conformationally rigid polycyclic systems to arrange aromatic nuclei in a face-to-face manner has been known. For example, Cristol and Lewis constructed Janusene **10**, a face-to-face arranged system, using a polycyclic system (see Figure 3).<sup>9</sup> Moreover, cyclopropane-fused [2.2]paracyclophane **11** was successfully synthesized to examine its structural properties.<sup>10</sup> In this category, the photoreaction mentioned above was developed to obtain various cyclophane systems possessing cyclobutane tethers. The cyclobutane rings make the cyclophane systems rigid and force them to keep the unstable conformation. The method is now known to have a variety of synthetic applications, because many finely designed vinylarenes are available to form tailor-made cyclophane skeletons. Accordingly, as mentioned below, many cyclophanes have been obtained by this method which has led to the study of some structural chemical problems.<sup>5</sup> For example, using a conformationally stable [2.5]metacyclophane derivative, the cone-fixed

calix[4]arene analogue **12** was successfully made with free phenol moieties, which had not been attained by other modification (see Figure 3).<sup>11</sup> These special calixarene-based ionophores have a wide lower rim to bind larger K<sup>+</sup> and Rb<sup>+</sup> ions rather than the Na<sup>+</sup> ion which is usually bound most efficiently by ordinary calix[4]arenes **9**.<sup>8</sup>

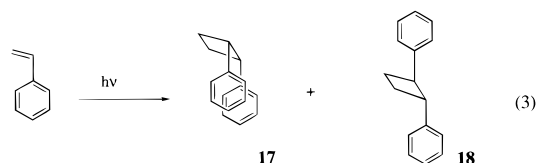
## Rigidifying the Cyclophane Tether by Fusing a Cyclobutane Ring

The dihedral angles of small rings, cyclopropane and cyclobutane, are calculated to be 0° and 23°, respectively. Therefore, cyclopropane and cyclobutane rings are useful to maintain the ethano tether at eclipsed or synperiplanar conformation effectively, where they are fused.

From the synthetic point of view, cyclopropane formation from a trimethylene moiety is much superior to cyclobutane formation from a tetramethylene moiety, according to Baldwin's rule.<sup>12</sup> Actually, Truesdale and Hutton made **11** by this reaction,<sup>10a</sup> but it needs two steps from linear precursors, i.e., cyclization and transformation. On the other hand, if a one-step cyclization like reactions (1) and (2) accompanies a small ring fusion, cyclobutane-fusion is much more easily accomplished, because only simple **15** is needed, instead of complex **13** having a C=C double bond and carbene precursor at each end.



Taking the above analysis into consideration, [2 + 2] photocycloaddition of vinylarenes and their derivatives was chosen for the cyclophane synthesis. As the simplest model case, the reaction of styrene was studied in detail. Although the reaction of styrene (**3**) has been known for more than three decades,<sup>13</sup> it was ignored for a long time as a preparative method.<sup>5</sup> On the other hand, Caldwell analyzed [2 + 2] and [4 + 4] photocycloadditions theoretically and proposed a predictor  $\gamma(r_c)$ . By the predictor he classified reactions into three groups: the first group has less than 20 kcal/mol of the predictors and shows facile reaction leading to products; the second has between 20 and 25 kcal/mol and does not always give products; and the third has above 25 kcal/mol and does not have any successful reactions.<sup>14</sup> According to Caldwell's calculation, styrene gave a predictor of 12.1 kcal/mol, which means high reactivity.



Recently, we followed the calculation (see Figure 4), using singlet and triplet energies evaluated by PM3-CI,<sup>15</sup>

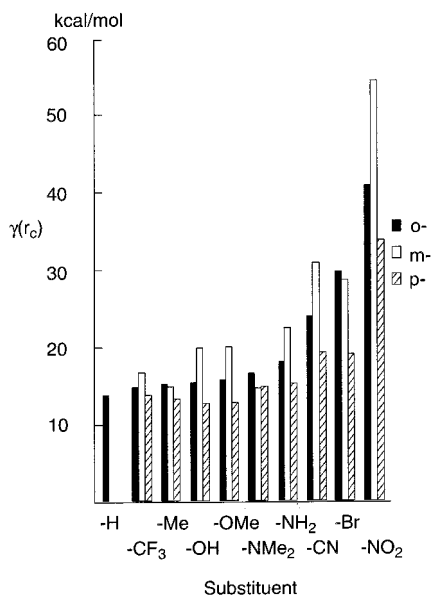


FIGURE 4. Caldwell's  $\gamma(r_c)$  values calculated for styrene and its derivatives

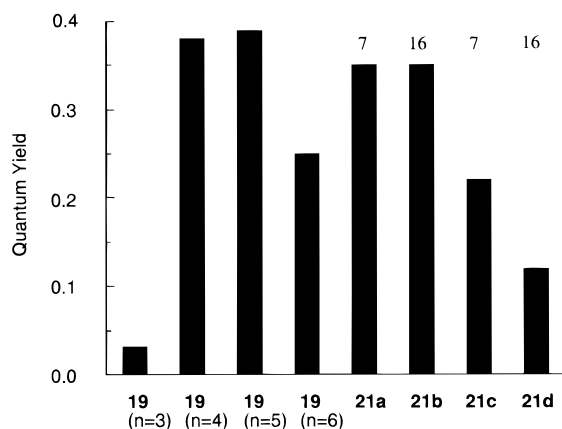
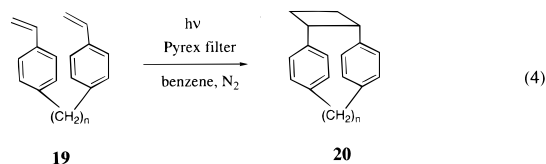


FIGURE 5. Quantum yields of intramolecular [2 + 2] photocyclization of styrene derivatives. Numbers in the graph indicate the numbers of atoms connecting two styrene moieties.

and found that the prediction could well agree with experimental results for styrene and vinylnaphthalene derivatives. Vinylphenanthrenes, however, record  $\gamma(r_c) = 40$ –51 kcal/mol, although they successfully gave photocyclization products or phenanthrenophanes in good yields.

Under sufficiently dilute conditions,  $\alpha,\omega$ -bis(*p*-vinylphenyl)alkanes **19** were subjected to photocyclization (4) in benzene.<sup>5</sup> Although no cyclophanes are formed in the case

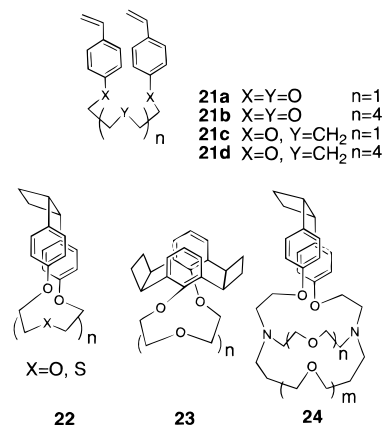


of  $n \leq 2$  due to a highly strained transition state, the corresponding [2.*n*]paracyclophanes **20** ( $n \geq 3$ ) are obtained in quite high quantum yields (see Figure 5). Thus, the fundamental styrene photocyclodimerization is proved to be a good preparative photoreaction. Wulff and co-

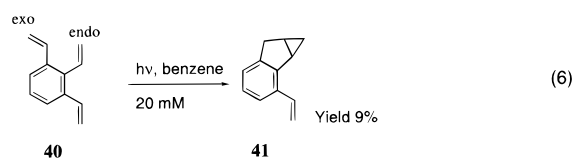
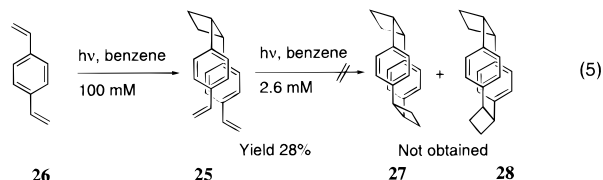
workers found large  $\Delta\epsilon$  differences in CD spectra between a naphthalenophane and a precursor olefin. Astonishingly, the precursor olefin cyclizes by itself during CD spectroscopic measurements.<sup>16</sup> This demonstrates how high the quantum yield is for the [2 + 2] photocycloaddition of vinylarenes. Related to this intramolecular regio- and stereoselective photocycloaddition, syntheses of intriguing natural products such as taxanes have been reported, for example, by Sieburth's group.<sup>17</sup>

Now many inter- and intramolecular reactions of vinylarenes are recognized to be facile and useful.<sup>5</sup> For example, *p*-methyl-, *o*-methoxy-, *p*-dimethylamino-, and *p*-bromostyrenes gave the corresponding cyclic dimers and compounds related to **20**, proving their predicted reactivities (see Figure 4).

Generally, the longer the oligomethylene tether between styrene moieties becomes, the more sharply the quantum yield declines and the less useful the method becomes. Since the C–O–C ether bond is more flexible than the C–C–C bond, an oligooxyethylene tether is more useful than a rigid oligomethylene, in order for two vinyl groups to encounter each other intramolecularly. In fact, the quantum yield did not decrease much for ethers (see Figure 5, **21a** vs **21b**),<sup>18</sup> and many reactions of this sort gave almost quantitative isolated yields.<sup>5b</sup> The products are unique crown ethers such as **22**–**24**.<sup>5,19</sup>



In reaction 4, substrate **19** ( $n = 2$ ) did not give cyclophane **20** ( $n = 2$ ), and even favorably oriented *cis*-1,2-bis(*p*-vinylphenyl)cyclobutane **25** did not cyclize itself to form the corresponding paracyclophanes **27** and **28**, so that one of the factors preventing the cyclization seems to be the strain at the transition state.<sup>20a</sup>



**Table 1. Strain Energy of 1,2-Ethano[2.*n*]paracyclophane **20****

<i>n</i>	strain energy (kcal/mol) <sup>a</sup>	remarks <sup>b</sup>
2	52.0	not obtained by the reaction
3	41.1	14% yield
4	33.9	61% yield

<sup>a</sup> Calculated by HDE method. <sup>b</sup> Reference 5a.

To evaluate the strain limitation of the reaction, we took two cyclophanes; one is 1,2-ethano[2.2]paracyclophane **20** (*n* = 2) which had not been obtained previously, and the other is 1,2-ethano[2.3]paracyclophane **20** (*n* = 3) available by reaction 4 (see Table 1). The strain energies were calculated by the homodesmotic destabilization energy (HDE) method.<sup>21</sup> As shown in Table 1, strain energies of **20** (*n* = 3 and *n* = 2) were calculated to be 41 and 52 kcal/mol, respectively, so that the reaction can overcome the strain loaded in the products at least more than 41 but less than 52 kcal/mol.

## Synthesis of Cyclophanes Possessing Cyclobutane-Fused Tethers






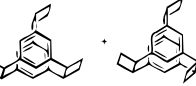







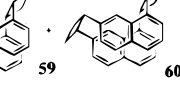

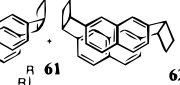



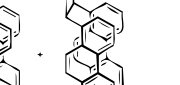


Cyclophanes, naphthalenophanes, phenanthrenophanes, and heterophanes have been obtained from vinylarenes by the photocyclization. In Tables 2 and 3, results of inter- and intramolecular photocyclization are summarized, respectively.

Orthocyclophane **30** and metacyclophanes **32–34** were obtained. Although paracyclophanes **27** and **28** could not be formed from *p*-divinylbenzene **26** (see reaction 5), cyclophanes such as [2<sub>3</sub>](1,3,5)- **36** and **37** and [2<sub>4</sub>](1,2,4,5)-cyclophanes **39** have been produced despite their high strain energies.<sup>20</sup> Their formation is believed to proceed in a stepwise manner using a zipper effect, dividing the strain of final cyclophanes into each step.<sup>20a</sup> The intermolecular reaction has a drawback in that it does not produce a [2<sub>3</sub>](1,2,3)cyclophane from 1,2,3-trivinylbenzene **40**, which takes always *exo,endo*-conformation between two vinyl groups to lead to indane derivative **41** after a facile intramolecular photoreaction.<sup>22</sup>

Two perisubstituents located side-by-side on polycondensed aromatics generally suffer severe steric hindrance from each other. In vinylnaphthalenes and vinylphenanthrenes having vinyl groups at *peri* positions, the steric repulsion between vinyl-methylene and *peri*-hydrogen is large. Therefore, for example,  $\alpha$ -vinylnaphthalene prefers exclusively the *exo*-conformation. This conformational rigidity results in the exclusive formation of an *exo, syn*-di( $\alpha$ -naphthyl) moiety (see **43** in Table 3).<sup>5</sup> This moiety does not undergo any internal ring rotation if it is incorporated into [2.*n*]naphthalenophanes.

Since 1,2-ethano[2.*n*](1,4)naphthalenophanes **43** can be converted to [4.*n*](1,4)naphthalenophanes **45** in excellent yields by means of Birch reduction,<sup>5</sup> we investigated how large the naphthalenophane ring system should be for internal naphthalene-ring rotation (see Scheme 1). Eventually, *syn*-[2.3](1,4)- **43** (*n* = 3) and [3.3](1,4)naphthalenophanes did not change their conformation, but *syn*-[3.4](1,4)naphthalenophane **45** (*n* = 3) could be transformed

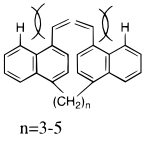
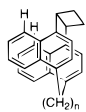
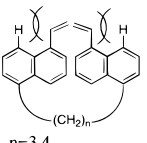
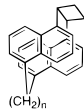
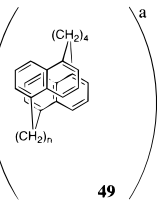
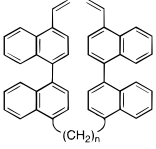
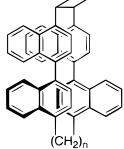
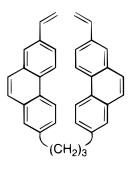
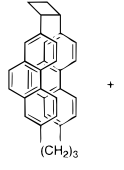
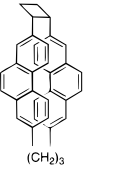
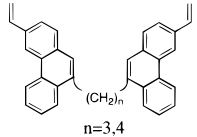
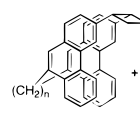
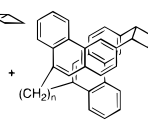
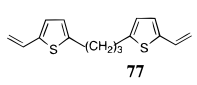
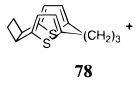
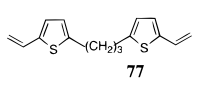
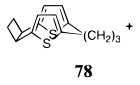
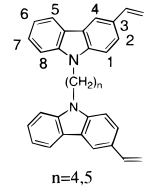
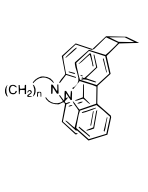
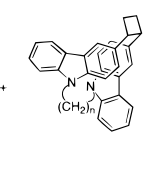
**Table 2. Intermolecular [2 + 2] Photocycloaddition toward Cyclophanes**

Polyvinyl compd.	Cyclophane	Yield, %	Isomer ratio
		11	
		5	56:28:16
		1	74:26
		0.6	
		8	
		18	
		15	65:35
		18	65:35
		(R=COOEt) 47 (R=Ph) 42	
		33	60:40
		46	54:41:5

to the anti-conformer **46** (*n* = 3) during the transformation. This result is completely compatible with Cram's results on the ring rotation of [*m.n*]paracyclophane.<sup>2</sup>

Using the rigid conformation of the *exo, syn*-1,2-di( $\alpha$ -naphthyl)cyclobutane moiety, for the first time, we successfully made partly locked binaphthylophane **51** com-

**Table 3. Intramolecular [2 + 2] Photocycloaddition toward Cyclophanes**

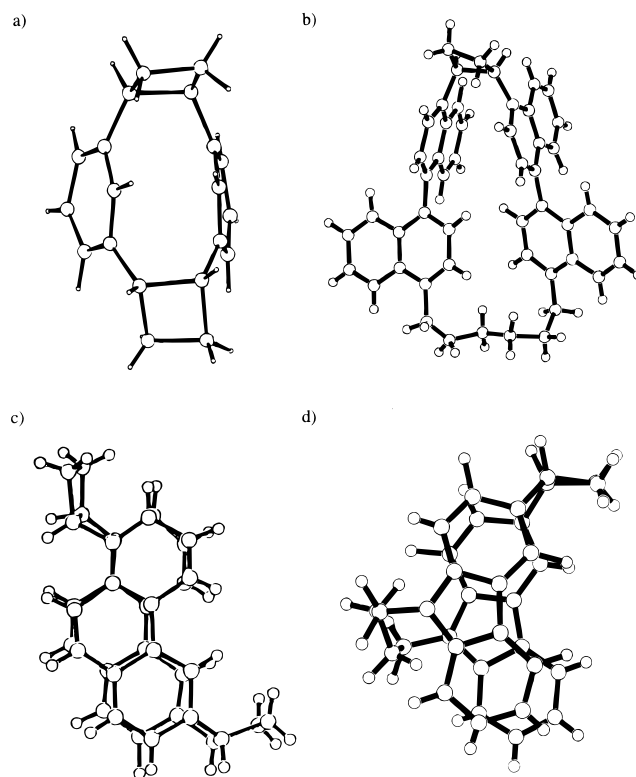
Divinyl compd.	Cyclophane	Yield, % Isomer ratio
 n=3-5	 (CH <sub>2</sub> ) <sub>n</sub>	33-35
 n=3,4	 (CH <sub>2</sub> ) <sub>n</sub>	29-38 (61-65) <sup>a</sup>
	 (CH <sub>2</sub> ) <sub>n</sub>	
 n=6,7	 (CH <sub>2</sub> ) <sub>n</sub>	45-47
 (CH <sub>2</sub> ) <sub>3</sub>	 (CH <sub>2</sub> ) <sub>3</sub>	40 1:1.3
	 (CH <sub>2</sub> ) <sub>3</sub>	
 n=3,4	 (CH <sub>2</sub> ) <sub>n</sub>	40-44 1:3-6
	 (CH <sub>2</sub> ) <sub>n</sub>	
 (CH <sub>2</sub> ) <sub>3</sub>	 (CH <sub>2</sub> ) <sub>3</sub>	4 1:0.6
 (CH <sub>2</sub> ) <sub>3</sub>	 (CH <sub>2</sub> ) <sub>3</sub>	4 1:0.6
 n=4,5	 (CH <sub>2</sub> ) <sub>n</sub>	39-77 1:0.3-5
	 (CH <sub>2</sub> ) <sub>n</sub>	

<sup>a</sup> After Birch reduction.

posed of only carbon and hydrogen atoms.<sup>23</sup> The X-ray structure of **51** is depicted in Figure 6.

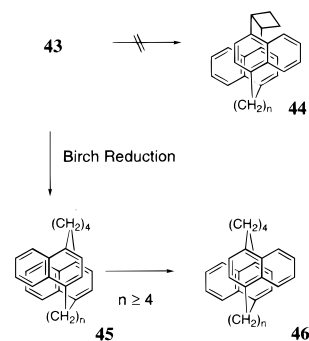
[2.2]Naphthalenophanes **57–63** were obtained by the intermolecular dimerization of divinyl naphthalenes and derivatives **52–56** (see Table 2), although the reaction has the same drawback as that of divinylbenzenes; i.e., no formation of [2.2](1,4)- or [2.2](1,2)naphthalenophanes due to steric energy loaded at the cyclization or facile intramolecular side reaction.<sup>24</sup>

It is noteworthy that various regioisomers are possible for mono- and divinylphenanthrenes due to the low



**FIGURE 6.** Structures determined by X-ray crystallography. (a) 1,2,9,10-Bisethano-*syn*-[2.2]metacyclophane **32**, (b) 1,2-ethano-*syn,anti*-[3.6](4',4'')binaphthylophane **51**, (c) 1,2,17,18-bisethano-*syn*-[2.2](3,6)phenanthrenophane **67**, and (d) 1,2-ethano-*syn*-[2.4](3,9)carbazolophane **81**.

**Scheme 1. Conformational Interconversion of [m.n](1,4)Naphthalenophane**



symmetry of the phenanthrene nucleus. Among them, the vinylphenanthrenes and their derivatives shown in Tables 2 and 3 successfully gave the corresponding phenanthrenophanes by the inter-<sup>25</sup> or intramolecular<sup>26–28</sup> photocycloaddition. Both 1,6- (**64**) and 3,6-divinylphenanthrenes (**65**) efficiently afforded *syn*-[2.2]phenanthrenophanes **66** and **67** and **68–70**, respectively, whereas 2,7-divinylphenanthrene failed to give the corresponding phenanthrenophane, probably for steric reasons, similar to the case of *p*-divinylbenzene and 1,4-divinyl naphthalene. [2.*n*]Phenanthrenophanes **73–76** obtained by the intramolecular photoreactions of **71** and **72** are composed of both *syn*- and *anti*-isomers, which were successfully separated by HPLC.

To date, efforts to make any pyrenophane by this [2 + 2] photocyclization of vinylarenes have been unsuccessful. Although this negative result cannot be fully explained yet, at least the  $\gamma(r_c)$  value is calculated to be more than 37 kcal/mol.

The method was extended to make heterophanes. Checking the reactivity by Caldwell's  $\gamma(r_c)$  value, some vinylthiophenes show a possibility ( $\gamma(r_c) = 14\text{--}21$  kcal/mol), whereas no vinylpyridines give promising values (34–58 kcal/mol). The intramolecular photocyclization of vinylthiophene derivatives **77** ( $n = 2\text{--}5$ ) was systematically examined. No thiophenophane was obtained from **77** ( $n = 2$ ) because of its short linkage, similar to **19** ( $n = 2$ ). However, **77** ( $n = 3$ ) gave the desired [2.3](2,5)thiophenophanes; both *syn*-isomer **78** ( $n = 3$ ) and *anti*-isomer **79** ( $n = 3$ ) were isolated.<sup>29</sup> Synthesis of pyridinophanes from vinylpyridine derivatives has failed. According to our literature survey, no vinylpyridine has given the desired cyclic dimers through singlet excited-state photochemistry.

Regarding synthesis of carbazolophanes, prior to our work there had been only a single example, dioxo[3.3](3,6)-carbazolophane which was synthesized by Tani et al.<sup>30</sup> This compound, however, adopted the *anti*-conformation with a small overlap between the carbazoles. Recently, precursors **80** were subjected to intramolecular photoreaction.<sup>31</sup> Short-tethered **80** ( $n = 3$ ) failed to give any carbazolophanes, but long-tethered **80** ( $n = 4, 5$ ) afforded both *syn*-**81** and *anti*-isomer **82**. Notably, **81** ( $n = 4$ ) is isolated as the first example of *syn*-carbazolophanes.

## Structure and Fluorescence Emission of Cyclophanes Obtained

The cyclophanes obtained by the photochemical method are interesting from the structural point of view, and for the electronic and photophysical properties such as excimer formation, since the aromatic nuclei are arranged in a sufficiently fixed conformation with full or partial overlap. An excimer (excited state dimer) is a complex between a molecule in an electronically excited state and the same molecule in the ground state. They are generally characterized by broad and structureless fluorescence red-shifted relative to monomer fluorescence. Their formation is closely related to the arrangement of aromatic nuclei. 1,3-Diarylpropanes have usually been utilized for the examination of intramolecular excimer emission of condensed polycyclic aromatics. Cyclophanes, in which the relative arrangement of two chromophores is fixed rigidly, are the more desirable compounds for elucidation of the relationship between the chromophore arrangement and fluorescence emission properties. The naphthalenophanes, phenanthrenophanes, and carbazolophanes obtained here are appropriate model compounds for such study as that described below.

The cyclophanes prepared by the intermolecular reactions of di-, tri-, and tetravinylbenzenes (see Table 2) possess different structural features, from parallel-overlapped to tilted as well as fully to partially overlapped.

These features are clearly recognized by their electronic absorption spectra.<sup>20a</sup> Actually, tilted **30** absorbs light at almost the same wavelength as *o*-xylene with a little broadening, while the absorption maximum of **39** shifts bathochromically by ca. 45 nm compared to that of durene with considerable broadening.<sup>20</sup> [2.2]Metacyclopheane **32** was shown by X-ray crystallography to have the *syn*-conformation, in contrast with the parent [2.2]metacyclopheane, which adopted the *anti*-conformation,<sup>6</sup> although the two benzene rings of **32** are not arranged parallel but are considerably tilted from each other with a dihedral angle of ca. 30° (see Figure 6).<sup>32</sup>

The properties, especially the photophysical properties of [2.*n*]naphthalenophanes, have been attracting much attention. Their excimer fluorescence was examined thoroughly by Shizuka and co-workers, focusing on the effect of fine structural differences.<sup>33</sup> Formation of various excimers was recognized by their fluorescence wavelength and lifetime. In *anti*-isomer **46** ( $n = 4$ ) the so-called second excimer was observed with a short lifetime at 77 K, while similarly long-tethered **49** ( $n = 4$ ) was apt to give a longer-lived excimer than the locked **48** ( $n = 4$ ).

Among the naphthalenophanes, Yamaji found that [3.4]-(1,5)naphthalenophane **49** ( $n = 3$ ) formed a triplet excimer upon irradiation, which was clearly identified by the transient absorption spectra, but did not emit phosphorescence from its triplet excimer or locally excited species. This phenomenon was observed only for **49** ( $n = 3$ )<sup>34</sup> and is believed to be important evidence in the triplet excimer studies of naphthalene derivatives.<sup>35</sup>

The phenanthrenophanes obtained have provided further interesting information on the excimer formation of phenanthrene. In contrast with other aromatics such as anthracene and pyrene, unambiguous excimer fluorescence of phenanthrene has rarely been observed in solution under usual experimental conditions.<sup>36</sup> Note that before our work no pure *syn*-phenanthrenophanes had been isolated and their photophysical properties had not been examined in pure isomer-free forms.<sup>36b</sup> We were prompted to investigate the excimer from a structural point of view, using a variety of phenanthrenophanes prepared photochemically.

First, two unique *syn*-[2.2]phenanthrenophanes, (1,6)-isomer **67** and (3,6)-isomer **70**, were examined. The fluorescence spectra of **70** exhibited sharp vibrational structures, as in phenanthrene, suggesting the monomer fluorescence from the locally excited state. On the other hand, **67** afforded a broad and structureless emission with a maximum at 410 nm 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. This fluorescence spectral difference between **67** and **70** can be explained reasonably by the structure or arrangement of two phenanthrene rings. They are tightly held almost in parallel for **67**, according to the X-ray structural analysis (see Figure 6), while largely tilted by ca. 50° along the short axis for **70**, based on PM3 calculation.

To see the influence of the extent of orbital overlap on fluorescence emission, *anti*-phenanthrenophanes were taken where the two parallel phenanthrene rings are only partially overlapped. Staab and co-workers synthesized [2.2](2,7)phenanthrenophane as a mixture of *syn*- and *anti*-isomers, whose separation was not achieved.<sup>36b</sup> They observed excimer fluorescence from this mixture in a fluorene host crystal at 4.2 K, but the fluorescence of *anti*-phenanthrenophane still remains unknown. Therefore, *anti*-(2,7)phenanthrenophanes were designed by the photocycloaddition.<sup>27</sup> While the formation of [2.2](2,7)phenanthrenophane was unsuccessful from 2,7-divinylphenanthrene, *syn*- and *anti*-[2.3](2,7)phenanthrenophanes **73** and **74** were synthesized by applying reaction 4 (Table 3). According to PM3 calculations, the two phenanthrene rings are arranged almost in parallel for both **73** and **74**. Surprisingly, not only **73** but also **74** afforded structureless broad emission assignable as excimer fluorescence, though the maximal position (395 nm) of the latter was slightly blue-shifted relative to the former (405 nm).<sup>29</sup> The blue shift is ascribed to the lower stability in the excimer of **74** due to the smaller overlap of the two aromatic rings.

The photophysical properties of another *anti*-phenanthrenophane like **76**, with even less overlap, were studied in order to clarify the minimum overlap required for excimer formation. *anti*-[2.*n*](3,9)Phenanthrenophane **76** ( $n = 3, 4$ ), prepared by the intramolecular [2 + 2] photocycloaddition of vinylphenanthrene derivative **72** along with *syn*-isomer **75** ( $n = 3, 4$ ), is regarded as a candidate for such phenanthrenophanes.<sup>28</sup> The fluorescence of **75** ( $n = 3$ ) was composed of a broad structureless emission with a maximum at 420 nm red-shifted compared to **67** (410 nm). Interestingly, **76** ( $n = 3$ ) also exhibited a similar broad emission without any vibrational structures, where the maximal position (407 nm) was remarkably blue-shifted relative to **75** ( $n = 3$ ). As far as can be judged from the appearance, it is reasonable to interpret these emissions as excimer fluorescence rather than monomer fluorescence, although some kinetic investigation is necessary for the precise assignment. The blue shift in **76** ( $n = 3$ ) relative to **75** ( $n = 3$ ) is ascribed to smaller stabilization in the excimer due to the smaller overlap of the two aromatic rings. For **75** ( $n = 4$ ), similar broad structureless emission is observed with further blue shift ( $\lambda_{\text{max}} = 395$  nm). This is also assignable as excimer fluorescence. The blue shift in **75** ( $n = 4$ ) relative to **75** ( $n = 3$ ) is apparently derived from the difference in the bridging length; in the excited state of **75** ( $n = 4$ ), the two phenanthrene rings cannot approach each other as closely as in **75** ( $n = 3$ ). In contrast, **76** ( $n = 4$ ) afforded apparent vibrational structures characteristic of monomer fluorescence. The arrangement of **76** ( $n = 4$ ) appears to be no longer favorable for excimer formation. Thus, four phenanthrenophanes **75** and **76** ( $n = 3, 4$ ) exhibited quite different fluorescence from one another depending on the overlap and distance between the two aromatics. It is surprising that excimer fluorescence was observed even for **76** ( $n =$

3), where the phenanthrene nuclei overlap mainly at the single six-membered ring.

The carbazole chromophore is a constituent of poly-(*N*-vinylcarbazole) which is well known as a photoconductor, and the photophysical properties of its dimer model compounds and polymers have been extensively investigated. Carbazolophanes such as **81** and **82** are more suitable models for study of excimer formation. The fluorescence spectrum of carbazolophane **82** ( $n = 4$ ), composed of vibrational structures, is obviously different from the partial-overlap excimer fluorescence which is reported to show a broad band around 370 nm and is virtually interpreted as the monomer fluorescence of the carbazole chromophore.<sup>31</sup> This result contrasts with the expectation that **82** ( $n = 4$ ) is seemingly suitable for the partial-overlap excimer. Probably, the two carbazole rings are not sufficiently overlapped with each other. This is actually demonstrated by the <sup>1</sup>H NMR data of **82** ( $n = 4$ ). The high-field shifts of H1 (1.12 and 1.06 ppm) and H2 (1.45 and 1.07 ppm) of **82** ( $n = 4$ ) relative to **80** ( $n = 4$ ) are much larger than those of H4 (0.54 and 0.22 ppm), indicating that H1 and H2 are located over the opposite carbazole moiety, whereas H4 is not; the benzene rings on the cyclobutane side are only partially overlapped with each other.

On the other hand, **81** ( $n = 4$ ) afforded broad and structureless fluorescence with a peak at 415 nm, much red-shifted in comparison with **82** ( $n = 4$ ). This is apparently assigned as sandwich excimer fluorescence which usually appears around 420 nm, in agreement with the well-overlapped arrangement in **81** ( $n = 4$ ). According to the X-ray crystallographic analysis of **81** ( $n = 4$ ), the two carbazole rings favorably overlap with each other, although they are slightly deviated from parallel arrangement (19.4°) (see Figure 6). Therefore, the slight blue shift in **81** ( $n = 4$ ) relative to the typical position is believed to be associated with the deviation from parallel arrangement.

## Conclusion

The inter- and intramolecular [2 + 2] photocycloaddition of vinylarenes can force cyclophanes produced to adopt *syn*-conformations, where the nuclei usually overlap to the maximum extent. Although it cannot make severely strained cyclophanes, the method is a most efficient way to find and examine the electronic properties of face-to-face arranged arene ring systems, ranging from fully to partially overlapped and parallel to tilted. Most of the variation is attained by choosing ethano to tetramethylene tethers, whose preparation this method covers. Moreover, one can systematically provide several cyclophanes besides a single target from the same kind of starting materials and by the same reaction sequences, summarized in Tables 2 and 3.

Various phenanthrenophanes prepared emitted fluorescence from the excimer or only from locally excited species. The experimental results can be fully rationalized with the structural and electronic properties. Other cy-

clophanes such as carbazolophanes have also been investigated to elucidate their electronic properties. Consequently, the inter- and intramolecular [2 + 2] photocycloaddition of vinylarenes has supplied key materials, giving some important sets of experimental findings for theoretical development in structural organic chemistry.

We are indebted to co-workers, whose names are shown in references, for their outstanding contributions. The work was supported partly by grants from The Ministry of Education, Science, Sports, and Culture, Japan, and also from Japan Society for the Promotion of Science.

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