

## Cycloaddition reactions of cyclophanes

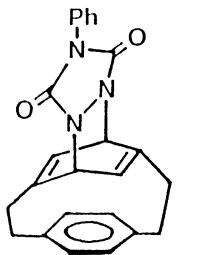
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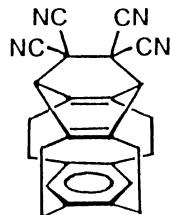
**Abstract** – Unusual thermal and photochemical cycloaddition reactions of the aromatic rings in some cyclophanes are described. For example, the benzene in paracyclo(9,10)anthracenophane functions as a dienophile in intramolecular Diels-Alder reaction and tetracyanoethylene reacts easily with a triple-layered cyclophadiyne even at room temperature to give a 1:1 cycloadduct, suggesting a concerted process of three isolated  $\pi$ -systems. The formation of cage compounds by photo-induced cycloaddition and their reverse, thermal ring opening reactions are observed with syn[2.2](1,4)anthracenophane and dihetero quadruple-layered cyclophanes. A quantitative photodimerization of (9,10)anthracenophadiyne and photoinduced bridge migration of multilayered metaparacyclophanes are discussed.

### INTRODUCTION

The most striking characteristic of [2.2]para- and metacyclophanes is anomalous behavior in electrophilic substitution of the two benzene rings, which is caused on the transannular  $\pi$ -electron interactions among the stacked benzenes to function just as one  $\pi$ -electron system. In addition, severe strain of benzene nuclei in such stacking systems, *i.e.* bending and twisting, brings about them some extent of thermodynamical destabilization or reduced aromatic character. As a result, the "superdienophile" 4-phenyl-1,2,4-triazoline-3,5-dione, for example, reacts with [2.2]paracyclophe to give a 1:2 cycloadduct 1 (99% yield) after 6 days at room temperature, although it does not add to benzene at room temperature even after several weeks (ref. 1). Also, tetracyanoethylene does not add to benzene and even to [2.2]paracyclophe at 100°C for 165 hr, whereas it gives readily a 1:1 adduct 2 (100% yield) of [2.2.2.2](1,2,4,5)cyclophane at 20 °C (ref. 2).



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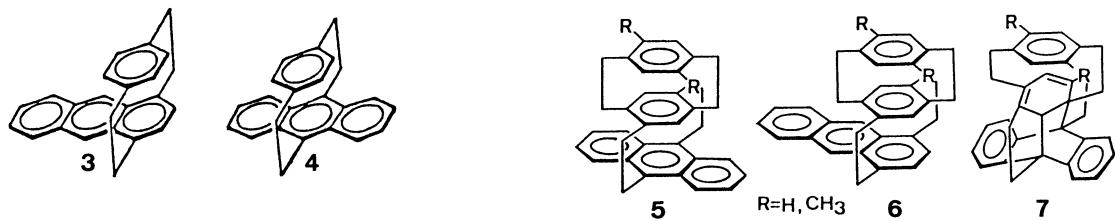
**2**

As model compounds to study the transannular  $\pi$ -electron interactions in stacked aromatic systems, we have synthesized various types of cyclophanes which contain some extended aromatics (ref. 3), diacetylene bond (ref. 4), and multistacked benzene systems (ref. 5). During the study on physical and chemical properties of these cyclophanes, we found that they often show remarkable non-catalytic reactions, *i.e.* thermal and photochemical cycloadditions, due to their severe strain and transannular  $\pi$ -electron interactions.

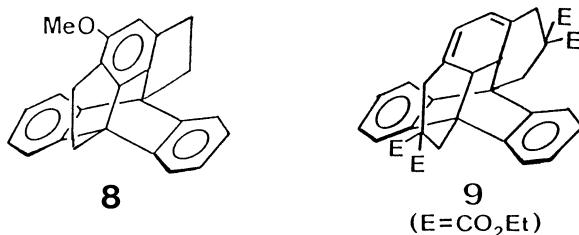
## THERMAL CYCLOADDITION

### Anthracenophanes

In anticipation of stronger transannular  $\pi$ -electron interactions in the cyclophanes of condensed aromatics than that in [2.2]paracyclophe, we prepared a series of anthracenophanes, i.e. benzene-anthracene, naphthalene-anthracene, and anthracene-anthracene systems (ref. 6). Some isomeric anthracenophanes are expected due to the difference in stacking mode of two aromatic rings. A longer wavelength shift in electronic spectrum of [2.2]paracyclo-(9,10)anthracenophane 4 was ascribed to stronger interaction between the two  $\pi$ -systems, compared to that of the corresponding (1,4)isomer 3 (ref. 6). Synthesis of isomeric triple-layered anthracenophanes, 5 and 6, was undertaken by employing the Hofmann elimination method of the corresponding ammonium bases. The isomer 5 was obtained in low yield, but in the case of anthracenophane 6(R=CH<sub>3</sub>) an isomeric cage compound 7(R=CH<sub>3</sub>) was isolated from the reaction mixture in 1.5% yield(7: R=H 8.7% yield)(ref. 7). The structures of 7 were determined by PMR and X-ray analysis.



The formation of 7 is illustrated by intramolecular Diels-Alder addition of the inner benzene ring as a dienophile to the 9,10-positions of the anthracene ring. This unusual cycloaddition under ordinary reaction conditions can be accounted for by close fixing of the anthracene ring against the inner benzene ring with two ethylene bridges, and by severe molecular strain in the intermediate 6, as same as in X-ray molecular structures of triple-(ref. 8) and quadruple-layered cyclophanes (ref. 9), in which both inner benzene rings are bent into twisted form. In other words, strain releasing is responsible for the unusual addition reaction. The thermal instability of anthracenophane 4, which polymerizes gradually even in crystalline state at room temperature, is also attributable to the same reason.



The formation of a bridged triptycene 8 is interpreted by a reaction sequence of Diels-Alder addition and following elimination of a methanol molecule (ref. 10). Although an attempt to regenerate the labile intermediate 6 by retro Diels-Alder reaction of 7 was unsuccessful, a cycloadduct having propylene bridges 9 showed a reversible reaction to the original anthracenophane(ref.11).

### Cyclophadiynes

In the course of a study on charge transfer complexes, 10 and 11, of [n]paracyclophadiyne or [m.n]paracyclophe with tetracyanoethylene (ref. 12),

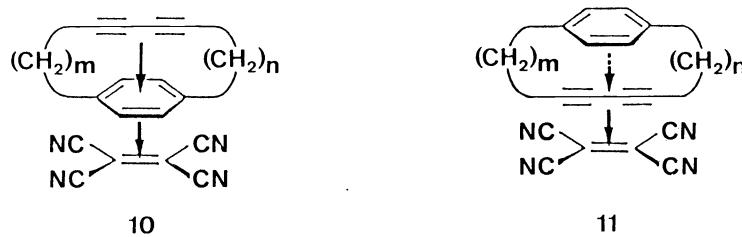
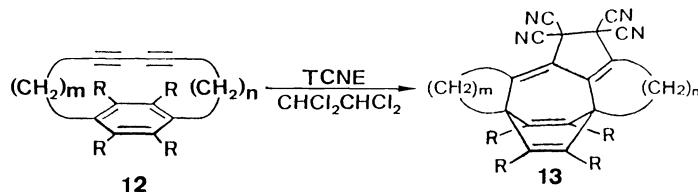


Table 1. Reaction conditions and yields of TCNE to [m.n]paracyclopadiynes 12.

[m.n]	R	Reac.temp.(°C)	Reac.time	yield(%)
[2.3]	H		---	---
[2.4]	H	140	30 min	76
[3.3]	H	140	30 min	73
[3.3]	CH <sub>3</sub>	75	19 hr	88
[3.4]	H	140	70 min	34
[4.4]	H	140		0



we found that a novel multicycloaddition took place among three isolated  $\pi$ -systems (ref. 13). Immediately after addition of TCNE to [3.3]paracyclopadiyne 12 in tetrachloroethane, the solution changes to blue color for a short time, suggesting the formation of CT complex, and it becomes quickly colorless. The structure of colorless product 13(R=H, m,n=3), isolated from the solution, is clearly confirmed by spectral analyses, that is, IR, UV, PMR and <sup>13</sup>C-NMR, which indicate the reaction to proceed with the disappearance of diacetylene bond and the inner benzene ring. In particular, NMR spectra show evidently the formation of unsymmetric structure 13 via 1,3-mode reaction of three kinds of cycloaddition modes as shown in Fig. 1.

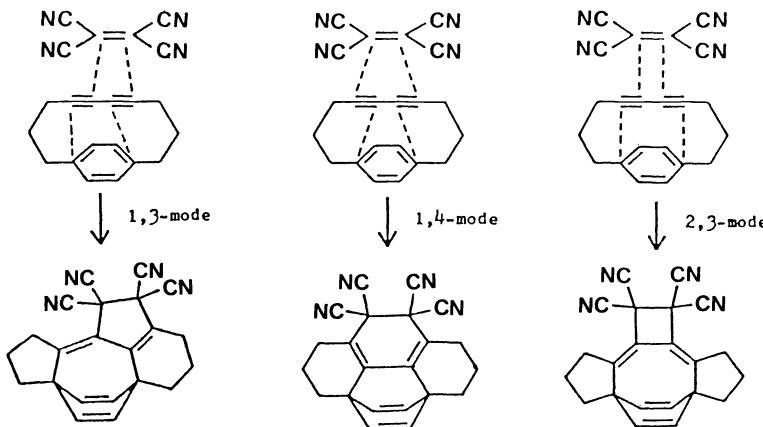
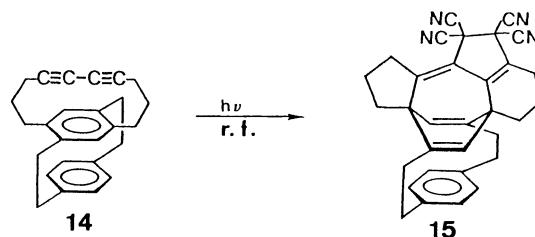


Fig. 1. Cycloaddition modes of TCNE to [3.3]paracyclopadiyne.

Such a cycloaddition reaction is also observed with higher homolog 12(R=H, m=3, n=4) to give lower yield of 13, but no formation of cycloadduct with 12 (R= H, m,n>4)(Table 1). On the other hand, tetramethyl derivative 12(R=CH<sub>3</sub>, m,n=3) of [3.3]paracyclopadiyne undergoes the cycloaddition under milder conditions and in higher yield, compared to those of the parent [3.3]- and an isomer [2.4]paracyclopadiyne 12(R=H, m=4, n=2) having the same length of the bridge.



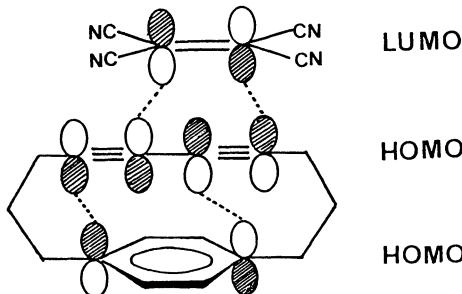
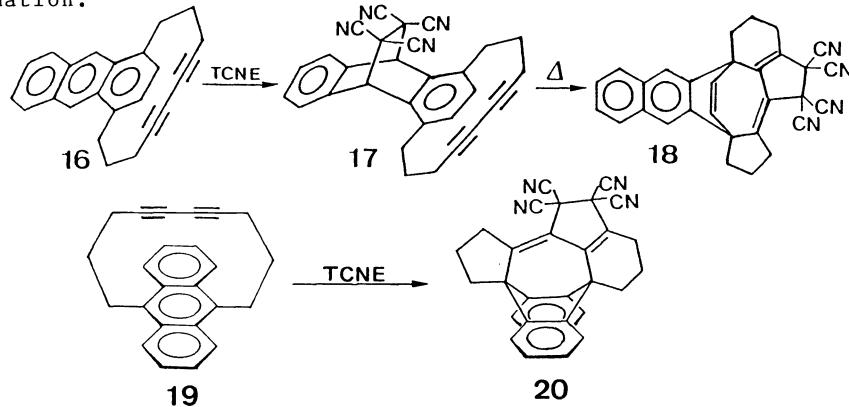


Fig. 2. The three  $\pi$ -system interaction orbital set for multicycloaddition of [3.3]paracyclopadiyne with TCNE.

On the other hand, more severely strained cyclophadiyne 14 (ref. 4) reacts readily with TCNE even at room temperature to give a cycloadduct 15 (ref. 13). On the basis of several examples above-stated, the easiness of this intriguing multicycloaddition is concluded to be depend strongly upon magnitudes of both the strain and the electron donating ability of the benzene ring faced to diacetylene group.

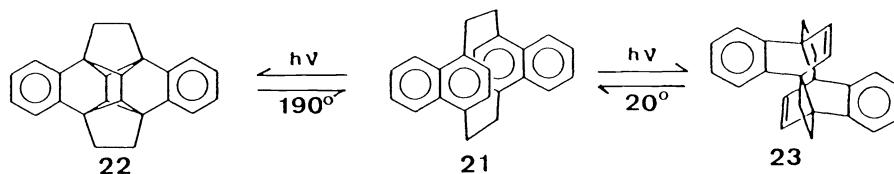
A mechanism of this multicycloaddition was first thought as an example of a thermally allowed  $[\pi 4s + \pi 2a + \pi 2s + \pi 2a]$  pericyclic process, provided that the cycloaddition proceeds in a concerted manner. Later the reactions were interpreted on the basis of molecular orbital theory, that is, in terms of three  $\pi$ -systems interaction among the HOMO of the benzene ring, the HOMO of the conjugated diacetylene group, and the LUMO of TCNE as shown in Fig. 2 (ref. 14). There the theory claimed that highly electron-deficient TCNE allows the HOMO-HOMO interaction, which is prohibited normally in thermal reaction, between the diyne group and the benzene ring for stabilization and bond formation.



In the case of [10](1,4)anthracenophane-4,6-diyne 16, TCNE is added exclusively to 9,10-positions of the anthracene ring to give quantitative yield of an adduct 17, because of ready CT complex formation and the following Diels-Alder addition reaction. When the adduct 17 in tetrachloroethane is refluxed, an isomeric 1:1 adduct 18 is given in 38% yield, probably through a retro Diels-Alder process followed by the above-stated multicycloaddition mechanism among three  $\pi$ -systems. Similarly, isomeric 9,10-anthracenophadiyne 19 yields a cycloadduct 20 with TCNE.

#### PHOTOCHEMICAL CYCLOADDITION

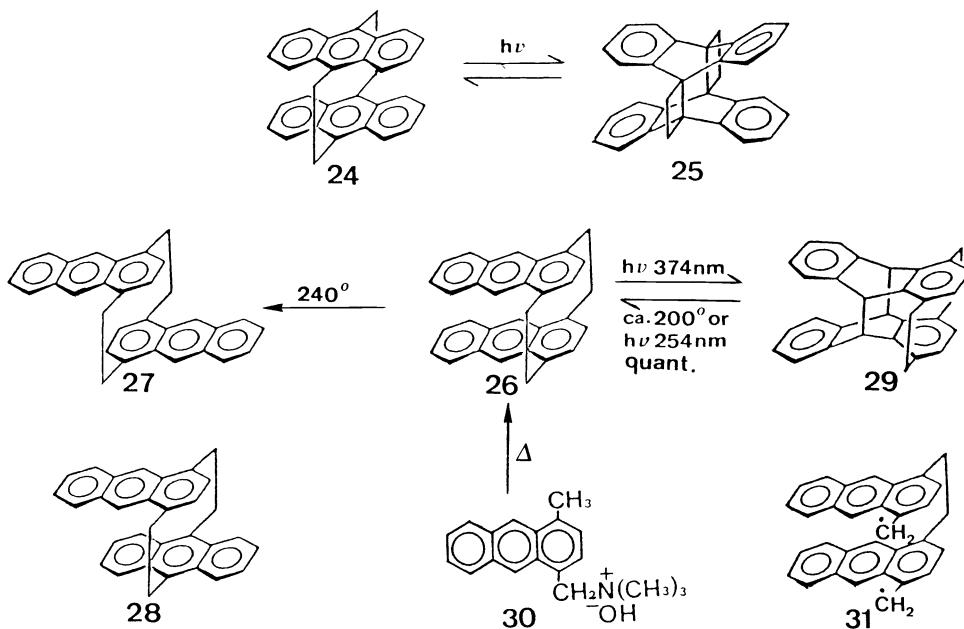
Two types of photoinduced cycloadditions on irradiation of anti[2.2](1,4)-naphthalenophane 21 are well-known as a typical example of condensed aromatics phane to give cycloadduct 22 by two consecutive  $[\pi 2 + \pi 2]$  reaction and cycloadduct 23 by  $[\pi 4 + \pi 4]$  reaction (ref. 15).



### Anthracenophanes

The first photoinduced cycloaddition of anthracenophane 24 to give a strained cage compound 25 which showed a reverse, thermal reaction to 24, that is, indicating the photochromism just as with naphthalenophane 21 (ref. 16).

In order to study the effect of sandwich type  $\pi$ -electron interaction on excimer fluorescence, photodimerization, and esr spectra of anthracene, we have synthesized a series of cyclophanes incorporating anthracene which has a lower ionization potential than either naphthalene and benzene. Using Hofmann elimination method of the corresponding quaternary ammonium bases, three isomeric [2.2]anthracenophanes 26-28 are obtained (ref. 6).



Irradiating with sunlight or monochromatic light at 374 nm in benzene, yellow syn[2.2](1,4)anthracenophane 26 gives an isomeric, colorless cage compound 29 in quantitative yield. The reverse, thermal reaction of cage compound 29 in solid state is performed to give quantitative yield of 26 under conditions at 198–199 °C for 6 hr in nitrogen atmosphere. On the other hand, when the pyrolysis is carried out in solution at ca.220 °C, a mixture of anti-isomer 27 and syn-isomer 26 of anthracenophane is given with a molar ratio of 21:19 as the reaction prolongs. This difference in pyrolytic reactions in both solid and solution can be understood as follows. In solution an anthracene  $sp^3$ - $sp^3$  biradical species 31 which is formed by homolytic cleavage of an  $sp^3$ - $sp^3$  single bond in ethylene bridges, can rotate with biradical pairing and regenerate the single bond to give thermodynamically stable anti-isomer 27. In solid state, on the other hand, the aromatic ring is unable to rotate due to less degrees of freedom for molecular motion and therefore more hindered syn-isomer 26 is selectively afforded. A photochemical interconversion between 26 and 29 is observed on irradiation of their THF solutions. Thus, when a THF solution of 29 is exposed to monochromatic light at 254 nm for 10 min, the formation of 26 is observed in the electronic spectrum of resulting solution, and conversely, 26 to 29 by irradiation of 374 nm light.

The molecular structure of 26, in which the two anthracene rings are fixed in nearly parallel with relatively short distances, is shown in Fig. 3 (ref. 17). The figure demonstrates considerable overlapping among the two anthracene  $2P_z$  electrons and thereby ready formation of covalent bonds between two pairs of  $C_9$  and  $C_{10}$  anthracene carbons.

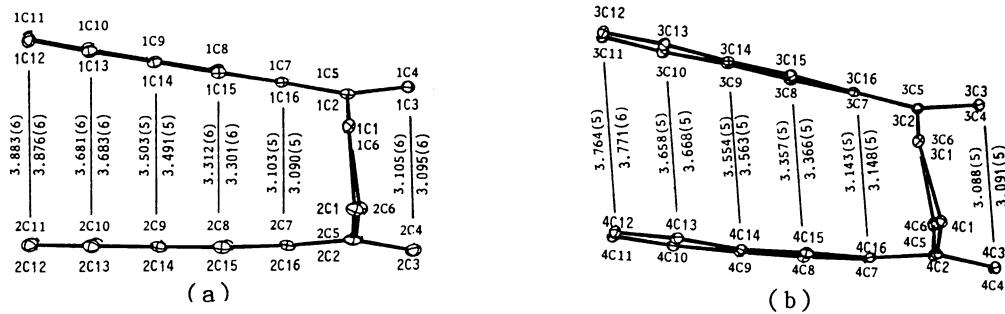
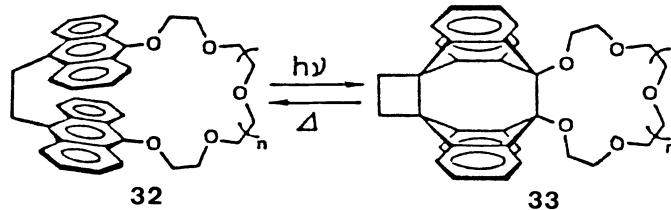


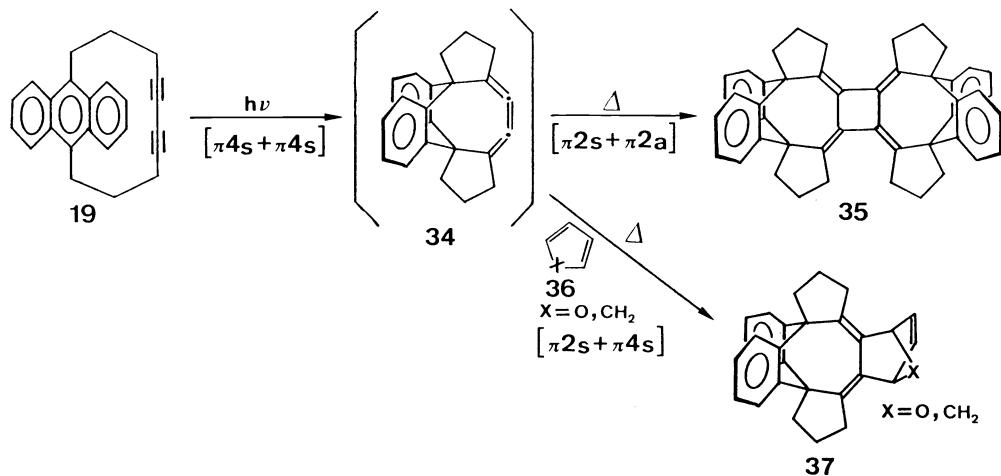
Fig. 3. A side view of syn-anthracenophane molecules, (a):A molecule, (b):B molecule.

As an application of anthracene photochromism above-stated, a macrocyclic anthracenophane 32 was synthesized by the Williamson synthesis with polyethyleneglycol ditosylate (ref. 18). In other words, the incorporation of 1,2-dianthrylethane group in a macrocyclic polyether ring offers a possibility of selective metalion complexation-transportation by means of photo-controlled and reversible modification of the macrocyclic cavity. The selective complexation of alkali metal ion with 32(n=1,2,3) was confirmed by measuring ion-dependent half-lives of thermal, dark reaction of 33 to 32, compared to that of ion-free case.



### Anthracenophadiyne

Besides being susceptible to multicycloaddition with TCNE as described before, anthracenophadiyne 19 gives, on exposure of a benzene solution to sunlight for 10 min, an interesting dimer  $C_{48}H_{40}$  in quantitative yield (ref. 3, 19). When 19 in large excess of furan or cyclopentadiene 36 ( $X=O$  or  $CH_2$ ) is exposed to sunlight for 30 min, a 1:1 adduct,  $C_{28}H_{24}O$  or  $C_{29}H_{26}$ , is obtained in quantitative yield. The structure of the photodimer 35 is determined by PMR and decoupled  $^{13}C$ -NMR spectra, lack of  $\text{C}\equiv\text{C}$  stretching band in IR, and similarity with [4]radialene in UV spectra. The structures of two 1:1 cycloadducts are similarly assigned to 37 ( $X=O, CH_2$ ) by spectral analyses.

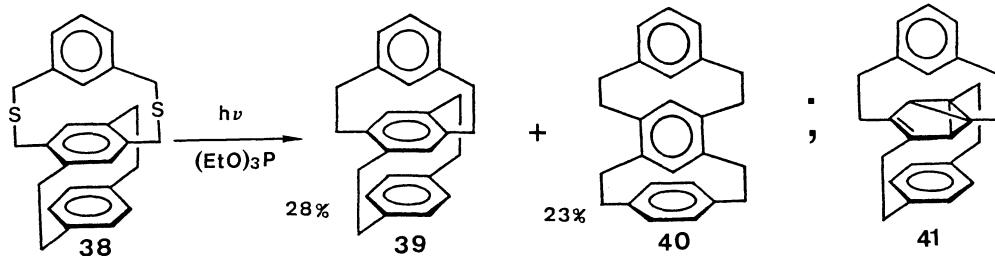


Extensive study on mechanism of the photoinduced dimerization elucidated an extremely strained butatriene derivative 34 to be the most likely intermediate on the basis of the following results: 1) all the reactions are independent of the concentration of reactant 19 with no detectable side reaction, 2) the reaction rate is proportional to the light intensity used for irradiation, 3) the intermediate 34 is trapped by repeated cycles of freezing-softening-UV

irradiation process with a matrix of 19 in glycerol-ethanol (1:1) at 77 K and it reverts quantitatively to the reactant 19 by irradiation with shorter wavelength light, 4) the intermediate 34 in the same matrix gives the dimer 35 by warming up to room temperature in the dark, and 5) the absorption spectrum of 35 is similar to that of tetra-tert-butylbutatriene except its absorption intensity. Taking into account that this photodimerization is not affected by the presence of oxygen or radical scavenger, the reaction is explained to proceed by a two-step mechanism involving photochemically allowed  $[\pi 4s + \pi 4s]$  and the following  $[\pi 2s + \pi 2a]$  thermal processes. Thereby the formation of the two cycloadducts 37 is interpreted also by a two-step mechanism of Diels-Alder cycloaddition of the first-formed intermediate 34 with furan or cyclopenta-diene.

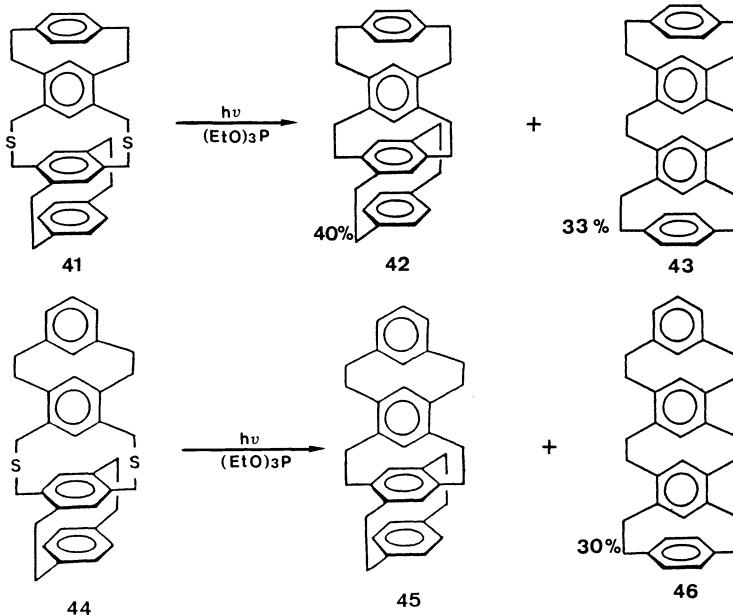
### Multilayered cyclophanes

A series of triple- and quadruple-layered [2.2]metaparacyclophanes is synthesized by a combination of general methods, since they have been of great interest on physical properties as intermediates between multilayered para- and metacyclophanes.

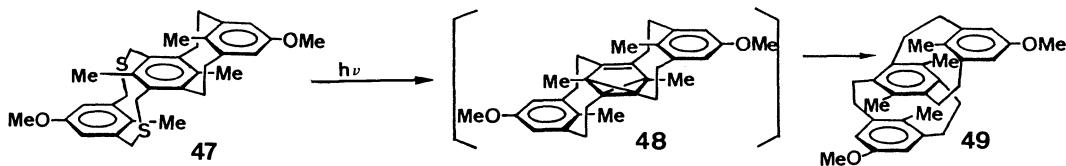


Photoinduced desulfurization of dithia[3.3]metaparacyclophanes is convenient as a general method for small scale preparation of [2.2]metaparacyclophanes (ref. 21). In the photodesulfurization of dithia triple-layered metaparacyclophane 38 in degassed triethyl phosphite with a high pressure mercury lamp, an unexpected isomeric triple-layered metaparacyclophane 40 is obtained in 23% yield together with about equal amounts of the desired metaparacyclophane 39 (ref. 22). For this case is not considered the intramolecular 1,2-shift of an ethylene bridge cation, which is assumed in the way of the skeletal rearrangement on treatment of triple-layered paracyclophane with Friedel-Crafts acids. A plausible mechanism is the exchange of two ethylene bridges, which may proceed through a benzvalene intermediate 41 from the first-formed product 39. This assumption is supported by the facts that a prolonged irradiation of 38 results in increased yield of 40 with a decreased yield of normal product 39, and that irradiation of 39 in degassed cyclohexane produces the isomer 40.

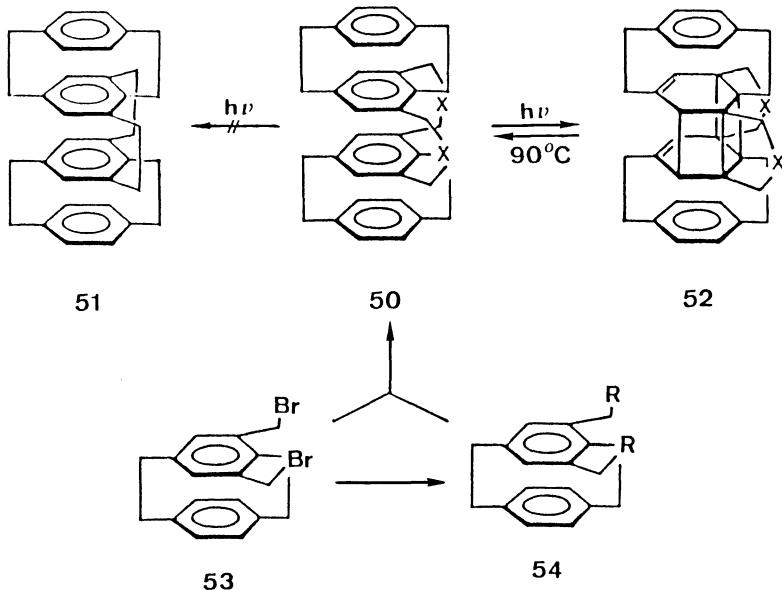
Similar photoinduced rearrangements are observed on irradiating dithia quadruple-layered metaparacyclophanes, 41 and 44, both of which have the



framework of 38 as a common molecular moiety, to give photorearranged quadruple-layered metaparacyclophanes, 43 and 46, respectively, in relative good yield (ref. 23). Such a benzvalene mechanism was also proposed for the formation of unexpected triple-layered metaparacyclophane 49 via intermediate 48 on irradiation of dithia triple-layered metacyclophane 47 (ref. 24).



Compared with the ready photodimerization of condensed aromatics, benzene is so stable on photoinduced reaction that it has often been used as a reaction medium. Even in highly strained [2.2]paracyclophane, the two benzene rings are inert to irradiation. As described before, a few multilayered metaparacyclophanes including the [2.2]paracyclophane framework shows the photochemical exchange of two ethylene bridges to release the strain of the twisted inner benzene ring.



On the other hand, a novel photochemical reaction of benzene rings was observed in the course of a study on the synthesis of new type of quadruple-layered cyclophane 51 by photoinduced desulfurization of dithiacyclophane 50b (ref. 25). Dihetera quadruple-layered cyclophanes 50a-c are synthesized together with nearly same amounts of their anti-conformers by coupling of a key intermediate 4,8-bis(bromomethyl)[2.2]paracyclophane 53 with the corresponding chalcogenatom-substituted [2.2]paracyclophanes 54a-c (see Table 2) (ref. 26, 27). Irradiating 50b and 50c in triethyl phosphite for extrusion of chalcogenatoms, unexpected cage compounds 52b and 52c, respectively, are produced as colorless fine crystals. The structures of these photoisomers are clearly confirmed by MS, NMR, and UV spectra, that is, disappearance of inner benzene rings and, instead, formation of olefins. The possibility of another structure containing two benzvalene rings is eliminated on the basis of PMR data. Similarly cage compound 52a is obtained in good yield by irradiation of 50a. The decreased yield of 52c, as shown in Table 2, is partly ascribed to a competitive photoinduced C-Se bond fission to give a byproduct, 4,8-dimethyl[2.2]paracyclophane in 15% yield.

After various examinations on thermal properties of the cage compounds 52a-c, the thermal ringopening reaction of 52 in THF solution is optimized to give the original quadruple-layered cyclophanes 50a-c as shown in Table 3. The table shows that the reaction proceeds with a relative rate of  $\text{Se} > \text{S} > \text{O}$ -compounds.

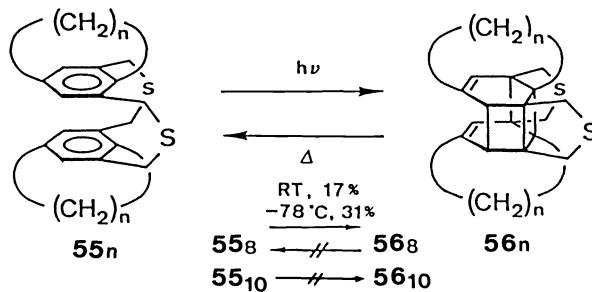
Table 2. Yields of 50, 54, and photoisomerization of 50.

	yield(%) <u>53</u> → <u>54</u>	yield(%) <u>53+54</u> → <u>50</u> + anti		yield(%) <u>50</u> → <u>52</u>
a	—	0	24	28
b	SH 81	S	33	23
c	SeCN 60	Se	27	36
				Se 47

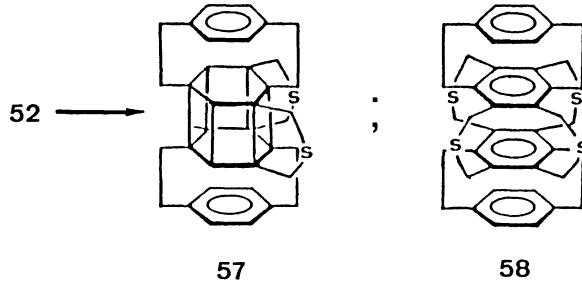
Table 3. Thermal isomerization of 52 to 50.

X	T <sub>1/2</sub> (t °C)	yield(%)
52a	0	2 hr(90)
b	S	30 min(90)
c	Se	25 min(90)

In order to search the driving forces for these unusual photodimerization of benzene nuclei in diheteracyclophanes 50, photochemical behavior of a series of model compounds was studied with respect to four factors: 1) magnitude of molecular strain, 2) effect of the two outer benzene rings in 50, 3) positions of four bridges at the inner benzenes, and 4) interfacial constraint of the particular two benzene rings. On irradiation, dithiacyclophane 55(n=8) containing [8]paracyclophane, in which the benzene ring is well-known by bending comparable to that of [2.2]paracyclophane, gives a photoisomer 56(n=8) in 31% yield at -78 °C and 17% at room temperature. On the other hand, reverse thermal reaction of 56(n=8) is not observed under various conditions. No photoisomer is given in the case of 55(n=10).



From photochemical examinations with various model compounds, it is concluded that the most important factor on the photodimerization is some extent of severe strain, but not too much, in the benzene ring. The outer benzene rings of photoisomers 52 are required for increased thermal stability of the inside cage framework but not necessarily for photodimerization. In other words, the two outer benzenes are essential to effective photochromism between 50 to 52.



An attractive theme is to synthesize a hexaprismane derivative 57 from 52. A [2+2]photocycloaddition of the remaining two double bonds was attempted by irradiation under many conditions. Unfortunately, the attempt resulted in the formation of small amounts of 4,8-dimethyl[2.2]paracyclophane in place of the desired hexaprismane derivative. The reasons that the reaction does not proceed are due to 1) unexpectedly long distance between the two double bonds, 2) photochemically symmetry-forbidden [ $\pi_2s+\pi_2s$ ]cycloaddition caused by a through-bond interaction of the double bond and  $\sigma$ -bond of adjacent cyclobutane (ref. 28), and 3) severe strain in hexaprismane framework. An attempt to synthesize a hexabridged tetrathiacyclophane 58 is now in progress.

#### Acknowledgement

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