Layered Compounds. LIX.[1] Facile Syntheses and Spectral Properties of [3.3]Cyclophanes and Related Cyclophanes

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A simple synthetic method of [3.3]cyclophanes *via* dithia[4.4]cyclophanes is presented. The spectra of a variety of cyclophanes were examined and compared to those of [2.2]analogues. It was concluded from the absorption spectra that the transannular π-π interactions of the cyclophanes were strongly dependent on both ring-to-ring distance and overlapping mode. From the emission spectra, it was described that cyclophanes of parallel sandwich type formed easily normal excimers, whereas [2.2]metacyclophane and [2.2]- and [3.3]metaparacyclophanes formed strained excimers showing marked red shifts of fluorescence bands.

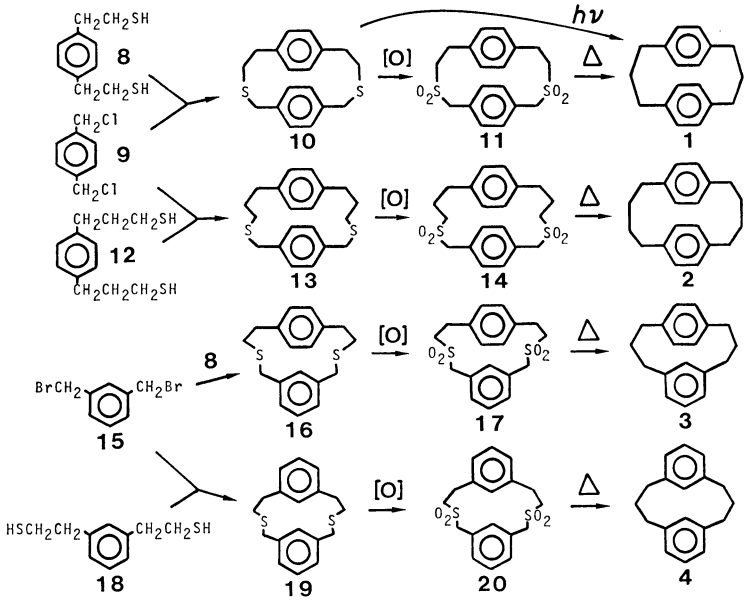
Cram and his coworkers reported the first synthesis of [3.3]paracyclophane **1** in the study of a series of [*m.n*]paracyclophanes and pointed out its unique properties, *e.g.*, the formation of a rather stronger tetracyanoethylene complex than [2.2]paracyclophane **31** in spite of longer ring-to-ring distance.[2] In this regard, an investigation was undertaken for comparing the strength of intramolecular charge-transfer interaction in a series of donor-acceptor [*n.n*]paracyclophanes, of which the [3.3]system was expected to provide the most stable intramolecular complex.[3]

It has been well known that [3.3]paracyclophane **1** might be the most suitable system for the transannular electronic interaction because **1** has a parallel sandwich structure of the two benzene rings with considerably short ring-to-ring distance and without severe ring strain.[4] However, further extensive study of **1** has been limited owing to tedius route in the initial synthesis. Although a few synthetic methods of **1** were developed by means of ring expansion of [2.2]paracyclophane,[5] 1,8-cycloaddition,[6] and condensation of malonic ester,[7] a general method has been expected for applying to a variety of [3.3]cyclophanes such as multibridged and multilayered types and donor-acceptor type.

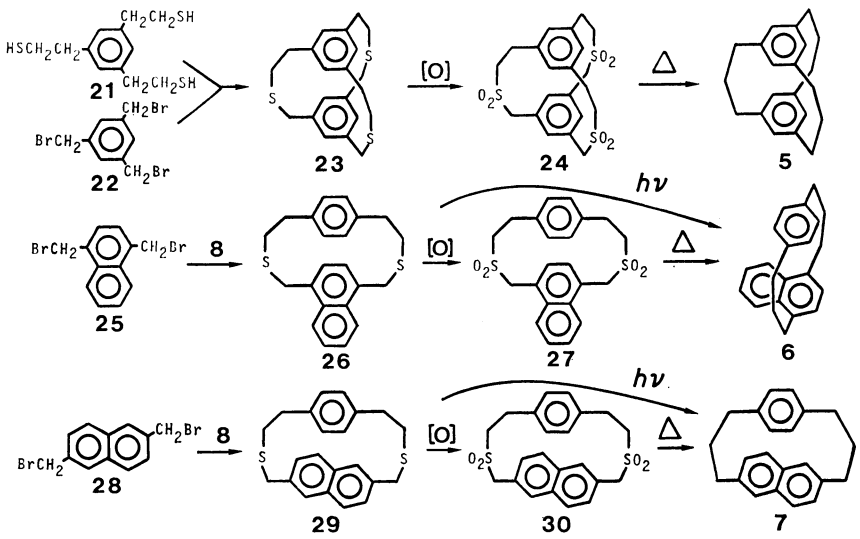
The synthesis of [2.2]cyclophanes by sulfur elimination from dithia[3.3]cyclophanes has proved to be very useful as a general method of [2.2]cyclophanes.[8] This successful approach results from a facile extrusion of sulfur atom bonded to two benzyl groups forming relatively stable radicals in desulfurization, in contrast to stubborn sulfur atom bonded to alkyl groups. When bonded to phenethyl or longer phenylalkyl groups, elimination of sulfur atom was difficult due to predominant decomposition. Recently we found that when either of two interposing groups was benzyl group, a similar extrusion of sulfur smoothly proceeded, and a series of [*n*]cyclophanes was prepared by desulfurization of such type of dithiacyclophanes.[9] Furthermore, this method made it possible to extend to the syntheses of higher homologues of [*n.n*]paracyclophanes. Here we present a general method for syntheses of [3.3]- and [4.4]paracyclophanes **1** and **2** and the application to a variety of [3.3]- and related cyclophanes **3**—**7**.[10] Their absorption and emission spectra are discussed together with those of [2.2]-analogues from view points of transannular electronic interaction and excimer formation.

Results and Discussion

Syntheses: All the starting materials required in



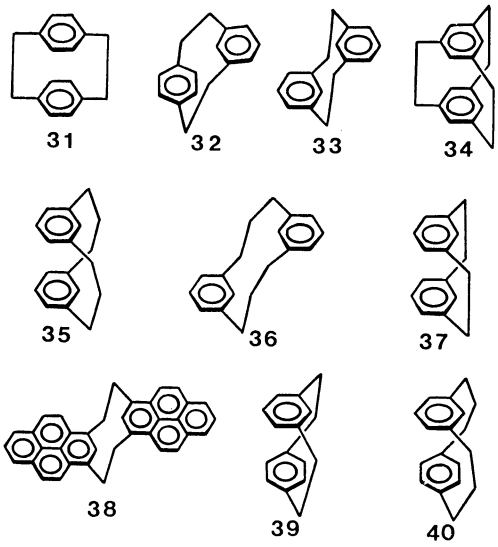
Scheme 1.



Scheme 2.

the general synthesis of cyclic thia compounds were prepared according to the literatures or conventional methods, except commercially available **9** and **15**.[11] Cyclic thia compounds **10**, **13**, **16**, **19**, **23**, **26**, and **29** were obtained in high yields (60—90%) by the corresponding coupling reactions of these precursors under high dilution conditions. [3.3]Paracyclophane **1** was produced by irradiation of 2,13-dithia[4.4]-paracyclophane **10** in triethyl phosphite with a high pressure mercury lamp for one week in 24% yield or with a low pressure mercury lamp for 15 h in 20% yield. As an alternative route, **10** was oxidized with hydrogen peroxide (95% yield) or *m*-chloroperbenzoic acid (81% yield) to disulfone **11**, and the subsequent pyrolysis of **11** gave **1** in 75% yield (flash pyrolysis) or in 33% yield (flow system pyrolysis).[12] [4.4]-Paracyclophane **2**[13] was similarly prepared by oxidation (97% yield) of 2,15-dithia[5.5]paracyclophane **13**, followed by pyrolysis (76% yield) of disulfone **14**. In this case, the direct photodesulfurization of **13** to **2** was unsuccessful. The pyrolytic method is widely applicable to the syntheses of all the other [3.3]-cyclophanes, *i.e.*, [3.3]metaparacyclophane **3** (40% yield), [3.3]metacyclophane **4**[7] (52%), [3.3.3](1,3,5)-cyclophane **5**[14] (16%), [3.3]paracyclo(1,4)naphthalenophane **6** (37%), and [3.3]paracyclo(2,6)naphthalenophane **7** (13%). The photochemical method was also applied with success for the synthesis of **6** (5.6%) and **7** (12%), but not for **3**, **4**, and **5**. All the new compounds were characterized by NMR and mass spectra and elemental analyses.

Electronic Absorption Spectra: Cram *et al.* reported that the electronic spectra of [*m.n*]paracyclophanes showed bathochromic shift and broadening of absorption bands due to an increasing transannular π-electronic interaction between the two benzenes as the number of *n* and *m* decreased.[2] As seen in the spectra of [2.2]- and [3.3]paracyclophanes (Fig. 1), these anoma-



Scheme 3.

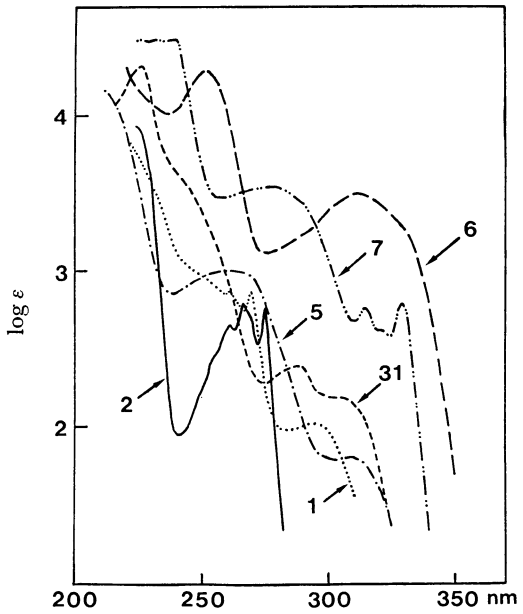


Fig. 1. Electronic spectra of cyclophanes **1**, **2**, **5**, **6**, **7**, and **31** in tetrahydrofuran.

lous phenomena become marked when the two benzene rings were more closely fixed within van der Waals contact.[4,15] It should be noted that the interaction depends not only on ring-to-ring distance but also on overlapping mode. Thus, the two benzenes of [2.2]paracyclophane **31** are well superposed on each other,[15] whereas those of [3.3]paracyclophane **1** are stacked with a little parallel displacement, so that the $p\pi$-$p\pi$ overlap somewhat diminishes.[4] The overlapping in [3.3.3](1,3,5)cyclophane **5** is very similar as in **31**, though the ring-to-ring distance is the almost same as that of **1**. If the ring-to-ring distance is main factor for the spectral anomalousness of cyclophanes, **5** should show a spectrum similar to that of **1**. In practice, however, it showed considerable red shift of the longest wavelength band compared to that of **1**, and its maxima (λ_{max} 261 and 310 nm) are, interestingly, quite similar to those (λ_{max} 258 and 312 nm) of the lower homologue, *i.e.*, [2.2.2]-(1,3,5)cyclophane **34**.[16] This result clearly indicates the significance of the overlapping mode rather than the ring-to-ring distance. The spectra of the two paracyclonaphthalenophanes **6** and **7** also reflect the difference in the overlapping mode. According to molecular model examination, the benzene ring of [3.3]paracyclo(2,6)naphthalenophane **7** is stacked above the center of the faced naphthalene ring, but $p\pi$-$p\pi$ overlapping may be less effective than that of [3.3]paracyclo(1,4)naphthalenophane **6**. In fact, the longest wavelength band (L_b transition) of **7** shows only a small red shift by *ca.* 5 nm as compared to that of 2,6-dimethylnaphthalene and retains a fine structure, while that of **6** shows a striking red shift by *ca.* 25—30 nm as compared to that of 1,4-dimethylnaphthalene.

[2.2]Metaparacyclophane **32** and [2.2]metacyclophane **33** exhibit weak transannular interaction due to partial overlapping of two benzene rings in the spectra (Fig. 2). [3.3]Metaparacyclophane **3** no longer

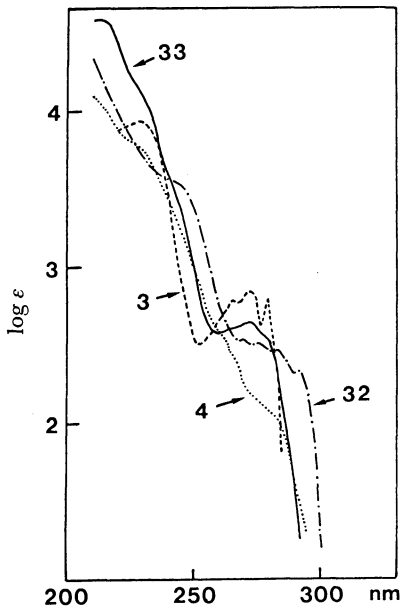


Fig. 2. Electronic spectra of cyclophanes **3** and **4** in tetrahydrofuran and **32** and **33** in cyclohexane.

demonstrates such an effect because the two benzene rings are far apart beyond van der Waals contact. However, [3.3]metacyclophane **4** is not the case, in spite of longer distance between the two benzene rings. Its absorption bands are more broad than that of the lower homologue **33**. This can be explained by a conformational flipping between syn and anti forms, which occurs much easily than the corresponding [2.2] system **33**. Thus, **33** exists only as the anti form,[17] which is hardly interconvertible to syn form, whereas **4** favors the syn form **35** over the anti form **36**, according to molecular model examination. In other words, the increased overlapping of the two benzene rings in the syn form seems to be responsible for the marked interaction in [3.3]system.

Emission Spectra: The emission spectra of paracyclophanes have been studied as a model for examining the structure of benzene excimer, *i.e.*, dimolecular associate in excited state.[18] For example, Vala *et al.* observed the excimer emissions of [2.2]- and [4.4]-paracyclophanes **31** and **2**, indicating that an excimer was formed when two benzene rings were stacked in parallel.[19] Study on the emission spectrum of [3.3]-paracyclophane, in which two benzenes are stacked with little strain, is expected to give further information about the excimer structure. Excimer fluorescences are readily distinguishable from the normal monomer fluorescences, because the former is characterized by large Stokes shifts, broadening, and weak intensity of emission bands.

Table 1 summarizes the emission data of the present cyclophanes measured at 77 K and room temperature (RT). [2.2]- And [3.3]paracyclophanes **31** and **1** and [3.3.3]cyclophane **5** exhibit excimer emissions at both temperatures, although their maxima appear at somewhat longer wavelength due to benzene ring warping than that (*ca.* 330 nm) of ordinary benzene excimer.[20] [4.4]Paracyclophane **4** shows an excimer emission at RT, but a monomer emission at 77 K. These results obviously indicate that the structures of **31** and **1** are favorable for strong π-π interaction even at the ground state, whereas **2** requires a conformational change to bring the two benzene rings close to a certain distance equal to or less than van der Waals contact for the excimer formation.[21]

Shizuka *et al.* reported that **33**, which is consisted of anti form alone in the ground state, exhibited an excimer fluorescence together with a normal fluorescence at RT but no excimer fluorescence at 77 K, and the excimer fluorescence was resulted from its syn form[22] A similar conversion of anti form to syn form in the excited state was observed with [2.2]-(1,3)pyrenophane **38**.[23] The fact that **33** exhibits excimer emission only at RT implies considerable activation energy for syn-anti conversion. In addition, significant red shift of the emission band (392 nm) reflects the severe strain in the syn form. On the other hand, [3.3]metacyclophane, which favors syn form in the ground state in contrast to anti form for **33**, emits an excimer fluorescence characteristic of less strained system even at 77 K.

[2.2]- and [3.3]metaparacyclophanes **32** and **3** exhibit both monomer and excimer emissions at RT and

Table 1. Emission spectra of [2.2]- and [3.3]cyclophanes in EPA

Compound	Temp	Fluorescence	Phosphorescence (nm)
[2.2]Paracyclophane **31**	77 K	354 (excimer)[a]	470[a]
	RT	350 (excimer)[a]	
[3.3]Paracyclophane **1**	77 K	361 (excimer)[a]	463[a]
	RT	358 (excimer)[a]	
[3.3.3](1,3,5)Cyclophane **5**	77 K	374 (excimer)[a]	446[a]
	RT	371 (excimer)[a]	
[4.4]Paracyclophane **2**	77 K	281 (monomer)[b]	379[b]
	RT	335 (excimer)[a]	
[2.2]Metacyclophane **32**	77 K	296 (monomer)[b]	372[b]
	RT	392 (excimer)[a]	
[3.3]Metacyclophane **4**	77 K	284 (monomer),[a] 349 (excimer)[a]	440[a]
	RT	348 (excimer)[a]	
[2.2]Metaparacyclophane **32**	77 K	310 (monomer)[b]	474[a]
	RT	314 (monomer),[a] 393 (excimer)[a]	
[3.3]Metaparacyclophane **3**	77 K	286 (monomer)[b]	398[b]
	RT	292 (monomer),[a] 393 (excimer)[a]	
[3.3]Paracyclo(1,4)naphthalenophane **6**	77 K	370 (excimer)[a]	554[b]
	RT	372 (excimer)[a]	
[3.3]Paracyclo(2,6)naphthalenophane **7**	77 K	346 (monomer)[b]	504[b]
	RT	346 (monomer)[b]	

a) Broad. b) Fine structure.

only monomer emission at 77 K. The maxima of their excimer bands lie at a wavelength comparable to that of **33**. The emission spectra suggest their structures to be of sandwich type with severe strain such as **39** and **40**, in which the two benzene rings are stacked with remarkably different mode compared to the syn form of **33**.

The orientation dependence of excimer formation was found in the case of paracyclonaphthalenophanes **6** and **7**. The 1,4-isomer **6** exhibits an excimer emission at RT and 77 K, whereas the 2,6-isomer **7** a monomer emission at both temperatures. Evidently, $p\pi$-$p\pi$ interaction is also an important factor for excimer formation.

Experimental

Melting points are uncorrected. All solvents are of reagent grade. NMR measurements were made with a Hitachi Perkin-Elmer R-20 spectrometer (60 MHz) or a JEOL JNM-FX100 in deuteriochloroform using tetramethylsilane as an internal standard. Mass spectra were determined on a Hitachi RMU-7 spectrometer at 70 eV using direct insertion technique. UV spectra were recorded on a Hitachi EPS-3T spectrophotometer. Emission spectra were taken on a Hitachi MPF-2A spectrophotometer attached with a HTV R-446F photomultiplier in EPA (ethyl ether–isopentane–ethanol of 5 : 5 : 2 volume ratio). A solution of about 1×10^{-3} M was prepared and degassed by freeze-pump-thaw method. Emission spectra were uncorrected.

1,4-Bis(2-mercaptoethyl)benzene ***8***. A mixture of 1,4-bis(2-bromoethyl)benzene[24] (19.70 g, 0.068 mol) and thiourea (12.32 g, 0.162 mol) in 200 ml of 95% ethanol was refluxed with stirring for 2.5 h. After evaporation of the solvent, the residue was refluxed with potassium hydroxide (80 g) in 400 ml of water for 7 h under nitrogen. The mixture was cooled in an ice bath and acidified with 1 : 1 of concd sulfuric acid–water. The resulting oil was extracted with benzene. The extract was washed with water, dried over anhyd magnesium sulfate, and evaporated to give a colorless oil, 12.83 g (96%), bp 125—127 °C/1 Torr.

NMR ($CDCl_3$, 60 MHz) δ=1.39(m, 2H, SH), 2.4—3.0 (m, 8H, CH_2), 7.14 ppm(s, 4H, ArH). Found: C, 60.29; H, 6.82; S, 32.14%. Calcd for $C_{10}H_{14}S_2$: C, 60.55; H, 7.11; S, 32.33%.

1,4-Bis(3-mercaptopropyl)benzene ***12***. Dithiol **12** was obtained in 97% yield from 1,4-bis(3-bromopropyl)benzene[25] in a similar manner as described in dithiol **8**; colorless oil, bp 165—167 °C/2 Torr.

NMR ($CDCl_3$, 60 MHz) δ=1.34(t, 2H, J=8 Hz, SH), 1.89(quint, 4H, J=7 Hz, CH_2), 2.48(t, 4H, J=7 Hz, CH_2S), 2.71(t, 4H, J=7 Hz, $ArCH_2$), and 7.09 ppm(s, 4H, ArH). Found: C, 63.81; H, 7.95; S, 28.13%. Calcd for $C_{12}H_{18}S_2$: C, 63.66; H, 8.01; S, 28.32%.

1,4-Bis(2-mercaptoethyl)benzene ***18***. Dithiol **18** was led from 1,3-bis(ethoxycarbonylmethyl)benzene[26] as described below.

A solution of 1,3-bis(ethoxycarbonylmethyl)benzene(1.65 g, 6.6 mmol) in 15 ml of dry tetrahydrofuran was slowly added into a suspension of lithium aluminium hydride (0.53g, 13.9 mmol) in 25 ml of dry THF over a period of 30 min at room temperature. After 30 min of reflux, a small amount of ethyl acetate, water, and dil hydrochloric acid were added successively. The mixture was saturated with sodium chloride and extracted with ethyl ether. The extract was washed with satd. aq NaCl solution and dried over magnesium sulfate. Evaporation gave a colorless oil of 1,3-bis(2-hydroxyethyl)benzene, 1.05 g (96%).

NMR ($CDCl_3$, 100 MHz) δ=2.75(t, 4H, J=6.7 Hz, $ArCH_2$), 3.27(bs, 2H, OH), 3.71(t, 4H, J=6.7 Hz, CH_2O), and 6.9—7.3 ppm(m, 4H, ArH).

The above 1,3-bis(2-hydroxyethyl)benzene (1.48 g, 8.9 mmol) was mixed with 100 ml of 48% hydrobromic acid and 6 ml of concd sulfuric acid. The mixture was refluxed for 1.5 h, cooled to room temperature, and extracted with benzene. The extract was washed with water and dried over anhyd magnesium sulfate. Evaporation gave a colorless oil of 1,3-bis(2-bromoethyl)benzene, 3.2 g (84%), bp 141 °C/2 Torr.

NMR ($CDCl_3$, 100 MHz) δ=3.12(A_2B_2m, 4H, $ArCH_2$), 3.53(A_2B_2m, 4H, CH_2Br), and 7.0—7.3 ppm(m, 4H, ArH).

The above dibromide was converted to 1,3-bis(2-mercaptoethyl)benzene **18** in 81% yield as described in the para analogue **8**; colorless oil, bp 115 °C/10 Torr.

NMR ($CDCl_3$, 60 MHz) δ=1.37(m, 2H, SH), 2.5—3.1 (m, 8H, CH_2), and 7.0—7.3 ppm(m, 4H, ArH). Found: C, 60.28; H, 6.81; S, 32.12%. Calcd for $C_{10}H_{14}S_2$: C, 60.55; H, 7.11; S, 32.33%.

General Method of Coupling Reaction. A solution of the corresponding thiol (0.01 mol) and halide (0.01 mol) in 100 ml of benzene was added dropwise into a refluxed ethanol solution (1 l) containing potassium hydroxide (1.78 g) in a nitrogen atmosphere. The addition was complete in 12 h. The mixture was refluxed an additional 12 h and then concentrated. The residue was taken up in benzene and chromatographed over silica gel with benzene–hexane (1 : 1) to give a crystalline solid of the desired cyclic dithia compound from the main fraction of eluates.

2,13-Dithia[4.4]paracyclophane ***10.*** Yield 62%, colorless plates from benzene, mp 183—185 °C.

NMR ($CDCl_3$, 60 MHz) δ=2.75(A_2B_2m, 8H, CH_2), 3.39(s, 4H, CH_2), and 6.80 ppm(s, 8H, ArH). MS *m/e* 300(M^+). Found: C, 71.75; H, 6.57; S, 21.11%. Calcd for $C_{18}H_{20}S_2$: C, 71.95; H, 6.71; S, 21.34%.

2,15-Dithia[5.5]paracyclophane ***13.*** Yield 91%, colorless scales from benzene–hexane, mp 153—153.5 °C.

NMR ($CDCl_3$, 60 MHz) δ=1.85(m, 8H, CH_2), 2.60 (m, 4H, $ArCH_2$), 3.55(s, 4H, $ArCH_2S$), 6.87(s, 4H, ArH), and 7.03 ppm (s, 4H, ArH). MS *m/e* 328(M^+). Found: C, 72.94; H, 7.36; S, 19.30%. Calcd for $C_{20}H_{24}S_2$: C, 73.12; H, 7.36; S, 19.52%.

3,12-Dithia[4.4]metaparacyclophane ***16.*** Yield 76%, colorless needles from benzene–hexane, mp 81—82 °C.

NMR ($CDCl_3$, 60 MHz) δ=2.83(bs, 8H, CH_2), 3.46(s, 4H, $ArCH_2S$), 6.40(bs, 1H, meta ArH), 6.88(s, 4H, para ArH), and 6.98 ppm(bs, 3H, meta ArH). MS *m/e* 300(M^+). Found: C, 71.78; H, 6.53; S, 21.61%. Calcd for $C_{18}H_{20}S_2$: C, 71.95; H, 6.71; S, 21.34%.

2,13-Dithia[4.4]metacyclophane ***19.*** Yield 79%, colorless prisms from benzene–hexane, mp 109—109.5 °C.

NMR ($CDCl_3$, 60 MHz) δ=2.74(A_2B_2m, 8H, CH_2), 3.65(s, 4H, $ArCH_2S$), 6.67(bs, 1H, ArH), 7.0—7.2(m, 3H, ArH), and 7.39 ppm(bs, 4H, ArH). MS *m/e* 300(M^+). Found: C, 72.06; H, 6.52; S, 29.49%. Calcd for $C_{18}H_{20}S_2$: C, 71.95; H, 6.71; S, 21.34%.

2,13,22-Trithia[4.4.4](1,3,5)cyclophane ***23.*** Yield 65%, colorless plates from benzene–hexane, mp 251—252 °C.

NMR ($CDCl_3$, 100 MHz) δ=2.71(A_2B_2m, 12H, CH_2), 3.31(s, 6H, $ArCH_2S$), 6.56(s, 3H, ArH), and 6.62 ppm (s, 3H, ArH). MS *m/e* 372 (M^+). Found: C, 67.87; H, 6.65; S, 25.57%. Calcd for $C_{21}H_{24}S_3$: C, 67.69; H, 6.49; S, 25.82%.

2,13-Dithia[4.4]paracyclo(1,4)naphthalenophane ***26.*** Yield 63%, colorless columns from benzene–hexane, mp 187—188 °C.

NMR ($CDCl_3$, 60 MHz) δ=2.3—3.1(A_2B_2m, 8H, CH_2), 3.86(s, 4H, $ArCH_2S$), 6.45(s, 4H, ArH), 6.72(s, 2H, ArH), 7.53(A_2B_2dd, 2H, J=7 and 3 Hz, ArH), and 8.02 ppm (A_2B_2dd, 2H, J=7 and 3 Hz, ArH). MS *m/e* 350(M^+). Found: C, 75.65; H, 6.17; S, 18.04%. Calcd for $C_{22}H_{22}S_2$: C, 75.38; H, 6.33; S, 18.29%.

2,13-Dithia[4.4]paracyclo(2,6)naphthalenophane ***29.*** Yield 89%, colorless plates from benzene–hexane, mp 198—200 °C.

NMR ($CDCl_3$, 60 MHz) δ=2.2—2.8(m, 8H, CH_2), 3.77 (s, 4H, $ArCH_2S$), 6.41(s, 4H, ArH), 7.26(ABd, 2H, J=8 Hz, ArH), 7.36(bs, 2H, ArH), and 7.53 ppm(ABd, 2H, J=8 Hz, ArH). Found: C, 75.52; H, 6.19; S, 18.51%. Calcd for $C_{22}H_{22}S_2$: C, 75.38; H, 6.33; S, 18.29%.

General Synthetic Method of Disulfone. A) With Hydrogen Peroxide: Cyclic disulfide (4 mmol) was mixed with 8 ml of acetic acid and 2.4 ml of 35% hydrogen peroxide, and heated at 100 °C with stirring for 6 h. The mixture was cooled in an ice bath, and the resulting white crystalline solid of disulfone was filtered, washed, and dried.

B) With m-Chloroperbenzoic Acid: A mixture of cyclic disulfide (1 mmol) and *m*-chloroperbenzoic acid (1.1 g, 6 mmol as 85% active) in 20 ml of dichloromethane was stirred at room temperature for 2 d. After some milliliters of dichloromethane was added to dissolve the resulting precipitate, the solution was washed successively with 3M NaOH solution and water, dried, and concentrated to give a white powder of disulfone. Disulfones thus obtained were essentially pure and used in the following pyrolysis without further purification.

2,13-Dithia[4.4]paracyclophane 2,2,13,13-tetraoxide **11**, yield 95%(method A) and 81%(method B), dec 330—340 °C. 2,15-Dithia[5.5]paracyclophane 2,2,15,15-tetraoxide **14**, yield 97%(by A), dec 310—320 °C. 3,12-Dithia[4.4]-metaparacyclophane 3,3,12,12-tetraoxide **17**, yield 90% (by A) and 67%(by B), mp 283—285 °C. 3,12-Dithia-[4.4]metacyclophane 3,3,12,12-tetraoxide **20**, yield 72% (by B), dec 320—325 °C with melting. 2,13,22-Trithia-[4.4.4](1,3,5)cyclophane 2,2,13,13,22,22-hexaoxide **24**, yield 83%(by A), dec 350 °C. 2,13-Dithia[4.4]paracyclo(1,4)-naphthalenophane 2,2,13,13-tetraoxide **27**, yield 82% (by B), dec 240 °C. 2,13-Dithia[4.4]paracyclo(2,6)naphthalenophane 2,2,13,13-tetraoxide **30**, yield 96%(by A), dec 320—330 °C.

General Synthetic Method of [3.3]-, [4.4]-, and [3.3.3]Cyclophanes. A)Flash Pyrolysis: Sulfone (100—500 mg) was packed in a Pyrex tube sealed at one end. The open end was connected to a rotary pump and the system was maintained under 0.1—0.5 Torr. The tube was placed in a furnace (15 cm in length, preheated to 650 °C) in such a way as the middle of the tube could be heated. The sample part was slidden smoothly inside the furnace. As soon as pyrolysis started, an oily product condensed at the opposite cool end. Column chromatography of the product on silica gel with hexane led to the isolation of the desired cyclophane as white crystals.

B) Flow System Pyrolysis: Sulfone (100 mg) was placed in a pyrolytic flow system modelled after that of Boekelheide *et al.*[27] The first furnace was set at 300 °C and the second at 600 °C. The whole system was maintained under 0.1 Torr. The pyrolysis was complete in a few hours. The resulting cyclophane was trapped in the cold finger and purified by column chromatography.

C) Photodesulfurization: Cyclic dithia compound (100 mg) was dissolved in 10 ml of benzene and 5 ml of triethyl phosphite in a quartz tube. The solution was irradiated with a high pressure mercury lamp in a nitrogen atmosphere (one week for [3.3]paracyclophane and 3 h for [3.3]paracyclonaphthalenophane). After removal of the solvent, the residue was chromatographed on silica gel to give white crystals of the desired product.

[3.3]Paracyclophane ***1.*** Yield 75% (method A), 33% (method B), and 24%(method C), colorless plates from methanol, mp 103—104 °C (lit[2], mp 104.3—105.3 °C).

NMR ($CDCl_3$, 60 MHz) δ=2.03(m, 4H, CH_2), 2.72 (t, 8H, CH_2), and 6.66 ppm(s, 8H, ArH). MS *m/e* 236 (M^+).

[4.4]Paracyclophane ***2.*** Yield 76%(by A), colorless

plates from ethanol, mp 147.5—149 °C (lit,[13] mp 146.2—147.3 °C).

NMR ($CDCl_3$, 60 MHz) δ=1.6(m, 4H, CH_2), 2.3(m, 4H, $ArCH_2$), and 6.68 ppm(s, 8H, ArH). MS *m/e* 264 (M^+).

[3.3]Metaparacyclophane ***3***. Yield 40% (by A), 20% (by B), colorless plates from hexane, mp 90—91 °C.

NMR ($CDCl_3$, 60 MHz) δ=1.9—2.9(m, 8H, CH_2), 2.71(t, 4H, J=6 Hz, CH_2), 5.55(bs, 1H, meta ArH), 6.63 (s, 4H, para ArH), and 6.6—7.2 ppm (m, 3H, meta ArH). MS *m/e* 236(M^+). Found: C, 91.25; H, 8.30%. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53%.

[3.3]Metacyclophane ***4***. Yield 52% (by A), 2.7% (by B), colorless plates from ethanol, mp 81—82 °C (lit,[7] 79—80 °C).

NMR ($CDCl_3$, 100 MHz) δ=1.92—2.15(m, 4H, CH_2), 2.74(t, 8H, J=5.8 Hz, $ArCH_2$), 6.54—6.84 (A_2B_2m, 6H, outer ArH), and 6.84 ppm(bs, 2H, inner ArH). MS *m/e* 236(M^+).

[3.3.3](1,3,5)Cyclophane ***5***. Yiled 16% (by A), colorless plates from pentane, mp 134—135.5 °C (lit,[14] mp 140 °C).

NMR ($CDCl_3$, 100 MHz) δ=2.18(m, 6H, CH_2), 2.75 (t, 12H, J=5.8 Hz, $ArCH_2$), and 6.52 ppm(s, 6H, ArH). MS *m/e* 276 (M^+).

[3.3]Paracyclo(1,4)naphthalenophane ***6***. Yield 13% (by A), 12% (by C), colorless fine crystals from pentane, mp 106—107 °C.

NMR ($CDCl_3$, 60 MHz) δ=2.0—3.0(m, 10H, CH_2), 3.4—3.8(m, 2H, CH_2), 5.95(bs, 2H, ArH), 6.70(s, 2H, ArH), 6.76(bs, 2H, ArH), 7.43(A_2B_2dd, 2H, J=7 and 3 Hz, ArH), and 7.94 ppm(A_2B_2dd, 2H, J=7 and 3 Hz, ArH). MS *m/e* 286(M^+). Found: C, 91.82; H, 7.32%. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74%.

[3.3]Paracyclo(2,6)naphthalenophane ***7***. Yield 37% (by A), 5.6% (by C), colorless plates from benzene-hexane, mp 160—161 °C.

NMR ($CDCl_3$, 60 MHz) δ=1.8—3.0(m, 12H, CH_2), 6.04(s, 4H, ArH), 7.01(bs, 2H, ArH), and 7.13 ppm(bs, 2H, ArH). MS *m/e* 286(M^+).

Found: C, 92.31; H, 7.51%. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74%.

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