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Layered Compounds. LXII.[1] Triple-layered [*m.m*][*n.n*]Paracyclophanes: Syntheses and Spectra

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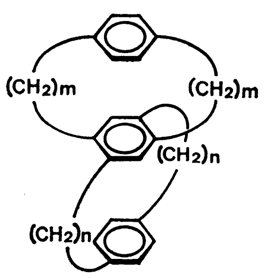
(Received August 7, 1979)

A series of the title cyclophanes ($m, n=2$—4) were synthesized by the thermal- and photo-desulfurization methods from dithia intermediates. Their absorption and emission spectra were measured to examine the transannular electronic interaction. The absorption spectra of the title compounds and their TCNE complexes gave the same order of the interaction as seen in the case of double-layered system: [2.2]>[3.3]>[4.4] in neutral state and [3.3]>[2.2]>[4.4] in CT state. The emission spectra are discussed in terms of the existence of excited trimer.

In the previous papers of this series we reported the physical and chemical properties of multilayered [2.2]paracyclophanes to be strongly affected by the transannular π-electronic interactions among the stacked benzene rings. In addition to the electronic interaction, their severe molecular strain due to rigid [2.2]phane framework gave rise to intriguing behaviors such as catalytic skeletal rearrangement.[3] In order to pursue only transannular electronic interaction without strain effect, it is more instructive to study some series of multilayered [*m*. *n*]paracyclophanes with longer bridging chain.

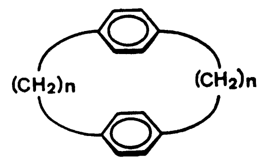
For example, [3.3]paracyclophane is much more suitable for this purpose because of far less strained sandwich framework compared to [2.2]paracyclophane. It was already pointed out that double-layered [3.3]-paracyclophane **8** is a better system for both intermolecular and intramolecular charge-transfer interactions than [2.2]paracyclophane **7**.[4,5] So, multilayered [3.3]paracyclophanes are expected to reveal more unique behaviors with the increase of layer number. In addition, it is interesting to see if [4.4]phane system exerts such a multilayer effect although [4.4]paracyclophane **9** exhibits less transannular interaction.

For the above-stated purpose, we have intended to investigate a series of triple-layered [*m.m*][*n.n*]paracyclophanes **1**—**6** with combined numbers of the bridging methylene, *i.e.*, m and $n=2$—4.[6] This paper presents their syntheses and spectral properties.



1, m = n = 2
2, m = 2, n = 3
3, m = n = 3
4, m = 2, n = 4
5, m = 3, n = 4
6, m = n = 4

Scheme 1.

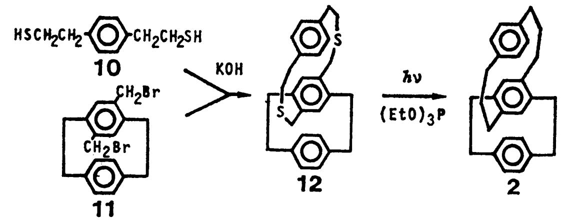


7, n = 2
8, n = 3
9, n = 4

Scheme 2.

Results and Discussion

Syntheses. Although the syntheses of [3.3]- and [4.4]paracyclophanes, **8** and **9**, were difficult before, new synthetic routes through sulfur extrusion of the corresponding dithia homologs have recently developed for the general use.[7] These methods are also useful to the syntheses of the present triple-layered [*m.m*][*n.n*]-paracyclophanes **2**—**6**, that is to say, by stepwise stacking of *para*-substituted benzenes. For example, in the case of [2.2][3.3]paracyclophane **2** the [2.2]-framework was at first constructed by the Hofmann elimination method as previously reported.[2] The resulting 4,7-bis(bromomethyl)paracyclophane **11**[8] was treated with 1,4-bis(2-mercaptoethyl)benzene **10**[7a] to give dithia[2.2][4.4]paracyclophane **12** in 25% yield. Irradiation of **12** in triethyl phosphite with a high pressure mercury lamp for 6 h led to the formation of the desired cyclophane **2** in 23% yield.



Scheme 3.

A similar route to derive [3.3][3.3]homolog **3** requires 5,8-bis(bromomethyl)[3.3]paracyclophane **20** as a key intermediate, which is not readily accessible.[9]

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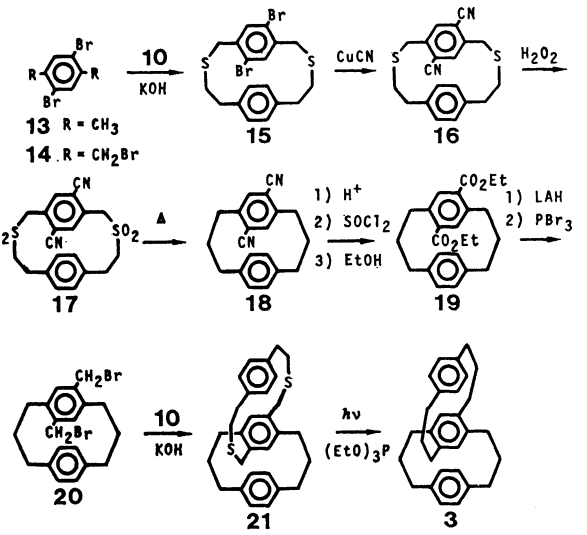
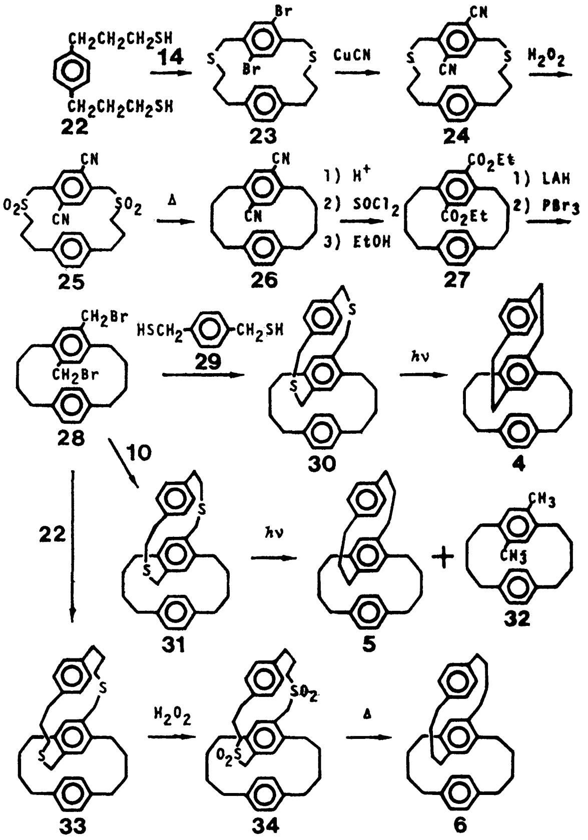
One successful but laborious approach has been developed. Treatment of 2,5-dibromo-*p*-xylene **13**[10] with NBS gave 2,5-dibromo-1,4-bis(bromomethyl)benzene **14** in 34% yield. A coupling reaction between **10** and **14** led to 16,19-dibromo-2,13-dithia[4.4]paracyclophane **15** in 62% yield, which was treated with copper(I) cyanide in *N*-methylpyrrolidinone to afford dicyano derivative **16** in 68% yield. 5,8-Dicyano-[3.3]paracyclophane **18** was obtained in 40% yield by oxidation of **16** with hydrogen peroxide to give disulfone **17**, followed by pyrolysis. Although hydrolysis of **18** in basic conditions failed, it was hydrolyzed in a boiling solution of sulfuric acid–acetic acid, and treatment of the resulting acid with thionyl chloride and then with absolute ethanol produced 5,8-bis(ethoxycarbonyl)[3.3]paracyclophane **19** in 46% yield. Reduction of **19** with lithium aluminium hydride followed by bromination with phosphorus tribromide gave the desired bromide **20** in satisfactory yield. [3.3][3.3]Paracyclophane **3** was derived from **20** in quite similar manner as described for **2**.



Scheme 4.

For [4.4]phane series, 6,9-bis(bromomethyl)[4.4]paracyclophane **28** was prepared according to the same reaction sequence. Dithiacyclophanes **30**, **31**, and **33** were similarly obtained by reactions of bromide **28** with dithiols **29**, **10**, and **22**, respectively, in high yields. Photodesulfurization of **30** proceeded smoothly to afford [2.2][4.4]paracyclophane **4** in 55% yield. A similar reaction of **31** was ineffective with a high pressure mercury lamp because of the poor absorbance of **31**. This was improved by use of a low pressure mercury lamp, and [3.3][4.4]paracyclophane (**5**) was formed in 12% yield together with 6,9-dimethyl[4.4]paracyclophane (**32**) as a by-product. On the other hand, the formation of [4.4][4.4]paracyclophane (**6**) was accomplished by the pyrolytic method (5% yield), for any photochemical attempt was unsuccessful.



Scheme 5.

Electronic Absorption Spectra. It is well known that the transannular electronic interaction in cyclophane results in the bathochromic and hyperchromic shifts of the absorption bands in its electronic spectrum and the magnitude of these shifts is simply utilized as a measure of the interaction.[2] As shown in Fig. 1, the shifts of a series of triple-layered paracyclophanes are in an order of [4.4][4.4]PC **6**<[3.3][4.4]PC **5**<[2.2][4.4]PC **4**<[3.3][3.3]PC **3**<[2.2][3.3]PC **2**<[2.2][2.2]PC **1** (PC: paracyclophane). It is evidently concluded

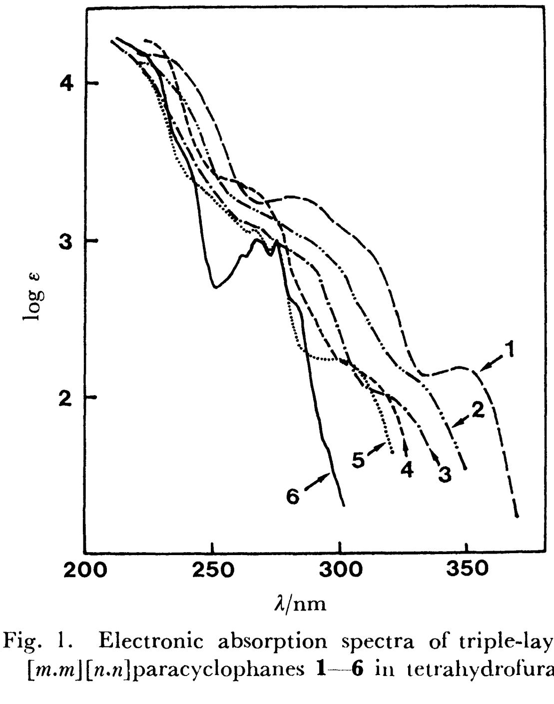


Fig. 1. Electronic absorption spectra of triple-layered [*m.m*][*n.n*]paracyclophanes **1**—**6** in tetrahydrofuran.

Table 1. Charge-transfer absorption maxima of cyclophane–TCNE complexes in dichloromethane

Compd		λ_{max}/nm	Compd		λ_{max}/nm
[2.2][2.2]PC[a]	**1**	530[b], 630	[4.4][4.4]PC[a]	**6**	423, 499
[2.2][3.3]PC	**2**	412, 640	[2.2]PC	**7**	521
[3.3][3.3]PC	**3**	421, 655	[3.3]PC	**8**	485, 600
[2.2][4.4]PC	**4**	425[b], 525,	[4.4]PC	**9**	475,
[3.3][4.4]PC	**5**	420, 546, 625[b]	*p*-xylene		420, 465[b]

a) PC: paracyclophane, b) Shoulder.

that the transannular interactions of triple-layered paracyclophanes depend mainly on a pair of the ring-to-ring distances in each molecule and [2.2]phane system with the shortest distance is most effective. [4.4]Phane system shows no interaction even when triply layered, that is, the $^1B_{2u}$ transition of **6** still retains fine structure, characteristic of alkylbenzenes. Also the spectral shapes of **4** and **5** are essentially same as those of [2.2]paracyclophane **7** and [3.3]paracyclophane **8**, respectively.[11]

Charge-transfer Complexes. The charge-transfer spectra of cyclophane–tetracyanoethylene complexes were measured to obtain further information concerning the transannular interaction. The π-donor character of the complexing benzene in cyclophane is enhanced by a transannular electron release from the remaining faced benzene ring. Cram *et al.* reported that double-layered [3.3]paracyclophane **8** was rather stronger π-donor than [2.2]paracyclophane **7**.[4] This indicates that [3.3]phane system is favored over [2.2]phane system for the transannular interaction in charge-transfer state. The CT spectra of a series of triple-layered paracyclophanes are shown in Fig. 2 and Table 1. The order of the shifts is the same as seen in double-layered case. Thus, [3.3][3.3]paracyclophane **3** is the strongest donor of all the triple-layered cyclophanes. The presence of the transannular interaction in CT complexes of [4.4]-phane system is supported by a red shift of the CT band of [4.4][4.4]paracyclophane **6** compared with *p*-xylene or [4.4]paracyclophane **9**.

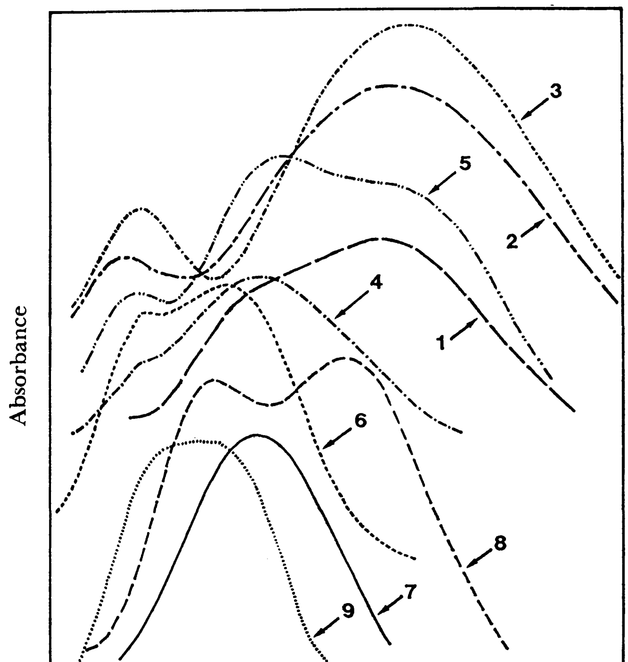


Fig. 2. Charge-transfer spectra of cyclophane–TCNE complexes in dichloromethane. Curves are all displaced on the vertical axis for separation.

Emission Spectra. Some of double-layered cyclophanes provide suitable models for the study of excimer which is well known to exist only in excited state and to show a fluorescence band in longer wavelength than the monomer fluorescence.[12] In the previous paper, we described on the basis of fluorescence spectra data that [2.2]- and [3.3]paracyclophanes, **7** and **8**, have structures resemble to the benzene excimer, whereas [4.4]paracyclophane **9** undergoes conformational change for the excimer formation.

An interesting question is whether any excited trimer exists or not. There has been found an example of termolecular exciplex composed of 2: 1 ratio of donor: acceptor.[13] The formation of neutral excited intramolecular trimer is also possible when considered a marked interaction in multilayered cyclophanes, although it is unfavorable on entropy to form intermolec-

Table 2. Emission data of triple-layered [*m.m*][*n.n*]-paracyclophanes and [*m.n*]paracyclophanes in EPA

Compd		Temp	Fluorescence λ_{max}/nm	Phosphorescence λ_{max}/nm
[2.2][2.2]PC[a]	**1**	77 K	380[c]	524, 542, 560
		RT[b]	384[c]	
[2.2][3.3]PC	**2**	77 K	381[c]	513
		RT	381[c]	
[3.3][3.3]PC	**3**	77 K	376[c]	474
		RT	377[c]	
[2.2][4.4]PC	**4**	77 K	358[c]	467
		RT	356[c]	
[3.3][4.4]PC	**5**	77 K	357[c]	457
		RT	356[c]	
[4.4][4.4]PC	**6**	77 K	285[d]	389
		RT	330[c], 395[c]	
[2.2]PC	**7**	77 K	354[c]	470
		RT	350[c]	
[3.3]PC	**8**	77 K	361[c]	463
		RT	358[c]	
[4.4]PC	**9**	77 K	281[d]	379
		RT	335[c]	

a) PC: paracyclophane. b) Room temperature. c) Excimer emission, broad. d) Monomer emission with fine structure.

ularly a termolecular aggregate. The present triple-layered paracyclophanes are expected to provide a helpful information about the excited trimer.

Their emission data are summarized in Table 2. The excimer fluorescences are characterized by broadening and large Stokes shift and are clearly distinguishable from ordinary monomer type of fluorescence. The excimer fluorescence bands of **1**, **2**, and **3** appear at much longer wavelength than those of double-layered paracyclophanes, **7** and **8**, indicating that the third stacked benzene obviously serves to stabilize the excited trimer state.

On the other hand, [4.4][4.4]paracyclophane **6** shows another type of excited trimer formation. It reveals monomer emission at low temperature but excimer emission at room temperature as seen for [4.4]paracyclophane **9**. However, the emission of **6** can be considered as superposition of two distinct excimer bands. Thus, the band at 330 nm is associated with excited dimer in analogy with the excimer band at 335 nm for **9** and another band at 395 nm is assigned to excited trimer emission.

Table 2 also shows large red shift of phosphorescence bands. There are rather correlated to absorption bands than fluorescence bands, indicating that the excimers are independent of triplet state.

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-FX 100 in deuteriochloroform using TMS 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 (diethyl 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.

Dithia[2.2][4.4]paracyclophane (12). A mixture of 1,4-bis(2-mercaptoethyl)benzene **10**[7a] (0.79 g, 4.0 mmol) and 4,7-bis(bromomethyl)[2.2]paracyclophane **11**[8] (1.73 g, 4.4 mmol) in benzene (200 ml) was slowly added into a refluxing ethanol solution (500 ml) of potassium hydroxide (0.71 g) under nitrogen. The addition took 6 h and the reflux was continued for further 6 h. The solvent was evaporated and the residue was chromatographed on silica gel with 1: 1 benzene–hexane to give the desired cyclic compound **12** (0.44 g, 25%), colorless plates from benzene–hexane, mp 156.5—158 °C.

NMR ($CDCl_3$, 60 MHz) δ=6.67 (4H, s, ArH), 6.37 (4H, A_2B_2m, ArH), 5.80 (2H, s, ArH), 3.51 (2H, ABd, J=14 Hz, $ArCH_2S$), 3.07 (2H, ABd, J=14 Hz, $ArCH_2S$), 2.3—3.1 (16H, m, CH_2); MS *m/e* 430 (M^+). Found: C, 78.06; H, 7.22; S, 15.11%. Calcd for $C_{28}H_{30}S_2$: C, 78.09; H, 7.02; S, 14.89%.

Triple-layered [2.2][3.3]Paracyclophane (2). Dithiacyclophane **12** (70 mg) was dissolved in a mixture of benzene (5 ml) and triethyl phosphite (5 ml) in a quartz tube and irradiated with a high pressure mercury lamp for 6 h in a nitrogen atmosphere. After evaporation to dryness, the residue was chromatographed on silica gel with 1: 9 benzene–hexane to give the desired product **2** from the first eluate, 13 mg (23%), colorless prisms from hexane, mp 161—162.5 °C.

NMR ($CDCl_3$, 60 MHz) δ=6.46 (4H, s, ArH), 6.35 (2H, A_2B_2dd, J=7 Hz, ArH), 6.14 (2H, A_2B_2dd, J=7 Hz, ArH), 5.57 (2H, s, ArH), 1.7—3.4 (20H, m, CH_2); MS *m/e* 366 (M^+). Found: C, 91.49; H, 8.29%. Calcd for $C_{28}H_{30}$: C, 91.75; H, 8.25%.

2,5-Dibromo-1,4-bis(bromomethyl)benzene (14). A mixture of 2,5-dibromo-*p*-xylene **13** (79 g, 0.3 mol) and NBS (111 g, 0.62 mol) in carbon tetrachloride (500 ml) was refluxed for 1 h using sunlight as a catalyst. The hot solution was filtered and the insoluble succinimide was washed with dichloromethane. The filtrate and the washings were combined, washed with water, and dried over anhyd magnesium sulfate. The solution was concentrated *in vacuo*, and the residue was recrystallized from benzene to give colorless columns, 43 g (34%), mp 160—161 °C.

NMR ($CDCl_3$, 60 MHz) δ=4.51 (4H, s, CH_2), 7.66 (2H, s, ArH). Found: C, 22.84; H, 1.35; Br, 75.50%. Calcd for $C_8H_6Br_4$: C, 22.78; H, 1.43; Br, 75.78%.

16,19-Dibromo-2,13-dithia[4.4]paracyclophane (15). A mixture of 1,4-bis(2-mercaptoethyl)benzene **10** (1.98 g, 0.01 mol) and 2,5-dibromo-1,4-bis(bromomethyl)benzene **14** (4.22 g, 0.01 mol) in benzene (300 ml) was slowly added into a refluxing ethanol (1 L) containing potassium hydroxide (1.78 g) under nitrogen. The addition took one day. After the addition was complete, the reflux was continued half a day. The mixture was concentrated, and the residue was chromatogphed on silica gel with 1: 1 benzene–hexane. The first eluate gave the desired coupling compound **15** (8.54 g, 62%), colorless scales from benzene–hexane, mp 181.5—182.5 °C.

NMR ($CDCl_3$, 60 MHz) δ=7.00 (2H, s, ArH), 6.89 (4H, s, ArH), 3.68 and 3.26 (4H, ABq, J=14 Hz, $ArCH_2S$), 3.6—2.3 (8H, m, CH_2); MS *m/e* 458 (M^+). Found: C, 46.94; H, 3.75; S, 13.92; Br, 34.67%. Calcd for $C_{18}H_{18}S_2Br_2$: C, 47.17; H, 3.96; S, 13.99; Br, 34.88%.

16,19-Dicyano-2,13-dithia[4.4]paracyclophane (16). A suspension of dithia compound **15** (6.79 g, 14.8 mmol) in *N*-methyl-2-pyrrolidinone (28 ml) was heated at 180 °C with stirring in a nitrogen atmosphere for 1.5 d. The hot mixture was poured into 15% ammonia water (50 ml) and cooled in an ice bath. The resulting cake was filtered and dried in the air. The desired product **16** was extracted from the cake with dichloromethane by use of a Soxhlet extraction and purified by chromatography on silica gel with dichloromethane, 3.53 g (68%), colorless scales from benzene–hexane, mp 259.5—261.5 °C.

NMR ($CDCl_3$, 60 MHz) δ=7.26 (2H, s, ArH), 6.90 (4H, s, ArH), 3.80 and 3.45 (4H, ABq, J=15 Hz, $ArCH_2S$), 3.5—2.5 (8H, m, CH_2). Found: C, 68.38; H, 5.00; N, 7.96; S, 18.29%. Calcd for $C_{20}H_{18}N_2S_2$: C, 68.53; H, 5.18; N, 7.99; S, 18.30%.

5,8-Dicyano[3.3]paracyclophane (18). Dithia[4.4]paracyclophane **16** (3.19 g, 9 mmol) was mixed with acetic acid (24.3 ml) and 35% hydrogen peroxide (6.1 ml) and heated at 100 °C for 5 h. The mixture was cooled in an ice bath and resulting colorless solid of disulfone **17** was collected by filtration, washed with water, and dried, 3.09 g (82%).

Disulfone **17** (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 0.5 mmHg. The tube was placed in a furnace (15 cm in length, preheated at 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 the pyrolysis started, an oily product condensed near the opposite cool end. Column chromatography of the product on silica gel with benzene gave pure dicyano[3.3]paracyclophane **18**, 176 mg (49%), colorless columns from benzene–hexane, mp 190.5—191.5 °C.

NMR ($CDCl_3$, 60 MHz) $\delta=7.11$ (2H, s, ArH), 7.01 (2H, A_2B_2dd, $J=8$, 2 Hz, ArH), 6.79 (2H, A_2B_2dd, $J=8$, 2 Hz, ArH), 3.4—1.8 (12H, m, CH_2); MS *m/e* 286 (M^+). Found: C, 83.61; H, 6.05; N, 9.73%. Calcd for $C_{20}H_{18}N_2$: C, 83.88; H, 6.34; N, 9.78%.

*5,8-Bis(ethoxycarbonyl)[3.3]paracyclophane (**19**).* Dicyano compound **18** (185 mg, 0.65 mmol) was mixed with 1 : 1 concd H_2SO_4–H_2O (3 ml) and acetic acid (1 ml), and refluxed with stirring for one day in a nitrogen atmosphere. The mixture was diluted with 30 ml of water. The resulting precipitate of 5,8-dicarboxy[3.3]paracyclophane was collected by filtration, washed with water, and dried, 184 mg (88%).

The above dicarboxylic acid (100 mg, 0.31 mmol) was treated under reflux with thionyl chloride (2 ml) in dry benzene (10 ml) for 1.5 h. After complete removal of thionyl chloride by distillation, absolute ethanol (5 ml) was added. The mixture was refluxed for 1 h and diluted with benzene (50 ml). The solution was washed with sat. aq NaCl and dried over anhyd magnesium sulfate. After evaporation, the residue was chromatographed on silica gel with benzene to give the desired diester **19**, 61 mg (52%).

NMR ($CDCl_3$, 100 MHz) $\delta=1.46$ (6H, t, $J=7.1$ Hz, CH_3), 2.05 (4H, m, CH_2), 2.70 (6H, m, CH_2), 3.65 (2H, m, CH_2), 4.42 (4H, q, OCH_2), 6.74 (4H, s, ArH), 7.34 (2H, s, ArH).

An analytical sample was purified by gel permeation liquid chromatography and recrystallized from pentane, colorless plates, mp 82.5—83 °C. Found: C, 75.81; H, 7.38%. Calcd for $C_{24}H_{28}O_4$: C, 75.76; H, 7.42%.

*5,8-Bis(bromomethyl)[3.3]paracyclophane (**20**).* Diester **19** (132 mg) was mixed with excess of lithium aluminium hydride in dry THF (20 ml) and refluxed for 30 min. After successive addition of ethyl acetate, water, dil hydrochloric acid, and NaCl, the mixture was extracted with ether. The extract was washed with sat. aq NaCl solution and dried over anyd magnesium sulfate. Evaporation of solvent gave a colorless solid of 5,8-bis(hydroxymethyl)[3.3]paracyclophane, 98 mg (96%).

NMR ($CDCl_3$, 100 MHz) $\delta=2.0$—3.0 (12H, m, CH_2), 4.68 (4H, center of ABq, $J=12.8$ Hz, CH_2O), 6.72 (4H, center of ABq, $J=8.0$ Hz, ArH), 6.76 (2H, s, ArH).

This diol was used in the following bromination without purification.

The above diol (98 mg) was stirred with phosphorus tribromide (0.5 ml) in dry benzene (20 ml) for 1 h at room temperature. The mixture was washed with sat. aq NaCl, dried over anhyd magnesium sulfate, and evaporated. The residue was filtered through a short column of silica gel with benzene to give the pure compound **20**, 104 mg (74%), colorless plates from hexane, mp 136.5—137.5 °C.

NMR ($CDCl_3$, 100 MHz) $\delta=1.9$—3.1 (12H, m, CH_2), 4.45 (4H, center of ABq, $J=10.3$ Hz, CH_2Br), 6.69 (2H, s, ArH), 6.77 (4H, center of ABq, $J=8.6$ Hz, ArH). Found: C, 56.74; H, 5.13; Br, 37.62%. Calcd for $C_{20}H_{22}Br_2$: C, 56.90; H, 5.25; Br, 37.85%.

*Dithia[3.3][4.4]paracyclophane (**21**).* Compound **21** was obtained in 63% yield from a coupling reaction of the above dibromide **20** and 1,4-bis(2-mercaptoethyl)benzene **10** in a similar manner as described for dithia[2.2][4.4]paracyclophane **12**, colorless prisms from benzene–hexane, mp 204—205 °C.

NMR ($CDCl_3$, 60 MHz) $\delta=6.63$ (4H, s, ArH), 6.57 (4H, s, ArH), 6.06 (2H, s, ArH), 3.69 (2H, ABd, $J=14$ Hz, $ArCH_2S$), 3.11 (2H, ABd, $J=14$ Hz, $ArCH_2S$), 3.5—1.5 (20H, m, CH_2); MS *m/e* 458 (M^+). Found: C, 78.27; H, 7.19; S, 13.94%. Calcd for $C_{30}H_{34}S_2$: C, 78.55; H, 7.47; S, 13.98%.

*Triple-layered [3.3][3.3]Paracyclophane (**3**).* Photodesulfurization of dithia compound **21** was carried out in similar manner as described in the synthesis of [2.2][3.3]analogue **2**. [3.3][3.3]Paracyclophane **3** was obtained in 16% yield, colorless plates from hexane, mp 166—168 °C.

NMR ($CDCl_3$, 100 MHz) $\delta=6.54$ (4H, A_2B_2dd, $J=6.7$, 0.7 Hz, ArH), 6.43 (4H, A_2B_2dd, $J=6.7$, 0.7 Hz, ArH), 5.89 (2H, s, ArH), 3.0—1.8 (24H, m, CH_2); MS *m/e* 394 (M^+). Found: C, 91.11; H, 8.68%. Calcd for $C_{30}H_{34}$: C, 91.31; H, 8.69%.

*18,21-Dibromo-2,15-dithia[5.5]paracyclophane (**23**).* Dithia compound **23** was prepared from 2 5-dibromo-1,4-bis(bromomethyl)benzene **14** and 1,4-bis(3-mercaptopropyl)benzene **22**[7a] in similar manner as for dithia[4.4]analogue **15**, yield 87%, colorless plates from hexane, mp 137—138 °C.

NMR ($CDCl_3$, 60 MHz) $\delta=7.45$ (2H, s, ArH), 6.99 (4H, s, ArH), 4.03 (2H, ABd, $J=14$ Hz, $ArCH_2S$), 3.44 (2H, ABd, $J=14$ Hz, $ArCH_2S$), 2.63 (4H, m, $ArCH_2$), 1.96 (8H, m, CH_2); MS *m/e* 486 (M^+). Found: C, 49.11; H, 4.60; S, 13.27; Br, 32.69%. Calcd for $C_{20}H_{22}S_2Br_2$: C, 49.39; H, 4.56; S, 13.19; Br, 32.86%.

*18,21-Dicyano-2,15-dithia[5.5]paracyclophane (**24**).* Dithia compound **24** was derived from dibromo derivative **23** in similar manner as for dithia[4.4]analogue (**16**), yield 53%, colorless plates from benzene, mp 164—165 °C.

NMR ($CDCl_3$, 60 MHz) $\delta=7.60$ (2H, s, ArH), 6.94 (4H, s, ArH), 4.02 (2H, ABd, $J=14$ Hz, $ArCH_2S$), 3.55 (2H, ABd, $J=14$ Hz, $ArCH_2S$), 2.65 (4H, m, $ArCH_2$), 1.92 (8H, m, CH_2); MS *m/e* 398 (M^+). Found: C, 70.05; H, 6.12; N, 7.47; S, 16.87%. Calcd for $C_{22}H_{22}N_2S_2$: C, 69.80; H, 5.86; N, 7.40; S, 16.94%.

*6,9-Dicyano[4.4]paracyclophane (**26**).* The above dicyano dithia compound **24** was oxidized to disulfone **25** in 96% yield. The pyrolysis as described in [3.3]analogue **18** gave the desired [4.4]paracyclophane **26** in 48% yield, colorless columns from benzene–hexane, mp 206.5—207.5 °C.

NMR ($CDCl_3$, 60 MHz) $\delta=7.12$ (2H, s, ArH), 6.76 (4H, s, ArH), 3.1—0.9 (16H, m, CH_2); MS *m/e* 314 (M^+). Found: C, 84.34; H, 7.08; N, 8.78%. Calcd for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05; N, 8.91%.

*6,9-Bis(ethoxycarbonyl)[4.4]paracyclophane (**27**).* Diester **27** was derived from dicyano compound **26** in similar manner as in the case of [3.3]analogue **19**, colorless plates from pentane, mp 59.5—61.5 °C, yield 77%.

NMR ($CDCl_3$, 100 MHz) $\delta=7.30$ (2H, s, ArH), 6.66 (4H, s, ArH), 4.37 (4H, q, $J=7.2$ Hz, OCH_2), 1.42 (6H, t, $J=7.2$ Hz, CH_3). Found: C, 76.69; H, 7.95%. Calcd for $C_{26}H_{32}O_4$: C, 76.44; H, 7.90%.

*6,9-Bis(bromomethyl)[4.4]paracyclophane (**28**).* Bromomethyl derivative **28** was prepared *via* 6,9-bis(hydroxymethyl)[4.4]paracyclophane from the above diester **27** in overall yield 72%, colorless prisms from hexane, mp 129—130 °C.

NMR ($CDCl_3$, 100 MHz) $\delta=6.75$ (2H, s, ArH), 6.67 (4H, s, ArH), 4.37 (4H, centered ABq, $J=10.2$ Hz, CH_2Br), 3.0—1.0 (8H, m, CH_2). Found: C, 58.97; H, 5.80; Br, 35.46%. Calcd for $C_{22}H_{28}Br_2$: C, 58.69; H, 5.82; Br, 35.49%.

*Dithia[3.3][4.4]paracyclophane (**30**).* The synthesis of **30** was accomplished by a reaction of dibromide **28** and 1,4-bis(mercaptomethyl)benzene **29** in similar manner as described in dithia[2.2][4.4]paracyclophane **12**, yield 88%, colorless columns from benzene–hexane, mp 206.5—208 °C.

NMR ($CDCl_3$, 100 MHz) $\delta=6.76$ (4H, centered A_2B_2, ArH), 6.51 (4H, s, ArH), 6.20 (2H, s, ArH), 3.79 (2H, ABd,

J=15 Hz, $ArCH_2S$), 3.71 (4H, s, $ArCH_2S$), 3.42 (2H, ABd, J=15 Hz, $ArCH_2S$), 2.9—1.0 (16H, m, CH_2); MS *m/e* 458 (M^+). Found: C, 78.29; H, 7.43; S, 13.71%. Calcd for $C_{30}H_{34}S_2$: C, 78.55; H, 7.47; S, 13.98%.

Triple-layered [2.2][4.4]Paracyclophane (4). Triple-layered cyclophane **4** was obtained in 55% yield by photodesulfurization of dithia[3.3][4.4]paracyclophane **30** as described in the case of **2**, colorless plates from pentane, mp 129—130 °C.

NMR ($CDCl_3$, 100 MHz) δ=6.53 (4H, s, ArH), 6.35 (2H, A_2B_2dd, J=7.4, 1.0 Hz, ArH), 6.20 (2H, A_2B_2dd, J=7.4, 1.0 Hz, ArH), 5.64 (2H, s, ArH), 3.2—1.0 (24H, m, CH_2); MS *m/e* 394 (M^+). Found: C, 91.32; H, 8.58%. Calcd for $C_{30}H_{34}$: C, 91.31; H, 8.69%.

Dithia[4.4][4.4]paracyclophane (31). The synthesis of **31** was accomplished by a reaction of 6,9-bis(bromomethyl)[4.4]paracyclophane **28** and 1,4-bis(2-mercaptoethyl)benzene **10** in similar manner as described in dithia[2.2][4.4]paracyclophane **12**, yield 77%, colorless plates from benzene–hexane, mp 280—282 °C.

NMR ($CDCl_3$, 100 MHz) δ=6.66 (4H, s, ArH), 6.53 (4H, s, ArH), 6.03 (2H, s, ArH), 3.46 (2H, ABd, J=14 Hz, $ArCH_2S$), 3.03 (2H, ABd, J=14 Hz, $ArCH_2S$), 3.2—0.9 (16H, m, CH_2). Found: C, 78.70; H, 7.63; S, 13.39%. Calcd for $C_{32}H_{28}S_2$: C, 78.96; H, 7.87; S, 13.17%.

Triple-layered [3.3][4.4]Paracyclophane (5) and 6,9-Dimethyl-[4.4]paracyclophane (32). The above dithia compound **31** (49 mg), triethyl phosphite (10 ml), and benzene (20 ml) were mixed in a Vycor tube, and the mixture was irradiated with a low pressure mercury lamp for 12 h in a nitrogen atmosphere. After evaporation of the solvent, the residue was chromatographed on silica gel with hexane. From the first eluate, compound **32** was obtained, 2 mg (7%), colorless prisms from hexane, mp 113—114.5 °C.

NMR ($CDCl_3$, 100 MHz) δ=6.67 (4H, s, ArH), 6.47 (2H, s, ArH), 2.07 (6H, s, CH_3), 2.8—1.1 (16H, m, CH_2); MS *m/e* 292 (M^+). Found: C, 90.18; H, 9.16%. Calcd for $C_{22}H_{28}$: C, 90.35; H, 9.65%.

From the second eluate, the desired triple-layered compound **5** was obtained in 12% yield (5 mg), colorless columns from pentane, mp 170—171 °C.

NMR ($CDCl_3$, 100 MHz) δ=6.60 (2H, ABd, J=7.1 Hz, ArH), 6.53 (2H, ABd, J=7.1 Hz, ArH), 6.51 (4H, s, ArH), 5.96 (2H, s, ArH), 2.8—1.3 (28H, m, CH_2); MS *m/e* 422 (M^+). Found: C, 91.20; H, 8.80%. Calcd for $C_{32}H_{38}$: C, 90.94; H, 9.06%.

Dithia[4.4][5.5]paracyclophane (33). Dithia compound **33** was obtained in 67% yield by the reaction of 6,9-bis(bromomethyl)[4.4]paracyclophane **28** and 1,4-bis(3-mercaptopropyl)benzene **22** in similar manner as described in dithia-[2.2][4.4]paracyclophane **12**, colorless prisms from pentane, mp 120—122 °C.

NMR ($CDCl_3$, 100 MHz) δ=6.80 (4H, s, ArH), 6.62 (4H, s, ArH), 6.44 (2H, s, ArH), 3.66 (2H, ABd, J=14.1 Hz, SCH_2), 3.28 (2H, ABd, J=14.1 Hz, SCH_2), 3.1—1.0 (28H, m, CH_2); MS *m/e* 514 (M^+). Found: C, 79.40; H, 8.32; S, 12.30%. Calcd for $C_{34}H_{42}S_2$: C, 79.32; H, 8.22; S, 12.46%.

Triple-layered [4.4][4.4]Paracyclophane (6). The above dithia compound **33** (290 mg) was mixed with acetic acid (2 ml) and 35% hydrogen peroxide (0.6 ml), and heated at 100 °C for 12 h to give colorless precipitate of disulfone **34** (190 mg, 58%).

The above disulfone **34** (50 mg) was pyrolyzed by the method described for 5,8-dicyano[3.3]paracyclophane **18**. The pyrolytic product was chromatographed on silica gel with benzene–hexane and recrystallized from benzene–hexane to give colorless columns of paracyclophane **6**, 2 mg (5%), mp 250 °C (dec).

NMR ($CDCl_3$, 100 MHz) δ=6.55 (8H, s, ArH), 5.99 (2H, s, ArH), 1.6—0.8 (32H, m, CH_2); MS *m/e* 450 (M^+). Found: C, 90.61; H, 9.39%.

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 847019 from the Ministry of Education, Science and Culture.

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