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Layered Compounds. XXXVII.[1] Syntheses and Properties of Quadruple-layered Metaparacyclophanes

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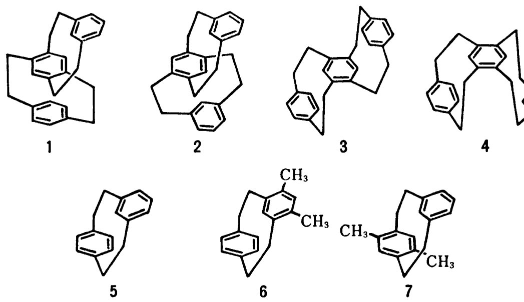
Six quadruple-layered [2.2]metaparacyclophanes have been synthesized by photo-induced desulfurization or the Hofmann elimination method. Their electronic spectra exhibit stronger transannular electronic interactions than those of the corresponding triple-layered [2.2]metaparacyclophanes and considerable dependence on the bridge substitution mode of the inside ring. The absorption spectra of the charge transfer complexes of a series of layered metaparacyclophanes and tetracyanoethylene have been studied with regard to the donor characters. It is concluded that the electron release from meta to para ring is significant, while the reverse is less effective.

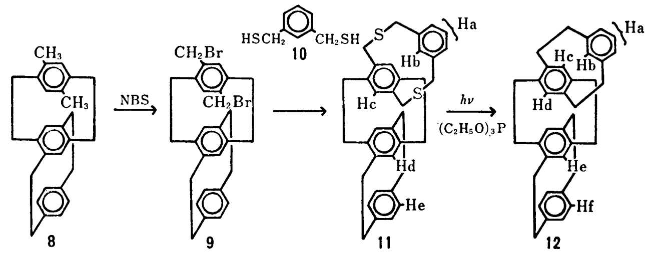
In preceding papers we reported the syntheses, structures, and properties of triple-layered [2.2]metaparacyclophanes **1**—**4**.[1] Although double-layered [2.2]metaparacyclophanes **5**—**7** show no remarkable transannular electronic interaction between benzene rings,[1] compounds **1** and **2**, the inside ring of which is doubly *para*-substituted with two pairs of methylene brigdes, exhibit strong interaction as in the case of multilayered [2.2]paracyclophanes. On the other hand, compounds **3** and **4** with doubly *meta*-substituted benzene reveal weak interaction as in the case of multilayered [2.2]metacyclophanes. In this paper we report the syntheses and properties of some quadruple-layered [2.2]metaparacyclophanes. The compounds are expected to give us further information on the relationship between structures and spectra.



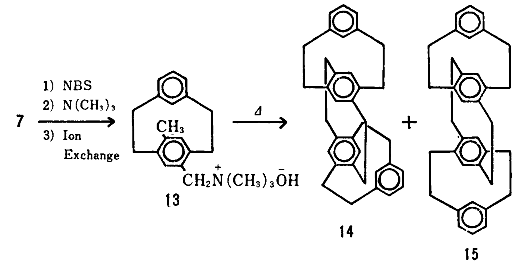
Scheme 1.

Results and Discussion

Syntheses and Structures. Dimethyl derivative **8**[2] of triple-layered [2.2]paracyclophane was brominated with *N*-bromosuccinimide and the resulting dibromide **9** was coupled with 1,3-bis(mercaptomethyl)benzene **10** to afford dithia compound **11** in 16% overall yield. Compound **11** was then converted into the desired quadruple-layered metaparacyclophane **12** in an excellent yield (81%) using photodesulfurization developed by Bruhin *et al.*[3] The structure of **12** was determined by its NMR spectrum. Most of the aromatic protons appear at high field due to the shielding effect of the other benzene rings. Hc and Hd protons are not equivalent, indicating fixation of meta ring as in the case of [2.2]metaparacyclophane **5**.[4]

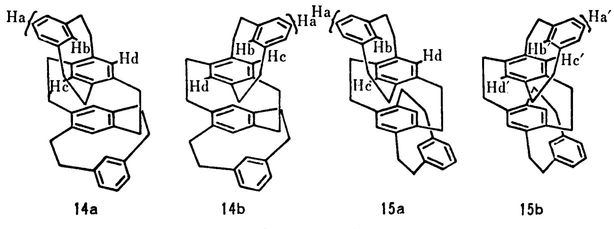


Scheme 2.



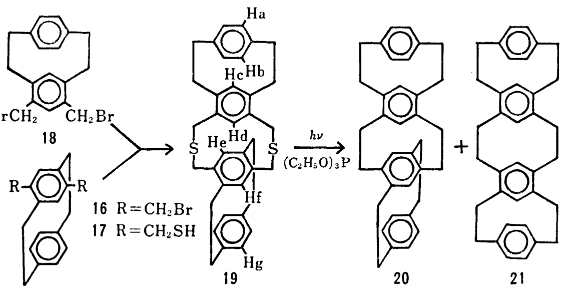
Scheme 3.

Hofmann elimination reaction, a convenient method for approach of multilayered [2.2]paracyclophanes,[2,5] was applied to the syntheses of quadruple-layered metaparacyclophanes **14** and **15**. 12,15-Dimethyl[2.2]metaparacyclophane **7**[1] was brominated with *N*-bromosuccinimide followed by treatment with trimethylamine and then ion exchange resin to give the quaternary ammonium hydroxide **13**. Pyrolysis of **13** in boiling xylene afforded a mixture of the desired cyclophanes **14** and **15**, which could be separated by utilizing the large difference in their solubility. In the same manner as for quadruple-layered [2.2]paracyclophanes,[2] the more soluble isomer was assigned to the structure **14**, and the less soluble one to the structure **15**. The eclipse of methylene bridges at two inside rings of **15** may be responsible for the lower yield (2.7%) than that of **14** (12%). Fixation of the meta rings of **14** gives two possible conformational structures **14a** and **14b**. They



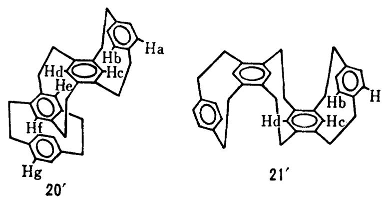
Scheme 4.

are not enantiometric with each other, but can not be distinguished on NMR analysis due to the equivalence of the corresponding aromatic protons. Two conformational structures are expected also for **15**. In this case the NMR spectrum demonstrates two sets of signals for aromatic protons, which correspond to **15a** and **15b**. The ratio was evaluated to be 1 : 1 on the basis of the integral intensities.



Scheme 5.

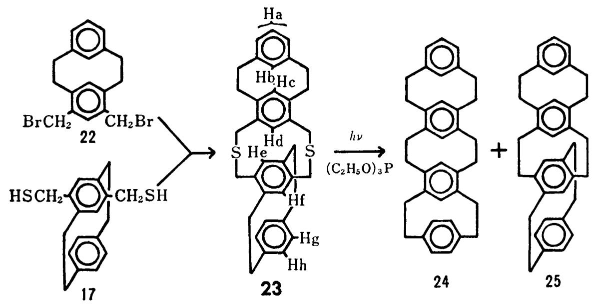
4, 7-Bis(bromomethyl) [2.2]paracyclophane **16**[1] was led to the corresponding dithiol **17** in 74% yield. Condensation of **17** with 4,6-bis(bromomethyl)[2.2]-metaparacyclophane **18**[1] gave dithia compound **19** in 25% yield. Photodesulfurization of **19** in triethyl phosphite afforded the desired quadruple-layered metaparacyclophane **20** in 40% yield and its isomer **21** in 33% yield. From the fact that triple-layered metaparacyclophane **1** is easily photo-isomerized to **4**,[1] **20** seems to isomerize to **21** during the photolysis.



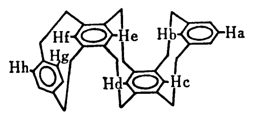
Scheme 6.

The geometry of **3** was confirmed to be a staircase-shape on the basis of NMR analysis[1] and X-ray crystallographic analysis.[6] Similarly, the structure of **20** is expected to have a staircase-shape as shown in **20′**. The NMR spectrum is in good accord with the present structure **20′**. In the same manner as in the case of multilayered[2.2]paracyclophanes,[7] the chemical shifts of the aromatic protons in **20** can be successfully evaluated by considering the anisotropy of the stacked rings. Three stereoisomers are possible for **21**. However, its NMR spectrum is simple and suggests that there is only one conformational isomer having a symmetrical structure. The structure was determined to be **21′** by comparison of the NMR spectrum with that of **4** which has a platform-shape differing from **3**.[1]

Condensation of 4,6-bis(bromomethyl)[2.2]metacyclophane **22**[8] with 4,7-bis(mercaptomethyl)[2.2]-paracyclophane **17** gave coupling compound **23** in 29% yield. Photodesulfurization of **23** afforded **24** in 30% yield. The product **24** is considered to be derived from **25** which was initially desired. Unfortunately **25**



Seheme 7.



Scheme 8.

could not be isolated because of contamination with oily by-products. Four conformational isomers are possible for **24**, but the NMR spectrum can be explained on a single isomer of zigzag structure **24′**. The assignment is consistent with the fact that in multilayered metacyclophanes, the structure of platform-shape is thermodynamically stable.[9]

Electronic Spectra. The electronic spectra of quadruple-layered [2.2]metaparacyclophanes are shown in Fig. 1. The explanation that bridge substitution mode is important for transannular electronic interaction of triple-layered metaparacyclophane[5] is also applicable to the present case. Compounds **12**, **14**, and **15** are formally regarded as if they are given by stacking another meta or para substituted benzene on the outside para ring of triple-layered metaparacyclophane **1**. As expected, their spectra exhibit much more bathochromic

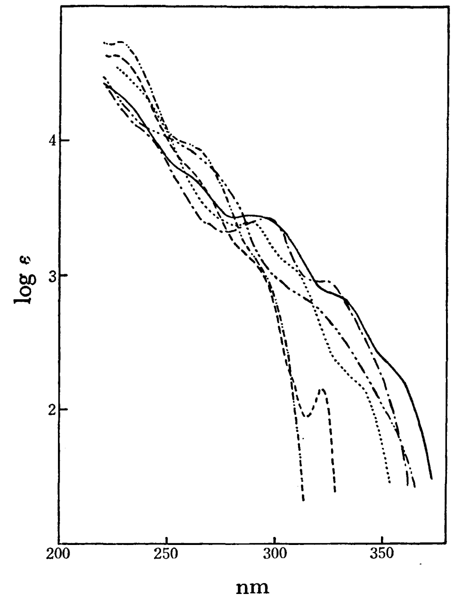


Fig. 1. Electronic spectra of quadruple-layered metaparacyclophanes **12** (——), **14** (-·---·-) in cyclohexane and **15** (–··–), **20** (·····), **21** (––––), **24** (--·--) in tetrahydrofuran.

shifts and stronger transannular electronic interactions than that of **1**. On the other hand, stacking of another *para*-substituted benzene on the outside meta ring of **1** gives the structure **20**, which is expected to provide spectral properties of both meta and para bridged types. In fact, the electronic spectrum of **20** is, in a short wavelength region, similar to that of **3** (meta type) and, in a long wavelength region, identical with that of **1** (para type). Compounds **21** and **24** are classified as a meta bridged type. Their spectra exhibit just a weak transannular electronic interaction as seen in multilayered [2.2]metacyclophanes.[8)]

Charge Transfer Spectra. It is well-known that an aromatic hydrocarbon forms a charge transfer complex with tetracyanoethylene (TCNE) and that absorption maximum of its charge transfer band gives information on π-basicity of the donor.[10)] The increased transannular electronic interaction of multilayered [2.2]paracyclophanes was observed to be reflected in the increase of π-basicity.[2,5)] Thus with increasing number of layers, the donor character of the cyclophanes increases and the absorption maximum of the charge transfer complex with TCNE shifts to longer wavelength.

It is interesting to study which of the two benzene rings in [2.2]metaparacyclophane **5** tends to more easily form a complex with TCNE and which of two types of transannular electron release in TCNE complexes is more effective, *viz.*, from the non-complexed meta or para ring to the complexed face ring. Absorption maximum wavelengths of layered metaparacyclophane–TCNE complexes are summarized in Table 1. The charge transfer complex of *m*-xylene with TCNE shows a CT absorption maximum at 440 nm in dichloromethane, and the complex of *p*-xylene two absorption maxima at 420 nm and 465 nm.[2)] The CT absorption maximum of [2.2]metaparacyclophane **5** with TCNE is at 457 nm which is situated between the above values of *m*-xylene and *p*-xylene. This suggests that both the meta and para benzenes form complexes with TCNE. The CT complexes of dimethyl derivatives **6** and **7** give us further information. Their absorption maxima appear around 490 nm, with an additional shoulder at 570 nm for **7**. This is considered to arise from the complex of the durene moiety with TCNE. Since durene–TCNE complex shows a CT band at 480 nm,[2)] the transannular electron release from the meta ring to the complexed durene moiety is more significant, whereas that from the para ring is less effective.

Table 1. Absorption maxima of layered [2.2]-metaparacyclophane–TCNE complexes in dichloromethane

Compound	λ_{max} (nm)
[2.2]MPC[a)]	
5	457
6	497
7	486, 570[b)]
MPC[a)] having meta-rings at both outsides	
2	473
14	472
15	476
MPC[a)] having para-rings at both outsides	
3	451, 547
20	545
MPC[a)] having a para- and a meta-rings at both outsides	
1	483, 585[b)]
4	428, 520[b)]
12	486, 710

a) Metaparacyclophanes. b) Shoulder.

In the case of multilayered metaparacyclophanes having meta rings on both outsides, TCNE exclusively forms a complex with the outside meta ring since TCNE is sterically unable to face the inside ring. Evidently these compounds have very weak π-basicity although their own electronic spectra exhibit remarkable transannular electronic interactions. It can be concluded that electron release from the para ring to the meta ring is less effective.

On the other hand, compounds **3** and **20** have para rings at both ends which exclusively face TCNE. The two absorption maxima of **3** at 451 and 547 nm exhibit outstanding bathochromic shifts as compared with the corresponding peaks of *p*-xylene–TCNE complex. Evidently there is reasonable electron release from the meta to the para ring as described in dimethyl[2.2]-metaparacyclophanes. In the case of **20**, the [2.2]-paracyclophane moiety is considered to form TCNE complex with relative ease. Comparing the CT absorption maximum (545 nm) with that (521 nm) of [2.2]-paracyclophane itself,[2)] we might expect some contribution of electron release from the third stacked benzene ring to the complexed face ring of the [2.2]paracyclophane moiety in TCNE complex of **20**.

Compounds **1** and **12** contain double- and triple-layered [2.2]paracyclophane moieties, respectively, which have more increased donor character than [2.2]-metaparacyclophane. In fact, the long wavelength maxima of the TCNE complexes shift to longer wavelength like multilayered [2.2]paracyclophanes[2)] and the donor characters of these cyclophanes increase progressively. The transannular electron release of **12** is particularly significant. The case of **4** seems to be more complicated because its structure is a platform-shape and the inside ring is also capable of forming a complex. Probably its CT spectrum appears as a mixture of all possible complexes.

Experimental

Mps are uncorrected. All the solvents are of reagent grade unless otherwise specified. NMR spectra were taken with a Hitachi-Perkin Elmer R-20 spectrometer (60 MHz) using tetramethylsilane as an internal std, electronic spectra with a Hitachi EPS-3T spectrophotometer, and mass spectra with a Hitachi RMU-7 spectrometer at 70 eV using a direct insertion technique.

Bis(bromomethyl)triple-layered[2.2]paracyclophane (9). A mixture of dimethyl derivative **8**[2)] (1.00 g, 2.7 mmol) of triple-layered [2.2]paracyclophane, *N*-bromosuccinimide (0.97 g, 5.4 mmol), and a small amount of benzoyl peroxide in 20 ml of carbon tetrachloride was refluxed for 3 h. After removal of insoluble succinimide by filtration, the soln was washed with water and dried over anhyd sodium sulfate. The solvent was evaporated to give the desired product as an oil (1.65 g). This was used in the next step without purification.

Dithia Compound (11). A soln of the above dibromide **9** in 35 ml of benzene and a soln of 1,3-bis(mercaptomethyl)-benzene **10** (0.54 g, 3 mmol) and sodium hydroxide (0.26 g, 6.5 mmol) in water (2 ml) and ethanol (33 ml) were added dropwise and simultaneously over a period of 2.5 h to a refluxing ethanol (100 ml) in a nitrogen atmosphere. After the solvent was removed, the residue was taken up in benzene and chromatographed on alumina (40 g) using benzene–hexane (1 : 1) for elution. The initial fraction gave the desired coupling compd **11** (0.23 g, 16% based on **8**), colorless needles from 1 : 1 benzene–ethanol, mp 217—218 °C.

Found: C, 81.29; H, 6.67; S, 12.16%. Calcd for $C_{36}H_{36}S_2$: C, 81.14; H, 6.87; S, 12.03%. NMR ($CDCl_3$, δ) 2.0—3.9 (m, 24H, CH_2), 5.29 (bs, 1H, Hb), 5.48 (s, 2H, Hd), 5.64 (s, 2H, Hc), 6.17 (s, 4H, He), 6.82 (m, 3H, Ha). MS *m/e* 532 (M^+), 104.

*Quadruple-layered Metaparacyclophane (*m-p,p-p,p-p*) (12).* The above coupling compd **11** (100 mg, 0.19 mmol) in 13 ml of purified triethyl phosphite was irradiated through a quartz tube with a high pressure mercury lamp for 3 h under a nitrogen atmosphere. The solvent was evaporated and the residue was chromatographed over silica gel (20 g) using 1 : 4 benzene–hexane for elution. The first fraction gave the desired product **12** (71 mg, 81%), colorless plates from 1 : 1 benzene–ethanol, mp 117—118 °C.

Found: C, 92.10; H, 7.60%. Calcd for $C_{36}H_{36}$: C, 92.24; H, 7.76%. NMR ($CDCl_3$, δ) 1.5—3.4 (m, 24H, CH_2), 4.67 (s, 1H, Hc), 5.05 (bs, 1H, Hb), 5.27 (s, 2H, He), 5.90 (s, 1H, Hd), 6.15 (s, 4H, Hf), 6.5 (m, 3H, Ha). MS *m/e* 468 (M^+), 234.

*Quadruple-layered Metaparacyclophane (*m-p,p-p,p-m*) (14 and 15).* A mixture of 12,15-dimethyl[2.2]metaparacyclophane **7**[1] (2.98 g, 13 mmol), *N*-bromosuccinimide (2.24 g, 13 mmol), and a small amount of benzoyl peroxide in 20 ml of carbon tetrachloride was refluxed for 5 h. After removal of succinimide by filtration, the soln was washed with water, dried over anhyd sodium sulfate, and then mixed with excess trimethylamine in ether. The mixture was stirred with ice cooling overnight. The resulting white ppt of quaternary ammonium bromide was extracted with a small amount of water. The aq soln was filtered, washed with xylene, and passed through a column containing strongly basic anion exchange resin, Dowex I-X8, 50—100 mesh. The aq soln of the quaternary ammonium hydroxide **13** was mixed with phenothiazine (100 mg) and xylene (50 ml). The mixture was heated with stirring under a nitrogen atmosphere, and water was removed by azeotropic distillation using a Dean-Stark type of water separator. After removal of water, the reflux was continued for additional 6 h. The solvent was removed and the residue was chromatographed over silica gel using 1 : 4 benzene–hexane for elution. The first fraction gave a mixture of **14** and **15**, which then separated by treatment with carbon tetrachloride. The more soluble isomer **14** (366 mg, 12%) was recrystd from toluene, colorless fine crystals, mp 191—192 °C.

Found: C, 92.27; H, 7.88%. Calcd for $C_{36}H_{36}$: C, 92.24; H, 7.76%. NMR ($CDCl_3$, δ) 1.2—3.4 (m, 24H, CH_2), 4.73 (s, 2H, Hc), 5.06 (bs, 2H, Hb), 5.94 (s, 2H, Hd), 6.4—7.0 (m, 6H, Ha). MS *m/e* 468 (M^+), 234, 104.

The less soluble isomer **15** (82 mg, 2.7%) was recrystd from toluene, colorless fine crystals, mp 265 °C (dec).

Found: C, 92.36; H, 7.61%. Calcd for $C_{36}H_{36}$: C, 92.24; H, 7.76%. NMR ($CDCl_3$, δ) 1.0—3.0 (m, 48H, CH_2), 4.68 (s, 2H, Hc′), 4.79 (s, 2H, Hc), 5.10 (bs, 4H, Hb, and Hb′), 5.94 (s, 2H, Hd), 6.07 (s, 2H, Hd′), 6.4—6.9 (m, 12H, Ha and Ha′). MS *m/e* 468 (M^+), 234.

4,7-Bis(mercaptomethyl)[2.2]paracyclophane (17). 4,7-Bis(bromomethyl)[2.2]paracyclophane **16**[1] (11.82 g, 30 mmol) was added portionwise to a boiling soln of thiourea (4.60 g, 61 mmol) in 50 ml of ethanol. The mixture was refluxed for 2 h and concd to dryness. The crude thiouronium salt was refluxed with potassium hydroxide (20 g) in 50 ml of water for 15 h. After filtration, the soln was acidified with dil sulfuric acid and the resulting solid was extracted with chloroform. The extract was washed with water, dried over anhyd sodium sulfate, and subjected to alumina column chromatography. Elution with 1 : 1 benzene–hexane gave the desired mercaptan **17** (6.70 g, 74%), colorless prisms from benzene–hexane, mp 92—93 °C.

Found: C, 72.23; H, 6.79; S, 21.03%. Calcd for $C_{18}H_{20}S_2$: C, 71.94; H, 6.72; S, 21.34%. NMR ($CDCl_3$, δ) 1.53 (t, J=8 Hz, 2H, SH), 2.6—4.0 (m, 12H, bridged CH_2 and CH_2-S), 6.25 (s, 2H, ArH), 6.40 and 6.63 (A_2B_2, J=8 Hz, 4H, ArH). MS *m/e* 300 (M^+).

Dithia Compound (19). A soln of 4,6-bis(bromomethyl)-[2.2]metaparacyclophane **18**[1] (1.30 g, 3.3 mmol) in 35 ml of benzene and a soln of 4,7-bis(mercaptomethyl)[2.2]paracyclophane **17** (0.99 g, 3.3 mmol) and potassium hydroxide (0.38 g, 5.8 mmol as 85% content) in water (7 ml) and ethanol (28 ml) were added dropwise and simultaneously over a period of 3 h to boiling ethanol (100 ml) in a nitrogen atmosphere. Reflux was continued for additional 12 h and the solvent was removed. The residue was taken up in benzene and chromatographed over alumina using 1 : 1 benzene–hexane for elution. The first fraction gave the desired product **19** (0.44 g, 25%), colorless fine crystals from toluene, mp 260 °C (with dec).

Found: C, 81.24; H, 6.67; S, 11.90%. Calcd for $C_{36}H_{36}S_2$: C, 81.14; H, 6.82; S, 12.03%. NMR ($CDCl_3$, δ) 1.8—4.2 (m, 24H, CH_2), 4.86 (s, 1H, Hc or Hd), 5.06 (s, 1H, Hd or Hc), 6.03 (bs, 2H, Hb), 6.15 (s, 1H, He or Hf), 6.43 (s, 1H, Hf or He), 6.3—6.7 (m, 4H, Hg), 7.13 (bs, 2H, Ha). MS *m/e* 532 (M^+).

*Quadruple-layered Metaparacyclophane (*p-m,m-p,p-p*) (20) and (*p-m,m-m,m-p*) (21).* The dithia compd **19** (100 mg, 0.19 mmol) and triethyl phosphite (14 ml) were placed in a quartz tube and irradiated with a high pressure mercury lamp for 3 h under bubbling nitrogen. The solvent was evaporated and the residue was treated with 1 : 4 benzene–hexane. The insoluble solid was filtered and washed with hexane to give the pure isomer **21** (29 mg, 33%), colorless plates from toluene, mp>300 °C.

Found: C, 91.99; H, 7.48%. Calcd for $C_{36}H_{36}$: C, 92.24; H, 7.76%. NMR ($CDCl_3$, δ) 1.5—3.5 (m, 24H, CH_2), 5.26 (s, 2H, Hd), 5.72 (s, 2H, Hc), 6.35 (bs, 4H, Hb), 7.47 (bs, 4H, Ha). MS *m/e* 468 (M^+).

The filtrate was subjected to silica gel column chromatography. Elution with 1 : 4 benzene–hexane afforded the other isomer **20** (35 mg, 40%), colorless plates from 1 : 1 benzene–hexane, mp 242—243 °C.

Found: C, 91.99; H, 7.54%. Calcd for $C_{36}H_{36}$: C, 92.24; H, 7.76%. NMR ($CDCl_3$, δ) 1.5—3.5 (m, 24H, CH_2), 4.62 (s, 1H, Hd), 4.69 (s, 1H, He), 4.75 (s, 1H, Hc), 5.55 (bs, 2H, Hb), 6.11 (s, 1H, Hf), 6.29 (bs, 4H, Hg), 7.09 (bs, 2H, Ha). MS *m/e* 468 (M^+), 364, 104.

Dithia Compound (23). A soln of 4,6-bis(bromomethyl)-[2.2]metacyclophane **22**[8] (1.36 g, 3.5 mmol) in 40 ml of benzene and a soln of 4,7-bis(mercaptomethyl)[2.2]paracyclophane **17** (1.04 g, 3.5 mmol) and potassium hydroxide (0.55 g, 8.3 mmol as 85% content) in water (10 ml) and ethanol (30 ml) were added dropwise and simultaneously over a period of 3.5 h to boiling ethanol (100 ml) in a nitrogen atmosphere.

Reflux was continued for additional 12 h. The solvent was removed, and the residue was taken up in benzene and subjected to alumina column chromatography. Elution with 1:1 benzene–hexane gave an oil which was then treated with hexane to solidify. The product **23** was filtered and washed with hexane (0.52 g, 29%), colorless fine crystals from toluene, mp 230—231 °C.

Found: C, 81.26; H, 6.68; S, 11.94%. Calcd for $C_{36}H_{36}S_2$: C, 81.14; H, 6.82; S, 12.03%. NMR ($CDCl_3$, δ) 2.5—4.1 (m, 25H, CH_2 and Hc), 4.52 (bs, 1H, Hb), 5.23 (s, 1H, Hd), 6.20 (s, 2H, He and Hf), 6.40 and 6.60 (A_2B_2, J=7 Hz, 4H, Hh, and Hg, respectively), 7.1 (m, 3H, Ha). MS m/e 532 (M^+).

*Quadruple-layered Metaparacyclophane (*m-m,m-m,m-p*) (24).* The dithia compd **23** (50 mg, 0.09 mmol) and triethyl phosphite (13 ml) was placed in a quartz tube and irradiated with a high pressure mercury lamp (400 W) for 2 h under nitrogen. The solvent was evaporated and the residue was chromatographed over silica gel using 1:4 benzene–hexane for elution. After a mixture of **25** and an unknown oily compd, the desired product **24** was eluted (13 mg, 30%), colorless fine crystals from toluene, mp>300 °C.

Found: C, 92.23; H, 7.50%. Calcd for $C_{36}H_{36}$: C, 92.24; H, 7.76%. NMR ($CDCl_3$, δ) 1.5—3.7 (m, 24H, CH_2), 4.19 (s, 1H, Hc), 4.58 (s, 1H, He), 5.01 (bs, 1H, Hb), 5.62 (s, 1H, Hd), 5.71 (s, 1H, Hf), 6.50 (d, J=2 Hz, 2H, Hg), 7.1—7.4 (m, 3H, Ha), 7.50 (d, J=2 Hz, 2H, Hh). MS m/e 468 (M^+).

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