Layered Compounds. LIII.[1] Unique Skeletal Rearrangement of Multilayered [2.2]Paracyclophanes

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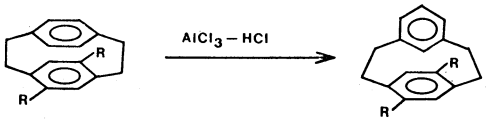
Skeletal rearrangements of multilayered [2.2]paracyclophanes to [2.2]metaparacyclophanes with several Friedel-Crafts acids have been studied. Two types of rearrangements depending on the catalyst were observed. Treatment of triple-layered paracyclophane(**8**) with $AlCl_3$–HCl gave mainly triple-layered metaparacyclophane(**9**), which was derived by migration of one of the ethylene bridges attached to the outer benzene rings. Treatment of **8** with mild protonic acids such as $SnCl_4$–HCl, $TiCl_4$–HCl, *etc.* afforded two kinds of metaparacyclophanes **10** and **11** in high yields, which arose from double migration of the two ethylene bridges attached to the inner benzene ring. Such a double migration of substitutents was also observed in the case of tertamethyl[2.2]paracyclophane and quadruple-layered one. The structures of products were determined by means of NMR spectra, alternative syntheses, and X-ray analyses. The mechanism of the rearrangements is discussed in view of protonation experiment.

[2.2]Paracyclophane(**1**), a typical layered compound, has been extensively investigated from the viewpoint of transannular π-electronic interaction. A number of anomalous physical and chemical behaviors have been reported.[2] Cram and his coworkers observed an interesting skeletal rearrangement of **1** to [2.2]metaparacyclophane(**2**) in the presence of aluminium chloride–hydrogen chloride.[3] This reaction is known to be the most practical and convenient method for the preparation of **2** since the starting material **1** is commercially available.

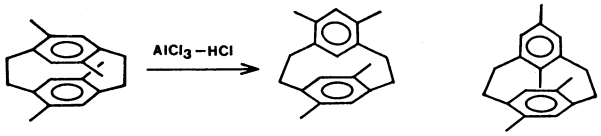


1: R = H 2: R = H
3: R = CH_3 4: R = CH_3

Multilayered [2.2]paracyclophane,[4] in which stronger electronic interaction[4a] and severer strain[5] than in **1** were observed, are expected to be highly reactive with Friedel-Crafts acid. In this paper, we report two types of skeletal rearrangement of double-, triple-, and quadruple-layered [2.2]paracyclophanes with several Friedel-Crafts acids to give unique multilayered metaparacyclophanes, and discuss their mechanisms.

Results and Discussion

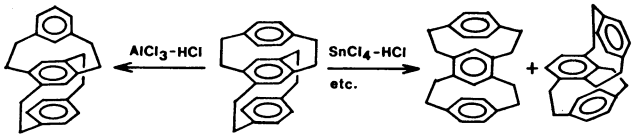
Rearrangement and Structure. Before starting with multilayered cyclophanes, methyl-substituted [2.2]-paracyclophanes were examined according to Cram's procedure.[3] Treatment of 4,7-dimethyl[2.2]paracyclophane(**3**) with $AlCl_3$–HCl at 0 °C for 30 min gave a 38% yield of 12,15-dimethyl[2.2]metaparacyclophane (**4**), which was formed by 1,2-migration of an ethylene bridge attached to the non-substituted benzene ring. Product **4** was identified by comparison of its melting point and NMR data with those of an authentic sample.[6a,b] Under the same conditions, D_2-symmetric 4,7,12,15-tetramethyl[2.2]paracyclophane(**5**) afforded 4,6,12,15-tetramethyl[2.2]metaparacyclophane(**6**) in 15% yield, which was derived by positional exchange



5 6 7

of a methyl group and an ethylene bridge attached to a benzene ring. The structure of **6** was easily assigned by comparing its NMR data with those of 4,6- and 12,15-dimethyl[2.2]metaparacyclophanes.[6b] Another isomer **7** expected to be formed by single 1,2-migration of an ethylene bridge was not obtained, probably because of severe steric repulsion between the inner methyl group and the faced para-bridging benzene ring.

Treatment of more highly strained triple-layered [2.2]paracyclophane(**8**)[5b] under the same conditions as in the case of double-layered ones gave only polymeric material. However, when the reaction was



9 8 10 11

carried out at a lower temperature (−17 °C) in a shorter time, triple-layered metaparacyclophane **9** was obtained in 39% yield, together with a small amount of two isomeric cyclophanes **10** and **11**. Compound **9** was identified with the authentic sample synthesized by an alternative, stepwise method.[6a,b]

On the other hand, when **8** was treated with a large excess of weak Friedel-Crafts acid $SnCl_4$–HCl at room temperature, a mixture of **10** and **11** in a 56:46 ratio was obtained in 80% yield along with a very small amount of polymeric substance, no detectable amount of isomer **9** being observed. Use of $TiCl_4$–HCl, BF_3–HCl, or $ZnCl_2$–HCl as a catalyst gave results similar to the case of $SnCl_4$–HCl as shown in Table 1. It is of great interest that the formation of **10** and **11** is achieved by double migration of the two ethylene bridges attached to the inner benzene ring and that a molar ratio of 1.2:1 of the two isomers remains unaltered even by

Table 1. Rearrangement conditions of cyclophane **8** in dry dichloromethane

Friedel-Crafts Acid	Temp (°C)	Time (min)	Yield (%)	Product ratios (%)[a]					
				8	**9**	**10**	**11**	**10** :	**11**
$AlCl_3$-HCl	−17	15	51	3	76	11	10	52	48
$SnCl_4$-HCl	29	30	80	—	—	54	46	54	46
	30	180	64	—	—	55	45	55	45
$TiCl_4$-HCl	29	30	72	—	—	54	46	54	46
	29—31	180	69	—	—	48	52	48	52
$BF_3 \cdot Et_2O$-HCl	−17	60	Recovery of starting material						
	29—31	30	74	15	—	47	38	55	45
	29—31	180	79	—	—	53	47	53	47
$ZnCl_2$-HCl	Reflux	180	80	1	—	56	43	56	44
HF	0	20	20	13	—	11	76	—	—

a) Determined by the intensities in NMR spectra (100 MHz).

elongation of the reaction time and by the use of different kinds of catalyst. Application of $GaCl_3$–HCl, $SbCl_5$–HCl, or $FeCl_3$–HCl as a catalyst gave rise to only the formation of polymeric material and/or the recovery of the starting cyclophane **8**. Hydrogen fluoride was found to catalyze the reaction to give a mixture of **10** and **11** in a low yield (Table 1), while no rearrangement takes place in the presence of hydrogen chloride or hydrogen bromide alone. Treatment of double-layered cyclophanes **3** and **5** with weak protonic acid $SnCl_4$–HCl caused no formation of migration products, indicating that triple-layered paracyclophane is much more reactive than a double-layered one.

Isomers **10** and **11** were separated by fractional crystallization from benzene. Gel permeation liquid chromatography was also useful for separating them. Cyclophane **10** is identical with an authentic sample.[6a,b] The structure of new cyclophane **11** having a prehnitene (1,2,3,4-tetramethylbenzene) framework as the inner benzene ring was assigned by its spectral data and elemental analysis. Its NMR signals are explained in terms of the anisotropic effect of benzene rings (Fig. 1). The molecular structure of **11** was confirmed by X-ray crystallographic analysis of its bromoderivative **12** which was derived by bromination of **11** almost quantitatively (Figs. 2 and 3).[7a] Analysis showed no appreciable nonbonding interaction between bromine and its neighboring atoms, *viz.*, a structural resemblance

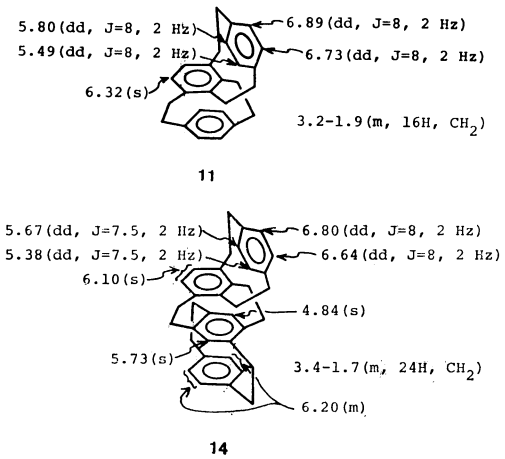


Fig. 1. NMR data of triple- and quadruple-layered [2.2]metaparacyclophanes **11** and **14** (δ values in $CDCl_3$, 60 MHz).

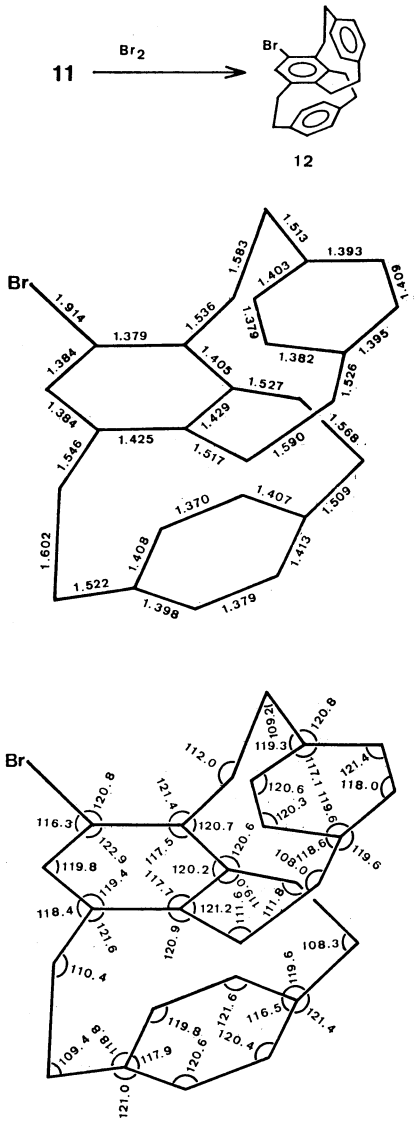


Fig. 2. Profile of the compound **12** together with bond lengths (Å) and angles (°).

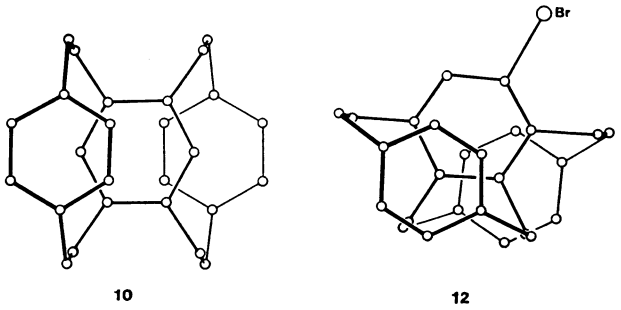
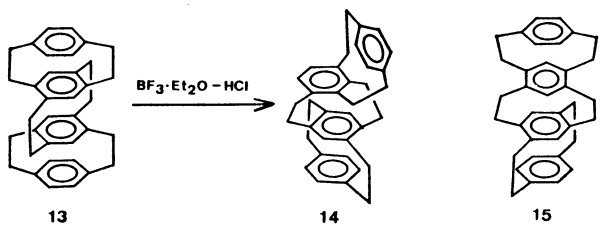


Fig. 3. Projection of the compounds **10** and **12** along the normal to the plane defined with the inner benzene ring.

of **12** to the parent hydrocarbon **11** is seen.

A similar rearrangement was observed in the treatment of quadruple-layered [2.2]paracyclophane(**13**) with boron trifluoride etherate–hydrochloric acid at 0 °C for 30 min. Compound **14** was isolated by column chromatography on silica gel from the reaction mixture.



However, there was no detectable isomer **15**, corresponding to **10** in the case of triple-layered series.[6c] No rearranged product was obtained from **13** by treatment with mild reagent $ZnCl_2$–HCl. The results indicate relatively low stability of **13** as compared with **1** and **8**. The structure of **14**, determined on the basis of its elemental analysis and NMR data (Fig. 1), can be assigned by considering the data of **11** and the anisotropic effect of an additional benzene ring.

In previous papers,[6b,c] the electronic spectra of multilayered metaparacyclophanes except for cyclophanes **11** and **14** having a prehnitene framework were reported and a discussion on the relationship between structure and spectrum was given. The spectra of compounds **10**, **11**, and **14**, derived from skeletal rearrangement on the inner benzene ring, are shown in Fig. 4 together with the spectrum of compound **15**. The spectral resemblance between **10** and **11** can be attributed to the same extent of overlapping between the inner and the two outer benzene rings (Fig. 3), although their modes of overlapping differ to some extent. A similarity was observed in the spectra of quadruple-layered metaparacyclophanes **14** and **15**.

Mechanism. Cram *et al.* reported the NMR spectral measurement of protonated compound **16** formed by dissolving **1** in fluorosulfuric acid–sulfuryl chloride fluoride–dichloromethane at −98 °C, and proposed a mechanism of the rearrangement of **1** to **2**, the first step of which is the protonation at a bridgehead carbon, followed by 1,2-migration of the ethylene bridge attached to the protonated carbon and finally by deprotonation.[3b]

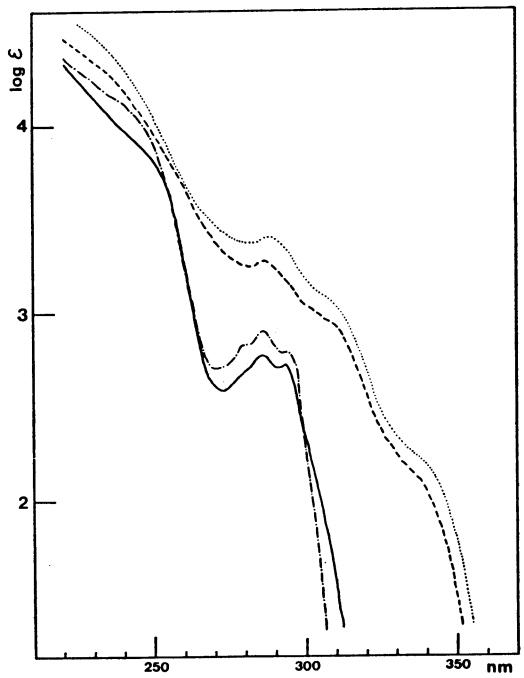
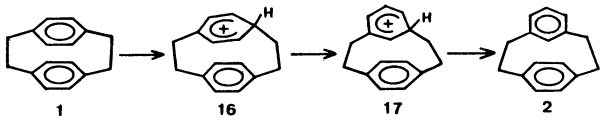


Fig. 4. Electronic spectra of cyclophanes **10** (—·—), **11** (——), **14** (----), and **15** (·····) in tetrahydrofuran.



A similar treatment of cyclophane **8** in the same reagent at −78 °C gave a deep red solution, in which a single protonated species **18** was confirmed as the main product by NMR analysis. As seen in Fig. 5, the aromatic protons of the inner benzene ring appear at δ 7.21 and 6.11 ppm as singlets showing downfield shifts by 1.81 and 0.71 ppm, respectively, as compared to the corresponding protons of **8**. Such downfield shifts are comparable to the values (1.80 and 1.12 ppm)[3b] observed in protonation of [2.2]para-

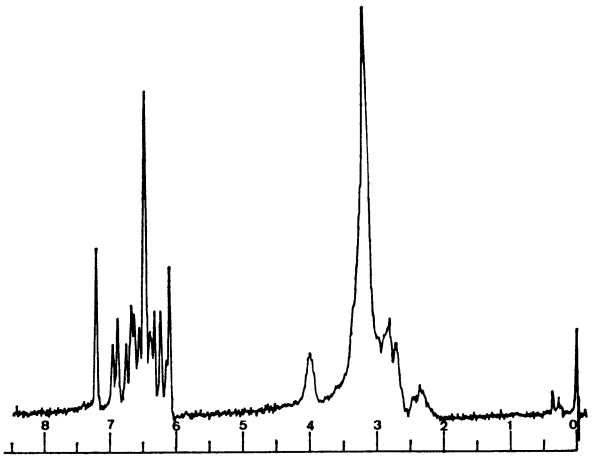
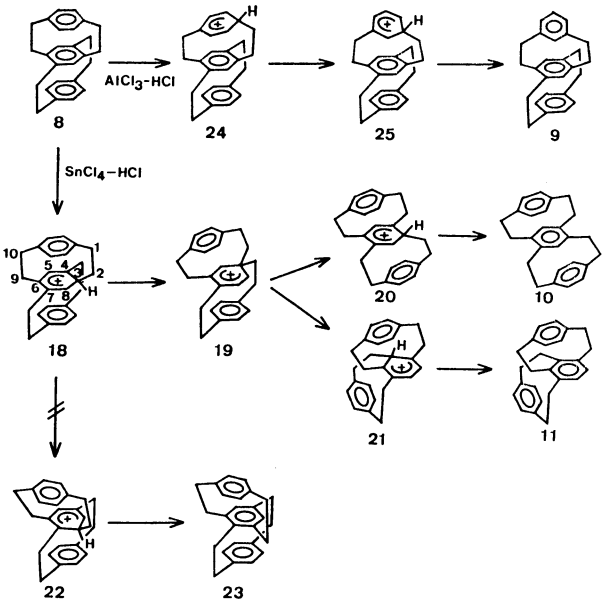


Fig. 5. NMR spectrum (100 MHz) of protonated triple-layered [2.2]paracyclophane **18** in FSO_3H-SO_2ClF-CD_2Cl_2 at −100 °C.

cyclophane. The fact that protonation occurred preferentially at a bridgehead carbon of the inner benzene is ascribed to a stronger basicity than that of the outer benzene ring due to the difference in the number of alkyl substituent and to considerable relief of bond angle strain, *viz.*, π-π repulsive strain between two benzene rings. On the other hand, the protonation of **10** occurred at bridgehead carbons of the two outer benzenes in preference to more basic inner one to give diprotonated species under marked strain release. The results of protonation demonstrate the strain relief to be a more important factor than π-basicity.

We propose a mechanism of the rearrangement of **8** to **10** and **11** as follows. At the initial stage, a proton would add to a bridgehead carbon (C_3) in the inner



benzene ring of **8** to form a cation (**18**), releasing bond angle strain of **8**. Although the same extent of strain relief is considered for another possible protonated species **24**, the difference in π-basicity of the inner and the outer benzene rings and the difference in relative stability of the two cations **18** and **24** due to transannular π-electronic delocalization are probably responsible for the predominance of **18**. The ethylene bridge attached to the protonated carbon would migrate intramolecularly to the adjacent bridgehead carbon C_4 to yield cation **19**, in which considerable strain reduction might result between the inner ring and both outer rings. Cation **19** is probably a common intermediate for the two rearranged products **10** and **11**, since a constant ratio was obtained for these products in the reaction mixtures regardless of the kind of weak protonic acid, reaction time, and temperature (Table 1), no interconversion between **10** and **11** being found under the same conditions. Finally, another ethylene bridge attached to the carbon C_4 would migrate in two ways, *viz.*, to C_3 and C_5 to give cations **20** and **21**, respectively, from which products **10** and **11** would be formed by deprotonation. No other possible migration of **18** to cation **22** was realized due to severe strain in the structure **23** as expected from the examination with molecular models.

In the rearrangement with aluminium chloride–hydrogen chloride, the initial protonation might take place at a bridgehead carbon of the outer benzene rings under strain relief, followed by bridge migration to cation **25** and deprotonation to **9**. Predominance of such a different type of initial protonation may be associated with the strong acidity and/or the bulkiness of this protonic acid.

The results suggested that the relief in molecular strain functions as a driving force in both the rearrangements **8**→**9** and **8**→**10**+**11**, and the relative π-basicity serves as an additional factor in the case of the latter rearrangement.

Experimental

Melting points are uncorrected. All the solvents are of reagent grade unless otherwise stated. Commercial Lewis acids were used. Chromatography was carried out on silica gel (Merck, activity II) or neutral alumina (Woelm, activity I). PMR spectra were taken with Hitachi-Perkin-Elmer R-20 (60 MHz) and Nihon Denshi JNM-TS-100 (100 MHz) spectrometers using TMS as an internal standard, MS with Hitachi RMU-7 spectrometer at 70 eV using a direct insertion technique, IR with Jasco DS-402 and UV with Hitachi EPS-3T spectrophotometers. Multilayered [2.2]paracyclophanes were synthesized according to the 1,6-Hofmann elimination method.[4a,c]

Rearrangemnet of 4,7-Dimethyl[2.2]paracyclophane ***3*** *to 12,15-Dimethyl[2.2]metaparacyclophane* ***4***. After dry hydrogen chloride gas had been bubbled into a stirred solution of anhyd aluminium chloride (1.694 g, 12.7 mmol) in dry dichloromethane (50 ml) for 30 min, 4,7-dimethyl[2.2]paracyclophane **3** (500 mg, 2.12 mmol) was added at once to the solution. The resulting blood red complex solution was vigorously stirred at 4—6 °C for 180 min, cooled to −15 °C, and decomposed with 6*N*-hydrochloric acid. The aqueous layer was extracted with dichloromethane and the combined organic layer was successively washed with water, saturated aq sodium hydrogencarbonate and water. After drying and evaporation of the solvent, the residual oil was filtered through neutral alumina (6 g) with hexane. The crystals obtained from the filtrate were recrystallized from pentane to give 192 mg (38%) of **4**, colorless plates, mp 66.5—67.5 °C (lit, 65—66 °C).[6a]

Rearrangement of D_2*-symmetric 4,7,12,15-Tetramethyl[2.2]paracyclophane* ***5*** *to 4,6,12,15-Tetramethyl[2.2]metaparacyclophane* ***6***. A suspension of anhyd aluminium chloride (2.28 g, 17.1 mmol) in dry dichloromethane (150 ml) was saturated with dry hydrogen chloride and cooled to −15 °C. Compound **5** (750 mg, 2.84 mmol) was added in one portion to the solution and the resulting deep red solution was stirred at −9——10 °C for 100 min under slow bubbling of dry hydrogen chloride. The reaction mixture was worked up in the same way as in the case of **4**. Chromatography on silica gel (80 g) with hexane gave, after elution of unidentified oily products, 112 mg (15%) of 4,6,12,15,-tetra methyl[2.2]metaparacyclophane **6**, white columns from hexane, mp 78—81 °C. Further recrystallization from the same solvent gave pure **6**, mp 81—82 °C.

Found: C, 90.60; H, 9.18%. Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.15%. NMR($CDCl_3$, δ ppm): 6.88(s, 1H, ArH), 6.62 (s, 1H, ArH), 5.69(s, 1H, ArH), 5.34(s, 1H, ArH), 3.4—1.9 (m, 8H, CH_2), 2.45(s, 3H, CH_3), 2.22(s, 6H, CH_3), 1.65 (s, 3H, CH_3): MS (rel intensity): 264(M^+, 52), 249(57),

133(63), 132(100), 117(30), 91(18); UV λ_{max} in THF, nm(ε): 279(520), 287.5(540).

When the above reaction was carried out at −20——21 °C for 15 min, the starting material was recovered, a tarry material only being produced at 0 °C for 1 h.

Rearrangement of Triple-layered [2.2]Paracyclophane ***8***.

a) With Aluminium Chloride–Hydrogen Chloride: A suspension of powdered anhyd $AlCl_3$ (472 mg, 3.54 mmol) in dry dichloromethane (40 ml) was saturated with dry HCl and cooled to −20 °C. Triple-layered [2.2]paracyclophane **8** (200 mg, 0.59 mmol) was added to the solution at once and the resulting deep red solution was stirred at −17 °C for 15 min. After cold 6M-HCl had been added, the separated aqueous layer was extracted with dichloromethane. The combined organic solution was washed with water, dried over anhyd magnesium sulfate, and evaporated to dryness. The residual oil was chromatographed on silica gel (30 g) with hexane. From the first eluate, triple-layered [2.2]metaparacyclophane **9** was obtained and recrystallized from benzene–ethanol to give 60 mg of colorless plates, mp 141—142 °C (lit, 144—145 °C).[6a]

The mother liquor and the following eluates gave a mixture of cyclophane (42 mg) consisting of **8**:**9**:**10**:**11**=3:76:11:10 on the basis of NMR analysis (100 MHz).

b) With Stannic Chloride–Hydrogen Chloride: To a stirred solution of anhyd $SnCl_4$ (460 mg, 1.75 mmol) in dry dichloromethane (20 ml) saturated with hydrogen chloride was added **8** (100 mg, 0.30 mmol). The resulting purple red solution was stirred at 29 °C for 30 min and quenched with cold dil hydrochloric acid. The reaction mixture was worked up as above and the product was purified by filtration through alumina (7 g) with 10% benzene–hexane to give a mixture of **10** and **11** (79.7 mg, 80% yield). Repeated recrystallization of the mixture from benzene gave two forms of crystal, colorless plates **10** and colorless prisms **11**, which were separated with tweezers and purified by recrystallization. The mixture was also separated into **10** and **11** by gel permeation chromatography (Nihon Bunsekikogyo LC-08). Cyclophane **10** gave spectral data and melting point (259—260 °C) identical with those of an authentific sample.[6a] Data of the new cyclophane **11** are as follows: mp 209—210 °C (partly sublime).

Found: C, 92.42; H, 7.63%. Calcd for $C_{26}H_{26}$: C, 92.26; H, 7.74%. The NMR datum is given in Fig. 1. MS (rel intensity): 338(M^+, 100), 233(38), 219(47), 104(92). UV λ_{max} in THF, nm(ε): 285(590), 293(530).

The rearrangement of **8** was carried out with the other protonic acids, $TiCl_4$–HCl, BF_3–HCl, and $ZnCl_2$–HCl in the same way as in the case of $SnCl_4$–HCl. The results are given in Table 1. A similar treatment with $GaCl_3$–HCl (at 28 °C, 30 min), $SbCl_5$–HCl (−5——2 °C, 60 min), and $FeCl_3$–HCl (29 °C, 10 min) gave only polymeric substances; with $SbCl_5$–HCl (−40——30 °C, 60 min) and HCl (reflux, 180 min) or HBr alone (22 °C, 60 min) the starting cyclophane **8** was recovered .

c) With Hydrogen Fluoride: Hydrogen fluoride (5 ml) was distilled in a solution of **8** (100 mg, 0.30 mmol) in dichloromethane (20 ml) which had been cooled in a Dry Ice–acetone bath. The resulting purplish red solution was gradually warmed up to 0 °C under stirring over a period of 20 min, stirring being continued at the temperature for 20 min. After HF had been removed, the reaction mixture was poured into a saturated aq. sodium hydrogencarbonate solution and worked up as described above. A mixture (20 mg, 20%) of **8**, **10**, and **11** was obtained in the ratio given in Table 1.

6-Bromo[2.2]paracyclo(4,8)[2.2]metaparacyclophane ***12***.

To a stirred solution of bromine (14.2 mg, 0.11 mmol) in carbon tetrachloride (0.3 ml) was added triple-layered metaparacyclophane **11** (37.2 mg, 0.11 mmol) in dry dichloromethane (1.5 ml) at 0 °C. The mixture was slowly warmed up to room temperature and then stirred for 15 min. After filtration through neutral alumina (1 g) and removal of the solvent, the residue was chromatographed on silica gel (10 g) with 10% benzene–hexane to give 45.1 mg (98%) of the desired bromoderivative **12**, colorless prisms from benzene–ethyl acetate, mp 242—243 °C with decompn. (in a sealed tube).

Found: C, 74.70; H, 5.96; Br, 18.82%. Calcd for $C_{26}H_{25}Br$: C, 74.82; H, 6.04; Br, 19.14%. NMR($CDCl_3$, δ ppm): 6.91 (dd, J=8, 2 Hz, 2H, ArH), 6.75(dd, J=8, 2 Hz, 1H, ArH), 6.62(s, 1H, ArH), 6.05(dd, J=8, 2 Hz, 1H, ArH), 5.92(dd, J=8, 2 Hz, 1H, ArH), 5.63 (dd, J=8, 2 Hz, 1H, ArH), 5.62(dd, J=8, 2Hz, 1H, ArH), 3.3—1.7 (m, 16H, CH_2). MS (rel intensity): 416(M^+, 32), 418(M^++2, 33), 337(37), 314(6), 312(6), 233(15), 104(100), 91(10). UV λ_{max} in THF, nm(ε): 285(620), 294(280), 305(210)(sh).

Rearrangement of Quadruple-layered [2.2]Paracyclophane ***13*** *with Boron Trifluoride Etherate–Hydrogen Chloride.* To a solution of boron trifluoride etherate (0.49 ml, 3.82 mmol) in dry dichloromethane (60 ml) saturated with dry HCl was added quadruple-layered [2.2]paracyclophane **13** (300 mg, 0.64 mmol) at once under stirring. The purplish blue solution was stirred at 0 °C for 30 min and then decomposed with dil hydrochloric acid. The mixture was worked up as usual. Chromatography of the product on silica gel (20 g) with 2% benzene–hexane gave quadruple-layered metaparacyclophane **14**, colorless prisms from benzene–hexane, mp 336.5—337.5 °C, yield 25 mg (8%).

Found: C, 92.53; H, 7.60%. Calcd for $C_{36}H_{36}$: C, 92.26; H, 7.74%. The NMR datum is given in Fig. 1. MS (rel intensity): 468(M^+, 100), 363(44), 349(34), 245(32), 104(44). UV λ_{max} in THF, nm(ε): 286(1790).

Protonation of Triple-layered [2.2]Para- and Metapara-cyclophanes ***8***, ***10***, *and* ***11***. Protonation was carried out according to the general procedure for **8** described below.

Sulfuryl chloride fluoride (0.6 ml) and fluorosulfuric acid (0.2 ml, freshly distilled) were carefully added successively at −78 °C to a solid of **8** (40 mg) placed in an NMR tube. When the tube was shaken, the solution turned clear deep red. After the NMR spectrum of protonated species **19** was measured, the solution was poured into water, compound **8** being recovered quantitatively. Cyclophane **10** was also protonated in a similar manner to yield diprotonated species, which was analyzed by NMR spectrum.

Diprotonated species of **10**, NMR(SO_2ClF–FSO_3H–CD_2Cl_2, δ ppm): 8.70(br d, J=8 Hz, 2H), 7.91(br d, J=8 Hz, 2H), 7.48(br d, J=8 Hz, 2H), 6.51(br d, J=8 Hz, 2H), 5.98(br s, 2H), 4.16(br s, 2H), 4.0—2.0(m, 16H).

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