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Layered Compounds. XV.[1] Synthesis and Properties of Multilayered Cyclophanes

Tetsuo Otsubo, Shigeyoshi Mizogami, Ikuko Otsubo, Zenzaburo Tozuka, Akiko Sakagami, Yoshiteru Sakata, and Soichi Misumi

The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565

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A series of multilayered cyclophanes up to sixfold were synthesized by 1,6-Hofmann elimination method. Odd layered and some dissymmetric ones were derived by means of cross-breeding pyrolysis of mixed quaternary ammonium hydroxides. The electronic spectra, absorption, emission, and CT absorption of charge-transfer complexes, of these cyclophanes exhibited remarkable transannular π-electronic interaction among chromophores closely stacked by methylene bridges. The interaction is increased eminently when the layer is varied from single to quadruple, but becomes less effective from quadruple to fivefold and no longer appreciable for more than fivefold one.

Aromatic compounds in which two or more chromophores are closely bound by methylene bridges, *i.e.*, layered compounds, are known as quite suitable models for the study of the transannular π-electronic interaction. [2.2]Paracyclophane,[2] one of the typical layered compounds, has been extensively studied by Cram and his co-workers from the viewpoints of the transannular interaction which results from the face-to-face proximity of two benzene rings to one another and many unusual chemical and physical behaviors have been reported to appear.[3] Such a face-to-face compression of the benzene rings brings about extreme molecular deformation or strain to the molecule, *i.e.*, extraordinarily short ring-to-ring distances, elongated benzyl–benzyl σ-bonds, and boat-shaped benzene rings.[4] These striking characteristics have attracted many organic and physical chemists' attentions and thereafter led to a great development of the chemistry of "cyclophane,"[5] *e.g.*, paracyclophanes,[3] metacyclophanes,[6] layered condensed aromatic cyclophanes,[7] and heterophanes.[8]

In these studies the emphasis has been on the exploration of the double layered aromatic compounds, and there have been reported only two of more than two layered cyclophanes so far. A triple-layered cyclophane was synthesized by Hubert[9] and a quadruple-

1) Part XIV: T. Kaneda, T. Ogawa, and S. Misumi, *Tetrahedron Lett.*, **1973**, 3373.

2) C. J. Brown and A. C. Farthing, *Nature*, **164**, 915 (1949).

3) D. J. Cram, *Rec. Chem. Progr.*, **20**, 71 (1959) and references cited therein.

4) C. J. Brown, *J. Chem. Soc.*, **1953**, 3265; D. K. Lonsdale, H. J. Milledge, and K. V. Rao, *Proc. Roy. Soc. Ser. A*, **255**, 82 (1960); H. Hope, J. Bernstein, and K. N. Trueblood, *Acta Crystallogr.*, **B28**, 1733 (1972).

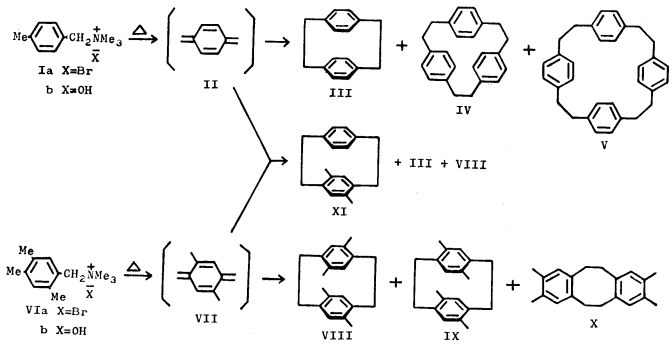
5) For nomenclature of cyclophane see B. H. Smith, "Bridged Aromatic Compounds," Academic Press Inc., New York, N. Y. (1964); F. Vögtle and P. Neumann, *Tetrahedron Lett.*, **1969**, 5329; *Tetrahedron*, **26**, 5847 (1970); K. Hirayama, *Tetrahedron Lett.*, **1972**, 2109.

6) F. Vögtle and P. Neumann, *Angew. Chem.*, **84**, 75 (1972), and references cited therein.

7) T. Toyoda, I. Otsubo, T. Otsubo, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, **1972**, 1731; M. Haenel and H. A. Staab, *ibid.*, **1970**, 3585; H. H. Wasserman and P. M. Keehn, *J. Amer. Chem. Soc.*, **91**, 2374 (1969).

8) H. E. Winberg, F. S. Fawcett, W. E. Mochel, and C. W. Theobald, *ibid.*, **82**, 1428 (1960); "Organic Syntheses," Vol. 42, p. 83 (1963).

9) A. J. Hubert, *J. Chem. Soc.*, (*C*), **1967**, 13.



Scheme 1.

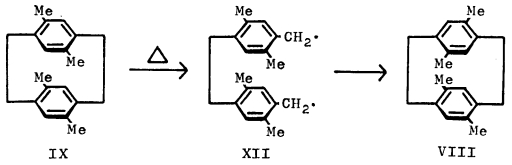
layered one by Longone,[10] but both ones were considered as mixture of configurational isomers and no report for separation was described.

In order to study the transannular interaction in more detail, we have designed syntheses of a series of multiple-layered cyclophanes. The synthesis of [2.2]-paracyclophane has been achieved by pyrolysis of *p*-xylene,[2,11] intramolecular Wurtz reaction,[12] 1,6-Hofmann elimination reaction,[8] and recently by photolysis of sulfide.[13] Of those procedures we took up the 1,6-Hofmann elimination method for synthesis of all multilayered paracyclophanes since the intermediate products were relatively accessible.

Results and Discussion

Synthesis of Double-Layered Cyclophanes (Scheme 1). On a pyrolysis of *p*-methylbenzyltrimethylammonium hydroxide (Ib), [2.2]paracyclophane(III) was obtained in 10—17% yield.[8] It is considered to proceed through *p*-xylylene intermediate II.[14] After examining a number of pyrolytic conditions we observed that when a small amount of xylene was used in the place of toluene as a solvent, its yield was raised to 29% and [2.2.2]-paracyclophane (IV)[15] and [2.2.2.2]paracyclophane (V)[16] were concomitantly obtained in 8.4 and 2.2% yields, respectively.

Longone and Chow obtained 4,7,12,15-tetramethyl-[2.2]paracyclophane (VIII) in a 20% yield along with 2,3,8,9-tetramethyl-*sym*-dibenzocyclooctadiene (X) by pyrolysis of duryltrimethylammonium hydroxide (VIb).[10] On dimerization of the intermediate VII, the dimer structure VIII where methyl groups on both rings are positioned in staggered form and the other one IX where all methyl groups are eclipsed are properly considered as the producible isomers. They reported that the product was assigned to dissymmetric form VIII on the basis of optical resolution by the Newman resolving agent and that the symmetric form IX couldn't be afforded owing to mutual overcrowding of four methyl groups.[17] By treatment with a small amount of *n*-pentane, however, we could separate a very slight amount (0.1% yield) of the sparingly soluble, eclipsed form IX (C_{2h} symmetry) from the readily soluble, staggered form VIII (D_2 symmetry).

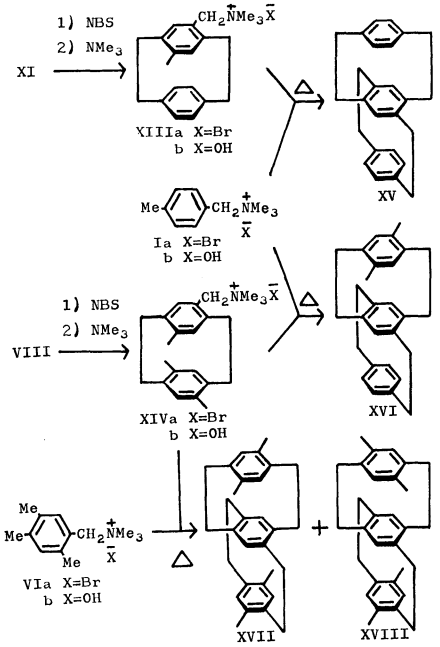


The mass spectra of both forms show entirely identical pattern, supporting an isomeric relationship with each other. Fairly higher melting point of IX than that of VIII suggests that the former is more symmetric. Moreover, a definitive evidence for this isomeric relationship could be provided by the conversion of IX to VIII in the thermochemical process. Thus, when a solution of IX in *n*-tridecane or hexachlorobutadiene was heated at *ca.* 195 °C for 3 hr, VIII was afforded almost quantitatively, probably through a biradical intermediate (XII).[18] In addition, the structural assignment of two isomers was made on the basis of the nuclear Overhauser effect and the steric compression effect as described in the next paper.[20]

Cross-breeding pyrolysis of an equimolar mixture of Ib and VIb gave [2.2]paracyclophane (III) and its methyl derivatives VIII and XI. 4,7-Dimethyl[2.2]-paracyclophane (XI) was isolated by fractional crystallization.

Synthesis of Triple-Layered Cyclophanes (Scheme 2). Quaternary ammonium salts XIIIa and XIVa were prepared from the corresponding methyl derivatives of [2.2]paracyclophanes, XI and VIII, by successive treatments with *N*-bromosuccinimide and trimethylamine according to Longone's procedure.[10] Cross-breeding pyrolysis of a quaternary ammonium hydroxide XIIIb, derived by ion exchange from XIIIa, with Ib gave non-substituted triple-layered cyclophane (XV) together with double-layered one III and quadruple-layered ones, XIX and XX. Column chromatography on silica gel gave a 1.3% yield of XV in a pure state.

10) D. T. Longone and H. S. Chow, *J. Amer. Chem. Soc.*, **86**, 3898 (1964); *ibid.*, **92**, 994 (1970).
11) L. A. Errede and J. P. Cassidy, *ibid.*, **82**, 3650 (1960).
12) D. J. Cram and H. Steinberg, *ibid.*, **73**, 5691 (1951).
13) J. Bruhin and W. Jenney, *Tetrahedron Lett.*, **1973**, 1215.
14) M. Szwarc, *Nature*, **160**, 403 (1947); *J. Chem. Phys.*, **16**, 128 (1948); L. A. Errede and B. F. Landrum, *J. Amer. Chem. Soc.*, **79**, 4952 (1957); L. A. Errede, *ibid.*, **83**, 949 (1961); L. A. Errede and W. A. Pearson, *ibid.*, **83**, 954 (1961).
15) W. Baker, J. F. W. McOmie, and J. M. Norman, *J. Chem. Soc.*, **1951**, 1114.
16) L. A. Errede, R. S. Gregorian, and J. M. Hoyt, *J. Amer. Chem. Soc.*, **82**, 5218 (1960).
17) D. T. Longone and M. T. Reetz, *Chem. Commun.*, **1967**, 46.
18) H. J. Reich and D. J. Cram, *J. Amer. Chem. Soc.*, **91**, 3517 (1969).

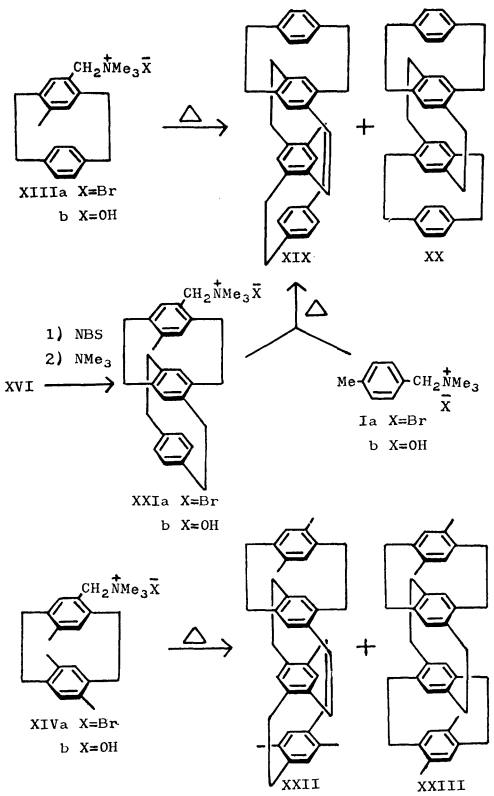


Scheme 2.

Dimethyl triple-layered cyclophane XVI was similarly prepared from XIVb and Ib in a 1.8% yield.

Tetramethyl triple-layered ones were obtained by cross-breeding pyrolysis of XIVb with VIb. Careful and elaborate column chromatography on silica gel gave a 1.1% yield of XVII and a 1.1% yield of XVIII. The structure of these isomers was determined on the basis of the chemical shifts of aromatic protons on NMR spectra. Thus, in the former isomer two signals of aromatic protons appear in a 1:2 ratio of integral strength which corresponds to the ratio of inner-to-outer aromatic protons, whereas in the latter isomer three signals appear in a 1:1:1 ratio which indicates the existence of two types of outer protons different in magnetic environment. One can easily see from the structures, XVII and XVIII, that the differences in magnetic shielding and steric crowding give rise to those aromatic proton ratios. In contrast to large difference in yields of tetramethyl double-layered compounds, VIII and IX, the formation of XVII and XVIII in a same yield may be best accounted for assuming that the steric crowding between methyl and benzylmethylene groups mutually eclipsed in XVIII might be less than that crowding between two methyl groups in IX because the methylene groups in problem would be bent toward the remaining benzene ring.

Synthesis of Quadruple-Layered Cyclophanes (Scheme 3). Pyrolysis of XIIIb in boiling xylene afforded a mixture of non-substituted quadruple-layered compounds, XIX (D_2 symmetry) and XX (C_{2h} symmetry). By treatment of the mixture with carbon tetrachloride–acetone (1:3), the readily soluble compound (1.1% yield) was separated from the sparingly soluble one (0.75% yield). The both compounds show similar NMR, IR, UV spectra, identical mass spectrum and empirical formula. It indicates obviously an isomeric relationship of both compounds. Although the structure of both isomers seemed to be difficult to determine, the easily soluble isomer could be assigned to the structure



Scheme 3.

XIX by direct comparison with an independently synthesized sample as described below. Thus, cross-breeding pyrolysis of an ammonium hydroxide XXIb, derived from dimethyl triple-layered cyclophane XVI in the usual manner, with Ib afforded only the dissymmetric isomer XIX which was proved to be identical in all respects with the readily soluble isomer obtained by pyrolysis of XIIIb. Consequently the other, sparingly soluble isomer should be assigned to more symmetric structure XX.

Longone reported the formation of a mixture of isomeric tetramethyl quadruple-layered cyclophanes,

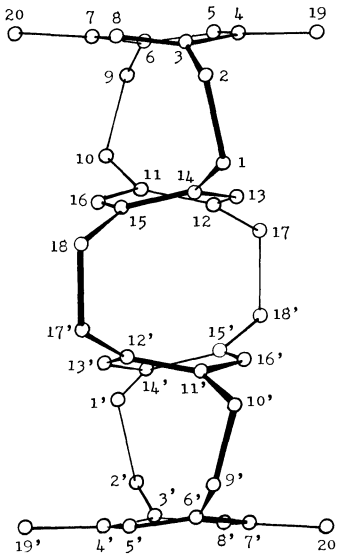


Fig. 1. Profile of quadruple-layered cyclophane XXIII viewed down the b axis.

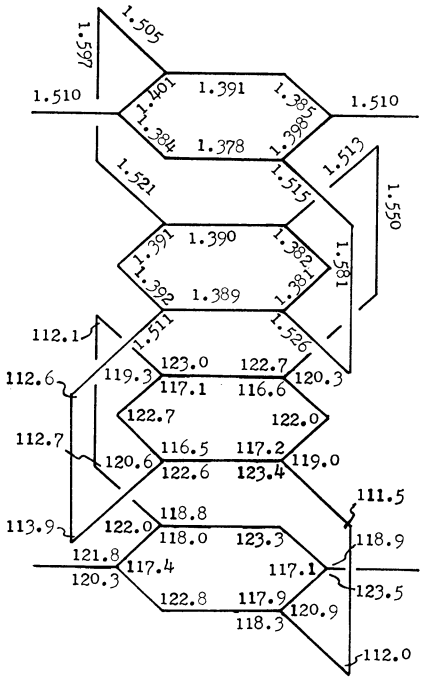


Fig. 2. Bond lengths and angles. The standard deviations are 0.010 Å in bond lengths and 0.6 ° in bond angles.

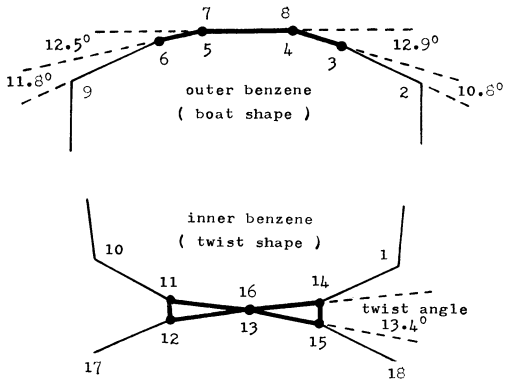
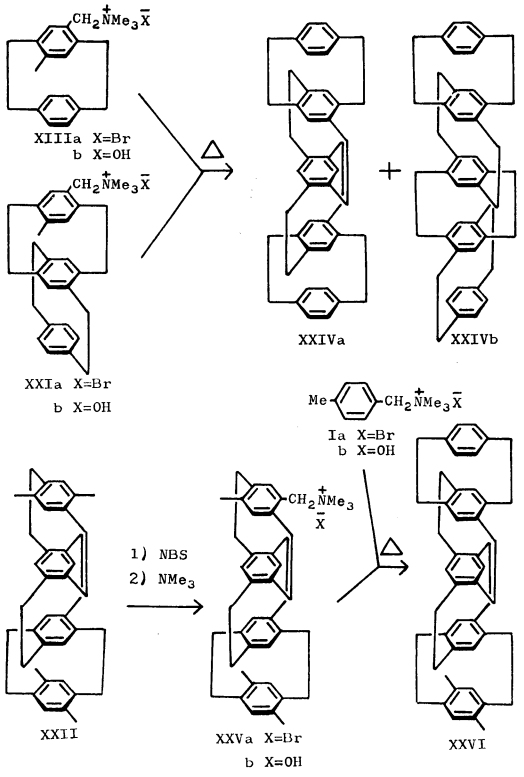


Fig. 3. Distortion of outer and inner benzene rings.

XXII (D_2 symmetry) and XXIII (C_{2h} symmetry), by pyrolysis of a quaternary base XIVb, but failed in separating them.[10] By treatment of a mixture of the isomers with the same solvent as in the case of non-substituted system, the readily soluble isomer (3.2% yield) was separated from the sparingly soluble one (1.6% yield). For the structures of two isomers we tentatively assigned the more soluble isomer to XXII (D_2 symmetry) and the less soluble one to XXIII (C_{2h} symmetry) by comparison of isomers ratio, solubility, and electronic spectra with non-substituted system. Recently the exact molecular structure of the less soluble isomer was determined by X-ray crystallographic analysis as shown in Figs. 1—3.[19] The figures show that the less soluble isomer has a C_{2h} symmetric structure and four benzene rings are closely stacked in a manner to be well superposed. Also the figures demonstrate significant strain of the molecule in such a manner that outer benzene rings are bent into boat shape as in the case of [2.2]paracyclophane (III),[4] whereas the inner rings are forced to be distorted remarkably by both π-electron repulsion between benzene rings and tension with two pairs of methylene bridges above (C_1–C_2 and C_9–C_{10} in Fig. 1) and below (C_{17}–C_{18}' and C_{18}–C_{17}') the benzene moiety and consequently deformed into a twist form as shown in Figs. 1 and 3. The four benzene layers are stacked with about equal ring-to-ring distances, that is, two outer-to-inner and one inner-to-inner. The mean value of those distances is 3.03 Å which is comparable to that of [2.2]paracyclophane and about independent of the increase of layers. Accordingly such a structural situation must be applied to all of other multilayered cyclophanes.



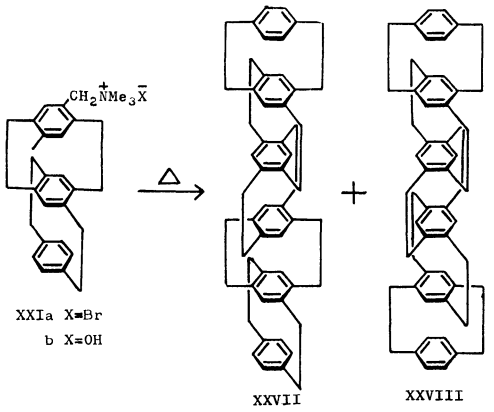
Scheme 4.

Synthesis of Fivefold-Layered Cyclophanes (Scheme 4). Pyrolysis of an equimolar mixture of quaternary bases XIIIb and XXIb afforded non-substituted fivefold-layered cyclophane XXIV along with quadruple-layered ones (XIX and XX) and polymers. Separation by liquid chromatography gave a 5% yield of pure XXIV which is probably a mixture of two isomers, XXIVa (D_2 symmetry) and XXIVb (C_2 symmetry).

Dimethyl derivative XXVI was obtained in a 1.1% yield by cross-breeding pyrolysis of Ib and XXVb which was prepared from tetramethyl quadruple-layered cyclophane XXII having D_2 symmetric configuration.

Synthesis of Sixfold-Layered Cyclophanes (Scheme 5). Sixfold-layered cyclophanes were obtained by pyrolysis of a quaternary base XXIb in boiling toluene. After column chromatography, a readily soluble product was

19) H. Mizuno, K. Nishiguchi, T. Otsubo, S. Misumi, and N. Morimoto, *Tetrahedron Lett.*, **1972**, 4981.



Scheme 5.

separated from a less soluble one in a 2:1 product ratio by treatment with benzene. The NMR, IR, and UV spectra of both isomers are fairly similar. On analogy with quadruple-layered cyclophanes, it is presumed that the structure of the readily soluble, major isomer is XXVII (D_2 symmetry), whereas the sparingly soluble, minor one is XXVIII (C_{2h} symmetry).

Properties. All of the multilayered cyclophanes are stable under ordinary conditions in spite of considerably strained structure. However, when the compounds are allowed to stand for a long time in halogenated hydrocarbon solvents, they decompose gradually. The isomer bearing higher symmetry generally displays higher melting point compared with the other isomer. All of more than three layered [2.2]paracyclophanes decompose with color change to brown and without melting at temperature above 240 °C.

The NMR, IR, and mass spectral data are consistent with the structures of above multilayered cyclophanes. The NMR spectra reveal a striking feature that all the aromatic protons appear at considerably higher field due to diamagnetic shielding effect.[20]

Infrared Spectra. The IR spectra of [2.2]paracyclophane system are known to reveal obvious features as follows. One is the increase of the intensity of a band in 1580—1600 cm^{-1} region, which relates to the increased double bond character due to the distortion of the benzene rings.[21] The other is the appearance of a strong new maximum at 720 cm^{-1} for [2.2]paracyclophane III and at 709 cm^{-1} for 4,7,12,15-tetramethyl[2.2]paracyclophane VIII as shown in Table 1. Longone stated that these bands might be associated with the distorted benzene rings.[22] In practice, other layered cyclophanes also exhibit the characteristic band around 700 cm^{-1}, whereas [2.2.2]paracyclophane IV bearing less strained benzene rings shows a weak band at 721 cm^{-1}, and [2.2.2.2]paracyclophane V and *p,p'*-dimethylbibenzyl bearing strain-free rings no band in this region.

More detailed examination of more than two layered, non-substituted cyclophanes shows that two bands

Table 1. IR spectra of layered cyclophanes around 700 cm^{-1} [a]

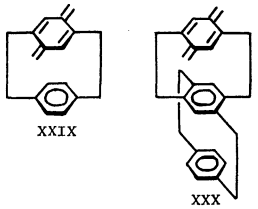
Compound	Wave number (cm^{-1})
III	720(s)
XI	715(s)
VIII	709(s)
IX	708(s)
XV	708(s), 680(s)
XVI	710(w), 695(s), 673(m)
XVII	693(s), 660(m)
XVIII	688(s), 660(m)
XIX	713(s), 674(s)
XX	710(s), 687(s)
XXII	692(s), 665(m)
XXIII	696(s), 669(m)
XXIV	714(m), 671(s)
XXVI	712(w), 693(m), 672(s), 665(s)
XXVII	713(m), 673(s)
XXVIII	715(m), 677(s)

a) KBr disc.

appear near 710 cm^{-1} comparable to characteristic, lower wavenumber band of double-layered cyclophanes and near 680 cm^{-1} and that the more the number of benzene layers increases, the stronger the relative intensity of the lower wave number band to the higher one becomes. It is reasonable to assume that the higher band is associated with the boat-shaped outer benzene rings and the lower band with twist-shaped inner benzene rings.

The spectra of dimethyl compounds XVI and XXVI show a strong new peak near 695 cm^{-1} together with above two bands of which the band at 680 cm^{-1} becomes broad. On the other hand, tetramethyl derivatives XVII, XVIII, XXII, and XXIII show two absorption bands near 695 and 665 cm^{-1}. By comparing the spectra of the three groups of cyclophanes, *i.e.*, non-substituted, dimethyl, and tetramethyl compounds, the band near 695 cm^{-1} of dimethyl and tetramethyl compounds probably originates from outer benzene rings more distorted by methyl groups, whereas the band near 665 cm^{-1} of tetramethyl compounds from the twist-shaped inner benzene rings. It is also observed that the two peaks of those methylated compounds appear in slightly lower wave number than the corresponding ones of non-substituted compounds owing to methyl substituents.

Mass Spectra. [2.2]Paracyclophane exhibits a characteristic mass spectrum where molecular ion peak and a fragment one corresponding to *p*-xylylene appear as predominant signals. In the spectra of multilayered cyclophanes, it is observed in general that the molecular ion is a base peak and the more layered



20) The discussions of NMR spectra of multilayered cyclophanes will be described in detail in Part XVI: This Bulletin, **46**, No. 12 (1973) in press.

21) D. J. Cram and H. Steinberg, *J. Amer. Chem. Soc.*, **73**, 5691 (1951).

22) D. T. Longone and C. L. Warren, *ibid.*, **84**, 1507 (1962).

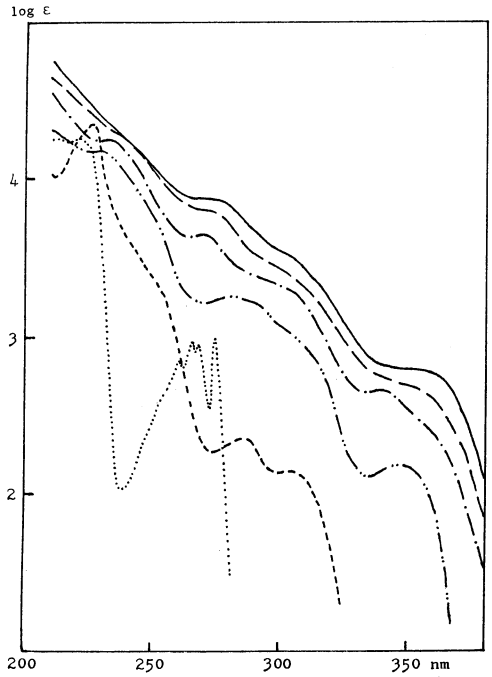


Fig. 4. UV spectra of layered cyclophanes in cyclohexane; ····· *p,p'*-dimethylbibenzyl, ---- III, -·-· XV, -·-·- XIX, — — XXIV, —— XXVII.

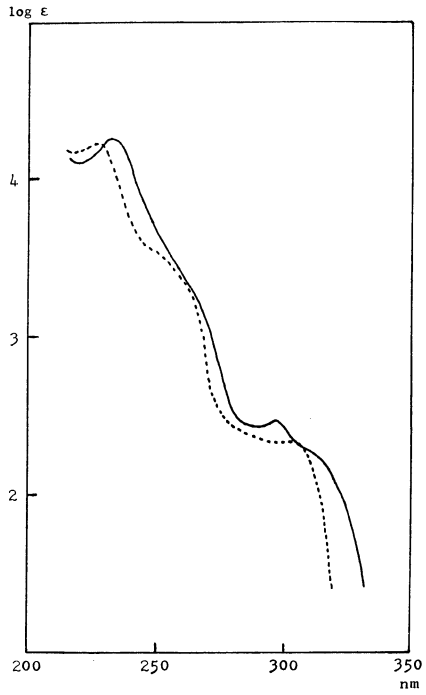


Fig. 5. UV spectra of tetramethyl[2.2]paracyclophanes in cyclohexane; ---- VIII, —— IX.

p-xylylene fragment ions such as XXIX and XXX become greater. This appears to be caused by the stabilization due to transannular charge delocalization.

Electronic Absorption Spectra. Figure 4 shows the electronic absorption spectra of non-substituted multilayered cyclophanes. The absorption curves are hardly affected by methyl substitution and show no difference in configurational isomers. The figure demonstrates strong bathochromic and hyperchromic effects as the number of layers increases successively. In particular those effects are prominent as the layer is varied from single to double. Thus a band at 270 nm associated with $^1B_{2u}$ transition of *p,p'*-dimethylbibenzyl disappears in the spectrum of [2.2]paracyclophane (III), and new peaks are observed to appear at 244, 286, and 302 nm instead. These spectral features have been explained by two predominant effects, that is, distortion of benzene ring and transannular π-electronic interaction between two rings.[23] In order to study the former effect, a series of [m]paracyclophanes were synthesized and examined.[24] The absorption bands of [m]paracyclophanes are somewhat shifted to longer wavelength with the decrease of methylene number, but the extent of deformation in absorption curves is not so large for [8]paracyclophane[25] which is considered as strain molecule comparable to [2.2]paracyclophane and even for extremely strained [7]paracyclophane.[26] Such a minor effect of the ring torsion on electronic spectra is also observed in the spectra of isomeric tetramethyl[2.2]-paracyclophanes, VIII and IX (Fig. 5). In spite of severe ring strain due to steric repulsion of mutually eclipsed methyl groups, the latter isomer shows a spectrum comparable to that of the former. As the layer is altered from double to triple, the absorption curve becomes further structureless with large bathochromic shift, increased intensity of the band near 290 nm, and appearance of a new peak at 347 nm. In this case the ring distortion effect is hardly considered to be responsible for such marked bathochromic shift because the extent of ring torsion is not so different between the double-layered and triple-layered compounds. Accordingly, the spectral change must be explained mainly by the transannular π-electronic interaction or delocalization. In theory, the configurational interactions of charge-transfer and neutral excitation states were applied with success for interpretation of the spectra of the layered paracyclophanes.[27]

With increasing layer number from the tripled to the fivefold, the absorption curves become broader successively, but the intensity per unit chromophore increases gradually. However, the spectrum of the sixfold one shows that the curve shape and the intensity per unit chromophore are nearly equal to that of the fivefold one, supporting no further increase of the transannular π-electronic interaction.

Emission Spectra. A study of the emission spectra

23) D. J. Cram, N. L. Allinger, and H. Steinberg, *J. Amer. Chem. Soc.*, **76**, 6132 (1954).

24) N. L. Allinger, L. A. Freiberg, R. B. Hermann, and M. A. Miller, *ibid.*, **85**, 1171 (1963).

25) D. J. Cram, C. S. Montgomery, and G. R. Knox, *ibid.*, **88**, 515 (1966).

26) N. L. Allinger and T. J. Walter, *ibid.*, **94**, 9267 (1972); A. D. Wolf, V. V. Kane, R. H. Levin, and M. Jones, Jr., *ibid.*, **95**, 1680 (1973).

27) M. T. Vara, Jr., I. H. Hillier, S. A. Rice. and J. Jortner, *J. Chem. Phys.*, **44**, 23 (1966); I. H. Hillier, L. Glass, and S. A. Rice, *J. Amer. Chem. Soc.*, **88**, 5063 (1966); S. Iwata, K. Fuke, M. Sasaki, S. Nagakura, T. Otsubo, and S. Misumi, *J. Mol. Spectrosc.*, **46**, 1 (1973).

Table 2. Emission spectra of layered cyclophanes (77 K)

Compound	Solvent	Fluorescence maximum (nm)	Phosphorescence maximum (nm)	Lifetime of phosphorescence (s)
Durene	EPA	279, 284, 289, 294	358, 368, 380, 391, 403, 415, 428	6.8 ±0.8
III	EPA	354	470	3.5 ±0.3
XI	EPA	355	470	2.2 ±0.1
VIII	EPA	347	469	2.3 ±0.3
XV	EPA	380	524, 542, 560	0.49±0.02
XVI	EPA	378	518, 532, 555	0.56±0.02
XVII	EPA	375	512, 529, 551, 570	0.77±0.06
XIX	EPA	396	527, 546, 567	0.37±0.03
XIX	TA	395	528, 546, 565	0.41±0.03
XXII	EPA	390	521, 538, 560, 573	0.41±0.04
XXIV	TA	397	527, 546, 567	0.42±0.04
XXVII	TA	398	528, 547, 570	0.41±0.03

a) EPA: ether–isopentane– alcohol (5: 5: 2). b) TA: tetrahydrofuran–alcohol (1: 1).

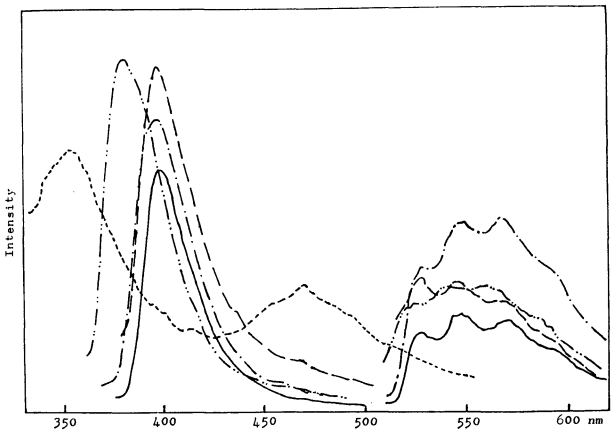


Fig. 6. Emission spectra of layered cyclophanes; ---- III, -·-·- XV, -·-·- XIX in EPA, and —— XXIV, —— XXVII in THF–alcohol (1: 1) at 77 K. Phosphorescences are enlarged by about four times fluorescences except III.

was carried out to obtain further information concerning the transannular interaction. The spectra are shown in Table 2. Both fluorescence and phosphorescence spectra exhibit large bathochromic shifts with successive increase of layer number as well as the absorption spectra just described above (Fig. 6). Such a shift is particularly remarkable as the layer is altered up to the tripled. In contrast to ambiguous positions of the longest wavelength bands in the absorption spectra, the emission maxima are clearly distinguishable for the tripled and the quadrupled cyclophanes. These spectra also indicate no further increase of transannular π-electronic interaction for more than five fold-layered cyclophanes.

Lifetime of Phosphorescence. The effect of the transannular π-electronic interaction on the various spectra of multilayered compounds can also be discussed from the lifetime of phosphorescence. As shown in Table 2, the lifetime tends to become progressively shorter and to converge in the same manner as band shifts on absorption and fluorescence spectra. It is well explainable by the postulate that the transannular π-electronic interaction lowers the energy gap between the ground and the triplet states and thereby increases the probability of radiationless deactivation.

Charge-Transfer Complexes. It is well known that in a series of π-complexes consisted of methylated benzenes and tetracyanoethylene (TCNE), there is a correlation between the position of the long-wavelength band and the association constant, K, of the complexes.[28] Increased transannular electronic interaction was also reported to be reflected in π-basicity of multilayered cyclophanes.[10,29] The transannular electron release to the complexed face ring from the remaining benzene rings is expected to take place. Table 3 and Fig. 7, indeed, show that with increasing number of layers in this series of cyclophanes, the long-wavelength maxima of TCNE complexes shift to longer wavelength and hence the donor character of the cyclophanes increases progressively. It is noteworthy that even in the case of fivefold one, such electron release is still effective for stabilization of the complex XXXI. Unfortunately, the spectrum of the sixfold compound

Table 3. Absorption maximum wavelengths of layered cyclophane-TCNE complexes in dichloromethane

Compound	λ_{max} (nm)
p-xylene	420, 465[a] (460)[b]
p,p'-dimethylbibenzyl	420, 465[a]
durene	480
III	521
XI	555
VIII	584 (580)[c]
IX	595
XV	530[a], 630
XVI	430[a], 650
XVII	430[a], 655
XVIII	430[a], 643
XIX	530, 710
XXII	720 (690)[c]
XXIV	540, 750

a) Shoulder. b) Ref. 28. c) Ref. 10.

28) R. E. Merrifield and W. D. Phillip, *J. Amer. Chem. Soc.*, **80**, 2778 (1958).
29) D. J. Cram and R. H. Bauer, *ibid.*, **81**, 5971 (1959).

Table 4. Equilibrium constants for 1,3,5-trinitrobenzene–layered cyclophane complexes in chloroform

Compound	λ_{max} (nm)	K_X	ε(cm^{-1}. mol^{-1}. l)
Xylenes[a)]	312	2.08	4080
p,p'-Dimethylbibenzyl (non-substituted cyclophane)	312		
[2.2]Paracyclophane (III)	362 (365)[b)]		
Triple-layered XV	405	6.84	1820
Quadruple-layered XIX	400, 450(sh)	7.46	1490
Fivefold-layered XXIV	400, 470(sh)		
Sixfold-layered XXVII (methylated cyclophane)	400, 470(sh)	11.1	950
Tetramethyl[2.2]paracyclophane VIII	405	10.2 (9.6)[b)]	2440 (2500)[b)]
Dimethyl triple-layered XVI	430	15.9	1280
Tetramethyl quadruple-layered XXII	430	15.7 (21.6)[b)]	1810 (1430)[b)]

a) A. Bier, *Rec. Trav. Chim. Pays-Bas*, **75**, 866 (1956). b) Ref. 10.

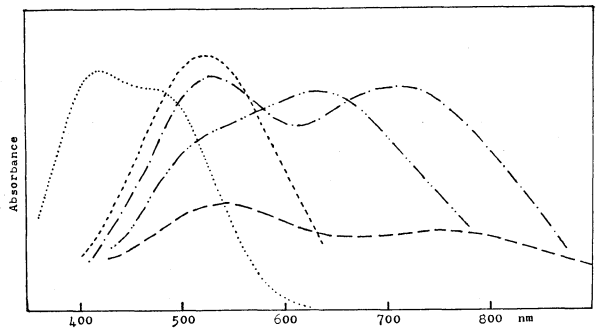
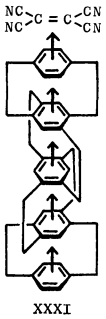


Fig. 7. Charge-transfer absorption spectra of layered cyclophane-TCNE complexes in dichloromethane; ····· *p,p'*-dimethylbibenzyl, ---- III, -·-· XV, -·-· XIX, —— XXIV.

failed to be measured owing to very low solubility of its dark blue TCNE complex.



XXXI

The use of 1,3,5-trinitrobenzene (TNB) as an acceptor makes possible to measure the complex spectrum of sixfold-layered compound and also shows a tendency analogous to TCNE complexes as summarized in Table 4. Thus, the long-wavelength bands of charge-transfer complexes display marked bathochromic shift and the equilibrium constants, K_x, increase significantly as the layers increase. It is noteworthy that the complexes of fivefold and sixfold compounds exhibit quite identical spectra. In other words, there is no difference in transannular electron-releasing between them.

Experimental

Melting points are uncorrected. All solvents are of reagent grade unless otherwise specified. Chromatography was done with neutral alumina (Woelm, activity I) or silica gel (Merck, activity II—III) of about 20 to 100 times of mixture to separate. The use of a long column often results in the decomposition of multilayered cyclophanes. General procedure for Hofmann pyrolysis was described in detail in the experiment for [2.2]paracyclophane (III).

NMR measurements were made with a Hitachi Perkin-Elmer R-20 spectrometer (60 MHz) on dilute solutions in carbon tetrachloride or deuteriochloroform using tetramethylsilane as an internal standard. Infrared spectra were taken on a Jasco DS-402 spectrophotometer. 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 at liquid nitrogen temperature 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) or tetrahydrofuran–ethanol (1:1 volume ratio). All solvents were of spectroscopic grade (Merck or Tokyo Kasei Kogyo) and used without further purification. A solution of about 1×10^{-3} M was prepared and degassed by freeze-pump-thaw method. Emission spectra were uncorrected. Lifetimes of phosphorescences were calculated from the exponential decay curves which were recorded on a synchroscope screen and photographed. The experimental errors are within $\pm5\%$.

[2.2]Paracyclophane (III), *[2.2.2]Paracyclophane (IV)*, *and [2.2.2.2]Paracyclophane (V)*. A solution of *p*-methylbenzyltrimethyl ammonium bromide (Ia, 10 g, 41 mmol) in 200 ml of distilled water was passed through a column containing strongly basic anion exchange resin, Amberite IRA-400[30] which is converted to its hydroxide form with large excess of 2 M sodium hydroxide solution. A mixture of the resulting aqueous solution (500 ml) of quaternary base (Ib), distilled xylene (50 ml), and phenothiazine (1 g) was placed in a three-necked, pear-shaped flask fitted with a mechanical stirrer and a water separator of Dean-Stark type attached

30) Instead of Amberite IRA-400, Dowex 1-X8, 50—100 mesh is currently available for ion exchange.

to a reflux condenser. The mixture was heated with stirring and water was removed as xylene azeotrope over a period of 4 hr. When the removal of water had been approximately completed, trimethylamine began to evolve and some polymers precipitated. After additional heating with stirring for 6 hr, the reaction mixture was allowed to cool and insoluble solid was separated by filtration. The solid was washed eight times with each 30 ml of hot benzene. The combined benzene washing was evaporated to dryness to give 0.83 g of crude [2.2]paracyclophane (III). The filtrate was chromatographed on neutral alumina (Woelm, activity I). Elution with benzene–hexane (1:9) gave first 0.39 g of [2.2]paracyclophane (III), then 0.36 g (8.4%) of [2.2.2]paracyclophane (IV), and finally 0.095 g (2.2%) of [2.2.2.2]-paracyclophane (V).

The combined [2.2]paracyclophane, 1.22 g (29%), was recrystallized from chloroform, colorless prisms, mp 285 °C in a sealed tube (lit, [8]285—287 °C in a sealed tube). NMR (CCl_4) τ 3.65 (s, 8H, ArH), 6.99 (s, 8H, CH_2); mass *m/e* 208 (M^+, 56), 104 (100); IR (KBr disc, cm^{-1}) 3030 (w), 3005 (w), 2947 (w), 2920 (m), 2893 (w), 2847 (w), 1589 (m), 1497 (m), 1412 (m), 1087 (m), 936 (m), 893 (m), 806 (s), 720 (s), 622 (s), 508 (s).

[2.2.2]Paracyclophane was recrystallized from acetone, colorless plates, mp 162—163 °C (lit,[15] 166—167 °C). NMR (CCl_4) τ 3.43 (s, 12H, ArH), 7.12 (s, 12H, CH_2); mass *m/e* 312 (M^+); IR (KBr disc, cm^{-1}) 2995 (m), 2890 (s), 2830 (m), 1512 (s), 1438 (s), 1094 (m), 916 (m), 803 (m), 787 (s), 721 (w), 583 (s), 468 (s).

[2.2.2.2]Paracyclophane was recrystallized from acetone, colorless plates, mp 179—181 °C (lit,[16] 179—182 °C). NMR (CCl_4) τ 3.39 (s, 16H, ArH), 7.19 (s, 16H, CH_2); mass *m/e* 416 (M^+); IR (KBr disc, cm^{-1}) 2995 (m), 2910 (s), 2835 (m), 1510 (s), 1435 (s), 1198 (m), 1094 (m), 928 (m), 812 (s), 583 (s), 566 (m).

Staggered and Eclipsed 4,7,12,15-Tetramethyl[2.2]paracyclophanes (VIII and IX). The ammonium hydroxide aqueous solution (*ca.* 1 l) derived from 20.0 g (73.5 mmol) of duryltrimethylammonium bromide (VIa) in the usual way was mixed with 500 ml of distilled xylene and three spatulas of phenothiazine, and heated with stirring. After water was removed by azeotropic distillation, further reflux was continued for 12 hr and the mixture was cooled. The insoluble polymers (4.53 g) were removed by filtration and the filtrate was dried over anhydrous magnesium sulfate. After the solvent was evaporated, the residue was subjected to column chromatography on silica gel (Merck, activity II—III) using petroleum ether as eluent. From the first eluate was isolated a mixture of two isomeric 4,7,12,15-tetramethyl[2.2]paracyclophanes, VIII and IX. The minor isomer IX was separated from the readily soluble, staggered form VIII by treatment with a small amount of pentane. From the next eluate was isolated 2,3,8,9-tetramethyl-*sym*-dibenzocyclooctadiene (X) in a 0.4% yield.

The staggered form VIII was recrystallized from petroleum ether (yield 20%), colorless prisms, mp 106—107 °C (lit,[10] 105—107 °C). NMR (CCl_4) τ 3.75 (s, 4H, ArH), 6.8—7.6 (A_2B_2, 8H, CH_2), 8.04 (s, 12H, CH_3); mass *m/e* 264 (M^+, 66), 132 (100); IR (KBr disc, cm^{-1}) 2994 (m), 2937 (s), 2855 (m), 1604 (m), 1495 (s), 1444 (s), 1394 (m), 1367 (m), 1247 (m), 1030 (m), 902 (s), 850 (m), 819 (m), 709 (s), 512 (m), 466 (m), 440 (m).

The eclipsed form IX was recrystallized from 1:3 carbon tetrachloride–acetone, 0.1% yield, colorless plates, mp 230—232 °C in a sealed tube. NMR (CCl_4) τ 3.93 (s, 4H, ArH), 6.5—7.7 (A_2B_2, 8H, CH_2), 7.85 (s, 12H, CH_3); mass *m/e* 264 (M^+, 66), 132 (100); IR (KBr disc, cm^{-1}) 2908 (s), 2853 (m), 1598 (m), 1497 (s), 1454 (m), 1392 (s), 1370 (m), 1030 (m), 895 (s), 708 (s), 510 (m), 434 (m). Found: C, 90.55; H, 9.14%. Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.15%.

The compound X was recrystallized from ethyl acetate, colorless prisms, mp 239—240 °C after sintering at *ca.* 210 °C in a sealed tube (lit,[10] crystallized from chloroform, mp 209—211 °C in a sealed tube). Mass *m/e* 264 (M^+); NMR ($CDCl_3$) τ 3.18 (s, 4H, ArH), 7.04 (s, 8H, CH_2), 7.83 (s, 12H, CH_3); IR (KBr disc, cm^{-1}) 3000 (m), 2965 (w), 2937 (m), 2920 (m), 2855 (w), 1496 (m), 1448(s), 1328 (m), 1024 (m), 997 (m), 933 (m), 892 (s), 554 (s).

4,7-Dimethyl[2.2]paracyclophane (XI). The aqueous solution (*ca.* 600 ml) of quaternary bases, Ib and VIb, derived from a mixture of 10.0 g (40.1 mmol) of Ia and 11.1 g (40.8 mmol) of VIa in the usual way, was mixed with 100 ml of distilled xylene and 0.6 g of phenothiazine, and water was removed by azeotropic distillation with stirring. Evolution of trimethylamine began and further reflux was continued for 15 hr. The reaction mixture was cooled, insoluble polymers were filtered off, and then the filtrate was dried over anhydrous magnesium sulfate. After concentration the residue was treated with a small amount of petroleum ether, and insoluble [2.2]paracyclophane (III) was filtered off. The filtrate was chromatographed on silica gel (Merck, activity II—III) using petroleum ether for elution to give a mixture of 4,7-dimethyl[2.2]paracyclophane (XI) and 4,7,12,-15-tetramethyl[2.2]paracyclophane (VIII). The dimethyl derivative XI was purified by fractional crystallization from petroleum ether and carbon tetrachloride–acetone (1:3), successively (yield 5.6%), colorless plates, mp 154—155 °C. NMR (CCl_4) τ 3.32 (dd, J=8 Hz, J'=2 Hz, 2H, ArH), 3.74 (dd, J=8 Hz, J'=2 Hz, 2H, ArH), 4.12 (s, 2H, ArH), 6.5—7.7 (m, 8H, CH_2), 7.95 (s, 6H, CH_3); mass *m/e* 236 (M^+, 68), 132 (100), 104 (45); IR (KBr disc, cm^{-1}) 2920 (s), 2850 (m), 1594 (m), 1496 (m), 1435 (m), 941 (m), 907 (s), 873 (m), 797 (s), 715 (s), 587 (m), 533 (m). Found: C, 91.32; H, 8.49%. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53%.

Quaternary Ammonium Bromides, XIIIa, XIVa, XXIa, and XXVa. All the quaternary ammonium bromides, XIIIa, XIVa, XXIa, and XXVa, were prepared from the corresponding methyl derivatives according to the general procedure described below.

A given methyl cyclophane was brominated with a less amount than the equivalent of *N*-bromosuccinimide in carbon tetrachloride under reflux. After removal of insoluble succinimide, the solution was washed with water, dried over anhydrous magnesium sulfate, and then treated with an excess amount of trimethylamine in ether. The resulting white precipitate of quaternary ammonium bromide was filtered off and washed repeatedly with carbon tetrachloride. The ammonium salt thus obtained in good yield was used to the following reaction without purification.

These quaternary ammonium bromides were recrystallized from distilled water to give hydrated white crystals. XIIIa: mp 167—170 °C; NMR ($CDCl_3$) τ 3.23 (AB doublet, J=8 Hz, 1H, ArH), 3.41 (s, 1H, ArH), 3.46 (s, 2H, ArH), 3.61 (AB doublet, J=8 Hz, 1H, ArH), 3.80 (s, 1H, ArH), 5.17 (AB quartet, 2H, NCH_2), 6.69 (s, 9H, NCH_3), 6.5—7.5 (m, 8H, CH_2), 7.47 (s, H_2O), 7.89 (s, 3H, CH_3); IR (Nujol mull, cm^{-1}) 3400 (s, H_2O), 1595 (m), 975 (m), 925 (m), 875 (s), 795 (m), 717 (s), 595 (m). XIVa: dec>210 °C with melting; NMR ($CDCl_3$) τ 3.10 (s, 1H, ArH), 3.46 (s, 1H, ArH), 3.64 (s, 1H, ArH), 3.94 (s, 1H, ArH), 5.28 (AB quartet, 2H, NCH_2), 6.65 (s, 9H, NCH_3), 6.5—7.5 (m, 8H, CH_2), 7.84 (s, 3H, CH_3), 7.94 (s, 6H, CH_3), 8.11 (s, H_2O); IR (Nujol mull, cm^{-1}) 3400 (s, H_2O), 1595 (m), 975 (m), 930 (m), 885 (s), 720 (s). XXIa: dec>240 °C; NMR ($CDCl_3$) τ 3.78 (s, 5H,

ArH), 4.02 (s, 1H, ArH), 4.20 (s, 1H, ArH), 4.50 (s, 1H, ArH), 5.49 (AB quartet, 2H, NCH_2), 6.79 (s, 9H, NCH_3), 6.6—7.6 (m, 16H, CH_2), 8.08 (s, 3H, CH_3), 8.25 (s, H_2O); IR (Nujol mull, cm^{-1}) 3380 (s, H_2O), 980 (s), 880 (s), 795 (m), 710 (s), 685 (m), 515 (m).

Triple-layered [2.2]Paracyclophane (XV). A mixture of 3.5 g (9.4 mmol) of the quaternary ammonium bromide XIIIa and 2.3 g (9.4 mmol) of *p*-methylbenzyltrimethylammonium bromide (Ia) dissolved in distilled water was converted to the hydroxides, XIIIb and Ib, in the usual way using ion exchange resin. The resulting solution (*ca.* 800 ml) was mixed with 200 ml of distilled xylene and a spatula of phenothiazine, and dehydrated by azeotropic distillation under nitrogen atmosphere. After water was removed, the reaction mixture was refluxed for an additional 17 hr and allowed to cool. The insoluble polymers were removed by filtration and the filtrate was dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was chromatographed on silica gel (Merck, activity II—III). Elution with petroleum ether gave first double-layered cyclophane (III), then triple-layered one (XV), and finally quadruple-layered ones (XIX and XX).

Triple-layered compound (XV) was recrystallized from carbon tetrachloride–acetone (1:3) (yield 1.3%), colorless plates, mp 230 °C dec. in a sealed tube. NMR (CCl_4) τ 3.92 (s, 8H, ArH), 4.65 (s, 2H, ArH), 6.8—7.7 (m, 16H, CH_2); mass *m/e* 338 (M^+, 100), 234 (66), 104 (14); IR (KBr disc, cm^{-1}) 2980 (m), 2910 (s), 2840 (m), 1584 (m), 1495 (m), 1427 (s), 1405 (m), 1198 (m), 1177 (m), 968 (m), 937 (m), 901 (s), 863 (s), 794 (s), 708 (s), 680 (s), 605 (m), 517 (s). Found: C, 92.31; H, 7.72%. Calcd for $C_{26}H_{26}$: C, 92.26; H, 7.74%.

Dimethyl Triple-layered [2.2]Paracyclophane (XVI). In the same manner as non-substituted triple-layered compound XV, dimethyl triple-layered compound XVI was synthesized from quaternary ammonium bromides, XIVa and Ia. Dimethyl derivative XVI was purified by column chromatography on silica gel (Merck, activity II—III) and recrystallization from petroleum ether (yield 1.8%), colorless plates, mp 146—148 °C. NMR (CCl_4) τ 3.88 (s, 4H, ArH), 4.30 (s, 2H, ArH), 4.36 (s, 2H, ArH), 6.8—8.1 (m, 16H, CH_2), 8.17 (s, 6H, CH_3); mass *m/e* 366 (M^+, 100), 262 (10), 234 (34), 132 (12), 104 (7); IR (KBr disc, cm^{-1}) 2840 (s), 1577 (m), 1426 (s), 1165 (m), 895 (s), 870 (s), 792 (m), 710 (w), 695 (s), 673 (m), 593 (m), 520 (s). Found: C, 91.55; H, 8.29%. Calcd for $C_{28}H_{30}$: C, 91.75; H, 8.25%.

Tetramethyl Triple-layered [2.2]Paracyclophanes (XVII and XVIII). The hydroxide solution (*ca.* 1.8 l), derived from a mixture of quaternary ammonium bromides XIVa (15.6 g, 38.8 mmol) and VIa (10.7 g, 39.3 mmol) in the usual way, was mixed with 300 ml of distilled xylene and 2.0 g of phenothiazine, and then pyrolyzed as described for non-substituted compound XV. After polymers were removed, the reaction mixture was chromatographed on silica gel (Merck, activity II—III). Elution with petroleum ether gave first double-layered cyclophane (VIII), second a mixture of isomeric triple-layered ones, XVII and XVIII, and finally quadruple-layered ones, XXII and XXIII. The isomer XVII was separated from XVIII by careful chromatography, where the former was eluted first. Tetramethyl derivative XVII was recrystallized from acetone–ethanol (1:1) (yield 1.1%), colorless plates, mp 245—246 °C in a sealed tube. NMR (CCl_4) τ 3.94 (s, 2H, ArH), 4.33 (s, 4H, ArH), 6.7—7.7 (m, 16H, CH_2), 8.11 (s, 12H, CH_3); mass *m/e* 394 (M^+, 100), 262 (58), 132 (35); IR (KBr disc, cm^{-1}) 2920 (s), 2850 (s), 1590 (m), 1490 (s), 1432 (s), 1164 (m), 895 (s), 693 (s), 660 (m), 537 (m), 508 (m), 452 (m). Found: C, 91.27; H, 8.83%. Calcd for $C_{30}H_{34}$: C, 91.31; H, 8.69%.

The other isomeric tetramethyl derivative XVIII was recrystallized from acetone-ethanol (1:1) (yield 1.1%), colorless plates, mp 204—205 °C. NMR ($CDCl_3$) τ 4.17 (s, 2H, ArH), 4.21 (s, 2H, ArH), 4.28 (s, 2H, ArH), 6.7—7.8 (m, 16H, CH_2), 8.10 (s, 12H, CH_3); mass *m/e* 394 (M^+, 100), 262 (72), 132 (35); IR (KBr disc, cm^{-1}) 2900 (s), 2850 (s), 1585 (m), 1490 (s), 1440 (s), 1391 (m), 1367 (m), 1250 (m), 1025 (m), 889 (s), 688 (s), 660 (m), 537 (m), 507 (m), 451 (m). Found: C, 91.38; H, 8.84%. Calcd for $C_{30}H_{34}$: C, 91.31; H, 8.69%.

Quadruple-layered [2.2]Paracyclophanes (XIX and XX). a) From Quaternary Salt XIIIa: The aqueous solution (*ca.* 400 ml) containing the quaternary ammonium hydroxide XIIIb, which was derived from 1.4 g (3.7 mmol) of the bromide XIIIa, was heated in the presence of 50 ml of distilled xylene and a spatula of phenothiazine under nitrogen atmosphere for azeotropic distillation. Insoluble polymers were removed from the reaction mixture and the filtrate was dried over anhydrous magnesium sulfate. After evaporation the residue was chromatographed on neutral alumina (Woelm, activity I). Elution with benzene–petroleum ether (2:8) gave a mixture of isomeric quadruple-layered compounds, XIX and XX. The readily soluble isomer XIX was separated from the sparingly soluble isomer XX by treatment with carbon tetrachloride–acetone (1:3).

The quadruple-layered cyclophane XIX was recrystallized from carbon tetrachloride–acetone (1:3) (yield 1.1%), colorless plates, dec>240 °C. NMR (CCl_4) τ 4.02 (s, 8H, ArH), 4.88 (s, 4H, ArH), 6.7—7.9 (m, 24H, CH_2); mass *m/e* 468 (M^+, 100), 364 (41), 234 (69), 104 (33); IR (KBr disc, cm^{-1}) 2915 (s), 2840 (m), 1582 (m), 1424 (s), 1180 (m), 980 (m), 933 (m), 897 (m), 868 (s), 795 (s), 713 (s), 674 (s), 603 (m), 521 (s). Found: C, 92.12; H, 7.80%. Calcd for $C_{36}H_{36}$: C, 92.26; H, 7.74%.

The other isomeric quadrupled one XX was recrystallized from toluene (yield 0.75%), colorless prisms, dec>250 °C. NMR (CCl_4) τ 4.02 (s, 8H, ArH), 4.90 (s, 4H, ArH), 6.7—7.9 (m, 24H, CH_2); mass *m/e* 468 (M^+, 100), 364 (34), 234 (42), 104 (24); IR (KBr disc, cm^{-1}) 2915 (s), 2840 (m), 1582 (s), 1428 (s), 1178 (m), 934 (m), 895 (s), 865 (s), 794 (s), 710 (s), 687 (s), 598 (m), 516 (s). Found: C, 91.99; H, 7.69%. Calcd for $C_{36}H_{36}$: C, 92.26; H, 7.74%.

b) Alternative Synthesis of XIX from Quaternary Salts, Ia and XXIa. A mixture of 0.60 g (2.5 mmol) of *p*-methylbenzyltrimethylammonium bromide (Ia) and 0.80 g (1.6 mmol) of quaternary ammonium bromide (XXIa) dissolved in distilled water was converted to the hydroxide form in the usual way. The resulting hydroxide solution (*ca.* 450 ml) was mixed with 20 ml of distilled toluene and 20 mg of phenothiazine, and heated with stirring under nitrogen. After water was removed by azeotropic distillation, further reflux continued for 6 hr. The reaction mixture was allowed to cool and the insoluble polymers (0.15 g) were filtered off. After drying over anhydrous magnesium sulfate, the filtrate was subjected to column chromatography on neutral alumina (Woelm, activity I). Elution with benzene–hexane (1:1) gave first 30 mg of [2.2]paracyclophane (III) and then 24 mg (3.2%) of quadruple-layered compound XIX. The properties of this product were quite identical with those of the readily soluble isomer obtained by pyrolysis of XIIIb.

Tetramethyl Quadruple-layered [2.2]Paracyclophanes (XXII and XXIII). The cyclophanes, XXII and XXIII, were synthesized from quaternary ammonium bromide XIVa in the same method as non-substituted quadruple-layered compounds, XIX and XX. The isomers, XXII and XXIII, were also separated by the treatment with the same solvent

as for non-substituted ones. The readily soluble isomer XXII was recrystallized from chloroform–ether–petroleum ether (1:1:1) and toluene, successively (yield 3.2%), colorless prisms, dec>240 °C. NMR (CCl_4) τ 4.43 (s, 4H, ArH), 4.53 (s, 4H, ArH), 6.8—8.1 (m, 24H, CH_2), 8.19 (s, 12H, CH_3); mass *m/e* 524 (M^+, 100), 392 (39), 262 (23), 132 (14); IR (KBr disc, cm^{-1}) 2900 (s), 2850 (s), 1585 (m), 1485 (m), 1428 (s), 1248 (m), 1185 (m), 1035 (m), 975 (m), 891 (s), 692 (s), 665 (m), 527 (m), 508 (m), 438 (m). Found: C, 91.35; H, 8.56%. Calcd for $C_{40}H_{44}$: C, 91.55; H, 8.45%.

The sparingly soluble isomer XXIII was recrystallized from toluene (yield 1.6%), colorless prisms, dec>240 °C. NMR (CCl_4) τ 4.45 (s, 4H, ArH), 4.52 (s, 4H, ArH), 6.8—8.1 (m, 24H, CH_2), 8.20 (s, 12H, CH_3); mass *m/e* 524 (M^+, 100), 392 (39), 262 (36), 132 (14); IR (KBr disc, cm^{-1}) 2900 (s), 2840 (s), 1583 (m), 1483 (m), 1445 (s), 1250 (m), 1165 (m), 1028 (m), 964 (m), 887 (s), 696 (s), 669 (m), 525 (m), 508 (m), 453 (m). Found: C, 91.77; H, 8.64%. Calcd for $C_{40}H_{44}$: C, 91.55; H, 8.45%.

Fivefold-layered [2.2]Paracyclophane (XXIV). The aqueous quaternary base solution (*ca.* 800 ml) derived from 1.2 g (3.2 mmol) of XIIIa and 1.5 g (2.9 mmol) of XXIa was added into 30 ml of distilled xylene and 50 mg of phenothiazine, and refluxed with stirring under nitrogen. After removal of water, heating was continued for an additional 6 hr. After cooling the insoluble polymers were filtered off and the filtrate was chromatographed on neutral alumina (Woelm, activity I) using benzene–hexane (2:8) as eluent to give a mixture of quadruple-layered compounds, XIX and XX, and fivefold-layered one XXIV. The separation of this mixture was performed by liquid chromatography using chloroform as eluent. This gave first XXIV and then a mixture of XIX and XX. The compound XXIV was recrystallized from carbon tetrachloride–acetone (1:3) (yield 5%), colorless microcrystals, dec>240 °C. NMR (CCl_4) τ 4.04 (s, 8H, ArH), 4.97 (s, 4H, ArH), 5.12 (b.s, 2H, ArH), 6.8—8.0 (m, 32H, CH_2); mass *m/e* 598 (M^+, 100), 494 (33), 364 (63), 234 (21), 104 (41); IR (KBr disc, cm^{-1}) 2910 (s), 2830 (m), 1585 (s), 1483 (m), 1425 (m), 1181 (m), 935 (m), 895 (m), 870 (s), 795 (s), 714 (m), 671 (s), 603 (m), 517 (s). Found: C, 91.67; H, 7.56%. Calcd for $C_{46}H_{46}$: C, 92.26; H, 7.74%.

Dimethyl Fivefold-layered [2.2]Paracyclophane (XXVI). Tetramethyl quadruple-layered [2.2]paracyclophane XXII (1.00 g, 1.91 mmol) was brominated with 0.27 g (1.52 mmol) of *N*-bromosuccinimide under reflux in 12 ml of carbon tetrachloride. After removal of succinimide, the solution was washed, dried over anhydrous magnesium sulfate, and then mixed with an excess amount of trimethylamine in ether under ice-cooling. The mixture was brought to room temperature slowly and the resulting white precipitate was collected and thoroughly washed with carbon tetrachloride. The quaternary ammonium bromide XXVa thus obtained was mixed with 0.5 g (2.1 mmol) of *p*-methylbenzyltrimethylammonium bromide (Ia) in 300 ml of distilled water and subjected to the ion exchange process. The resulting hydroxide solution (*ca.* 500 ml) was added into 15 ml of distilled xylene and 100 mg of phenothiazine, and heated with stirring under nitrogen. After removal of water, heating was continued for 6 hr. The insoluble polymers were filtered off and the filtrate was chromatographed on neutral alumina (Woelm, activity I). Elution with benzene–hexane (1:9) gave [2.2]paracyclophane (III) and [2.2.2]paracyclophane (IV). Further elution with 2:8 benzene–hexane gave dimethyl fivefold-layered [2.2]paracyclophane XXVI in a 1.1% yield based on NBS, colorless plates from 1:3 carbon tetrachloride–acetone, dec>250 °C. NMR (CCl_4) τ 4.04 (s, 4H, ArH), 4.47 (s, 2H, ArH), 4.64 (s, 2H, ArH), 4.96 (s, 2H, ArH), 5.08 (s, 2H, ArH), 6.9—8.1 (m, 32H, CH_2), 8.24 (s, 6H, CH_3); mass *m/e* 626 (M^+, 100), 522 (14), 494 (27), 392 (32), 364 (24), 262 (10), 234 (17), 132 (22), 104 (35); IR (KBr disc, cm^{-1}) 2910 (s), 2835 (m), 1584 (s), 1482 (m), 1425 (s), 1250 (m), 1178 (m), 892 (s), 790 (m), 712 (w), 693 (m), 672 (s), 665 (s), 600 (m), 518 (s). Found: C, 92.19; H, 7.93%. Calcd for $C_{48}H_{50}$: C, 91.96; H, 8.04%.

Sixfold-layered [2.2]Paracyclophanes (XXVII and XXVIII). The aqueous quaternary ammonium hydroxide solution (*ca.* 600 ml), prepared from 1.6 g (3.1 mmol) of the bromide XXIa in the usual way, was added into 30 ml of toluene and 20 mg of phenothiazine. The mixture was refluxed with stirring under nitrogen. After the removal of water was completed by azeotropic distillation, heating was continued for an additional 6 hr. After cooling to room temperature, the insoluble polymers (0.55 g) were separated. The filtrate was chromatographed on neutral alumina (Woelm, activity I) and elution with benzene–hexane (1:1) gave a mixture of isomeric sixfold-layered [2.2]paracyclophanes, XXVII and XXVIII. The readily soluble isomer XXVII was separated from the sparingly soluble one XXVIII by treatment of a minimum amount of benzene. The isomer XXVII was recrystallized from toluene (yield 4.7%), colorless plates, dec>250 °C. NMR (CCl_4) τ 4.06 (s, 8H, ArH), 5.00 (s, 4H, ArH), 5.20 (s, 4H, ArH), 7.1—8.3 (m, 40H, CH_2); IR (KBr disc, cm^{-1}) 2920 (s), 2840 (m), 1584 (s), 1472 (s), 1424 (s), 1183 (m), 974 (m), 935 (m), 894 (m), 875 (s), 794 (s), 713 (m), 673 (s), 602 (m), 518 (s). Found: C, 92.01; H, 7.64%; mol wt 734 (vapor pressure osmometry). Calcd for $C_{56}H_{56}$: C, 92.26; H, 7.74%; mol wt 729.

The other isomer XXVIII was recrystallized from xylene (yield 2.4%), colorless microcrystals, dec>250 °C. NMR ($CDCl_3$) τ 3.95 (s, 8H, ArH), 4.95 (s, 4H, ArH), 5.19 (s, 4H, ArH), 6.9—8.2 (m, 40H, CH_2); IR (KBr disc, cm^{-1}) 2920 (s), 2840 (m), 1584 (s), 1482 (s), 1425 (s), 1181 (m), 975 (m), 933 (m), 894 (m), 874 (s), 796 (m), 715 (m), 677 (s), 603 (m), 517 (s). Found: C, 92.07; H, 7.74%. Calcd for $C_{56}H_{56}$: C, 92.26; H, 7.74%.

Thermal Isomerization from Eclipsed Form (IX) to Staggered Form (VIII) of Tetramethyl[2.2]paracyclophane. Thermal isomerization from IX to VIII could be easily observed in NMR spectra. Thus, when IX in hexachlorobutadiene was heated at 190 °C, signals of VIII gradually appear with disappearance of signals of IX, and after 2 hr IX was completely transformed to VIII accompanying with insoluble black decomposition product. For preparative purpose, 10 mg of IX was dissolved in 0.5 ml of *n*-tridecane and degassed by freeze-pump-thaw method. The resulting solution in a sealed tube was heated at 195 °C for 3 hr. After cooling the product was chromatographed on silica gel (Merck, activity II—III). After *n*-tridecane, VIII was eluted with *n*-hexane in nearly quantitative yield.

Layered Cyclophane-TCNE and -TNB Complexes. Commercial tetracyanoethylene (TCNE) was recrystallized from chlorobenzene and then sublimed twice under reduced pressure. Commercial 1,3,5-trinitrobenzene (TNB) was recrystallized three times from ethanol and then three times from carbon tetrachloride. Dichloromethane and chloroform are of spectroscopic grade (Merck) and used without further purification. The charge-transfer spectra of layered cyclophane-TCNE and -TNB complexes were recorded on a Hitachi EPS-3T spectrophotometer. Most of the multilayered cyclophane complexes exhibit unchanged absorption maxima though the relative concentrations of two components are varied. Equilibrium constants and molar extinction coefficients for the TNB complexes were determined in the

manner described by Benesi and Hildebrand.[31] Measurements were carried out at four points in the presence of excess acceptor; the mole concentrations of the donor were varied from 0.003 to 0.005 M, while the TNB concentrations from 0.03 to 0.15 M. In the case of tetramethyl[2.2]paracyclophane (VIII), on the other hand, the donor concentration was varied from 0.025 to 0.15 M, while the acceptor concentration was kept constant at 0.002 M. Every complex of multilayered cyclophane here presented gave a good linear plots, supporting that the complex consists conclusively of 1 : 1 ratio one.

31) H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **71**, 2703 (1949).

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