Table I
^{13}C NMR Assignments of Benzocyclopropene,^{a} Benzocyclobutene, Indan, and o-Xylene^{b,c}

Compound	C-1	C-2	C-3	C-4	C-5	C-6	Aliphatic carbons	
							α	β
	125.4	125.4	114.7	128.8	128.8	114.7	18.4	
	145.6	145.6	122.1	126.6	126.6	122.1	29.4	
	144.0	144.0	124.4	126.2	126.2	124.4	33.8	25.4
	136.3	136.3	129.8	126.0	126.0	129.8	19.4	

^{a} The numbering scheme used here is consistent with that used for other benzocycloalkenes. The system devised by Halton[2] and used elsewhere[16,17] represents benzocyclopropene as a bond-fixed structure. ^{b} Data taken from ref 51. ^{c} δ values.

Since the data of Table I suggest that strain exerts the greatest effect on the chemical shifts of carbons at C-3 and C-6, it is interesting to compare the ^{13}C chemical shifts of these carbons in compounds **37**, **27**, **33**, and **39**. Compound **37** is probably the most highly
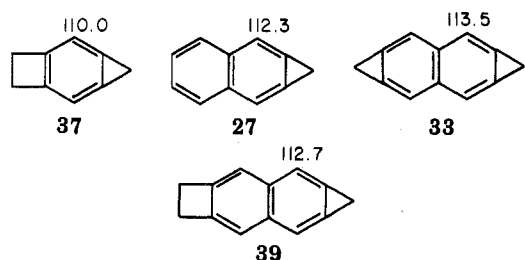
strained member of the benzocyclopropene family that has been reported and, as expected, experiences the greatest shielding at these positions. However, the naphthocyclopropenes fall in a narrow range, suggesting that the use of ^{13}C chemical may not provide a reliable method of ranking such compounds with regard to strain.

The infrared spectra of benzocyclopropenes exhibit a characteristic band around 1670 cm^{-1} thought to arise from a stretching vibration. This bond is commonly referred to as an "aromatic double bond". For benzocyclopropene this absorption appears at 1666 cm^{-1} and for naphtho[b]cyclopropene at 1673 cm^{-1}. Otherwise, infrared spectra of benzocyclopropenes are simple, indicating the high degree of symmetry in these molecules.

The ultraviolet spectra of the more highly strained benzocyclopropenes such as **37** exhibit strain-related bathochromic shifts when compared to benzocyclopropene. Benzocyclopropene itself does not differ appreciably from benzene, which suggests that the aromatic chromophore is not disrupted appreciably.

Chemistry of Multilayered Cyclophanes

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When two or more aromatic rings are stacked face to face, some transannular interaction is expected between their π-electronic systems. Such an interaction has been, in fact, observed in studies on many double-

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layered compounds, such as [2.2]paracyclophane (**1**), other cyclophanes, helicenes,[1] and janusenes.[2]

Unusual molecular deformation or strain is brought about by π-electron repulsion when the aromatic rings are closely fixed within van der Waals distance by virtue of short methylene bridges. For example, in [2.2]-paracyclophane (**1**) the two benzene rings are bent into a boat shape.[3] Because of these structural features,
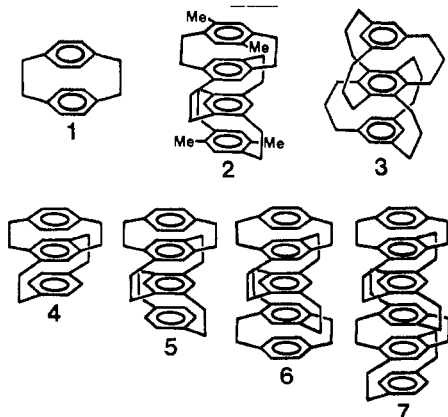
(1) R. H. Martin, *Angew. Chem.*, **86**, 727 (1974); *Angew. Chem., Int. Ed. Engl.*, **13**, 649 (1974); R. H. Martin and M. Baes, *Tetrahedron*, **31**, 2135 (1975).
(2) S. J. Cristol and D. C. Lewis, *J. Am. Chem. Soc.*, **89**, 1476 (1967).

Scheme I

Scheme II

Scheme III
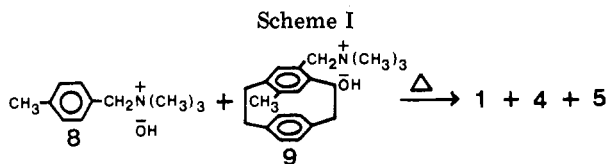
anomalous physical and chemical behavior has been observed for the layered compounds.[2,4]

Previously most investigations in this area were confined to double-layered compounds with the exception of one triple-layered (3)[5] and one quadruple-

layered cyclophane (2),[6] because of difficulties in the syntheses of multilayered compounds. The anticipation of stronger π-electronic interaction in these compounds than in their double-layered analogues prompted us to undertake a systematic study of a series of multilayered [2.2]paracyclophanes (4–7) as suitable models for basic research on organic semiconductors.

We prepared compounds 4–7 by means of the 1,6-Hofmann elimination method previously used for the synthesis of 2.[7] Subsequently, Nakazaki has obtained optically active multilayered cyclophanes (4–7) with known absolute configuration by a similar pyrolysis of chiral quaternary ammonium hydroxides.[8] Multilayered metacyclophanes and metaparacyclophanes are also interesting as alternative models for the study of transannular interaction, for their stacking modes may be very different from that of the para series discussed above.

Syntheses and Structures

Of a number of synthetic methods developed for double-layered [2.2]paracyclophanes, the 1,6-Hofmann elimination method is very convenient for the prepa-

Figure 1. Molecular structure of centrosymmetric tetramethyl quadruple-layered [2.2]paracyclophane (11).

ration of multilayered [2.2]paracyclophanes because the precursors, e.g., 8 and 9 in Scheme I, required for these reactions are relatively accessible. The yields, though poor in earlier reports, can be markedly improved by adjustment of the pyrolytic conditions, i.e., solvent, inhibitor, reaction temperature, and concentration.[9]

Recently the photodesulfurization method, reported as an alternative for the synthesis of multilayered cyclophanes, has proved to be versatile and convenient.[9,10] The triple-layered paracyclophane (4) was obtained by photolysis of cyclic dithia compound 10 which was derived by coupling the dibromide and the dimercaptan (Scheme II).

The molecular structures of multilayered paracyclophanes were demonstrated by X-ray crystallographic analyses, employing the bromo derivative in the case of the triple-layered [2.2]paracyclophane[11] and the tetramethyl derivative (11) for the quadruple-layered one (Figure 1).[12] Both structures show common features as described below. Firstly, the benzene rings are stacked at almost the same interval; that is, the ring-to-ring distance (3.03 Å) between the average planes of the deformed benzene rings has a value comparable to that of [2.2]paracyclophane (1). Secondly, all the outer

(3) C. J. Brown, *J. Chem. Soc.*, 3265 (1953); D. K. Lonsdale, H. J. Milledge, and K. V. Rao, *Proc. R. Soc. London, Ser. A*, **255**, 82 (1960); H. Hope, J. Bernstein, and K. N. Trueblood, *Acta Crystallogr., Sect. B*, **28**, 1733 (1972).

(4) For reviews, see (a) D. J. Cram, *Rec. Chem. Prog.*, **20**, 71 (1959); D. J. Cram and J. M. Cram, *Acc. Chem. Res.*, **4**, 204 (1971); (b) B. H. Smith, "Bridged Aromatic Compounds", Academic Press, New York, N.Y., 1964; (c) F. Vögtle, *Chem. Z.*, **95**, 668 (1971); F. Vögtle and P. Neumann, *Angew. Chem.*, **84**, 75 (1972); *Chimia*, **26**, 64 (1972); *Synthesis*, **85** (1973); (d) T. Sato, *Nippon Kagaku Zasshi*, **92**, 277 (1971); (e) S. Misumi, *Kagaku no Ryoiki*, **28**, 927 (1974); Y. Sakata, *ibid.*, **28**, 947 (1974).

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

(6) D. T. Longone and H. S. Chow, *J. Am. Chem. Soc.*, **86**, 3898 (1964); **92**, 994 (1970).

(7) T. Otsubo, S. Mizogami, Y. Sakata, and S. Misumi, *Chem. Commun.*, 678 (1971); *Tetrahedron Lett.*, 4803 (1971); 2457 (1973); T. Otsubo, Z. Tozuka, S. Mizogami, Y. Sakata, and S. Misumi, *ibid.*, 2927 (1972); T. Otsubo, S. Mizogami, I. Otsubo, Z. Tozuka, A. Sakagami, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **46**, 3519 (1973).

(8) M. Nakazaki, K. Yamamoto, and S. Tanaka, *J. Chem. Soc., Chem. Commun.*, 433 (1972); M. Nakazaki, K. Yamamoto, S. Tanaka, and H. Kametani, *J. Org. Chem.*, **42**, 287 (1977).
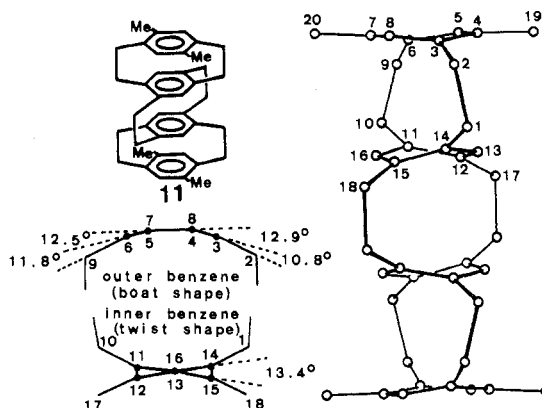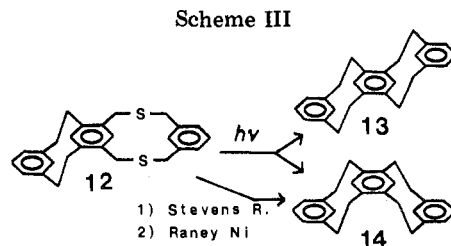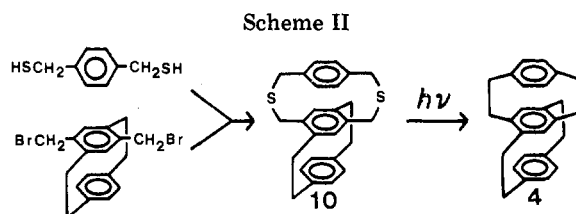
(9) T. Otsubo, H. Horita, and S. Misumi, *Synth. Commun.*, **6**, 591 (1976).

(10) T. Otsubo, M. Kitasawa, and S. Misumi, *Chem. Lett.*, 977 (1977).

(11) Y. Koizumi, T. Toyoda, H. Horita, and S. Misumi, presented at the 32nd National Meeting of the Chemical Society of Japan, Tokyo, April 1975, Summary I, p 184.

(12) H. Mizuno, K. Nishiguchi, T. Otsubo, S. Misumi, and N. Morimoto, *Tetrahedron Lett.*, 4981 (1972); H. Mizuno, K. Nishiguchi, T. Toyoda, T. Otsubo, S. Misumi, and N. Morimoto, *Acta Crystallogr., Sect. B*, **33**, 329 (1977).

benzenes are bent into a boat shape owing to severe repulsion between π-electron clouds. Their bending angles are nearly the same as those of 1. Thirdly, the inner benzenes are distorted into a twist form, because of tugging by the two pairs of ethylene bridges. Such a twisting gives rise to a higher strain energy than the bending into a boat shape. Thus, according to the thermodynamic measurements, the strain energy of triple-layered [2.2]paracyclophane (4) (247 kJ/mol or 59.0 kcal/mol) is twice as much as that of 1 (124 kJ/mol or 29.6 kcal/mol).[13] In other words, the twisted inner benzene bears almost twice the strain energy of the boat-shaped outer benzene.

Isomeric triple-layered [2.2]metacyclophanes, u,u-isomer (13) and u,d-isomer (14),[14] were synthesized by photodesulfurization of dithiacyclophane (12).[15] One isomer, 14, was also obtained by the Stevens rearrangement of 12 followed by Raney nickel desulfurization.[16] 13 and 14 were also prepared by another synthetic method.[17] (See Scheme III.)

In contrast to the difficult ring inversion of [2.2]-metacyclophane,[18] a thermal isomerization of u,u-isomer 13 to u,d-isomer 14 occurred easily at 100 °C. Thus 14 is thermodynamically more stable than 13. The difference (>4 kcal/mol)[19] in the stabilities of the two isomers is considered to depend largely upon the magnitude and type of deformation of the central benzene ring. X-ray crystallographic analysis shows that the central benzene of the u,u-isomer is deformed into a chair shape and the corresponding one of the u,d-isomer into a boat shape.[20]

The total energies of the above two types of bent benzenes were calculated using a semiempirical SCF-MO method, MINDO/2 approximation, and it was observed that the difference in their stabilities corresponds mostly to the difference in the resonance energy terms, that is, the difference in the overlapping of pπ orbitals of both benzenes.[21]

Introduction of a methyl group at the internal position of one of the outer benzenes is considered to diminish their energy difference, for there is considerable steric repulsion between the methyl group and the internal aromatic proton H_a in the u,d-isomer 16 but not in the u,u-isomer 15. Actually, it was demonstrated from an equilibrium experiment that 16 is still more stable by 2.1 kcal/mol than 15 and that the structure of the central benzene is a more important element for the stability of both isomers than the methyl–H_a repulsion.[15] When all the internal aromatic
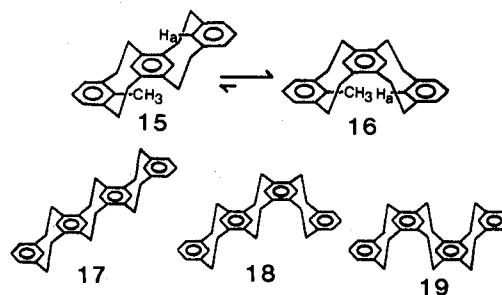
protons are replaced by methyl groups, the resulting methyl–methyl repulsion in the u,d-isomer becomes so significant as to overcome the deformation energy of benzene, so that only the u,u-isomer is obtained.[22]

Similarly, it is possible to separate the three conformers, u,u,u (17), u,u,d (18), and u,d,u (19), of quadruple-layered [2.2]metacyclophane, of which the u,d,u-isomer is the most stable on the basis of an equilibrium experiment.[15]

Triple-layered [2.2]metaparacyclophanes (20–23) and
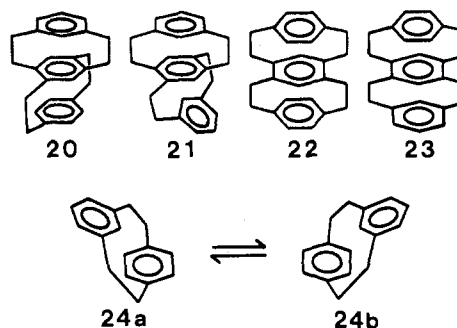
quadruple-layered homologues were generally synthesized by the combined use of conventional methods such as the Hofmann elimination, photodesulfurization of disulfide, and the Stevens rearrangement.[23] Some of them were also obtained by acid-catalyzed rearrangement of the triple-layered [2.2]paracyclophane (4) as described later.[24] Two structural isomers, 20 and 21, showed, as in the case of [2.2]metaparacyclophane (24), a dynamic mobility of the meta-bridged ring as followed by NMR spectral analysis at variable temperature.[25]

In analogy with the triple-layered metacyclophanes 13 and 14, two conformers are expected for the triple-layered metaparacyclophanes 22 and 23, respectively. However, they exist only as one stable isomer in each case, and their molecular structures were clarified by X-ray crystallographic analyses to be the u,u form for 22 and the u,d form for 23.[26] This stereochemical difference between 22 and 23 is elucidated by molecular model consideration that the endo aromatic protons of the two para-bridged benzenes of 22 are sterically overcrowded in its u,d-isomer compared to slight steric repulsion of a meta- and a para-bridged

(13) K. Nishiyama, M. Sakiyama, S. Seki, H. Horita, T. Otsubo, and S. Misumi, *Tetrahedron Lett.*, 3739 (1977).

(14) The prefixes u,u and u,d are used to discriminate between the conformers (14 and 15) of triple-layered metacyclophane (u and d mean up- and downstairs, respectively). The three conformers (17–19) of quadruple-layered one are similarly named.

(15) T. Umemoto, T. Otsubo, and S. Misumi, *Tetrahedron Lett.*, 1573 (1974).

(16) T. Umemoto, T. Otsubo, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, 593 (1973).

(17) H. Lehner, *Monatsh. Chem.*, 107, 565 (1976).

(18) T. Sato, S. Akabori, M. Kainosho, and K. Hata, *Bull. Chem. Soc. Jpn.*, 41, 218 (1968).

(19) Recently Lehner reported that the free-energy difference was 3.84 kcal/mol: H. Keller, C. Krieger, E. Langer, and H. Lehner, *Monatsh. Chem.*, 107, 1281 (1976).

(20) Y. Kai, N. Yasuoka, and N. Kasai, *Acta Crystallogr., Sect. B*, 33, 754 (1977); F. Hama, Y. Kai, N. Yasuoka, and N. Kasai, *ibid.*, 33, 3905 (1977).

(21) H. Iwamura, H. Kihara, S. Misumi, Y. Sakata, and T. Umemoto, *Tetrahedron Lett.*, 615 (1976).

(22) T. Otsubo, D. Stusche, and V. Boekelheide, *J. Am. Chem. Soc.*, to be published.

(23) N. Kannen, T. Umemoto, T. Otsubo, and S. Misumi, *Tetrahedron Lett.*, 4537 (1973); N. Kannen, T. Otsubo, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, 49, 3307 (1976); N. Kannen, T. Otsubo, and S. Misumi, *ibid.*, 49, 3208 (1976).

(24) H. Horita, N. Kannen, T. Otsubo, and S. Misumi, *Tetrahedron Lett.*, 501 (1974).

(25) N. Kannen, T. Otsubo, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, 49, 3203 (1976).

(26) Y. Koizumi, T. Toyoda, N. Kannen, H. Horita, and S. Misumi, presented at the Symposium on Molecular Structure, Nov, 1975, Osaka, Japan, Abstract p 455.
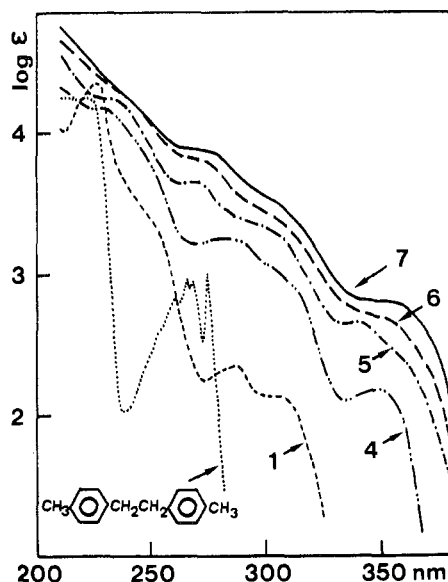
Figure 2. Electronic spectra of multilayered [2.2]paracyclophanes in cyclohexane.

ring in the u,d-isomer of **23**. As a result, the u,u structure is rather preferred for **22** despite the presence of an energetically disadvantageous chair form for the central benzene.

Physical Properties[27]

Transannular π-electronic interactions of layered compounds can be best understood by spectroscopic analyses. Figure 2 shows the electronic absorption spectra of some multilayered [2.2]paracyclophanes. The absorption curves demonstrate marked bathochromic and hyperchromic shifts successively as the number of layers increases.[6,7] The spectra were theoretically explained by considering the configuration interactions of charge transfer and neutral excitation states.[28] The emission spectra similarly exhibit large bathochromic shifts.[7]

In contrast, there is little characteristic in the electronic spectra of multilayered [2.2]metacyclophanes.[16] This weak transannular interaction is mainly attributable to the small overlap of the benzene rings of the metacyclophane series as compared with the paracyclophane series.

Multilayered metaparacyclophanes are anticipated to have intermediate properties between those of the para and the meta series. In the electronic spectra, compounds **20** and **21** show rather a para type of transannular interaction, whereas compounds **22** and **23** show a meta type behavior.[25] Apparently bridge substitution modes of the inside benzenes play an important role in the overlapping of the benzene rings and therefore in electronic interactions.

The marked electronic interaction of multilayered paracyclophanes is also reflected in their π basicity. The charge-transfer bands of their monotricarbonylchromium complexes (**25–27**)[29] as well as their tetracyanoethylene or 1,3,5-trinitrobenzene complexes[6,7] are
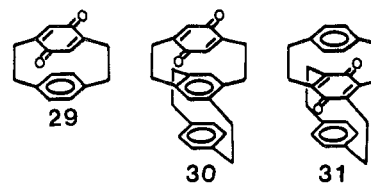
successively shifted to longer wavelength with an increase of the number of layers. Furthermore, IR spectral analysis of the chromium complexes shows that A_1 and E bands, associated with the carbonyl stretching vibrations, are shifted to lower wavenumber successively as the number of layer increases. These results indicate that an electronic donation from the cyclophane to chromium metal in both the ground state and the excited state is strengthened by transannular π-electron release induced in the cyclophanes with an increase of the number of layers.

A stronger bathochromic shift of bis(tricarbonylchromium) complexes, e.g., **28**, than the corresponding
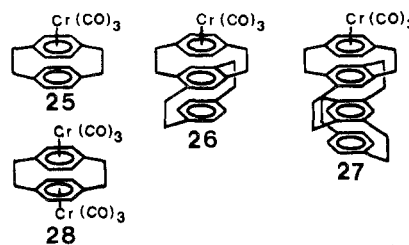
mono complexes (**25–27**) in their electronic spectra indicates that the excited state of the former is more stabilized by electron withdrawing of another tricarbonylchromium group.[29] The effect decreases with the increase of the distance between the two tricarbonylchromium groups, that is, with increase of the number of layers.

In recent years there has been noted an intramolecular donor–acceptor type of cyclophane. Cyclophane **29**[30] has been prepared as a simple model intramo-

lecular quinhydrone.[31] Its electronic absorption spectrum shows a charge-transfer band at 340 nm. The corresponding band of triple-layered cyclophanequinone (**30**) is remarkably shifted to 395 nm due to a transannular electron release.[32] Cyclophanequinone **31**, in which an acceptor is sandwiched by two donors, presents an interesting spectrum, that is, a CT band (435 nm) at a further longer wavelength region than **30**.

Two cyclophanes, **32** and **33**, containing a tropylium ion moiety are also regarded as a kind of intramolecular CT complex.[33] An increase of transannular electronic interaction in **33** is definitely indicated by the bathochromic shift of the CT band of **33** (λ_{max} 434 nm in CH_2Cl_2) relative to that (λ_{max} 354 nm in CH_2Cl_2) of **32**.

Triple-layered dicyanocyclophanes **34** and **35** show a weak donor–acceptor interaction at the ground state but can be expected to be a unique model system to

(27) For review: S. Misumi, *Mem. Inst. Sci. Ind. Res., Osaka Univ.*, **33**, 53 (1976).

(28) I. H. Hiller, L. Glass, and S. A. Rice, *J. Am. Chem. Soc.*, **88**, 5063 (1966); S. Iwata, K. Fuke, M. Sasaki, S. Nagakura, T. Otsubo, and S. Misumi, *J. Mol. Spectrosc.*, **46**, 1 (1973).

(29) H. Ohno, N. Horita, T. Otsubo, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, 265 (1977).

(30) D. J. Cram and A. C. Day, *J. Org. Chem.*, **31**, 1277 (1966).

(31) Recently Staab reported noteworthy syntheses of quinhydrone cyclophane and related intramolecular CT-type cyclophanes: W. Rebafka and H. A. Staab, *Angew. Chem.*, **85**, 831 (1973); **86**, 234 (1974); *Angew. Chem., Int. Ed. Engl.*, **12**, 776 (1973); **13**, 203 (1974); H. A. Staab, C. P. Hertz, and H.-E. Henke, *Tetrahedron Lett.*, 4393 (1974); H. A. Staab and H. Haffner, *ibid.*, 4397 (1974); D. Schweitzer, K. H. Hausser, V. Taglieber, and H. A. Staab, *Chem. Phys.*, **14**, 183 (1976).
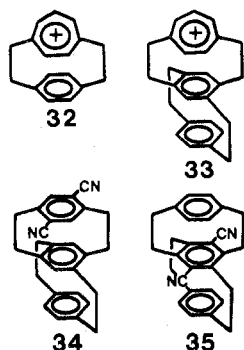
(32) H. Tatemitsu, T. Otsubo, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, 3059 (1975).

(33) H. Horita, T. Otsubo, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, 3899 (1976); H. Horita, T. Otsubo, and S. Misumi, *Chem. Lett.*, 1309 (1977).

32 33 34 35

elucidate the structure of excited termolecular complexes formed with two alkylbenzenes and one *p*-dicyanobenzene molecule.[34] A study of the fluorescence spectrum supported the hypothesis that the 2:1 donor–acceptor termolecular complex had the stacking mode of donor–donor–acceptor like 34 rather than of the donor–acceptor–donor like 35.
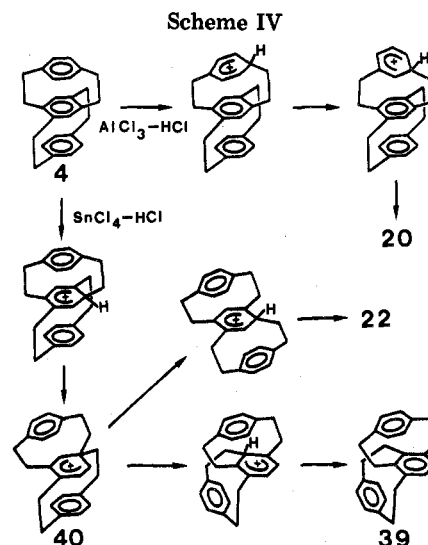
Chemical Properties

Substitution. Triple-layered [2.2]paracyclophane (4) gave the monobromo derivative 36 as a sole product
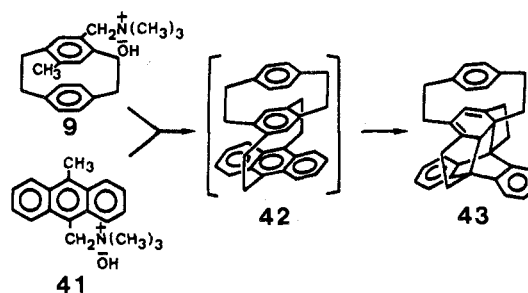

36 37 38
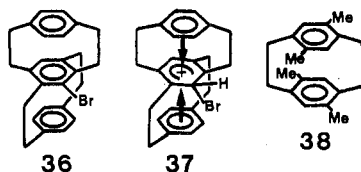
by treatment with bromine (36% yield) or pyridinium hydrobromide perbromide (60%) in the absence of a catalyst.[35] This electrophilic substitution indicates that the inner benzene is a stronger π base and is substituted more easily than the outer benzenes, in spite of the sterically unfavorable position for the formation of a stable intermediate π or σ complex (37). This reaction is probably accelerated by transannular electronic interaction in the transition states, and therefore multilayered cyclophanes are expected to undergo substitutions much faster than double-layered cyclophanes owing to the magnitude of transannular electronic stabilization in the transition states.

In a competitive bromination reaction using bromine, only triple-layered cyclophane (4) was brominated to give 36 while double-layered cyclophane 38 was entirely recovered. From this result and the fact that 38 was brominated 20 times faster than durene, it is concluded that a transannular charge delocalization in a possible intermediate complex (37) plays a significant contribution in providing an energetically favorable pathway for the reaction.

Skeletal Rearrangement. [2.2]Paracyclophane (1) was easily rearranged to [2.2]metaparacyclophane (24) in the presence of AlCl₃–HCl, releasing some of the severe π-electron repulsion.[36] Treatment of the more highly strained triple-layered [2.2]paracyclophane (4) with the same acid produced mainly triple-layered metaparacyclophane (20). On the other hand, when a

(34) M. Yoshida, H. Tatemitsu, Y. Sakata, S. Misumi, H. Masuhara, and N. Mataga, *J. Chem. Soc., Chem. Commun.*, 587 (1976); H. Masuhara, N. Mataga, M. Yoshida, H. Tatemitsu, Y. Sakata, and S. Misumi, *J. Phys. Chem.*, **80**, 879 (1977).
(35) S. Misumi et al., unpublished.
(36) D. J. Cram, R. C. Helgeson, D. Lock, and L. A. Singer, *J. Am. Chem. Soc.*, **88**, 1324 (1966); D. T. Hefelfinger and D. J. Cram, *ibid.*, **93**, 4754 (1971).

Scheme IV

4 20 22 40 39

Scheme V

9 41 42 43

weak proton acid such as SnCl₄–HCl, TiCl₄–HCl, or BF₃–HCl was used as a catalyst, a mixture of 22 and 39 in a ratio of 1.2:1 was obtained in 72–80% yield.

As shown in a presumed mechanism (Scheme IV), the former product (20) might be formed by protonation at a bridgehead carbon of the outer benzenes of 4, followed by 1,2 migration of the attached ethylene bridge. The other products, 22 and 39, might be produced by initial protonation at a bridgehead carbon of the tetrasubstituted inner benzene and then by successive migration of two ethylene bridges via a common intermediate 40 for a constant ratio of both products was attained regardless of varying reaction conditions such as catalyst, temperature, and concentration. Since the initial protonation is expected to be a key step to differentiate the two rearrangements, a protonation of 4 in FSO₃H–SOClF and NMR measurement of its protonated species were performed.[35] This result shows the protonation at the inner benzene carbon to be favored over that at the outer one. The preferred protonation at the outer benzene carbon in the case of Al₂Cl₆–HCl may be attributed to the acidity and/or bulkiness of the proton acid.

Cycloaddition. The synthesis of triple-layered anthracenophane (42) was attempted by a cross-breeding pyrolysis of the two ammonium bases 9 and 41 for the study of transannular interactions between anthracene and other aromatic rings. But an unexpected cycloadduct, 43, was obtained, and its structure was confirmed by X-ray analysis as well as its spectral properties.[37] (See Scheme V.) It is reasonable to

(37) T. Toyoda, A. Iwama, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, 3203 (1975); T. Toyoda, A. Iwama, T. Otsubo, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **49**, 3300 (1976).
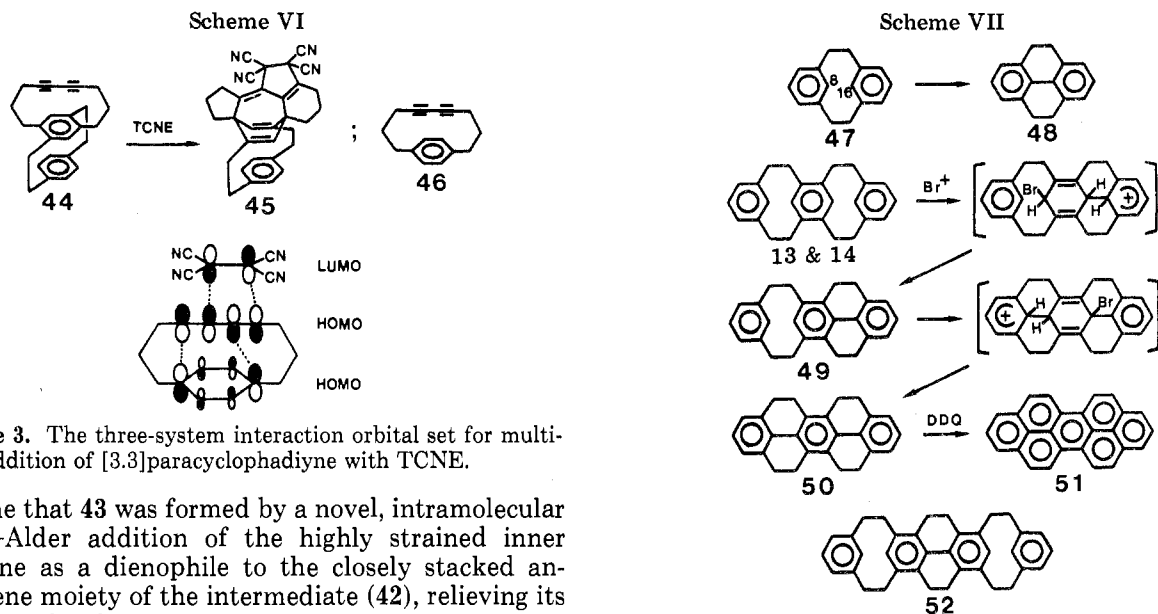
Scheme VI

Figure 3. The three-system interaction orbital set for multi-cycloaddition of [3.3]paracyclophadiyne with TCNE.

assume that **43** was formed by a novel, intramolecular Diels–Alder addition of the highly strained inner benzene as a dienophile to the closely stacked anthracene moiety of the intermediate (**42**), relieving its severe molecular strain.

High reactivity of such a strained benzene was also pointed out in the case of a multicycloaddition reaction as shown in Scheme VI.[38] Layered paracyclophadiyne (**44**) reacted smoothly with tetracyanoethylene at room temperature to give adduct **45**, whereas the similar reaction of paracyclophadiyne **46** proceeded only at a higher temperature (136 °C). The severe strain of the inside benzene of **44** is obviously responsible for acceleration of the cycloaddition.

We first thought that the multicycloaddition was an intriguing example of a thermally allowed $[_\pi 4_s + _\pi 2_a + _\pi 2_s + _\pi 2_a]$ pericyclic process, provided that it proceeded in a concerted manner. However, the mechanism of this reaction has recently been explained by molecular orbital theory, that is, in terms of a three-system interaction among the HOMO of the benzene ring, the HOMO of the diyne group, and the LUMO of TCNE as shown in Figure 3, in which highly electron-deficient TCNE allows the HOMO–HOMO interaction between the diyne group and the benzene ring to contribute to stabilization and bond formation between them.[39]

Transannular Reaction. [2.2]Metacyclophane (**47**) is known to undergo an interesting transannular dehydrogenation with the aid of electrophilic reagents to give tetrahydropyrene (**48**).[40] The reaction is based upon the fact that the C-8 and C-16 carbons of **47** are extremely close together (2.633 Å) and within their van der Waals distance.[20,41] A similar transannular reaction of triple-layered [2.2]metacyclophanes (**13** and **14**) proceeded more quickly under milder conditions to afford transannularly dehydrogenated products (**49** and **50**).[42] The transannular reaction of quadruple-layered

Scheme VII

metacyclophanes was also observed to proceed easily via the first transannular product (**52**).

A probable mechanism for this reaction is illustrated in Scheme VII. It is concluded that both the higher strain of the inner benzenes and the substituent effect of bridged ethylenes are responsible for the rapid transannular reactions of the multilayered metacyclophanes as compared with that of [2.2]metacyclophane (**47**). The bis-transannular product **50** was treated with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) to afford peropyrene (**51**) quantitatively. Teropyrene was similarly obtained from the tris-transannular product of quadruple-layered metacyclophane.[43] This reaction sequence is a useful synthetic method for preparing polynuclear aromatic hydrocarbons of the pyrene type.

Conclusion

We have described the syntheses and structures of multilayered paracyclophanes as well as multilayered metacyclophanes and metaparacyclophanes, and discussed their spectral properties and unusual reactions. It is shown that the strong transannular electronic interaction in the compounds of the para series and the severe molecular strain in the compounds of all series are significant factors to account for their anomalous spectral and chemical behaviors. We believe that more extensive studies of multilayered cyclophanes and of layered compounds composed of condensed aromatic nuclei might be of help toward understanding transannular and intermolecular electronic interactions and in the wide application of layered compounds in other fields.

(38) T. Kaneda, T. Ogawa, and S. Misumi, *Tetrahedron Lett.*, 3373 (1973); cf. multicycloaddition of anthracenophadiyne: T. Inoue, T. Kaneda, and S. Misumi, *ibid.*, 2969 (1974); T. Hayashi, N. Mataga, T. Inoue, T. Kaneda, M. Irie, and S. Misumi, *J. Am. Chem. Soc.*, **99**, 523 (1977).
(39) S. Inagaki, H. Fujimoto, and K. Fukui, *J. Am. Chem. Soc.*, **98**, 4693 (1976).
(40) T. Sato, M. Wakabayashi, Y. Okamura, T. Amada, and K. Hata, *Bull. Chem. Soc. Jpn.*, **40**, 2363 (1967), and references cited therein.
(41) C. J. Brown, *J. Chem. Soc.*, 3278 (1953).
(42) T. Umemoto, T. Kawashima, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, 463 (1975); *Chem. Lett.*, 837 (1975).

(43) T. Umemoto, T. Kawashima, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, 1005 (1975).