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Layered Compounds. XXXVI.[1] Structure and Properties of Triple-layered Metaparacyclophanes

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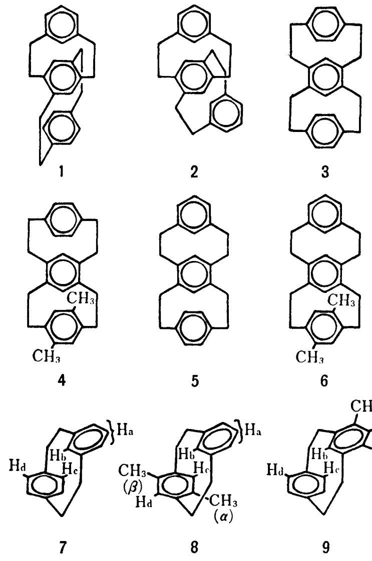
The geometrical structures of triple-layered metaparacyclophanes are discussed on the basis of the chemical shifts of the NMR spectra and their temperature dependence. [2.2]Metacyclo(4,7)[2.2]paracyclophane **1** and [2.2]metacyclo(12,15)[2.2]metaparacyclophane **2** proved to be mixtures of conformational isomers due to arrangement of meta-substituted ring. [2.2]Paracyclo(4,6)[2.2]metaparacyclophane **3** was confirmed to be a staircase-shape (*anti*-form), in contrast to a platform-shape (*syn*-form) of [2.2]metacyclo(4,6)[2.2]metaparacyclophane **5**. In their electronic spectra, **1** and **2** exhibit a transannular electronic interaction between the benzene rings similar to that of multilayered [2.2]paracyclophanes; **3** and **5** show one similar to that of multilayered [2.2]metacyclophanes. The difference between the former and the latter groups seems to arise from the substitution modes of methylene bridges attached to the inside benzene of triple-layered metaparacyclophanes.

In the preceding paper we reported the syntheses of triple-layered [2.2]metaparacyclophanes **1**—**6**.[1] The compounds are expected to consist of mixtures of conformational isomers due to fixation of meta-substituted benzene rings. In compounds **3**—**6** there seem to be two types of stacking which characterize either a staircase-shape (*anti*-form) or a platform-shape (*syn*-form) conformer. In this paper we discuss the assignment of the structures in detail and the conformational flipping of the meta ring at high temperature on the basis of NMR study. The transannular electronic interactions between benzene rings are considered in comparison with the electronic spectra of multilayered paracyclophane or metacyclophane.



Scheme 1.

Results and Discussion

Structure and NMR Spectra. The NMR spectra of layered metaparacyclophanes **1**—**9** are summarized in Table 1. The high field shift of the inner aromatic proton Hb of [2.2]metaparacyclophane **7** suggests that the proton is situated just above the faced para-substituted ring. The aromatic protons, Hc and Hd, of the para ring are nonequivalent at room temperature, becoming equivalent at higher temperature (T_C, *ca.* 140 °C). The behavior is interpreted in terms of conformational flipping of the meta ring which is fixed at room temperature.[2] The activation energy calculated is about 21 kcal/mol. Similarly two dimethyl derivatives **8** and **9** show the fixation of the meta ring at room temperature.

Table 1. Nmr spectra of metaparacyclophanes

Compound	δ Value in deuterochloroform
1	6.6 (m, 3H, Ha), 6.30 (bs, 4H, He), 6.17 (s, 1H, Hd), 5.12 (bs, 1H, Hb), 4.90 (s, 1H, Hc), 1.5—3.6 (m, 16H, CH$_2$)
2	6.4—7.1 (m, 12H, Ha and Ha′), 6.87 (s, 1H, Hc′), 5.60 (s, 2H, Hc), 5.37 (bs, 1H, Hb), 5.28 (bs, 1H, Hb′), 4.39 (s, 1H, Hd′), 1.5—3.5 (m, 32H, CH$_2$)
3	7.12 (bs, 4H, Ha), 5.66 (bs, 4H, Hb), 4.94 (s, 2H, Hc), 1.5—3.3 (m, 16H, CH$_2$)
4	7.09 (d, J=1 Hz, 2H, Ha), 6.79 (s, 1H, Hf), 5.63 (d, J=1 Hz, 2H, Hb), 5.48 (s, 1H, He), 5.05 (s, 1H, Hc), 4.90 (s, 1H, Hd), 1.7—3.2 (m, 16H, CH$_2$), 2.39 (s, 3H, CH$_3$-β), 1.44 (s, 3H, CH$_3$-α)
5	7.46 (d, J=2 Hz, 2H, Hf), 7.3 (m, 3H, Ha), 6.48 (d, J=2 Hz, 2H, He), 5.70 (bs, 1H, Hb), 5.62 (s, 1H, Hd), 3.66 (s, 1H, Hc), 1.5—3.5 (m, 16H, CH$_2$)
6	6.9—7.3 (m, 7H, Ha, Ha′, and Hf), 6.87 (s, 1H, Hf′), 6.21 (s, 1H, He), 5.80 (bs, 1H, Hb), 5.60 (s, 1H, He′), 5.39 (s, 1H, Hd), 5.07 (bs, 1H, Hb′), 4.20 (s, 1H, Hd′), 3.71 (s, 2H, Hc and Hc′), 1.7—3.2 (m, 32H, CH$_2$), 2.58 (s, 3H, CH$_3$-β), 2.44 (s, 3H, CH$_3$′-β), 1.98 (s, 3H, CH$_3$-α), 1.49 (s, 3H, CH$_3$′-α)
7	7.18 (d, J=2 Hz, 2H, Hd), 6.8 (m, 3H, Ha), 5.85 (d, J=2 Hz, 2H, Hc), 5.42 (bs, 1H, Hb), 2.0—3.3 (m, 8H, CH$_2$)
8	6.6—7.0 (m, 3H, Ha), 6.78 (s, 1H, Hd), 5.09 (s, 1H, Hc), 5.51 (bs, 1H, Hb), 1.9—3.4 (m, 8H, CH$_2$) 2.43 (s, 3H, CH$_3$-β), 1.65 (s, 3H, CH$_3$-α)
9	7.16 (d, J=1 Hz, 2H, Hd), 6.65 (bs, 1H, Ha), 5.83 (d, J=1 Hz, 2H, Hc), 5.22 (s, 1H, Hb), 1.7—3.3 (m, 8H, CH$_2$), 2.22 (s, 6H, CH$_3$)

The triple-layered metaparacyclophane **1** exhibits a NMR pattern similar to those of **7**—**9** except high field shifts of the protons, Hb, Hc, and Hd, due to the anisotropy of the additional third benzene ring. Figure 1

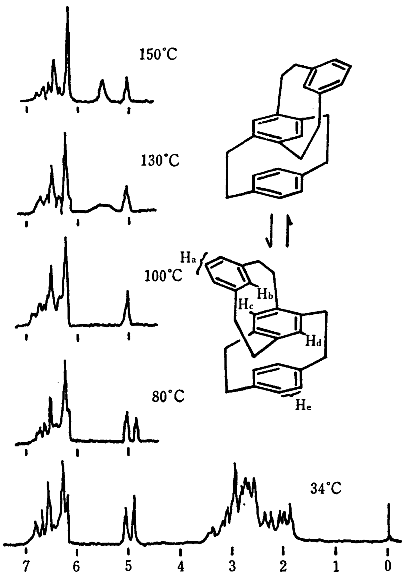


Fig. 1. NMR spectra of **1** in hexachlorobutadiene at various temperatures.

shows NMR spectra at various temperatures. The conformational flipping of meta ring occurs at 100 °C, a relatively low temperature which corresponds to 18 kcal/mol of activation energy. The difference in 3 kcal/mol as compared with [2.2]metaparacyclophane **7** is considered to arise from twisting of the inside ring, which is pulled up and down by two pairs of methylene bridges, to lower the steric energy barrier to the flipping of the meta ring.

For **2**, fixation of the meta ring is expected to give two conformational isomers, **2a** and **2b**, which should show quite different NMR spectra. In fact **2** reveals the NMR spectrum corresponding to 1: 1 equilibrium mixture of the two isomers at room temperature (Fig. 2). Thus the inner aromatic protons, Hb and Hb′, of meta rings appear at slightly different positions (δ 5.28 and 5.37 ppm) with equal integral intensity. Also, as expected from the structures in Fig. 2, the aromatic protons Hc at the inside ring of **2a** are equivalent (δ 5.60), but not those (Hc′ and Hd′) of **2b** (δ 4.39 and 6.87). The extraordinary upfield shift of the proton Hd′ is explained in terms of an additive shielding effect of two meta rings, between which the proton is sandwiched. The energy barrier for the conformational flipping of the meta rings is relatively low (19 kcal/mol). Above the coalescence temperature (116 °C) the inner aromatic protons of meta rings and the aromatic protons of the inside ring appear as a singlet at δ 5.63 and 5.30, respectively.

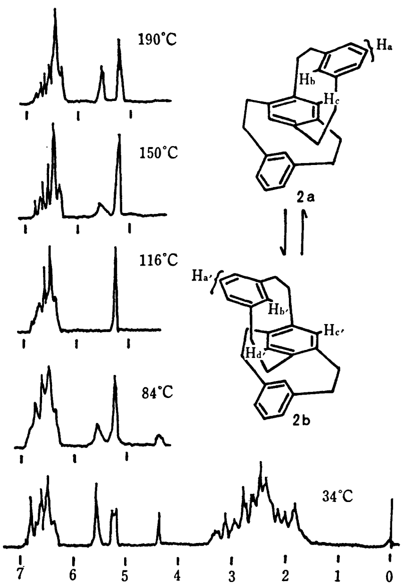
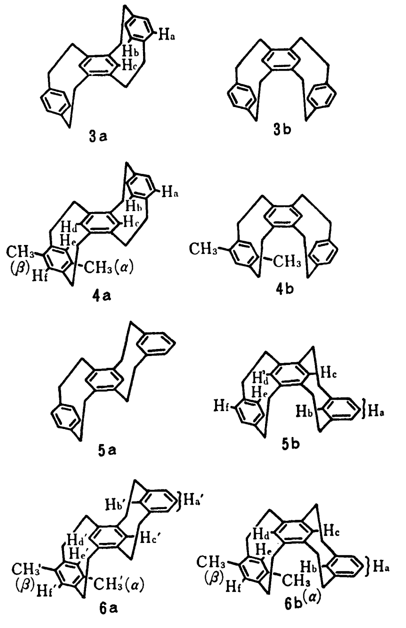


Fig. 2. NMR spectra of **2** in hexachlorobutadiene at various temperatures.



Scheme 2.

Two conformations, **3a** and **3b**, are possible for the structure of **3**. However, the NMR spectrum of **3** is very simple, suggesting that the compound consists of a symmetrical isomer. Dimethyl derivative **4** was prepared in order to facilitate the structure assignment of the parent compound **3**. Examination of the *syn*-form **3b** with a molecular model indicates that the *endo* aromatic protons of the two para rings are sterically crowded. When methyl groups are substituted to **3b**, more severe crowding is expected in the resulting *syn*-form **4b**. On the other hand, such methyl substitution in *anti*-form **3a** does not seem to influence the parent structure. The actual compound **4** is also composed of a single isomer and should have the same geometry as **3** since the aromatic protons, Ha and Hb, of nonsubstituted para ring of **4** show chemical shifts very close to those of **3**. *endo* Methyl protons CH_3-α (δ 1.44) of **4** appear at a slightly higher field than the corresponding protons (δ 1.65) of 12,15-dimethyl[2.2]metaparacyclophane **8**. If the geometry is of *syn*-form, the methyl signal should shift to downfield due to the deshielding effect of the third benzene ring or nonsubstituted para ring. Consequently, the staircase-shape (*anti*-form) structure is assigned to both **3** and **4**. Recently the validity of this assignment has been confirmed by X-ray crystallo-

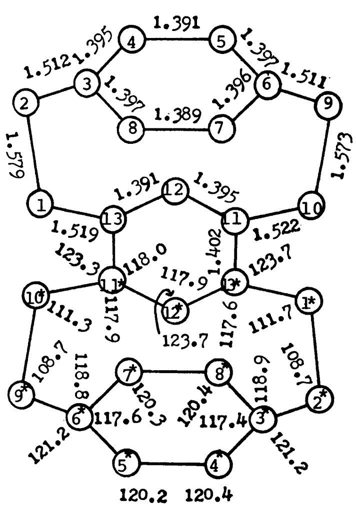


Fig. 3. Profile of triple-layered metaparacyclophane **3**. Bond lengths and angles.

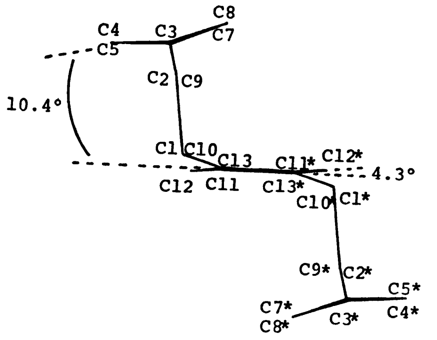


Fig. 4. Projection viewed down the vector C(1)–C(10).

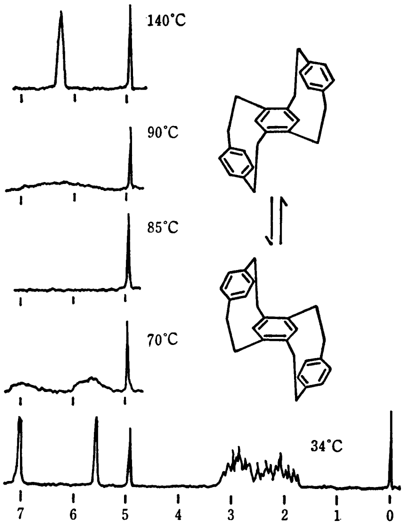


Fig. 5. NMR spectra of **3** in hexachlorobutadiene at various temperatures.

graphic analysis.3) The inside benzene is slightly overlapped with two para rings at *ca.* 10° angle, as shown in Figs. 3 and 4. By steric repulsion with the two para rings arranged in *anti*-form, the inside benzene ring is bent into a chair shape. This is the first example of a chair-shape benzene. There is a conformational flipping at elevated temperature also for compound **3** (Fig. 5). The nonequivalent aromatic protons, Ha and Hb, of para rings coalesce at 85 °C and appear as a singlet just in the middle of their initial positions at higher temperature. This spectrum indicates that the conformational change occurs between two *anti*-forms by means of double flipping of the two para rings, but not between *anti*- and *syn*-forms by one ring flipping.

A different conformational behavior was observed in the case of **5**. Two conformational isomers, *anti*-form **5a** and *syn*-form **5b**, are also possible for **5**. However, compound **5** shows no temperature dependence in its NMR spectrum, suggesting that it is composed of a single isomer, **5a** or **5b**. Methyl substitution makes the *syn*-form structure unstable as in the case of **3**. Actually the dimethyl derivative **6** was obtained as a mixture of two conformational isomers, **6a** and **6b**, in a 1 : 1 ratio (Table 1). The results may be explained by assuming that the *syn*-form conformer **5b** is assigned to the structure of compound **5** and the methyl substitution equalizes the stabilities of *syn*- and *anti*-forms by lowering the stability of the former. The assumption was confirmed by X-ray crystal analysis of **5** (Figs. 6 and 7).3) Differing from **3**, the inside benzene of **5** is bent into a boat shape.

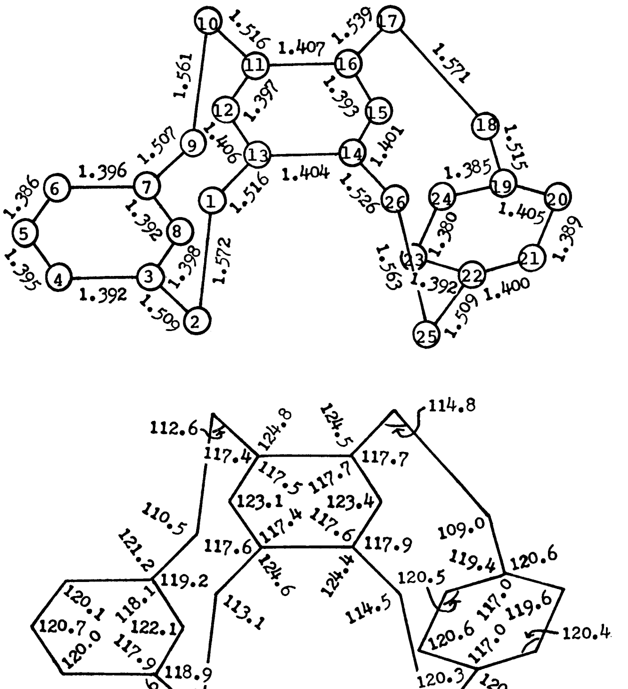


Fig. 6. Profile of triple-layered metaparacyclophane **5**. Bond lengths and angles.

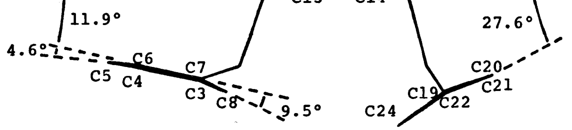


Fig. 7. Projection viewed down the vector C(3)–C(7).

Let us discuss the stereochemical difference between the two triple-layered metaparacyclophanes **3** and **5**. In a series of multilayered [2.2]metacyclophanes, the platform conformer is thermally more stable than the staircase one.[4] This seems to be related to the strained structure of the inside benzene ring. Thus the inside ring is bent into a boat form in the former and into a chair form in the latter. Molecular orbital calculation revealed that the boat-shape benzene is much more stable than the chair-shape one, mainly due to the difference in the resonance integral term.[5] The stability of *syn*-form **5b** can be explained in the same manner. On the other hand, molecular model examination of *syn*-form **3b** indicates that steric crowding between two para benzenes should be considerably large. The steric overcrowding energy presumably overcomes the energy difference between boat and chair forms of the inside benzene, making the *anti*-form geometry favorable for compound **3**.

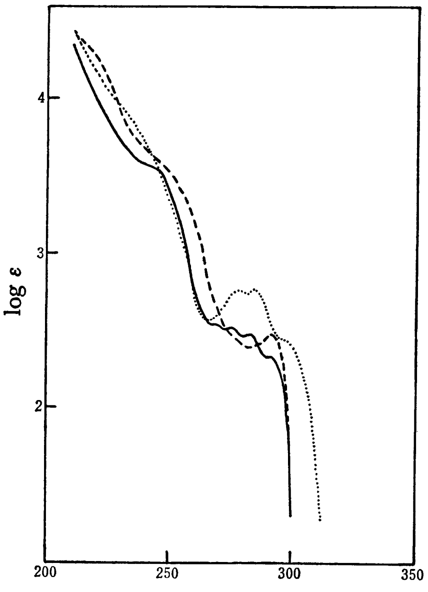


Fig. 8. Electronic spectra of [2.2]metaparacyclophane **7** (—) and the dimethyl derivatives **8**(···) and **9** (---) in cyclohexane.

Electronic Spectra. Electronic spectra of [2.2]-metaparacyclophane **7** and its dimethyl derivatives **8** and **9** are shown in Fig. 8. The most marked features are broadening and bathochromic shift of the absorption bands associated with B_{1u} and B_{2u} transitions of benzene. Such features were generally observed in the spectra of layered cyclophanes and mainly explained by π-electronic interaction between benzene rings.[6] In addition, bending of the benzene ring is responsible to some extent.[7] This is also the case for [2.2]metaparacyclophane, since its para ring is severely bent into a boat shape as demonstrated by X-ray crystal analyses.[3,8] Although [2.2]paracyclophane shows strong π-electron interaction due to sufficient overlapping of two faced benzenes, such a strong interaction can not be expected for the parent compound **7** of [2.2]metaparacyclophane series because of partial overlapping. However, the interaction in this cyclophane system is evidently realized by methyl substitution. Thus, two dimethyl derivatives **8** and **9** show rather different spectra from that of **7** besides the normal substituent effect. It is especially remarkable in the long wavelength region of **8**, *viz.*, the substitution at para ring is more effective than that at meta ring. This suggests that the transition of the para ring makes relatively large contribution to the transannular electronic interaction of [2.2]metaparacyclophane.

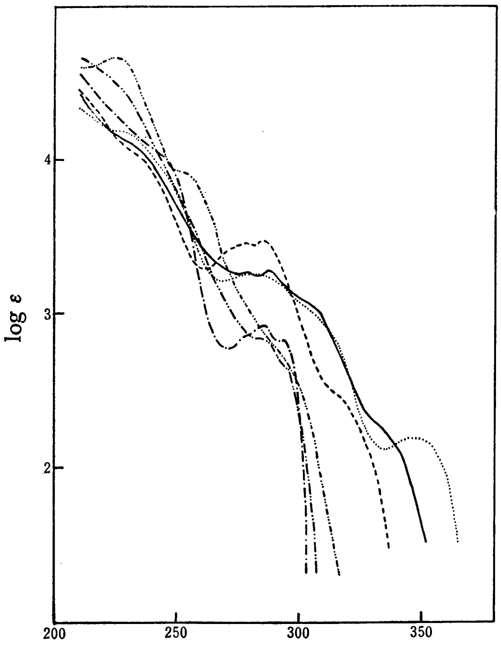
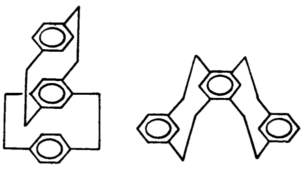


Fig. 9. Electronic spectra of triple-layered [2.2]metaparacyclophanes **1** (——), **2** (-----), **3** (-•-•-), and **5** (–•••–), together with triple-layered [2.2]paracyclophane **10** (······) and metacyclophane **11** (–···–) in cyclohexane.



10 **11**

Scheme 3.

A similar consideration can be extended to the present triple-layered metaparacyclophanes. As seen in Fig. 9, the electronic spectra of **1** and **2** show new bands around 330 and 315 nm, respectively, and an increase of intensity of the bands in the 260—310 nm region as compared with that of [2.2]paracyclophane or [2.2]-metaparacyclophane. Thus their absorption curves are similar to the curve of triple-layered [2.2]paracyclophane **10**,[9] indicating that a marked transannular electronic interaction also exists between the meta and para rings. On the other hand, the electronic spectra of **3** and **5** are similar to that of triple-layered [2.2]metacyclophane **11**[10] indicative of a weak electronic interaction. This is in marked contrast to the phenomenon of **1** and **2**.

There is no essential difference in the spectra due to conformational difference between *anti*- and *syn*-forms. Substitution modes of methylene bridges attached to the inside ring of triple-layered [2.2]metaparacyclophane serve as an important factor on overlapping of benzene rings and hence, on the electronic interaction.

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