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LAYERED COMPOUNDS. IX[1]. THE CRYSTAL STRUCTURE OF A QUADRUPLE-LAYERED CYCLOPHANE

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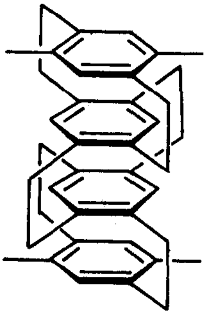
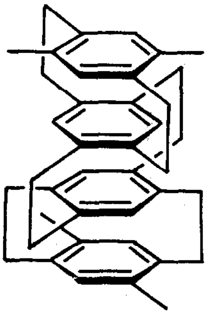
The molecular structures of unusually strained [2.2]paracyclophane and its derivatives have been described by several authors[2,3], in which the benzene rings are enormously bent due to intramolecular non-bonded interaction between closely situated aromatic nuclei. In the previous communication[4] of this series, concerning the configuration of isomeric tetramethyl derivatives of quadruple-layered cyclophane, we assumed the less soluble isomer as I and the more soluble one as II by comparison of their physical properties with clearly assigned, non-substituted quadruple-layered compounds. In order to determine definitely the geometrical structure of the two cyclophanes (I and II) and to investigate the distortion introduced by additionally stacked benzene nuclei, the present X-ray crystallographic analysis was undertaken.

The less soluble isomer, $C_{40}H_{44}$, was crystallized from toluene as colorless plates. The crystals are monoclinic with the cell dimensions, $a = 24.399$, $b = 8.924$, $c = 13.672$ Å, and $\beta = 95.53°$; $z = 4$. The space group is Cc or C2/c. The latter space group was confirmed in the course of the refinement of the structure.


I


II

The intensity data were collected on a computer controlled four-circle diffractometer using Zr-filtered Mo-Kα radiation and ω-2θ scan technique. The structure was deduced from the three-dimensional Patterson synthesis by assuming that the molecule occupies a center of symmetry in

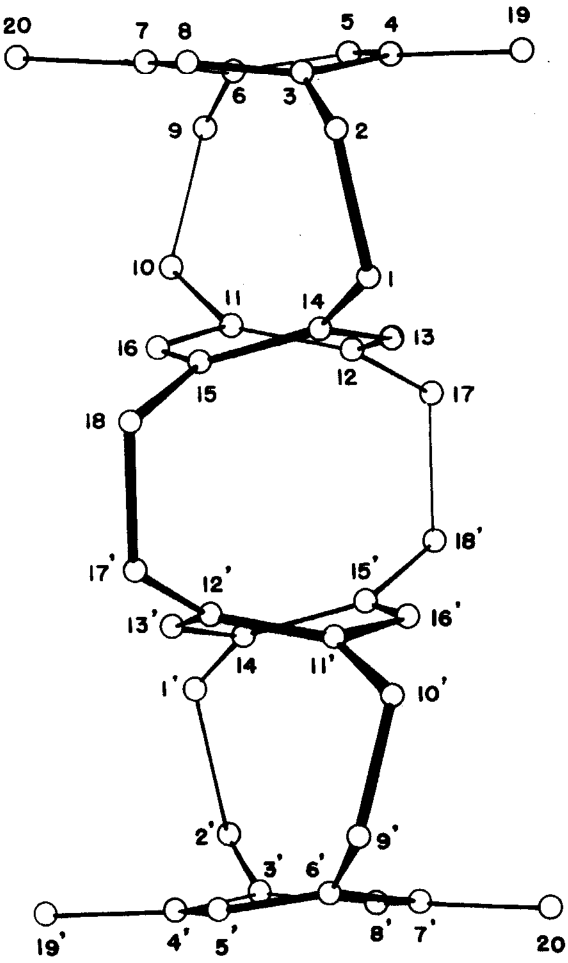


Fig. 1. Profile of the molecule viewed down the b axis.

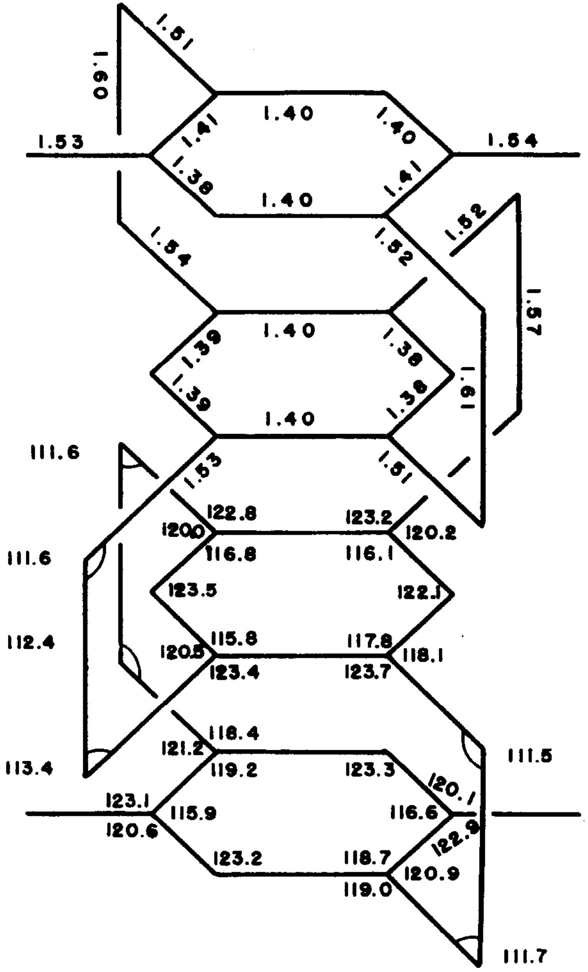
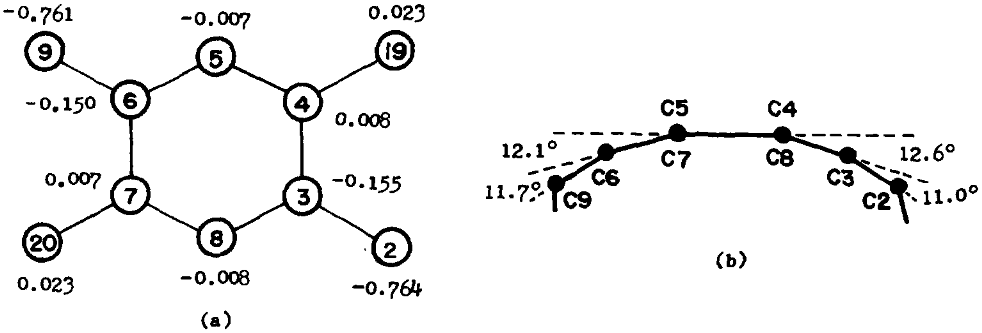


Fig. 2. Bond lengths and angles. The standard deviations are 0.010 Å in bond lengths and 0.6° in bond angles.



(a) (b)

Fig. 3. Two views of out-of-distortion in the outer benzene ring

the unit cell. The structure refinement was carried out by means of the block-diagonal least-squares method with the positional and anisotropic thermal parameters of all carbon atoms. The contributions of hydrogen atoms were included in the structure factor calculations. The final R-value was 0.11 for 1741 observed independent reflections. The molecular shape and the deviation of benzene atoms from the least-squares plane are shown in Figs. 1 and 3. Figs. 1 and 3b demonstrate that the outer benzene rings of the molecule are very similar to the boat-shaped benzene rings of [2.2]paracyclophane. As seen in Fig. 3a, however, two methyl carbon atoms, C_{19} and C_{20}, in the former are slightly displaced toward the outside of the molecule contrary to the inward displacement of the hydrogen atoms at the corresponding positions of the latter. This may be due to the steric requirement of the two methyl groups. On the basis of the structure of [2.2]paracyclophane, it is expected that the inner benzene rings of I are forced to distort remarkably by two pairs of methylene bridges above (C_1-C_2 and C_9-C_{10}) and below (C_{17}-C_{18}' and C_{18}-C_{17}') the benzene ring moiety. In fact, Fig. 1 shows such a striking deformation of the benzene ring into a twist shape.

The closest intramolecular contacts between atoms of two adjacent benzene rings are listed

Table 1. Intramolecular Contacts Between Atoms of Two Adjacent Benzene Rings

C_3 - C_{14}	2.78 Å	C_6 - C_{11}	2.79 Å	C_{13} - C_{16}'	3.02 Å
C_4 - C_{13}	3.06	C_7 - C_{16}	3.13	C_{14} - C_{11}'	3.31
C_5 - C_{12}	3.17	C_8 - C_{15}	3.26	C_{15} - C_{12}'	2.74

in Table 1, and are comparable to those of [2.2]paracyclophane[2] and its diolefin[3]. The intramolecular bond distances and angles are shown in Fig. 2. The C_1-C_2 ($C_{1'}$-$C_{2'}$) and C_9-C_{10} ($C_{9'}$-$C_{10'}$) bonds are longer by about 0.06 Å than the normal value of single bond while the C_{17}-$C_{18'}$ and C_{18}-$C_{17'}$ are slightly longer. It may be due to repulsions of non-bonded contacts, C_3.....C_{14} and C_6.....C_{11}. The C-C bond distances in the two types of benzene rings range from 1.38 to 1.41 Å and from 1.38 to 1.40 Å, respectively, and the mean C-C distances of 1.397 and 1.391 Å are in good agreement with the corresponding value of benzene[5]. On the other hand, C-C-C angles in the benzene rings show considerable change from 115.8 to 123.5°. The decrease of all the internal angles at the substituted carbon atoms in each benzene ring is compensated by greater increase of two internal angles at non-substituted carbon atoms. A similar effect is found in crystals of [2.2]paracyclophane.[2,3]

The present analysis clearly demonstrates our previous assumption that the less soluble isomer is of the molecular structure I bearing the center of symmetry while the structure II is assigned to the other isomer.

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