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The Crystal and Molecular Structure of 12-Bromo[2.2][2.2]triple-Layered Paracyclophane

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The molecular structure of 12-bromo[2.2][2.2]paracyclophane has been determined by means of X-ray diffraction. The crystal is orthorhombic, space group *Pbcn*, a=12.768(1), b=11.515(1), c=13.074(1) Å, Z=4. The structure was solved by the heavy-atom method, and refined anisotropically by the block-diagonal least-squares procedure; R=0.062. The Br–C····C–H axis of the central benzene ring lies on a crystallographic two-fold axis. The outer benzene rings take a boat form, and the central benzene ring is twisted.

Among the molecular structures of multi-layered paracyclophane, only that of tetramethyl quadruple-layered paracyclophane has been reported, hitherto.1) As to the structure of triple-layered ones, a preliminary result on isomers of tetramethyl triple-layered paracyclophanes has been presented, but the structure was reported disordered.2) This paper deals with the first example of the molecular structure of a triple-layered one, 12-bromo[2.2][2.2]paracyclophane, determined by means of X-ray diffraction. A brief sketch of the structure has been described previously.3)

Experimental

Crystal Data. $C_{26}H_{25}Br$, M=417.42, orthorhombic, space group *Pbcn*(No. 60, absent reflections, $0kl$: $k=2n+1$, $h0l$: $l=2n+1$, $hk0$: $h+k=2n+1$), a=12.768(1), b=11.515(1), c=13.074(1) Å, V=1922.1(2) Å^3, D_m=1.42 g cm^{-3}(by floatation in an aqueous solution of $ZnBr_2$), D_c=1.46 g cm^{-3} for Z=4.

Colorless octahedral crystal with approximate dimensions of 0.4×0.5×0.6 mm was mounted on a Rigaku automated, four-circle diffractometer. Zr-filtered Mo $K\alpha$ radiation(λ=0.71069 Å) was used.

Intensity data were collected by the θ—2θ scan technique at a 2θ rate of 2° min^{-1}. The scan range was from $\{2\theta(\alpha_1)-1.0\}$ to $\{2\theta(\alpha_2)+1.0\}°$. Backgrounds were counted for 15 s at both ends of a scan. Three standard reflections measured after every 50 reflections to monitor the stability and orientation of the crystal showed no significant decay throughout the data collection. A total of 1762 reflections was observed out of 2520($\sin\theta/\lambda<0.7$). Usual Lorentz and polarization corrections were made but absorption correction was ignored [μ(Mo)=23.5 cm^{-1}].

Structure Solution and Refinement

Since the space group is *Pbcn* and the unit cell contains four molecules, the molecule must lie on a special position, either two-fold axis or a center of symmetry. The structure was established by the heavy-atom method. The position of the bromine atom was found by the Patterson function. All the carbon atoms could be located on a Fourier map computed by using approximate phases based on the bromine atom. The structure was refined anisotropically by the block-diagonal least-squares procedure (*HBLS* V).4) The function minimized was $\sum(\Delta F)^2$. Hydrogen atoms were located on a difference Fourier map, which were included in the refinement with isotropic temperature factors. The R value converged to 0.062. Final atomic parameters are listed in Table 1.[††]

Atomic scattering factors were taken from International Tables for X-Ray Crystallography.5) Computations were done mainly on a NEAC 2200—500 computer at the Computation Center, Osaka University, and at the final stage an ACOS 850 computer was used at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Table 1. Final Atomic Coordinates of Non-hydrogen Atoms with Equivalent Isotropic Temperature Factors6)

Atom	x	y	z	B_{eq}/Å^2
Br	0.5000	0.56717(8)	0.2500	4.72
C(1)	0.3195(4)	0.4014(6)	0.1642(4)	3.93
C(2)	0.2313(4)	0.3803(5)	0.2467(5)	3.93
C(3)	0.2730(4)	0.3312(5)	0.3461(4)	3.12
C(4)	0.3289(4)	0.3999(5)	0.4139(4)	3.25
C(5)	0.4024(4)	0.3503(5)	0.4794(4)	3.23
C(6)	0.4199(4)	0.2307(5)	0.4791(3)	2.94
C(7)	0.3466(4)	0.1621(5)	0.4284(4)	3.31
C(8)	0.2749(4)	0.2120(5)	0.3620(4)	3.27
C(9)	0.5253(4)	0.1836(5)	0.5112(4)	3.77
C(10)	0.5989(4)	0.1614(6)	0.4158(4)	4.00
C(11)	0.5616(4)	0.2251(5)	0.3215(4)	3.10
C(12)	0.5781(4)	0.3436(5)	0.3059(3)	3.04
C(13)	0.5000	0.4005(6)	0.2500	2.80
C(14)	0.5000	0.1659(7)	0.2500	3.32

[††] Tables of anisotropic temperature factors, coordinates of hydrogen atoms, and observed and calculated structure factors are kept at the Chemical Society of Japan, Document No. 8612.

Results and Discussion

The molecular structure(*ORTEP*)[7] is drawn in Fig. 1 with the numbering scheme of non-hydrogen atoms. Bond distances and bond angles are given in Fig. 2. The molecule has a two-fold axis symmetry. The Br, C(13), C(14), and H(14) atoms lie on a crystallographic two-fold axis. Three benzene rings are displaced slightly in a helical way from the eclipsed position (Fig. 3a). The C(5)-C(4) and C(12)-(13) bonds projected onto the least-squares plane of the central benzene ring make an angle of 4.1°, and similarly the C(12)-C(13) and C(4′)-C(3′) bonds form 6.4°.

The outer benzene ring has a boat form (Fig. 3b). The bending angle p_1, i.e. the dihedral angle between the plane defined by the C(4), C(5), C(7), and C(8) atoms (Plane 1) and that formed by the C(3), C(4), and C(8)(Plane 2) is 12.0°, and the p_2, the dihedral angle between the plane made by the C(5), C(6), and C(7) atoms (Plane 3) and the Plane 1 is 12.1°. These are approximately equal to the corresponding angles in [2.2]paracyclophane [12.6°][8] and its derivatives[9,10] and tetramethyl quadruple-layered paracyclophane [12.5 and 12.9°].[1] The C(2)-C(3) bond makes an angle q_1 of 11.0° with the Plane 2, and the C(6)-C(9) bond an angle q_2 of 11.7° with the Plane 3. These values are almost the same as those of the [2.2]paracyclophanes. Six C-C bond distances in the outer ring are equal and have normal values [av. 1.393 Å]. Among the bond angles, the C(4)-C(3)-C(8) and C(5)-C(6)-C(7) angles [117.3(5) and 117.0(5)°], which are the angles at the bow and stern of the boat form, are smaller than 120°, whereas the other four angles have normal values [120.4(5) to 121.0(5)°].

The central benzene ring is twisted. The dihedral angle between the plane defined by the C(11), C(12), C(13), and C(14) atoms and that by the C(11′), C(12′), C(13), and C(14) is 5.1°. Bond distances in this ring seem normal, however, inner angles at the C(11) [117.6(5)°] and C(12) atoms [115.3(6)°] are much smaller, whereas that at the C(13)[124.1(6)] is larger than 120°. The C(1)-C(12′) bond bends by 6.6° away from the plane defined by the C(11′), C(12′), and C(13) and the C(10)-C(11) bond by 4.7° away from the C(11)-C(12)-C(14) plane (Fig. 3(b$_2$)).

In the ethylene bridges, two C_{sp^3}–C_{sp^3} bonds are equal in length[1.578(8) and 1.582(8) Å], which are comparable to those in 4,7-dimethy[2.2]paracyclophane[1.587(12) Å],[9] 4,7,13,16-tetramethyl[2.2]paracyclophane[1.580(10) Å],[9] and tricarbonylchromium complex of [2.2]paracyclophane[1.595(4) Å].[10] Torsional angles around the C(1)-C(2) and C(9)-C(10) bonds are 12.5 and 17.6°, respectively.

Because of the deformation of the outer and central benzene rings closest nonbonded atomic distances between these rings are observed between the C(6) and C(11) atoms [2.744(7) Å] and between the C(3) and C(12′)[2.754(7) Å] (Fig 3(b$_2$)). The nonbonded

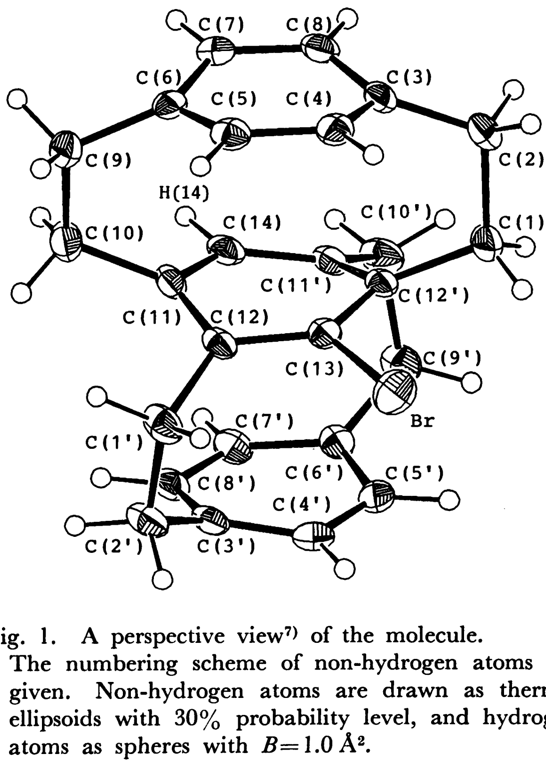

Fig. 1. A perspective view[7] of the molecule.
The numbering scheme of non-hydrogen atoms are given. Non-hydrogen atoms are drawn as thermal ellipsoids with 30% probability level, and hydrogen atoms as spheres with B=1.0 Å^2.

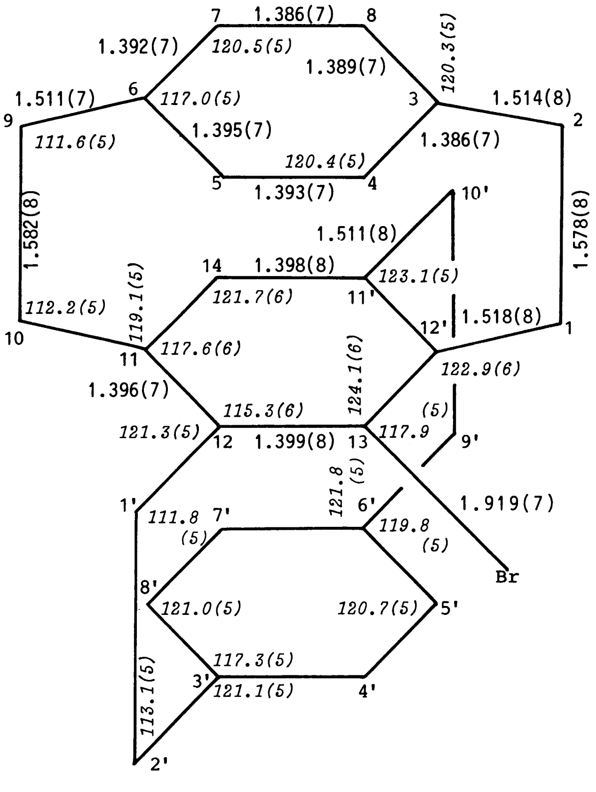

Fig. 2. Selected bond lengths and bond angles with estimated standard deviations in parentheses.

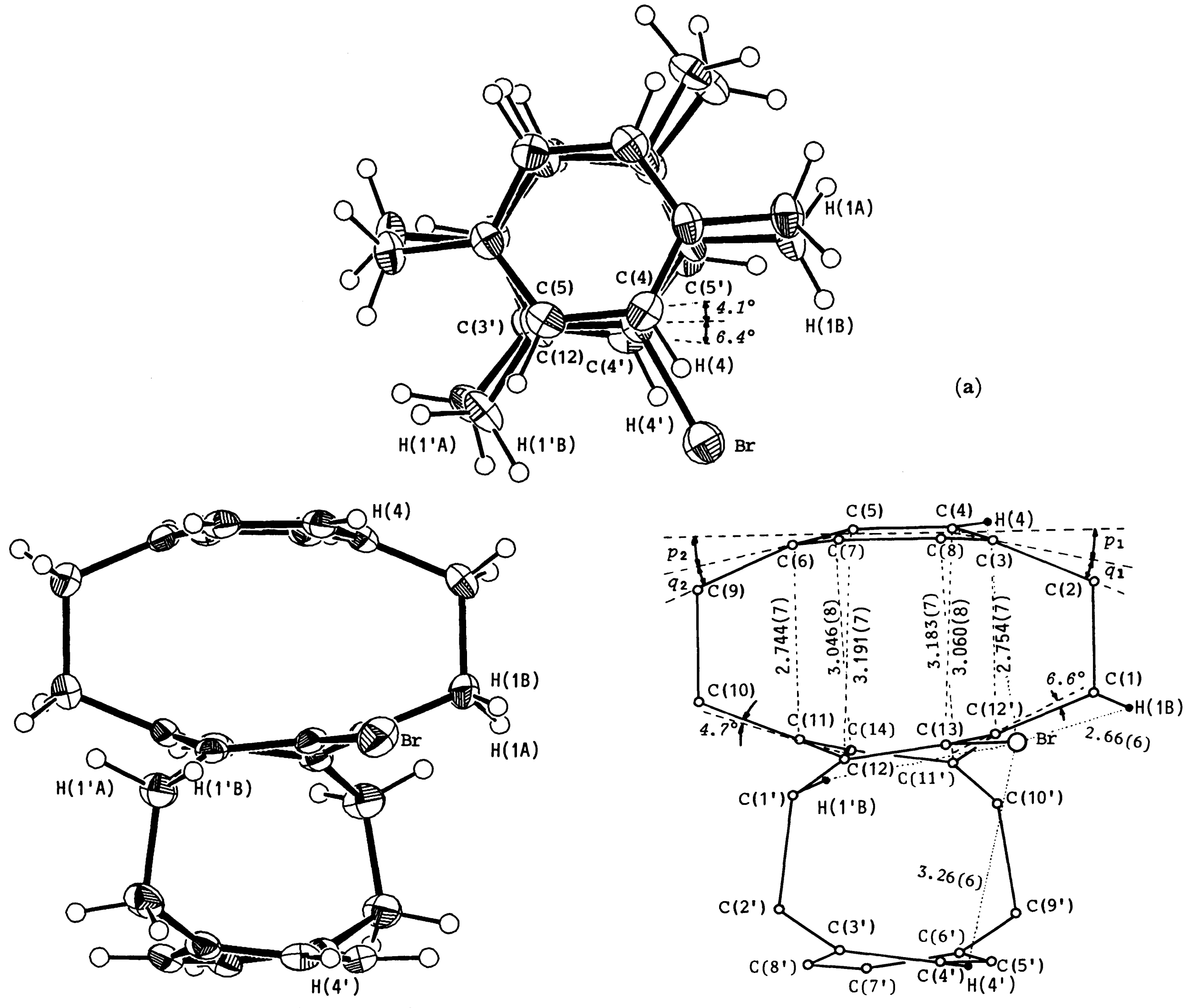

Fig. 3. Projections of the molecule.
(a): Projected along the C(6)→C(11) vector.⁷⁾ (b$_1$): Projected along the normal to the plane defined by the C(6), C(11), and C(12′) atoms.⁷⁾ (b$_2$): Schematic drawing of (b$_1$) with nonbonded atomic distances between the outer and central benzene rings[l/Å]. p, q, and other angles are also given.

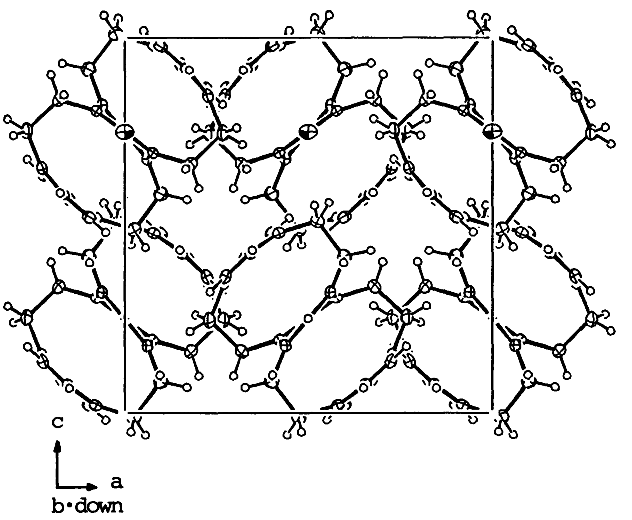

Fig. 4. Crystal structure projected along the b axis.⁷⁾

distance between the Br and the pseudo-gem proton, H(4) is a large value, 3.26(6) Å, which is equal to or rather larger than the ordinary van der Waals contact. In other words, the Br substitution provides little effect on the geometry of the present hydrocarbon, triple-layered paracyclophane. Among the nonbonded Br···H distances the closest is 2.66(6) Å of Br···H(4).

Crystal Structure. The packing of molecules in the crystal is shown in Fig. 4. Molecules are packed rather loosely. The closest intermolecular contact is observed between C(4)(x, y, z) and C(10)($-0.5+x$, $0.5-y$, $1-z$)[3.753(8) Å].

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