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The Crystal and Molecular Structure of 6-Bromo[2.2]paracyclo(4,8)[2. 2]metaparacyclophane

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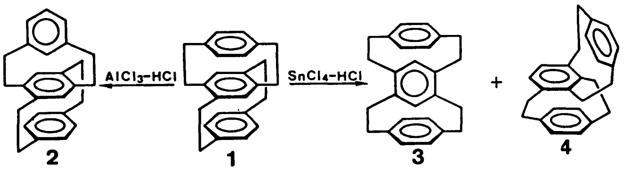
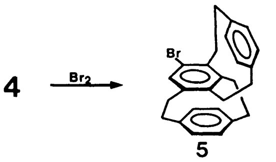
The molecular structure of the title compound has been determined by means of X-ray diffraction. $C_{26}H_{25}Br$, M 417.4, orthorhombic, space group $P2_12_12_1$, a=12.713(1), b=14.998(1), c=10.156(1) Å, V=1936.3(1) Å^3, D_m=1.43 g cm^{-3}, D_c=1.432 g cm^{-3} for Z=4.

Novel skeletal rearrangement of triple-layered [2.2]paracyclophane (**1**) to triple-layered [2.2]metaparacyclophanes (**2—4**) with several Friedel-Crafts acids has been reported by Misumi and coworkers.[1)]

Structures of [2.2]metacyclo(4,7)[2.2]paracyclophane (**2**) and [2.2]paracyclo(4,6)[2.2]metaparacyclophane (**3**) were determined by PMR and alternative syntheses,[2)]





and molecular structures of **2** and **3** have been reported recently.[3)] This paper deals with the molecular structure of **5** which was derived from the third rearranged isomer, [2.2]paracyclo(4,8)[2.2]metaparacyclophane (**4**) in quantitative yield. A preliminary result of the structure has been reported.[1)]

Experimental.

Colorless bipyramidal crystal, recrystallized from benzene-ethyl acetate, with approximate dimensions of 0.5×0.5×0.5 mm was mounted on a Rigaku automated, four-circle diffractometer. Unit cell dimensions and integrated intensities were measured on the diffractometer with Zr-filtered Mo $K\alpha$ radiation (λ=0.71069 Å). Intensity data were collected by the θ—2θ scan technique: The 2θ scan rate was 2° min^{-1}, and the scan width was from $\{2\theta(\alpha_1)-0.9\}$ to $\{2\theta(\alpha_2)+0.9\}°$. Backgrounds were measured for 10 s at both ends of a scan. Five standard reflections were measured after every 50 reflections, which showed no intensity decrease during the experiment. In total, 2833 reflections out of 3416 were observed. Usual Lorentz and polarization corrections were applied but an absorption correction was ignored [μ(Mo $K\alpha$)=23.7 cm^{-1}].

Structure Solution and Refinement

The structure was solved by the heavy atom method, and refined anisotropically by the block-diagonal least-squares procedure (*HBLS* V).[4)] The function minimized was $\sum w(\Delta F)^2$. Hydrogen atoms were located on the calculated positions, which were confirmed on the difference Fourier map. They were refined isotropically. The R value converged to 0.080 for non-zero (0.117 for all) reflections. The weighting schemes used were $w=(F_{\max}/|F_o|)^2$ for $|F_o|\geqq F_{\max}$, w=1 for $|F_o|<F_{\max}$, and w=0.1 for $|F_o|$=0. Atomic parameters are listed in Table 1.[††]

Table 1. Final Atomic Coordinates of Non-Hydrogen Atoms with Equivalent Isotropic Temperature Factors[5)] Estimated Standard Deviations in Parentheses

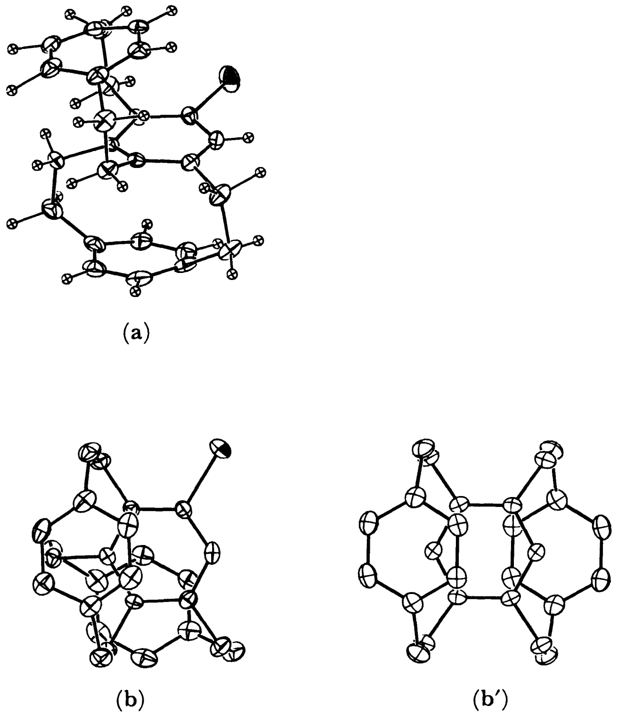
Atom	x	y	z	B_{eq}/Å^2
BR	0.28342(7)	0.46252(7)	0.42830(11)	5.4
C(1)	0.5080(6)	0.4725(5)	0.5654(8)	3.5
C(2)	0.4652(8)	0.5049(6)	0.7041(8)	4.5
C(3)	0.4748(7)	0.6051(6)	0.7129(7)	4.1
C(4)	0.5717(7)	0.6450(6)	0.7329(7)	4.0
C(5)	0.5953(8)	0.7286(6)	0.6794(8)	4.3
C(6)	0.5188(7)	0.7708(5)	0.6027(7)	3.7
C(7)	0.4174(7)	0.7399(6)	0.6076(8)	4.1
C(8)	0.3949(6)	0.6580(6)	0.6622(7)	4.0
C(9)	0.5514(8)	0.8316(5)	0.4902(9)	4.1
C(10)	0.5956(7)	0.7717(5)	0.3744(8)	3.5
C(11)	0.5337(5)	0.6863(4)	0.3598(7)	2.5
C(12)	0.4383(6)	0.6846(5)	0.2867(7)	3.1
C(13)	0.3691(6)	0.6138(6)	0.3043(8)	3.4
C(14)	0.3922(5)	0.5485(5)	0.3943(7)	2.9
C(15)	0.4885(5)	0.5415(5)	0.4571(7)	2.6
C(16)	0.5635(4)	0.6078(4)	0.4280(7)	2.3
C(17)	0.6797(5)	0.5919(5)	0.4611(7)	3.0
C(18)	0.7360(6)	0.5350(6)	0.3540(9)	4.1
C(19)	0.6946(6)	0.5626(6)	0.2199(8)	3.9
C(20)	0.6069(6)	0.5186(5)	0.1676(8)	3.5
C(21)	0.5361(7)	0.5621(5)	0.0866(8)	3.9
C(22)	0.5503(7)	0.6516(5)	0.0590(7)	3.8
C(23)	0.6483(8)	0.6893(6)	0.0854(8)	4.4
C(24)	0.7197(8)	0.6450(6)	0.1653(9)	4.5
C(25)	0.4546(8)	0.7102(6)	0.0358(8)	4.2
C(26)	0.4172(8)	0.7505(5)	0.1736(8)	4.0

[††] 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. 8646.

Atomic scattering factors used were taken from International Tables for X-Ray Crystallography.[6] Calculations 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.

Results and Discussion

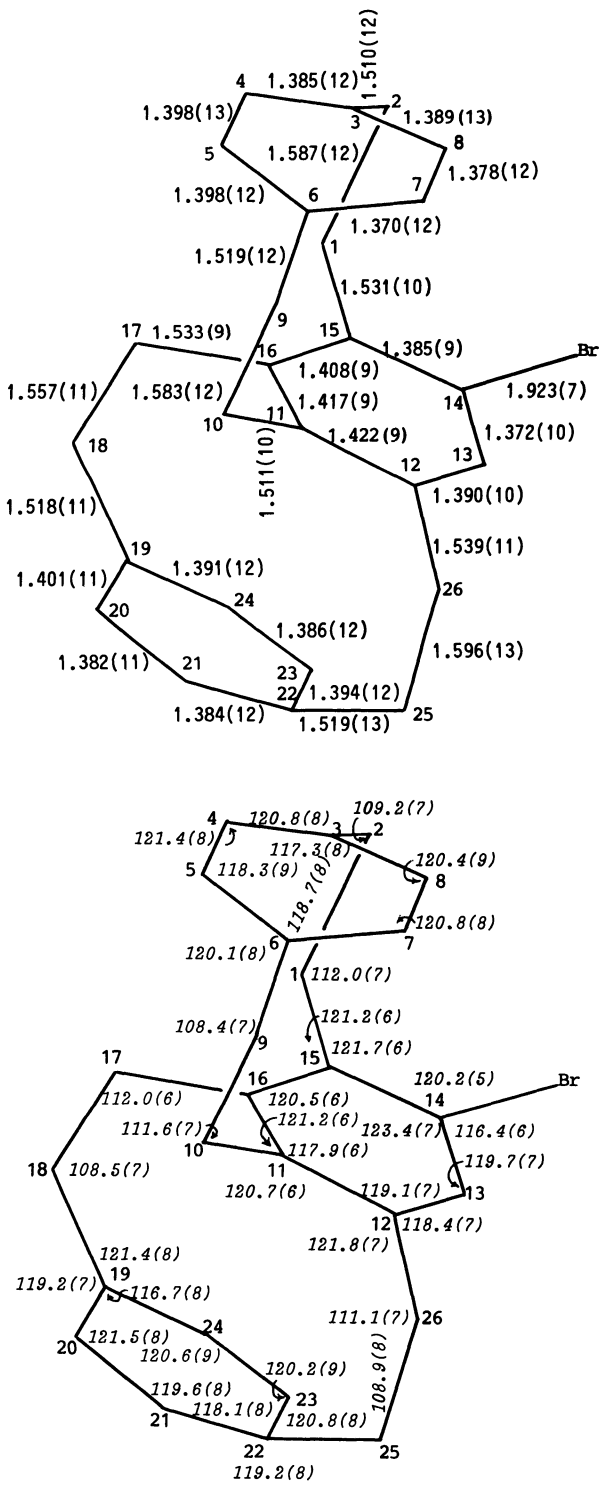
Molecular Structure. Structure of the molecule[7] is shown in Fig. 1. Bond distances and bond angles are given in Fig. 2. Both the upper and lower layer benzene rings are in boat form. The deformation angles[3] p_1 and q_1 at the C(3) atom (Fig. 3) are 11.6 and 16.4°, p_2 and q_2 at the C(6) 12.7 and 14.9°, p_3 and q_3 at the C(19) 11.7 and 16.0°, and p_4 and q_4 at the C(22) 13.6 and 13.7°. These benzene rings have normal bond distances [av. 1.387 and 1.390 Å]. Among the bond angles in these rings, the inner angles at the bow and stern of the boat form show a tendency to have the smaller angles than 120°, though it is not fully significant: C(4)-C(3)-C(8)=117.3(8), C(5)-C(6)-C(7)=118.7(8), C(20)-C(19)-C(24)=116.7(8), and C(21)-C(22)-C(23)=118.1(8)°.


(a)

(b) (b′)

Fig. 1. Molecular structure[7] of 6-bromo[2.2]paracyclo(4,8)[2.2]metaparacyclophane.
Non-hydrogen atoms are expressed by thermal ellipsoids with 30% probability level.
(a): A perspective view, Hydrogen atoms are expressed as spheres with B=1.0 Å^2 (b): Projected onto the plane defined by the C(11), C(12), C(14), and C(15) atoms, Hydrogen atoms are omitted for clarity. (b′): Similar projection as (b) of [2.2]paracyclo(4,6)[2.2]metaparacyclophane.[3]

The central four-bridged benzene ring is twisted. The dihedral angle between the plane made by the C(11), C(12), C(13) atoms and that by the C(14), C(15),



C(2)-C(3)-C(8) 119.2(8), C(14)-C(15)-C(16) 116.6(6)
C(7)-C(6)-C(9) 119.2(8), C(11)-C(16)-C(17) 119.6(6)
C(15)-C(16)-C(17) 119.7(6)

Fig. 2. Bond distances [l/Å] and bond angles [ϕ/°] with estimated standard deviations in parentheses.

and C(16) is 7.3°. The bending angles[3] of q_5 at the C(15) [6.4°] and q_6 at the C(12) [8.2°] are much larger then those of q_7 at the C(11) [4.8°] and q_8 at the C(16) [1.3°]. The Br–C(14) bond makes an angle of 1.3° with the plane formed by the C(13), C(14), and C(15) atoms.

In the four ethylene bridges between the outer and central benzene rings, four central C–C bonds [1.587(12), 1.583(12), 1.557(11), and 1.596(13) Å) can be compared with the corresponding distances in two triple-layered metaparacyclophanes [1.579(4) and 1.572 (4) Å and 1.558(8) and 1.572(6) Å].[3] Torsional angles around the C(1)–C(2) and C(25)–C(26) bonds [32.1 and 32.8°] are equal, which are much smaller than those around the C(9)–C(10) and C(17)–C(18) [38.1 and 38.0°]. It seems that the C(1)–C(2)–C(3), C(6)–C(9)–C(10), C(17)–C(18)–C(19), and C(22)–C(25)–C(26) angles [109.2(7), 108.4(7), 108.5(7), and 108.9(8)°] of the outer ring sides are smaller than the C(2)–C(1)–C(15), C(9)–C(10)–C(11), C(16)–C(17)–C(18), and C(12)–C(26)–C(25) [112.0(7), 111.6(7), 112.0(6), and 111.1(7)°, respectively]. The overlapping of three benzene rings (Fig. 1(b)) is larger than that of [2.2]paracyclo-(4,6)[2.2]metaparacyclophane (Fig. 1(b')).[3] The shortest atomic contact between the upper and central benzene rings is C(3)···C(15) [2.773(10) Å] and that between the lower and central rings is C(12)···C(22) [2.760(11) Å].

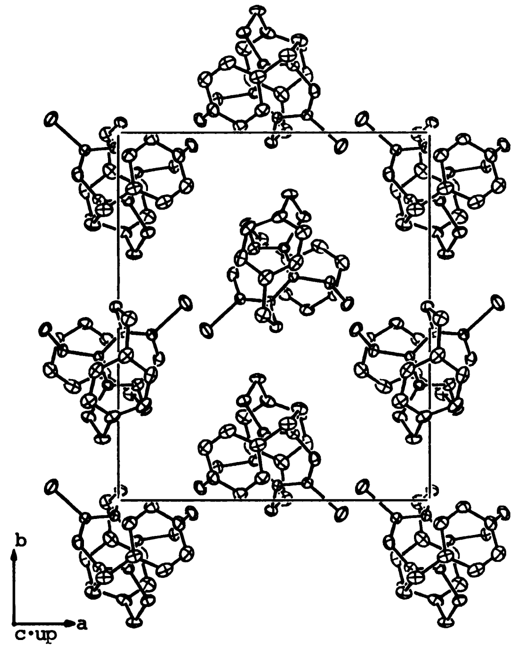


Fig. 4. Crystal structure projected along the *c* axis.[7] Non-hydrogen atoms are expressed as thermal ellipsoids with 30% probability level. Hydrogen atoms are omitted for clarity.

Crystal Structure. The packing mode of molecules in the crystal is drawn in Fig. 4. Molecules are packed rather loosely in the a and b directions, whereas very closely in the c direction: Shortest intermolecular atomic contacts are C(4)····C(22)(x, y, $1+z$)=3.325(12) and C(4)····C(25)(x, y, $1+z$)=3.555(13) Å.

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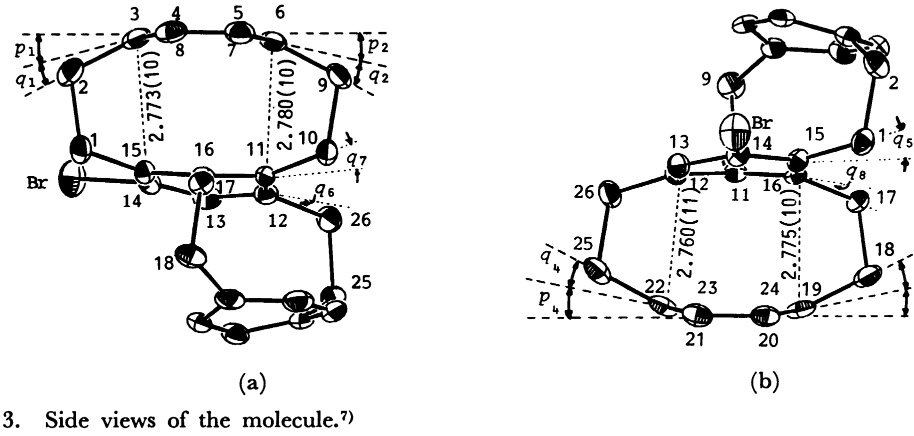
References

1) H. Horita, Y. Koizumi, T. Otsubo, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **51**, 2668 (1978).

2) N. Kannen, T. Otsubo, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **49**, 3307 (1976).

3) Y. Koizumi, T. Toyoda, N. Kasai, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **58**, 3158 (1985).

4) T. Ashida, *HBLS* V, "The Universal Crystallographic Computing System-Osaka," The Computation Center,



(a) (b)

Fig. 3. Side views of the molecule.[7]
Non-hydrogen atoms are expressed as thermal ellipsoids with 30% probability level. Hydrogen atoms are omitted for clarity.
(a): Projected along the C(4)···C(8) and parallel to the plane defined by the C(5), C(6), C(7), and C(8) atoms (b): Projected along the C(20)···C(24) and parallel to the plane defined by the C(20), C(21), C(23), and C(24) atoms.

Osaka Univ. (1978), p. 55.
5) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).
6) International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, Vol. IV (1974), p. 71.
7) C. K. Johnson, *ORTEP* II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, 1976.