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The Crystal and Molecular Structure of Two Triple-layered Metaparacyclophanes

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Molecular structures of triple-layered metaparacyclophanes containing two and one para-bridged, outside benzene rings([2.2]paracyclo(4,6)[2.2]metaparacyclophane (PMP) and [2.2]metacyclo(4,6)[2.2]metaparacyclophane (MMP), respectively) have been determined by means of X-ray diffraction. PMP: monoclinic, space group $P2_1/a$, a=15.989(1), b=9.932(1), c=5.991(1) Å, β=100.61(1)°, Z=2. MMP: monoclinic, space group $P2_1/c$, a=8.969(2), b=22.774(4), c=10.339(2) Å, β=119.32(1)°, Z=4. The structure of PMP was solved by the vector search method and that of MMP by the direct method. They are refined anisotropically by the least-squares procedure, final R values are 0.066 for PMP and 0.096 for MMP. Of the two possible conformers PMP has a centrosymmetric staircase structure(anti-form) whereas MMP takes a platform shape(syn-form).

Previously, a variety of triple-layered metaparacyclophanes has been synthesized by desulfurization of the corresponding dithiacyclophanes.1) There have been discussed the assignment of their structures in detail and the conformational flipping of the meta-bridged benzene ring at the high temperature based on the NMR studies, and also the transannular electronic interactions between benzene rings.2) In this paper, the crystal structure analysis of triple-layered metaparacyclophanes containing two and one para-bridged, outside benzene rings(PMP and MMP, respectively) is reported. A brief account of these metaparacyclophane structures has been given to prove the assigned structure in NMR studies.2)

Experimental

Crystal Data. PMP. $C_{26}H_{26}$, M 338.5, monoclinic, space group $P2_1/a$(No. 14, absent reflections, $h0l$: $h=2n+1$, $0k0$: $k=2n+1$), a=15.989(1), b=9.932(1), c=5.991(1) Å, β=100.61(1)°, V=935.14(6) Å^3, D_m=1.20 g cm^{-3}, D_c=1.202 g cm^{-3} for Z=2. MMP. $C_{26}H_{26}$, M 338.5, monoclinic, space group $P2_1/c$(No. 14, absent reflections, $h0l$: $l=2n+1$, $0k0$: $k=2n+1$), a=8.969(2), b=22.774(4), c=10.339(2) Å, β=119.32(1)°, V=1841.2 Å^3, D_m=1.23 g cm^{-3}, D_c=1.221 g cm^{-3} for Z=4.

Both crystals were recrystallized from toluene. A colorless, platelet crystal of PMP with approximate dimensions of 0.3×0.4×0.4 mm and a colorless, hexagonal crystal of MMP with 0.4×0.2×0.4 mm were selected for the X-ray experiment. A Rigaku automated, four-circle diffractometer was used for the determination of unit-cell dimensions and the measurement of integrated intensities.

Intensity data were collected by the θ—2θ scan technique at a 2θ rate of 4° min^{-1}. The scan range for PMP was from $\{2\theta(\alpha_1)-1.0\}°$ to $\{2\theta(\alpha_2)+1.0\}°$ for Zr-filtered Mo $K\alpha$ radiation and that for MMP from $\{2\theta(\alpha_1)-0.8\}°$ to $\{2\theta(\alpha_2)+0.8\}°$ for graphite monochromatized Mo $K\alpha$ radiation (λ=0.71069 Å). Backgrounds were counted for 10 s at both ends of a scan. Five standard reflections measured after every 50 reflections to monitor the stability and orientation of the crystals showed no significant decay throughout the data collection of both crystals. In total, 1864 non-zero reflections out of 2908 and 3152 out of 4499 were obtained for PMP and MMP, respectively($\sin\theta/\lambda<0.7$). Usual Lorentz and polarization corrections were made but absorption correction was ignored for both sets of data [μ(Mo)=0.72 cm^{-1} for PMP and MMP].

Structure Solution and Refinement

PMP. In order to obtain a clue to solve the structure, the benzene ring which is a main component of the molecule has been assumed as a rigid body, and the central benzene ring of the PMP molecule could be found by the vector search method(*XRICS*).3) Successive Fourier synthesis phased by the six carbon atoms of the benzene ring could locate the remaining carbon atoms. The structure was refined anisotropically by the block-diagonal least-squares procedure(*HBLS* V).4) The function minimized was $\sum w(\Delta F)^2$, where w=1. Hydrogen atoms were located on a difference Fourier map, which were included in the refinement with isotropic temperature factors. The R value converged to 0.066 for 1864 non-zero reflections. Final atomic parameters of carbon atoms are listed in Table 1a.††

MMP. The structure was solved by the direct method (*MULTAN*),6) and refined by using the *HBLS* V program with anisotropic temperature factors and unit weight for all reflections. Hydrogen atoms were located on the calculated positions, which were confirmed on a difference Fourier map. They were refined isotropically. The final R value was 0.096 for 3152 non-zero reflections. Atomic parameters are given in Table 1b.††

Atomic scattering factors were taken from International Tables for X-Ray Crystallography.7) Computations were done mainly on a NEAC 2200-500

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†† Tables of anisotropic temperature factors, atomic parameters of hydrogen atoms, and observed and calculated structure factors are kept at the Chemical Society of Japan, Document No. 8550.

Table 1. Atomic parameters of carbon atoms in PMP and MMP with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq}/Å^2 [5]
a. PMP				
C(1)	−0.2531 (5)	0.2142 (3)	0.0661 (2)	3.6
C(2)	−0.1772 (6)	0.3508 (3)	0.0291 (3)	4.3
C(3)	−0.1415 (5)	0.3264 (3)	−0.0608 (2)	3.6
C(4)	−0.3244 (5)	0.3092 (3)	−0.1277 (2)	3.9
C(5)	−0.3073 (5)	0.2227 (4)	−0.1946 (2)	4.0
C(6)	−0.1051 (5)	0.1528 (3)	−0.1957 (2)	3.6
C(7)	0.0893 (5)	0.1961 (3)	−0.1402 (2)	3.6
C(8)	0.0718 (5)	0.2825 (3)	−0.0735 (2)	3.5
C(9)	−0.1069 (6)	0.0138 (4)	−0.2343 (2)	4.3
C(10)	−0.1901 (5)	−0.0898 (3)	−0.1723 (2)	3.7
C(11)	−0.0939 (5)	−0.0568 (3)	−0.0798 (2)	2.7
C(12)	−0.2143 (4)	0.0328 (3)	−0.0379 (2)	2.6
C(13)	−0.1247 (4)	0.0946 (3)	0.0391 (2)	2.7
b. MMP				
Atom	x	y	z	B_{eq}/Å^2
C(1)	1.0441 (6)	0.1437 (3)	0.5876 (5)	3.8
C(2)	1.0340 (6)	0.0749 (3)	0.5856 (5)	4.1
C(3)	0.9087 (6)	0.0537 (2)	0.6334 (5)	3.7
C(4)	0.9589 (7)	0.0451 (3)	0.7828 (6)	4.4
C(5)	0.8358 (8)	0.0420 (3)	0.8278 (6)	5.0
C(6)	0.6648 (7)	0.0523 (3)	0.7285 (6)	4.2
C(7)	0.6120 (6)	0.0607 (2)	0.5789 (5)	3.5
C(8)	0.7342 (6)	0.0566 (2)	0.5334 (5)	3.5
C(9)	0.4402 (6)	0.0871 (3)	0.4756 (6)	4.0
C(10)	0.4503 (6)	0.1554 (2)	0.4780 (5)	3.7
C(11)	0.5740 (6)	0.1782 (2)	0.4296 (5)	3.0
C(12)	0.7485 (6)	0.1727 (2)	0.5292 (5)	3.0
C(13)	0.8743 (5)	0.1727 (2)	0.4857 (5)	3.1
C(14)	0.8269 (5)	0.1941 (2)	0.3438 (5)	3.0
C(15)	0.6576 (6)	0.2122 (2)	0.2556 (5)	3.1
C(16)	0.5270 (5)	0.1991 (2)	0.2870 (5)	3.0
C(17)	0.3407 (6)	0.2053 (2)	0.1600 (5)	3.7
C(18)	0.2697 (6)	0.1503 (3)	0.0555 (5)	4.1
C(19)	0.4080 (6)	0.1263 (3)	0.0266 (5)	3.9
C(20)	0.4631 (7)	0.1586 (3)	−0.0578 (5)	4.2
C(21)	0.6329 (7)	0.1550 (3)	−0.0247 (5)	4.4
C(22)	0.7491 (6)	0.1206 (3)	0.0928 (5)	4.0
C(23)	0.6803 (7)	0.0785 (3)	0.1465 (6)	4.2
C(24)	0.5123 (7)	0.0814 (3)	0.1141 (5)	4.1
C(25)	0.9339 (6)	0.1389 (3)	0.1844 (6)	4.5
C(26)	0.9443 (6)	0.1950 (3)	0.2748 (6)	4.1

computer at the Computation Center, Osaka University and at the final stage an ACOS 850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University was used.

Results and Discussion

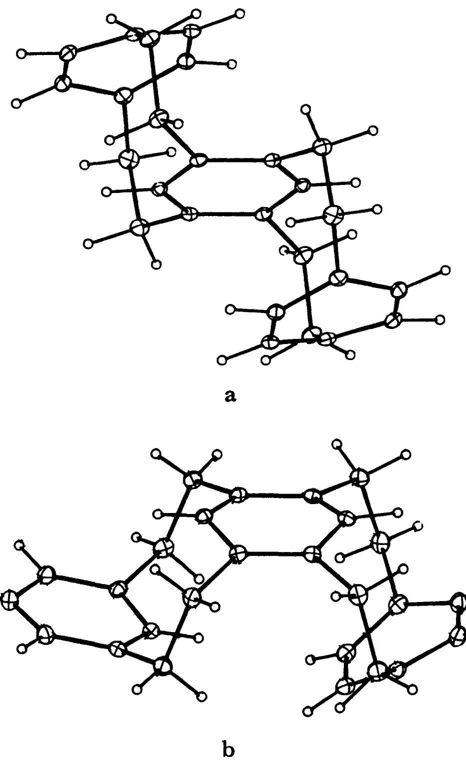


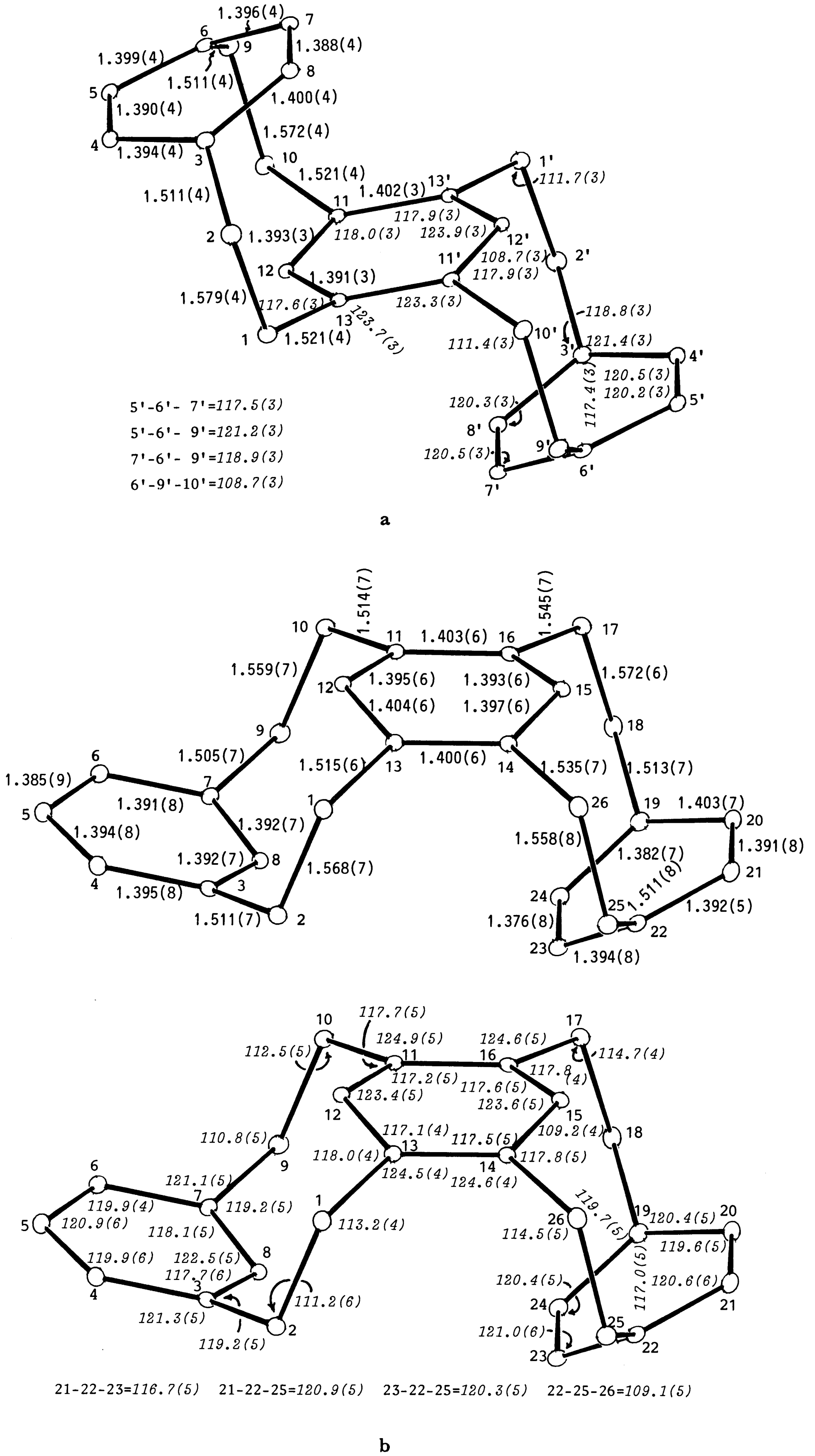
Fig. 1. A perspective view[8] of PMP (a) and MMP (b) molecules. Carbon atoms are represented by thermal ellipsoids with 10% probability level, hydrogen atoms as spheres with $B = 1.0$ Å^2.

Molecular Structure. *PMP.* The molecule has a centrosymmetric staircase structure, which is depicted in Fig. 1a(*ORTEP*).[8] Bond distances and bond angles are given in Fig. 2a.

The outside para-bridged benzene ring is in a boat form as is found usually, the deformation angle p_1 at the C(3) atom(the dihedral angle between the plane defined by the C(4), C(5), C(7), and C(8) (Plane 1) and that by the C(3), C(4), and C(8) (Plane 2)) is 13.6° and that at the C(6), p_2 is 12.8°. The angle q_1 at the C(3) atom made by the C(2)–C(3) bond and the plane 2 is 15.4° and the corresponding angle q_2 at the C(6) is 15.2°, which are much larger than those in [2.2]paracyclophane.[9] The inner angles, C(4)–C(3)–C(8) and C(5)–C(6)–C(7) [117.4(3) and 117.5(3)°, respectively] in the benzene ring are smaller than 120°.

The center of the inside four-bridged benzene ring lies on a crystallographic center of symmetry, and this ring takes a chairform (Fig. 3a). The bending angle at the C(12) atom is 4.3°. The C(11)–C(12)–C(13) and C(11′)–C(12′)–C(13′) angles [both 123.9(3)°] are larger, and the other four angles [117.9(3) and 118.0(3)°] are smaller, than 120°.

In the ethylene bridges between the inside and outside benzene rings, the central C$_{sp^3}$–C$_{sp^3}$ bonds are equal in length [1.579(4) and 1.572(4) Å]. Different from the corresponding angles in [2.2]paracyclophane and those of related compounds, the C(1)–C(2)–C(3) and C(6)–C(9)–C(10) angles[both 108.7(3)°] are smaller than the C(2)–C(1)–C(13) and C(9)–



5'-6'- 7'=117.5(3)
5'-6'- 9'=121.2(3)
7'-6'- 9'=118.9(3)
6'-9'-10'=108.7(3)

21-22-23=116.7(5) 21-22-25=120.9(5) 23-22-25=120.3(5) 22-25-26=109.1(5)

Fig. 2. Bond distances and bond angles in PMP (a) and MMP (b). Estimated standard deviations in parentheses.

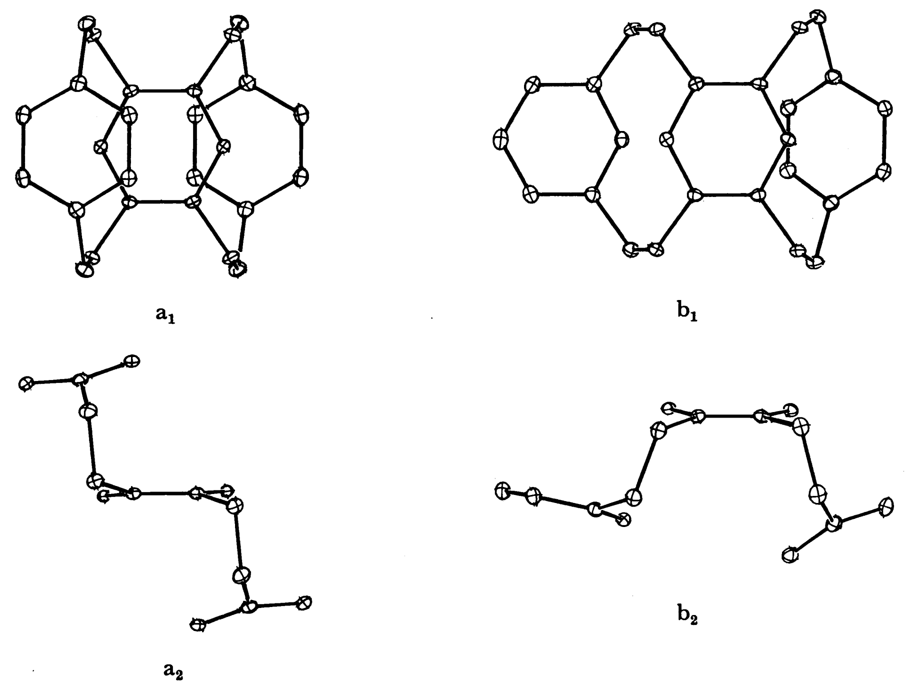

a_1 b_1 a_2 b_2

Fig. 3. Projections of molecules.
a_1: PMP molecule projected onto the plane defined by the C(11), C(13), C(11′), and C(13′) atoms.
a_2: PMP molecule projected along the vector passing through the midpoints of the C(11)–C(13′) and C(11′)–C(13) bonds.
b_1: MMP molecule projected onto the plane defined by the C(11), C(13), C(14), and C(16) atoms.
b_2: MMP molecule projected along the vector passing through the midpoints of the C(13)–C(14) and C(11)–C(16) bonds.

C(10)–C(11) angles [111.7(3) and 111.4(3)°, respectively]. This fact is one of the features of [2.2]metaparacyclophane and the similar compounds.

The overlapping of three benzene rings is small: Between the outside and inside benzene rings the Plane 1 and the plane defined by the C(11), C(13), C(11′), and C(13′) atoms makes an angle of 11.6°. Short nonbonded distances between atoms in the outside and inside benzene rings are given in Table 2, the closest distance, C(6)⋯C(11), is 2.780(4) Å.

MMP. A perspective view(*ORTEP*) of the molecule is drawn in Fig. 1b. The molecule has a platform shape(syn-form). Bond distances and bond angles are given in Fig. 2b. The projection of the molecule onto the least-squares plane of the C(11), C(13), C(14), and C(16) atoms and that along the vector passing through the midpoints of the C(13)–C(14) and C(11)–C(16) bonds are presented in Fig. 3b.

The outside meta-bridged benzene ring takes a boatform, the deformation angle p_1 at the C(5) atom is 4.9° and p_2 at the C(8) 9.2°. The C(4)–C(3)–C(8) [117.7(6)°] and C(6)–C(7)–C(8)[118.1(5)°] angles are smaller than 120°.

The central four-bridged benzene ring is also in a boatform, the deformation angle at the C(12) atom[14.8°] is larger than that at the C(15)[12.6°].

TABLE 2. SHORT NONBONDED DISTANCES LESS THAN 3.6 Å BETWEEN CARBON ATOMS IN BENZENE RINGS (l/Å) ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

PMP		MMP	
C(5)⋯C(11)	3.442(4)	C(7)⋯C(11)	3.024(7)
C(6)⋯C(11)	2.780(4)	C(8)⋯C(11)	3.061(7)
C(7)⋯C(11)	2.974(4)	C(3)⋯C(12)	3.010(7)
C(8)⋯C(11)	3.510(4)	C(7)⋯C(12)	2.982(7)
C(3)⋯C(12)	2.981(4)	C(8)⋯C(12)	2.649(7)
C(4)⋯C(12)	3.111(4)	C(3)⋯C(13)	3.051(7)
C(5)⋯C(12)	3.103(4)	C(8)⋯C(13)	3.068(7)
C(6)⋯C(12)	2.970(4)	C(14)⋯C(21)	3.441(7)
C(7)⋯C(12)	3.117(4)	C(14)⋯C(22)	2.871(7)
C(8)⋯C(12)	3.126(4)	C(14)⋯C(23)	3.193(7)
C(3)⋯C(13)	2.793(4)	C(15)⋯C(19)	3.042(7)
C(4)⋯C(13)	3.451(4)	C(15)⋯C(20)	3.081(7)
C(7)⋯C(13)	3.497(4)	C(15)⋯C(21)	3.084(7)
C(8)⋯C(13)	2.982(4)	C(15)⋯C(22)	3.034(7)
		C(15)⋯C(23)	3.288(7)
		C(15)⋯C(24)	3.292(7)
		C(16)⋯C(19)	2.885(7)
		C(16)⋯C(20)	3.447(7)
		C(16)⋯C(24)	3.188(7)

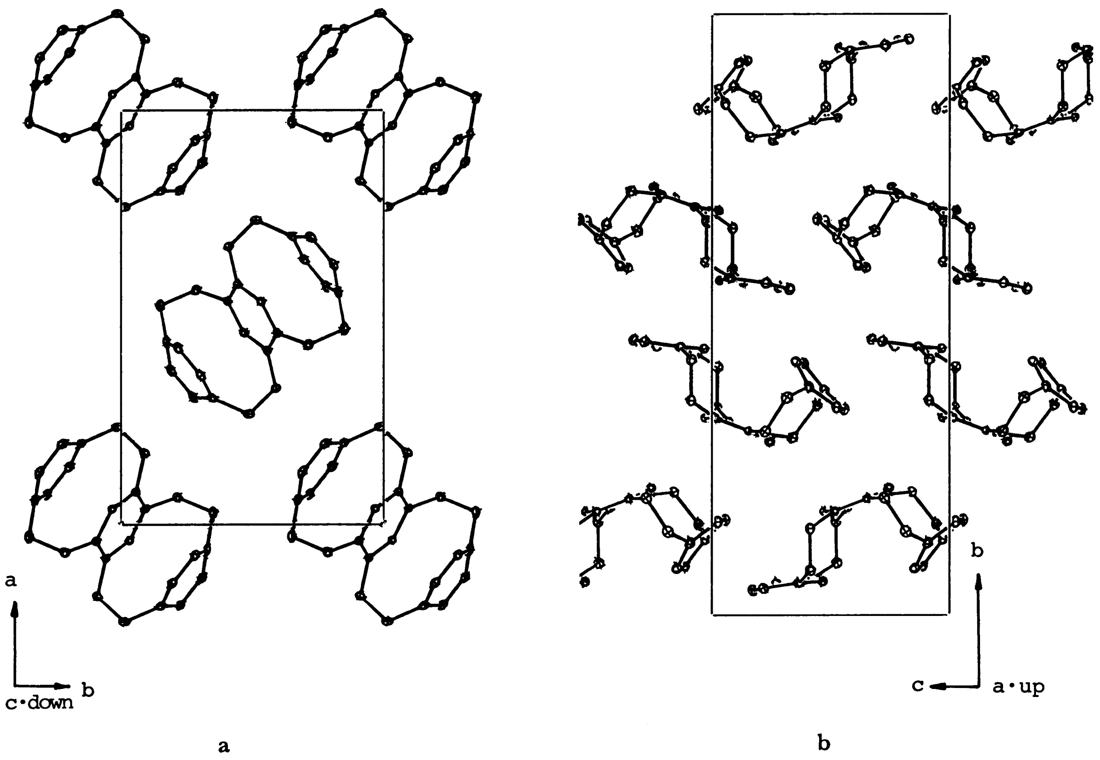


Fig. 4. Crystal structure[8] of PMP (a) and MMP (b) projected along an axis of the unit-cell. Carbon atoms are drawn as thermal ellipsoids with an arbitrary probability level.

The C(11)-C(12)-C(13) and C(14)-C(15)-C(16) angles are 123.4(5) and 123.6(5)°, respectively (Fig. 2b), which are larger than 120°. The other four inner angles [117.1(4) to 117.5(5)°] are smaller than 120°.

As a whole, the structure of the [2.2]metacyclophane moiety, consisting of the meta-bridged benzene and central benzene rings mentioned above and two ethylene bridges (Fig. 3b), is very similar to that of the two-third of the triple-layered metacyclophane-(*ud* isomer).[10,11] The closest intramolecular atomic contact is C(8)···C(12)[2.649(7) Å] (Table 2).

The third para-bridged benzene ring is also in a boatform. The deformation angles p_1 and q_1 at the C(19) atom are 13.9 and 14.9°, respectively, and those at the C(22) are p_2=14.8° and q_2=14.4°. These values of q's are larger than the corresponding angles in [2.2]paracyclophane.

Ethylene bridges in the [2.2]metaparacyclophane moiety, *i.e.* those between the central and third para-bridged benzene rings, have similar structure to those in the [2.2]metaparacyclophane moiety in PMP but slightly different structure from those in [2.2]paracyclophane moiety. The C(14)-C(26)[1.535(7) Å] and C(16)-C(17)[1.545(7) Å] bonds are longer, and the C(14)-C(26)-C(25)[114.5(5)°] and C(16)-C(17)-C(18) [114.7(4)°] angles are larger than the corresponding bond distances and bond angles in many [2.2]paracyclophanes, respectively. The torsion angles around the C(17)-C(18) and C(25)-C(26) bonds are equal[40.6 and 42.9°, respectively] but they are smaller than those around the C(1)-C(2)[59.8°] and C(9)-C(10) bonds[60.5°] in the [2.2]metacyclophane moiety of the present molecule.

The overlapping of the central and third para-bridged benzene rings are small. These two rings make an angle of 27.4°, which is much larger than the corresponding angle in the PMP molecule. Short nonbonded interatomic distances in the [2.2]metaparacyclophane moiety are C(14)···C(22) [2.871(7) Å] and C(16)···C(19)[2.885(7) Å].

Crystal Structure. The packing of PMP and MMP molecules in the crystal is shown in Fig. 4. In these two crystals molecules are packed rather loosely, and no short intermolecular contact less than 3.6 Å is found between non-hydrogen atoms.

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