References

BERGMAN, G. & SHOEMAKER, D. P. (1954). *Acta Cryst.* 7, 857–865.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* 53, 1891–1898.

FRANK, F. C. & KASPER, J. S. (1959). *Acta Cryst.* 12, 483–499.

GUPTA, K. P. (1964). *Trans. AIME*, 230, 253–254.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.

KOMURA, Y., SLY, W. G. & SHOEMAKER, D. P. (1960). *Acta Cryst.* 13, 575–585.

KRIPYAKEVICH, P. I. & YARMOLYUK, YA. P. (1971). *Dopov. Akad. Nauk. Ukr. RSR*, A33, 460–463.

MANOR, P. C., SHOEMAKER, C. B. & SHOEMAKER, D. P. (1972). *Acta Cryst.* B28, 1211–1218.

SHOEMAKER, C. B. & SHOEMAKER, D. P. (1963). *Acta Cryst.* 16, 997–1009.

SHOEMAKER, C. B. & SHOEMAKER, D. P. (1969). *Developments in the Structural Chemistry of Alloy Phases*, edited by B. C. GIESSEN, pp. 107–139. New York: Plenum.

SHOEMAKER, C. B. & SHOEMAKER, D. P. (1971a). *Acta Cryst.* B27, 227–235.

SHOEMAKER, C. B. & SHOEMAKER, D. P. (1971b). *Mh. Chem.* 102, 1643–1666.

SHOEMAKER, C. B. & SHOEMAKER, D. P. (1976). *Acta Cryst.* B32, 2306–2313.

ZACHARIASEN, W. H. (1963). *Acta Cryst.* 16, 1139–1144.

Structural Chemistry of Layered Cyclophanes.
I. Molecular Structure of a Triple-Layered [2.2]Metacyclophane (*ud* Isomer) and of a [2.2]Metacyclophane Redetermined at −160°C

BY YASUSHI KAI, NORITAKE YASUOKA AND NOBUTAMI KASAI

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565, Japan

The molecular structure of one of the two geometrical isomers of triple-layered [2.2]metacyclophane was determined from three-dimensional X-ray data collected on a four-circle diffractometer. The *ud* isomer crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell; $a = 11.659$ (1), $b = 11.715$ (1), $c = 14.678$ (1) Å and $\beta = 107.69$ (1)°. The structure was solved by the direct method and refined by block-diagonal least squares to an R of 0.048 for 2569 observed reflexions. The mean length of the methylene bridges is 1.565 Å. The bond distance between the bridging C and central benzene is 1.515 Å, which is significantly longer than that between the bridging C and terminal benzene, 1.506 Å. The molecular structure of [2.2]metacyclophane was redetermined from the X-ray data at −160°C to obtain standard data of high accuracy for the cyclophane compounds. The final R value was 0.050 for 2287 observed reflexions and the e.s.d.'s were $\sigma(C–C) = 0.001$ Å, $\sigma(C–C–C) = 0.1°$. The bond distance between the bridging C atoms is 1.568 Å. A comparison of these compounds shows an interesting addition effect of the two terminal benzene rings on the out-of-plane deformation of the central benzene ring.

Introduction

Layered cyclophanes are compounds which are expected to have highly strained molecular structures and specific physical properties. The structural chemistry of double-layered cyclophanes has been actively studied so far, but only a few structural studies have been reported for the multilayered cyclophanes. As the multilayered cyclophanes are supposed to have more constrained structures than those of double-layered cyclophanes, the determination of their molecular structures will reveal more remarkable physical properties than those found in their constituent double-layered cyclophanes.

Triple-layered [2.2]metacyclophanes have been synthesized by Umemoto, Otsubo & Misumi (1974). Two geometrical isomers were postulated from the nuclear Overhauser effect in PMR spectra. To distinguish these isomers, the symbols *ud* (*u* = up, *d* = down) and *uu* were given to the zigzag and stair-like isomers respectively. Easy thermal isomerization of the *uu* isomer to *ud* was observed by PMR investigations in toluene-d_8

at 100°C in contrast to the difficult conformational flapping of [2.2]metacyclophane (Sato, Akabori, Kainosho & Hata, 1968). Triple-layered [2.2]meta-cyclophanes are interesting compounds from the following points of view: (1) the central benzene ring must have a somewhat different structure from that of the terminal benzene rings, (2) the bulky substituent R may cause an asymmetrical deformation in the central benzene ring and (3) in the *ud* isomer, non-bonded atomic repulsion is expected between the two terminal benzene rings. As part of a study of cyclophane compounds the structure determination of triple-layered [2.2]metacyclophanes (I and II) and their methylated derivatives (III and IV) has been carried out. In this paper the molecular and crystal structure of I will be described.

ud isomer
(I) R =H
(III) R = CH$_3$

uu isomer
(II) R = H
(IV) R = CH$_3$
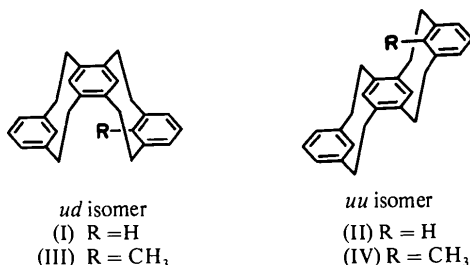
[2.2]Metacyclophane is the standard compound in the study of the structural chemistry of cyclophanes. The crystal structure of V was determined by Brown (1953b), just after his pioneer work on [2.2]paracyclophane (Brown, 1953a). The molecular structure reported was, however, limited in precision because of the rather low quality of experimental data and computational facilities available at that time. Recently, we have redetermined the molecular structure of V from X-ray data obtained at −160°C. The molecular and crystal structure of V will also be described in this paper and compared with that of I.

(V)
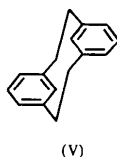
Experimental

Triple-layered [2.2]metacyclophane (I)

Crystals of I are colourless short prisms and are stable in air. The unit-cell dimensions were determined by the least-squares treatment of 23 2θ values [λ(Cu $K\alpha_1$) = 1·54051 Å] of high-angle reflexions (100° < 2θ < 120°) obtained on a Rigaku automated four-circle single-crystal diffractometer (AFC) at 20 ± 2 °C. The crystal density was measured by the flotation method in an aqueous solution of zinc bromide. The space group

was uniquely determined by the systematic absences of reflexions (*h0l* for *l* odd and 0*k*0 for *k* odd). The crystal data are listed in Table 1.

The intensity data were measured on a Rigaku AFC diffractometer with Cu $K\alpha$ (λ = 1·5418 Å) radiation and a graphite monochromator. The size of the crystal used was 0·2 × 0·2 × 0·25 mm. The integrated intensity of each reflexion was measured by a θ–2θ scan through the range $\Delta\theta$ = (1·0 + 0·15 tan θ_c)°, where θ_c was the calculated Bragg angle for λ(Cu $K\alpha_1$). The scan speed was 2·0° min^{-1} in 2θ, and backgrounds were counted for 10 s at both ends of the scan. The scans were repeated up to three times when the structure factor magnitude F was less than 3$\sigma(F)$, where $\sigma(F)$ was the standard deviation estimated from the counting statistics. In the repeated scans the counting time of the background was optimized to give the lowest $\sigma(F)$. 2847 independent reflexions were measured within a sphere of sin θ/λ = 0·562 (2θ ≤ 120°), among which 2569 were above background. Intensity data were corrected for Lorentz and polarization effects but not for absorption.

[2.2]Metacyclophane (V)

[2.2]Metacyclophane crystals are colourless and of short prismatic shape. The unit-cell dimensions were determined at both low and room temperatures by the least-squares method. At −160°C, the 2θ values [λ(Mo $K\alpha_1$) = 0·70926 Å] of 25 high-angle reflexions (59° <

Table 1. *Crystal data of triple-layered* [2.2]*metacyclophane* (*ud isomer*)

Monoclinic	C$_{26}$H$_{26}$
Space group $P2_1/c$	F.W. 338·5
a = 11·659(1) Å	Z = 4
b = 11·715(1)	D_x = 1·177 g cm^{-3}
c = 14·678(1)	D_m = 1·176
β = 107·69(1)°	$F(000)$ = 728
U = 1909·9(2) Å^3	μ(Cu $K\alpha$) = 5·03 cm^{-1}

Table 2. *Crystal data of* [2.2]*metacyclophane*

Monoclinic		C$_{16}$H$_{16}$	
Space group $P2_1/c$		F.W. 208·1	
$F(000)$ = 224		μ(Mo$K\alpha$) = 0·71 cm^{-1}	
	−160°C		20°C
a	5·838(1) Å		5·842(1) Å
b	8·179(2)		8·243(2)
c	11·959(2)		12·174(2)
β	93·72(1)°		94·55(2)°
U	569·8(2) Å^3		584·5(2) Å^3
Z	2		2
D_x	1·213 g cm^{-3}		1·182 g cm^{-3}
D_m			1·178*

* Brown (1953b).

$2\theta < 70°$) were measured. At room temperature, however, these high-angle reflexions did not give sufficient intensity, so another set of 25 reflexions with Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) was measured and used in the least-squares treatment. The crystal data are listed in Table 2.

The intensity data were collected on a Rigaku AFC diffractometer with Mo $K\alpha$ radiation and a graphite monochromator. A rather large crystal, 0·3 × 0·3 × 0·35 mm, was chosen in order to obtain enough measurable intensity. During the experiment the temperature of the crystal was kept constant at −160 ± 0·5 °C by Rigaku low-temperature equipment with the liquid-nitrogen gas-flow method. The scan mode was θ–2θ, and the scan range was $\Delta\theta = (1.0 + 0.35 \tan \theta_c)°$. Other experimental conditions were the same as for I. 2525 independent reflexions were measured within a sphere of $\sin\theta/\lambda = 0.807$ ($2\theta \leq 70°$) among which 2287 were greater than $3\sigma(F)$. No absorption correction was made.

Structure determination and refinement

Triple-layered [2.2]*metacyclophane*

The structure was solved by a local version of *MULTAN* (Germain, Main & Woolfson, 1971) from

Table 4. *Fractional atomic coordinates* (×10³) *and isotropic thermal parameters* (Å²) *of the hydrogen atoms* (I)

The numbering follows that of the carbon atoms to which the hydrogen atoms are attached.

	x	y	z	B
H(1A)	916 (2)	−55 (2)	434 (2)	2·1 (4)
H(1B)	849 (2)	59 (2)	454 (1)	2·9 (4)
H(2A)	727 (2)	−131 (2)	338 (1)	2·4 (4)
H(2B)	730 (2)	−110 (2)	448 (1)	2·6 (4)
H(4)	592 (2)	30 (2)	486 (1)	2·8 (4)
H(5)	451 (2)	187 (2)	435 (2)	3·9 (5)
H(6)	417 (2)	268 (2)	277 (2)	5·0 (6)
H(8)	620 (2)	7 (2)	210 (1)	2·4 (4)
H(9A)	517 (2)	145 (2)	87 (1)	3·2 (5)
H(9B)	455 (2)	262 (2)	121 (1)	3·4 (5)
H(10A)	641 (2)	319 (2)	103 (1)	3·1 (5)
H(10B)	650 (2)	331 (2)	219 (2)	3·7 (5)
H(12)	757 (2)	197 (2)	333 (1)	2·0 (4)
H(15)	936 (2)	31 (2)	118 (1)	2·0 (4)
H(17A)	715 (2)	241 (2)	3 (1)	3·5 (5)
H(17B)	835 (2)	168 (2)	−6 (1)	3·6 (5)
H(18A)	596 (2)	63 (2)	−11 (1)	2·9 (4)
H(18B)	644 (2)	87 (2)	−106 (2)	4·4 (5)
H(20)	800 (2)	−40 (2)	−139 (2)	4·5 (5)
H(21)	941 (2)	−198 (2)	−87 (2)	3·7 (5)
H(22)	981 (2)	−276 (2)	71 (1)	3·6 (5)
H(24)	700 (2)	−81 (2)	110 (1)	2·8 (4)
H(25A)	813 (2)	−212 (2)	235 (1)	2·5 (4)
H(25B)	932 (2)	−282 (2)	222 (1)	3·4 (5)
H(26A)	1002 (2)	−130 (2)	335 (1)	3·1 (5)
H(26B)	1043 (2)	−106 (2)	239 (1)	3·5 (5)

Table 3. *Fractional atomic coordinates and anisotropic thermal parameters* (×10⁴) *of the non-hydrogen atoms* (I)

Anisotropic thermal parameters are expressed in the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. The estimated standard deviations, given in parentheses, refer to the last significant figures.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	8480 (2)	−8 (2)	4049 (1)	78 (2)	81 (2)	44 (1)	−2 (3)	17 (2)	4 (2)
C(2)	7286 (2)	−704 (2)	3874 (1)	85 (2)	73 (2)	53 (2)	−14 (3)	35 (2)	15 (2)
C(3)	6202 (2)	61 (2)	3530 (1)	74 (2)	68 (2)	53 (1)	−23 (3)	36 (2)	−12 (2)
C(4)	5694 (2)	573 (2)	4166 (1)	89 (2)	94 (2)	54 (1)	−22 (3)	50 (2)	−5 (2)
C(5)	4895 (2)	1480 (2)	3877 (2)	101 (2)	114 (2)	68 (1)	18 (4)	73 (3)	−13 (3)
C(6)	4683 (2)	1942 (2)	2971 (2)	88 (2)	105 (2)	68 (1)	38 (3)	51 (3)	−6 (3)
C(7)	5177 (2)	1438 (2)	2316 (1)	70 (2)	94 (2)	53 (1)	16 (3)	26 (2)	−1 (2)
C(8)	5847 (2)	437 (2)	2590 (1)	70 (2)	77 (2)	50 (1)	−10 (3)	28 (2)	−14 (2)
C(9)	5233 (2)	2054 (2)	1430 (2)	89 (2)	104 (2)	58 (1)	63 (3)	36 (2)	23 (3)
C(10)	6439 (2)	2735 (2)	1627 (2)	118 (2)	72 (2)	65 (1)	37 (3)	64 (3)	24 (2)
C(11)	7531 (2)	1955 (2)	1922 (1)	83 (2)	53 (1)	56 (1)	−12 (2)	40 (2)	5 (2)
C(12)	7909 (2)	1575 (2)	2866 (1)	81 (2)	63 (1)	53 (1)	−25 (3)	36 (2)	−16 (2)
C(13)	8567 (2)	566 (2)	3151 (1)	63 (2)	65 (1)	45 (1)	−24 (2)	15 (2)	−6 (2)
C(14)	9103 (2)	73 (2)	2512 (1)	60 (1)	68 (2)	51 (1)	−13 (2)	18 (2)	−2 (2)
C(15)	8933 (2)	616 (2)	1629 (1)	69 (2)	69 (2)	56 (1)	−18 (3)	41 (2)	−1 (2)
C(16)	8052 (2)	1452 (2)	1277 (1)	82 (2)	62 (1)	55 (1)	−20 (3)	44 (2)	13 (2)
C(17)	7614 (2)	1635 (2)	204 (1)	112 (2)	82 (2)	58 (1)	24 (3)	63 (3)	33 (2)
C(18)	6752 (2)	663 (2)	−340 (1)	103 (2)	109 (2)	48 (1)	33 (3)	25 (2)	14 (3)
C(19)	7390 (2)	−471 (2)	−183 (1)	85 (2)	91 (2)	48 (1)	−10 (3)	25 (2)	−13 (2)
C(20)	8081 (2)	−832 (2)	−756 (1)	110 (2)	98 (2)	51 (1)	−21 (3)	51 (3)	−15 (2)
C(21)	8910 (2)	−1703 (2)	−453 (2)	107 (2)	94 (2)	66 (1)	−19 (3)	72 (3)	−39 (3)
C(22)	9136 (2)	−2164 (2)	455 (2)	96 (2)	76 (2)	65 (1)	−2 (3)	52 (3)	−27 (2)
C(23)	8451 (2)	−1831 (2)	1040 (1)	89 (2)	63 (2)	58 (1)	−13 (3)	41 (2)	−11 (2)
C(24)	7522 (2)	−1050 (2)	671 (1)	80 (2)	77 (2)	53 (1)	−19 (3)	39 (2)	−11 (2)
C(25)	8867 (2)	−2064 (2)	2100 (1)	110 (2)	64 (2)	60 (1)	23 (3)	54 (3)	8 (2)
C(26)	9708 (2)	−1085 (2)	2646 (1)	82 (2)	82 (2)	54 (1)	21 (3)	28 (2)	7 (2)

359 $|E|$ values greater than 1·50. From the E map calculated by the set of phases which gave the highest figure of merit, all 26 C atoms were easily located. The refinement of the molecular structure was carried out by the block-diagonal least-squares method with *HBLS*-V (Ashida, 1973). The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Five cycles of isotropic refinement gave a conventional R index of 0·137. Three successive cycles of refinement with anisotropic temperature factors assumed for all C atoms reduced R to 0·117. At this stage the difference Fourier map was calculated, which revealed all the H atoms clearly. The H atoms with isotropic temperature factors were then included in the refinement. The weighting scheme used was $w = F_{wt}$ for $|F_o| = 0·0$, $w = 1·0$ for $0·0 < |F_o| \leq F_{max}$ and $w = (F_{max}/F_o)^2$ for $F_{max} < |F_o|$, where $F_{wt} = 0·3$ and $F_{max} = 20·0$. After eight cycles of refinement R converged to 0·048 for non-zero intensities and to 0·057 for all reflexions. In the final cycle of refinement the shifts in the atomic parameters for H atoms were less than 0·1σ for positional parameters and less than 1·0σ for thermal parameters. The weighted R index, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$, was 0·056. The final atomic parameters for C and H atoms are given in Tables 3 and 4 respectively.*

[2.2]Metacyclophane

The refinement of the molecular structure was started from the positional parameters for eight C atoms reported by Brown (1953*b*) with an isotropic temperature factor of 4·0 Å^2 assumed for each C atom. Successive anisotropic refinements (three cycles) converged to R 0·092. H atoms were located from a difference Fourier map and refined isotropically. The atomic scattering factors for H were taken from Stewart, David-

---

* A list of structure factors for each compound, I and V, has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32100 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

son & Simpson (1965) and those of C were from *International Tables* (1974). The weighting scheme used was $w = F_{wt}$ for $|F_o| = 0·0$ and $w = [\sigma(F_o)^2 + a|F_o| + b|F_o|^2]^{-1}$ for $|F_o| > 0·0$, where F_{wt}, a and b were adjusted during the refinement. The parameters used in the final refinement were $F_{wt} = 3·765$, $a = 0·0347$ and $b = 0·0014$, and the shifts of positional and thermal parameters for the H atoms were less than 0·1σ and 0·5σ respectively. The final R was 0·050 for non-zero intensities and 0·059 for all reflexions. The weighted R was 0·083. The final atomic parameters for C and H atoms are given in Tables 5 and 6.*

Table 6. *Fractional atomic coordinates* ($\times 10^3$) *and isotropic thermal parameters* (Å^2) *of the hydrogen atoms* (V)

The numbering follows that of the carbon atoms to which the hydrogen atoms are attached.

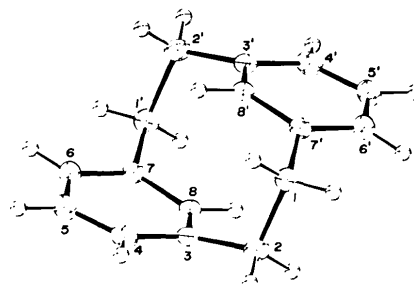|	x	y	z	B
H(1A)	−52 (2)	121 (2)	222 (1)	2·8 (3)
H(1B)	223 (3)	104 (2)	271 (1)	3·5 (3)
H(2A)	346 (3)	216 (2)	101 (1)	3·3 (3)
H(2B)	173 (3)	347 (2)	160 (1)	3·5 (3)
H(4)	−205 (3)	410 (2)	62 (1)	3·2 (3)
H(5)	−494 (3)	356 (2)	−85 (2)	4·0 (4)
H(6)	−459 (2)	125 (2)	−204 (1)	2·7 (3)
H(8)	208 (2)	51 (2)	−66 (1)	2·2 (3)

Fig. 1. The molecular structure and atomic numbering scheme of [2.2]metacyclophane. The thermal ellipsoids include 50% probability and hydrogen atoms are drawn as spheres of radius 0·1 Å.

Table 5. *Fractional atomic coordinates and anisotropic thermal parameters* ($\times 10^5$) *of the non-hydrogen atoms* (V)

Anisotropic thermal parameters are expressed in the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. The estimated standard deviations, given in parentheses, refer to the last significant figures.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	11103 (16)	9849 (11)	19989 (7)	1775 (22)	701 (10)	212 (4)	−202 (24)	33 (15)	−64 (11)
C(2)	18158 (16)	23606 (11)	11747 (7)	1607 (21)	619 (10)	280 (5)	−412 (23)	−29 (15)	−87 (11)
C(3)	2425 (14)	23448 (10)	1222 (7)	1255 (18)	477 (9)	260 (4)	−184 (19)	115 (14)	50 (9)
C(4)	−17955 (16)	32432 (11)	475 (8)	1652 (22)	555 (10)	350 (5)	220 (23)	291 (17)	26 (11)
C(5)	−34977 (16)	29028 (12)	−7913 (8)	1417 (21)	772 (11)	390 (6)	525 (25)	147 (17)	222 (13)
C(6)	−32546 (14)	15849 (12)	−15132 (8)	1241 (19)	819 (11)	303 (5)	67 (23)	−90 (15)	209 (12)
C(7)	−12296 (14)	6722 (10)	−14568 (6)	1263 (18)	601 (9)	203 (4)	−105 (20)	56 (13)	93 (9)
C(8)	5621 (13)	11586 (10)	−6959 (6)	1062 (16)	517 (9)	227 (4)	−61 (19)	159 (13)	68 (9)

Results and discussion

[2.2]Metacyclophane

A perspective view of the molecule with the atom numbering is shown in Fig. 1 by an *ORTEP* (Johnson, 1965) drawing. The interatomic bond distances and bond angles are listed in Table 7, with estimated standard deviations. The molecular structure determination is sufficiently accurate [σ(C—C) = 0·001 Å, σ(C—C—C) = 0·1°] to allow detailed discussion of the structure as a standard for cyclophane compounds. In Fig. 2 are shown the projections of the molecule along the vector passing through the midpoint of the C(1)—C(2) bond and the centre of symmetry (Fig. 2a), and on to the least-squares plane of C(3), C(4), C(6) and C(7) atoms (Fig. 2b). The deviations of atoms from the least-squares plane are shown in Fig. 2(a) and selected bond distances and bond angles in Fig. 2(b).

Four C atoms, C(3), C(4), C(6) and C(7) lie within 0·001 Å of the least-squares plane, which is taken as the basal plane. Both C(5) and C(8) deviate from the basal plane toward the outer part of the molecule, and
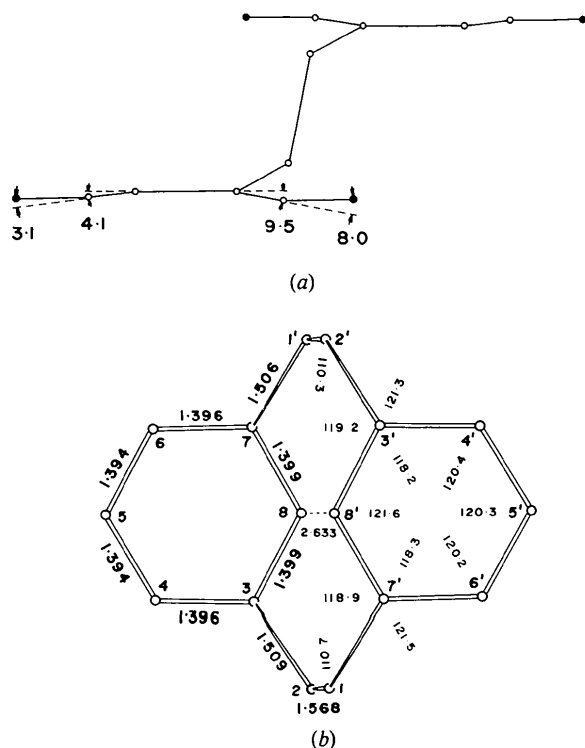
the benzene ring [C(3) through C(8)] adopts an asymmetrically distorted boat form, the deviation of C(8) being more than twice that of C(5). H atoms attached to C(8) and C(5), however, deviate from the plane toward the inner part of the molecule and the deviation of H(8) is also more than twice that of H(5) (Fig. 2a).

The intra-ring bond distances of the benzene rings are quite significant. Bond distances in the most crowded parts of the molecule are the longest, 1·399 Å, those in the least crowded parts are the shortest, 1·394 Å, and the rest are 1·396 Å. These differences are considered significant because of the good correlation between the bond distances of chemically equivalent but crystallographically independent parts of the molecule. Good correlation is also observed among the bond angles between chemically equivalent parts of the molecule.

In addition to the crystallographic centre of symmetry, the molecule has an extra mirror plane of symmetry passing through the centre of symmetry and C(5) and C(5') and perpendicular to the plane defined by C(3), C(4), C(6) and C(7). The molecule itself has, therefore, approximate 2/m symmetry. The bond distance between bridging C atoms is 1·568 (1) Å, which is 0·027 Å longer than the normal C—C single-bond distance of 1·541 Å.

The molecular structures of some derivatives of [2.2]metacyclophane (VI–IX) have been reported since

(a)

(b)

Fig. 2. Molecular projections of [2.2]metacyclophane (a) along the vector passing through the midpoint of the C(1)—C(2) bond and the centre of symmetry, and (b) on the least-squares plane of C(3), C(4), C(6) and C(7). In (a) atomic deviations (°) from the least-squares plane are given and in (b) selected bond distances (Å) and bond angles (°). Filled circles denote hydrogen atoms.

Table 7. *Interatomic bond distances (Å) and bond angles (°) in [2.2]metacyclophane*

Standard deviations, in parentheses, refer to the last significant figures.

C(3)—C(4)	1·396 (1)	C(4)—H(4)	1·00 (2)
C(4)—C(5)	1·394 (1)	C(5)—H(5)	1·00 (2)
C(5)—C(6)	1·394 (1)	C(6)—H(6)	1·01 (2)
C(6)—C(7)	1·396 (1)	C(8)—H(8)	1·03 (2)
C(7)—C(8)	1·399 (1)	C(1)—H(1A)	1·03 (2)
C(3)—C(8)	1·399 (1)	C(1)—H(1B)	1·04 (2)
C(2)—C(3)	1·509 (1)	C(2)—H(2A)	1·01 (2)
C(7)—C(1')	1·506 (1)	C(2)—H(2B)	1·04 (2)
C(1)—C(2)	1·568 (1)	C(8)—C(8')	2·633 (2)
C(2)—C(3)—C(4)	121·25 (7)	C(3)—C(8)—C(7)	121·61 (7)
C(2)—C(3)—C(8)	119·18 (7)	C(7)—C(8)—H(8)	119·2 (8)
C(4)—C(3)—C(8)	118·16 (7)	C(3)—C(8)—H(8)	118·5 (8)
C(3)—C(4)—C(5)	120·38 (8)	C(2)—C(1)—C(7')	110·71 (7)
C(3)—C(4)—H(4)	119 (1)	C(2)—C(1)—H(1A)	108·6 (9)
C(5)—C(4)—H(4)	120 (1)	C(2)—C(1)—H(1B)	108 (1)
C(4)—C(5)—C(6)	120·25 (9)	C(7')—C(1)—H(1A)	110·3 (9)
C(4)—C(5)—H(5)	120 (1)	C(7')—C(1)—H(1B)	110 (1)
C(6)—C(5)—H(5)	119 (1)	H(1A)—C(1)—H(1B)	109 (1)
C(5)—C(6)—C(7)	120·23 (9)	C(1)—C(2)—C(3)	110·33 (7)
C(5)—C(6)—H(6)	119·4 (9)	C(1)—C(2)—H(2A)	107·1 (9)
C(7)—C(6)—H(6)	120·3 (9)	C(1)—C(2)—H(2B)	107 (1)
C(6)—C(7)—C(8)	118·32 (8)	C(3)—C(2)—H(2A)	112·1 (9)
C(6)—C(7)—C(1')	121·54 (8)	C(3)—C(2)—H(2B)	112 (1)
C(8)—C(7)—C(1')	118·85 (7)	H(2A)—C(2)—H(2B)	108 (1)

the work of Brown (1953*b*) on V. The structural data of these compounds are summarized in Table 8. The bond distances between the bridging C atoms in VI and VII are also longer than the normal single-bond distance, as in V. Corresponding distances in VIII and IX are, however, similar to the normal C=C double-bond distance of 1·337 Å. The widening of the bond angles of the bridging C atoms from the tetrahedral angle in V–VII is small (1·0–3·0°). The corresponding values of widening of the trigonal angle in VIII and IX are, however, relatively large (5·9–6·0°).
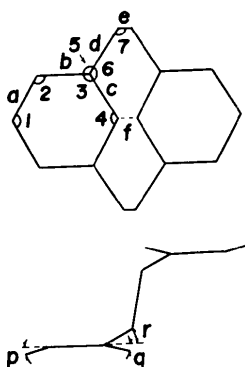
(VI) R = CH₃
(VII) R = CH₂Br
(VIII) R = H
(IX) R = F
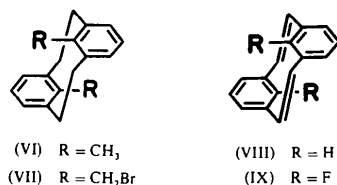
Table 8. *Molecular structures of* [2.2]*metacyclophane and its derivatives*

	V(i)	V(ii)	VI	VII	VIII	IX
a	1·387 Å	1·394 Å	1·389 Å	1·381 Å	1·383 Å	1·387 Å
b	1·383	1·396	1·397	1·387	1·396	1·398
c	1·389	1·399	1·411	1·407	1·404	1·390
d	1·535	1·508	1·517	1·519	1·483	1·474
e	1·559	1·568	1·573	1·568	1·341	1·330
f	2·689	2·633	2·819	2·77	2·567	2·66
σ		0·001	0·003	0·008	0·003	0·005
1	118·8°	120·3°	119·0°	121·1°	120·7°	120·1°
2	121·4	120·3	120·9	120·5	120·0	120·9
3	117·3	118·3	118·9	118·5	117·7	115·7
4	122·3	121·6	118·5	119·4	119·9	122·3
5	121·6	121·4	120·2	120·3	119·8	119·9
6	120·2	119·1	120·1	120·4	121·3	123·0
7	110·3	110·5	111·5	112·5	126·0	125·9
σ		0·1	0·3	0·5	0·2	0·3
p	3·5ᶜ	4·1°	7·3°	6·7°	6·6°	6·7°
q	11·9	9·2	15·4	14·7	19·1	19·3
r	13·9	15·8	16·7	16·2	19·3	20·2

References: V(i) Brown (1953*b*). V(ii) Present work. VI Hanson (1962). VII Mathew (1968). VIII Hanson & Röhrl (1972). IX Hanson (1975).

Significant differences between the three intra-ring bond distances are observed in these compounds (Table 8). The order of these bond distances is $c > b > a$ in V–VIII but $b > c > a$ in IX. The shortening of bond c in IX is interpreted by the substituent effect of fluorine. It is well known that the substituent effect of benzene derivatives causes the p character of an atom to tend to concentrate in the hybrid orbitals directed towards electron-withdrawing substituents (Walsh, 1947). This implies a decrease in the p character of the other two hybrid orbitals of C, and therefore causes (1) an increase in the endocyclic angle and (2) a decrease in the length of adjacent C—C bonds. The opposite is true for an electron-releasing substituent.

By comparing the molecular structures of VIII and IX, it is clear that the strong electron-withdrawing F atom causes a widening of angle 4 (Table 8) from 119·9 to 122·3° and a decrease of length c from 1·404 to 1·390 Å. The opposite effect is observed in V and VI, in which the electron-releasing substituent CH₃ causes a decrease of angle 4 from 121·6 to 118·5° and increase of length c from 1·399 to 1·411 Å. These facts show that the order of lengths of intra-ring bond distances $(c > b > a)$ is considered to be the common feature in the molecular structures of [2.2]metacyclophane and its derivatives. The common feature observed in the endocyclic angles is that angle 3 deforms to a few degrees below 120°. This may be because of the change in hybrid state of the C atom at 3 caused by the strains induced by the bridging.

The angles p and q show the deformation of the benzene ring from planarity. In compound V $p = 4·1$ and $q = 9·5°$, which are considered to be standard values for [2.2]metacyclophane and related compounds. In compounds VI and VII p and q are greater than in V because of the substitution of bulky CH₃ or CH₂Br groups in the 8 and 8′ positions (Fig. 1). Much deformation is induced, especially in angle q, by the ethylenic bridging in compounds VIII and IX.

Triple-layered [2.2]*metacyclophane* (*ud isomer*)

A perspective view of the molecule with the atom numbering is shown in Fig. 3 by an *ORTEP* drawing. The analysis of the molecular thermal vibrations in the
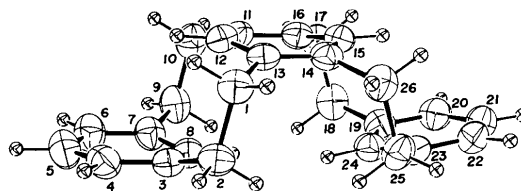
Fig. 3. The molecular structure and atomic numbering scheme of triple-layered [2.2]metacyclophane. The thermal ellipsoids include 50% probability and the hydrogen atoms are drawn as spheres of radius 0·1 Å.

crystal was undertaken by the method of Cruickshank (1956) with the *RSMV*-4 program of *UNICS* (Ito & Sakurai, 1967). The anisotropic translational (T) and rotational (ω) vibration tensors of the molecule were determined from the vibrational tensors of individual atoms. The results are given in Table 9. The interatomic bond distances and bond angles are listed in Table 10 together with the bond distances corrected for thermal vibrations. Differences between the corrected and uncorrected bond distances lie in the range 0·001–0·004 Å, *i.e.* $\le 1\cdot 0\sigma$ of the observed C—C distances. Discussions will be made, therefore, on the structure uncorrected for thermal vibrations.

The projection of the molecule along the vector passing through the midpoints of the C(13)—C(14) and C(11)—C(16) bonds is shown in Fig. 4(*a*), in which deviations of atoms from the least-squares plane of each benzene ring are also shown. Selected bond distances and bond angles are shown in Fig. 4(*b*) which is a projection of the molecule on the least-squares plane of C(11), C(13), C(14) and C(16). These figures indicate that the molecule has approximate *mm*2 symmetry. The correlation of the bond distances and bond angles of chemically equivalent parts of the molecule is very good. As a measure of the correlation the es-

timated standard deviations of the mean values of the bond lengths and angles are listed in Table 11 with the ranges of the observed values. Hereafter, discussion will be made of these average bond distances and bond angles.

Table 9. *Analysis of molecular vibrations of triple-layered* [2.2]*metacyclophane by the rigid-body approximation*

Translational, T (Å^2), and rotational, ω (deg^2), tensors

$$T = (\sigma T) \begin{pmatrix} 0\cdot 050 & -0\cdot 001 & -0\cdot 001 \\ (1) & (1) & (1) \\ & 0\cdot 041 & 0\cdot 000 \\ & (1) & (1) \\ & & 0\cdot 034 \\ & & (2) \end{pmatrix} \quad \omega = (\sigma \omega) \begin{pmatrix} 14\cdot 9 & -1\cdot 5 & -0\cdot 5 \\ (10) & (4) & (4) \\ & 4\cdot 2 & -0\cdot 4 \\ & (4) & (3) \\ & & 4\cdot 8 \\ & & (3) \end{pmatrix}$$

R.m.s. displacements along, and directions of, the principal vibrational axes

		R.m.s. displacements	Direction cosines of principal vibrational axes p along inertial axes I*		
			l_1	l_2	l_3
T	p_1	0·186 (Å)	0·0472	−0·0394	0·9981
	p_2	0·202	−0·0675	−0·9971	−0·0361
	p_3	0·225	0·9966	−0·0657	−0·0497
ω	p_1	1·94 (°)	0·1447	0·8964	0·4189
	p_2	2·24	0·0170	0·4211	−0·9069
	p_3	3·89	0·9893	−0·1383	−0·0457

* The inertial axes I are defined by I = m . a, where the elements of m are

$$\begin{pmatrix} -0\cdot 0406 & 0\cdot 0338 & 0\cdot 0447 \\ -0\cdot 0425 & 0\cdot 0559 & -0\cdot 0505 \\ 0\cdot 0682 & 0\cdot 0550 & 0\cdot 0238 \end{pmatrix}$$

and a is the column vector composed of the dimensions of the three crystal axes *a*, *b* and *c*.

Table 10. *Interatomic bond distances* (Å) *and bond angles* (°)

Standard deviations in parentheses refer to the last significant figure. The columns of bond distances headed by an asterisk show the values corrected for thermal vibration.

C(3)—C(4)	1·386 (3)	1·387*	C(6)—C(7)	1·392 (3) 1·393*
C(3)—C(8)	1·385 (3)	1·388	C(7)—C(8)	1·398 (3) 1·401
C(4)—C(5)	1·391 (3)	1·394	C(2)—C(3)	1·506 (3) 1·509
C(5)—C(6)	1·387 (3)	1·389	C(7)—C(9)	1·506 (3) 1·508
C(11)—C(12)	1·394 (3)	1·396	C(15)—C(16)	1·399 (3) 1·403
C(11)—C(16)	1·401 (3)	1·403	C(10)—C(11)	1·519 (3) 1·521
C(12)—C(13)	1·402 (3)	1·405	C(1)—C(13)	1·511 (3) 1·513
C(13)—C(14)	1·400 (3)	1·402	C(14)—C(26)	1·514 (3) 1·516
C(14)—C(15)	1·403 (3)	1·405	C(16)—C(17)	1·516 (3) 1·518
C(19)—C(20)	1·395 (3)	1·396	C(22)—C(23)	1·395 (3) 1·396
C(19)—C(24)	1·392 (3)	1·395	C(23)—C(24)	1·394 (3) 1·397
C(20)—C(21)	1·382 (3)	1·385	C(18)—C(19)	1·506 (3) 1·509
C(21)—C(22)	1·387 (3)	1·389	C(23)—C(25)	1·506 (3) 1·509
C(1)—C(2)	1·566 (3)	1·569	C(17)—C(18)	1·567 (3) 1·570
C(9)—C(10)	1·566 (3)	1·569	C(25)—C(26)	1·562 (3) 1·565

Mean† C—H = 1·03 (2) (1·00–1·08)

C(2)—C(3)—C(4)	121·2 (2)	C(5)—C(6)—C(7)	120·4 (2)
C(2)—C(3)—C(8)	119·4 (2)	C(6)—C(7)—C(8)	118·0 (2)
C(4)—C(3)—C(8)	118·3 (2)	C(6)—C(7)—C(9)	121·9 (2)
C(3)—C(4)—C(5)	120·6 (2)	C(8)—C(7)—C(9)	118·9 (2)
C(4)—C(5)—C(6)	119·8 (2)	C(3)—C(8)—C(7)	121·7 (2)
C(10)—C(11)—C(12)	117·4 (2)	C(13)—C(14)—C(15)	117·7 (2)
C(10)—C(11)—C(16)	123·9 (2)	C(13)—C(14)—C(26)	124·6 (2)
C(12)—C(11)—C(16)	117·8 (2)	C(15)—C(14)—C(26)	117·2 (2)
C(11)—C(12)—C(13)	123·1 (2)	C(14)—C(15)—C(16)	122·7 (2)
C(12)—C(13)—C(14)	117·6 (2)	C(11)—C(16)—C(15)	117·7 (2)
C(1)—C(13)—C(12)	117·4 (2)	C(11)—C(16)—C(17)	124·4 (2)
C(1)—C(13)—C(14)	124·3 (2)	C(15)—C(16)—C(17)	117·4 (2)
C(18)—C(19)—C(20)	121·6 (2)	C(21)—C(22)—C(23)	120·4 (2)
C(18)—C(19)—C(24)	118·9 (2)	C(22)—C(23)—C(24)	117·8 (2)
C(20)—C(19)—C(24)	118·0 (2)	C(22)—C(23)—C(25)	121·3 (2)
C(19)—C(20)—C(21)	120·3 (2)	C(24)—C(23)—C(25)	119·2 (2)
C(20)—C(21)—C(22)	120·5 (2)	C(19)—C(24)—C(23)	122·0 (2)
C(2)—C(1)—C(13)	112·4 (2)	C(7)—C(9)—C(10)	110·9 (2)
C(1)—C(2)—C(3)	111·0 (2)	C(9)—C(10)—C(11)	112·0 (2)
C(16)—C(17)—C(18)	112·8 (2)	C(23)—C(25)—C(26)	110·6 (2)
C(17)—C(18)—C(19)	110·6 (2)	C(14)—C(26)—C(25)	113·3 (2)

Mean† C—C—H (aromatic) = 119 (1) (117–121)
C—C—H (aliphatic) = 109 (1) (107–113)
H—C—H = 108 (2) (105–109)

† Only mean values of bond distances and bond angles involving hydrogen atoms are listed. The individual e.s.d.'s are in the first set of parentheses after the value and the ranges are in the second set.

Table 11. *Mean* $(\bar{x})$, *estimated standard deviations of the mean* $[\sigma(\bar{x})]$ *and ranges* (R) *of the bond distances and bond angles of chemically equivalent parts of the ud isomer of triple-layered* [2.2]*metacyclophane*
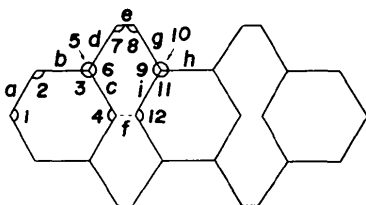
Mean: $\bar{x} = \Sigma x_i/n$ where x_i is the individual bond distance or bond angle observed, n is the number of chemically equivalent bond distances or bond angles. Variance: $s^2 = \Sigma(x_i - \bar{x})^2/(n - 1)$. Estimated standard deviation of mean: $\sigma(\bar{x}) = (s^2/n)^{1/2}$. Range: $R = (x_i)_{max} - (x_i)_{min}$.

	$\bar{x}$	$\sigma(\bar{x})$	R		$\bar{x}$	$\sigma(\bar{x})$	R
a	1·3868 Å	0·0019 Å	0·009 Å	1	120·15°	0·35°	0·7°
b	1·3920	0·0021	0·009	2	120·43	0·06	0·3
c	1·3923	0·0027	0·013	3	118·03	0·10	0·5
d	1·5060	0·0	0·0	4	121·85	0·15	0·3
e	1·5653	0·0011	0·005	5	121·50	0·16	0·7
f	2·6665	0·0049	0·007	6	119·10	0·12	0·5
g	1·5150	0·0017	0·008	7	110·78	0·10	0·4
h	1·4005	0·0005	0·001	8	112·63	0·28	1·3
i	1·3995	0·0020	0·009	9	117·35	0·05	0·2
				10	124·30	0·15	0·7
				11	117·70	0·04	0·2
				12	123·30	0·60	1·2

The bridging bond distances, e, in I and V have very similar values, 1·565 and 1·568 Å respectively. The bond distance between the bridging C and the terminal benzene C, d, in I (1·506 Å) agrees well with that in V (1·508 Å). The bond distance between the bridging C and the central benzene C, g, is, however, significantly longer than d. This may be because of the intramolecular strain which is more concentrated in g than d. This fact is also reflected in the larger deviations from the trigonal valence angle around the central benzene C atom bonded to the bridging C atom (angles 9, 10 and 11) than around the corresponding terminal benzene C atom (angles 3, 5 and 6). The intra-ring bond distances in the central benzene ring (h and i) are significantly longer than those in the terminal benzene ring (a, b and c). The shortest non-bonded atomic contact (f) in I (2·667 Å) is slightly longer than that in V (2·633 Å).

The comparison of out-of-plane deformations of the benzene rings in I and V is interesting. The average deviation of C(8) and C(24) from the basal plane [defined by C(3), C(4), C(6) and C(7), and C(19), C(20), C(22) and C(23)] is 10·0° (Fig. 4a), whereas the corresponding value for C(5) and C(21) is 4·9°. These are not significantly different from the corresponding values observed in V, the standard compound, 9·5° for C(8) and 4·1° for C(5). The deformation of the central benzene ring in I is much greater than that of the ter-
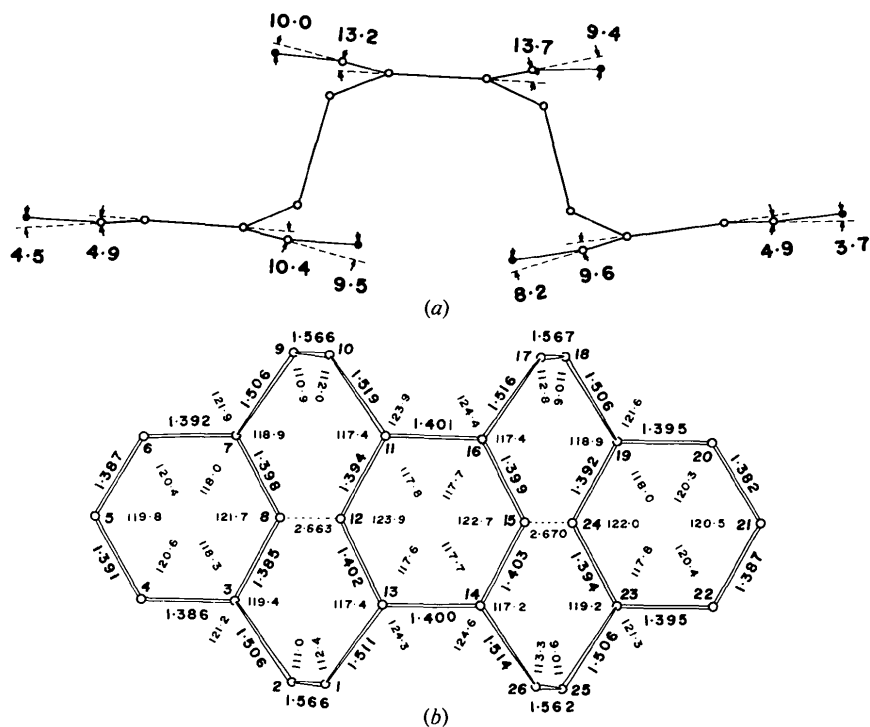

(a)

(b)

Fig. 4. The molecular projections of triple-layered [2.2]metacyclophane (a) along the vector passing through the midpoints of the C(13)—C(14) and C(11)—C(16) bonds and (b) on the least-squares plane of C(11), C(13), C(14) and C(16). In (a) atomic deviations (°) from the least-squares plane are given and in (b) selected bond distances (Å) and bond angles (°). Filled circles denote hydrogen atoms.

minal rings, the average deviation of C(12) and C(15) being 13·5°, which corresponds to the sum of the deviations in V (9·5° + 4·1° = 13·6°). This fact points to an interesting addition effect of the two terminal benzene rings on the deformation of the central benzene
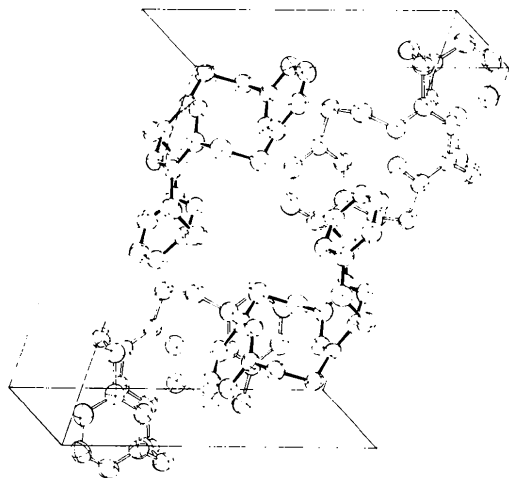

Fig. 5. The crystal structure of triple-layered |2.2|metacyclophane. The direction of view is close to **b**; **a** is nearly horizontal; **c** is nearly vertical. The parallelepiped outlined has dimensions *a*, *b* and *c*.

ring. The left terminal benzene ring causes C(12) and C(15) to deviate away from the basal plane defined by C(11), C(13), C(14) and C(16) by 9·5 and 4·1° respectively. The right terminal benzene ring deforms the two atoms in the same direction as the left, but by reversed amounts, 4·1° for C(12) and 9·5° for C(15). As a result C(12) and C(15) show the same amount of deviation, of 13·2 and 13·7° respectively, from the basal plane.

The dihedral angle between the basal planes of the left and central benzene ring is 1·3° and that between the right and central ring is 10·4°: the right benzene ring deviates significantly from the parallel position. This may result partly from the non-bonded repulsion between H(8) and H(24) atoms. The distance between these atoms is 2·22 (3) Å, which is shorter than the sum of the van der Waals radii of H. The reason why only the right benzene ring deviates from the parallel position, however, is not clear.

Crystal structure

The crystal structures of I and V are shown in Figs. 5 and 6 respectively. No intermolecular atomic contact shorter than the van der Waals distance is found in these crystals.
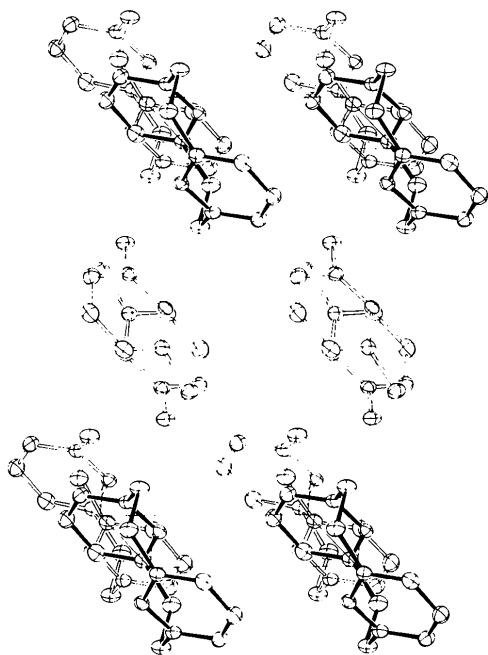
Fig. 6. The crystal structure of [2.2]metacyclophane. The direction of view is close to **b**; **a** is nearly horizontal; **c** is nearly vertical. The parallelepiped outlined has dimensions *a*, *b* and *c*.

References

ASHIDA, T. (1973). *The Universal Crystallographic Computing System – Osaka*, pp. 55–61. The Computation Center, Osaka Univ.
BROWN, C. J. (1953*a*). *J. Chem. Soc.* pp. 3265–3270.
BROWN, C. J. (1953*b*). *J. Chem. Soc.* pp. 3278–3285.
CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 757–758.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.
HANSON, A. W. (1962). *Acta Cryst.* **15**, 956–960.
HANSON, A. W. (1975). *Acta Cryst.* B**31**, 2352–2354.
HANSON, A. W. & RÖHRL, M. (1972). *Acta Cryst.* B**28**, 2032–2037.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
ITO, T. & SAKURAI, T. (1967). *The Universal Crystallographic Computing System* (I), edited by T. SAKURAI. Tokyo: The Crystallographic Society of Japan.
JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
MATHEW, M. (1968). *Acta Cryst.* B**24**, 530–534.
SATO, T., AKABORI, S., KAINOSHO, M. & HATA, K. (1968). *Bull. Chem. Soc. Japan*, **41**, 218–221.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
UMEMOTO, T., OTSUBO, T. & MISUMI, S. (1974). *Tetrahedron Lett.* pp. 1573–1576.
WALSH, A. D. (1947). *Discuss. Faraday Soc.* **2**, 18–25.