The Crystal Structure of 4,12-dimethyl(2,2)metacyclophane

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The crystal is monoclinic, probably $C2/c$, with

$$a = 12 \cdot 62, \quad b = 9 \cdot 25, \quad c = 10 \cdot 97 \text{ Å}; \quad \beta = 91 \cdot 56°; \quad Z = 4 .$$

The structure was determined from a three-dimensional Patterson synthesis, and refined by differential syntheses. Allowance was made for thermal anisotropy. The two benzene rings are displaced stepwise, and distorted to a boat shape to avoid too close mutual contact. The methyl groups appear to be stationary, but may be in a condition of strongly hindered rotation.

Introduction

Para- and meta-cyclophanes and some related compounds have been the subject of recent crystallographic study (Brown, 1953*a*, *b*; Gantzel, Coulter & Trueblood, 1960). 4,12-Dimethyl(2·2)metacyclophane (Lindsay, Stokes, Humber & Boekelheide, 1961) is a derivative of (2·2)metacyclophane (otherwise called di-*m*-xylylene (Brown, 1953*b*)). The latter molecule is considerably distorted by steric forces, and the present study was undertaken to determine what further distortion might be introduced by the additional methyl groups. The structural formula is given in Fig. 1.
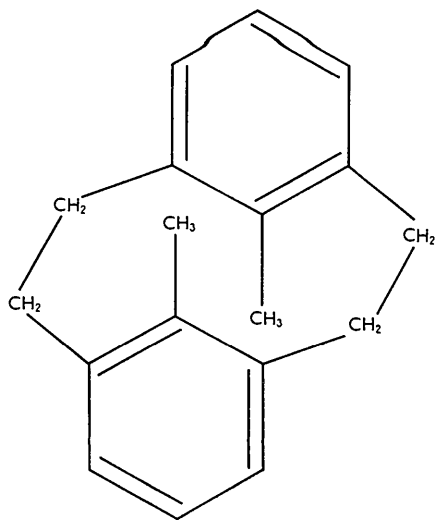

Fig. 1. Structural formula.

Experimental details

Crystal data: monoclinic.

$$a = 12 \cdot 62 \pm 0 \cdot 01, \quad b = 9 \cdot 25 \pm 0 \cdot 01, \quad c = 10 \cdot 97 \pm 0 \cdot 01 \text{ Å};$$
$$\beta = 91 \cdot 56 \pm 0 \cdot 02°.$$

$V = 1280 \cdot 1$ Å³. Formula weight 236·34.
D_m (measured density) = $1 \cdot 22 \pm 0 \cdot 01$ g.cm.$^{-3}$.
D_x (calculated density) = $1 \cdot 226 \pm 0 \cdot 003$ g.cm.$^{-3}$.
$Z = 4$.
$\mu = 6 \cdot 2$ cm.$^{-1}$ (Cu $K\alpha$) and 0·8 cm.$^{-1}$ (Mo $K\alpha$).

Space group Cc (C_s^4) or $C2/c$ (C_{2h}^6) from examination of Weissenberg and precession photographs. The latter space group is confirmed by the X-ray analysis.
Molecular symmetry: centre.

Two distinct habits are observed for the crystal. One is the prism {111}, variously terminated by {100}, {11$\bar{1}$}, and other forms. The data given above were obtained from a specimen of this habit. The prism {111} is present in the other habit also, but the pinacoid {100} is developed to such a degree that the crystals are better described as thin plates. It was found that for crystals of this habit *a* is about 0·05 Å, or 0·4%, greater than the value given above. No significant difference was observed for the other parameters. While crystals of the second habit are extremely small, and the unit-cell measurements consequently less accurate, the difference in *a* is believed to be real. No explanation is offered for this surprising result, but two possibly relevant facts may be mentioned. The X-ray intensity distributions for the two habits are at least approximately, and probably exactly, the same. Crystals of the first habit are of a much higher degree of perfection than those of the second; total mosaic spreads for two typical specimens are 0·05° and 0·30°.

The cell parameters and the relative intensities were obtained from a crystal of the first type, having extreme dimensions 0·2 and 0·4 mm. All measurements were made on the General Electric XRD5 spectrogoniometer and goniostat, with a scintillation counter. Cu $K\alpha$ radiation was used, and reasonable monochromatization was achieved by means of a $K\beta$ filter and a reverter (pulse-height analyser). The 'moving-crystal

moving-counter' method of Furnas was used (1957). The required goniostat settings were precomputed. Absorption corrections were deemed to be unnecessary, and were not made. In order to detect extinction, however, the more intense reflections were remeasured with Mo $K\alpha$ radiation. Comparison of the results indicated a small extinction effect, and errors were reduced somewhat by using the suitably scaled Mo $K\alpha$ results for the reflections affected. Of the 1420 reflections accessible to the spectrogoniometer (that is, those for which $2\theta \leq 165\cdot4°$) 1258 were observed.

Structure determination

A three-dimensional Patterson synthesis was first computed, and the orientation of a plausible molecule (assumed to occupy a centre of symmetry) was readily deduced. Refinement by three-dimensional structure-factor calculations and differential syntheses proceeded smoothly. McWeeny's (1951) scattering factor curves were used throughout. When the agreement residual had been reduced to about 0·14, comparison of observed and calculated central curvatures indicated appreciable anisotropic thermal motion. This was simulated in structure-factor calculations by substituting for each atom four atoms of one quarter weight, distributed at the corners of the appropriate rectangle (Kartha & Ahmed, 1960). At this stage also, a three-dimensional difference synthesis revealed the positions of all the hydrogen atoms, including those of the apparently stationary methyl group. The contributions of these atoms were included in sub-
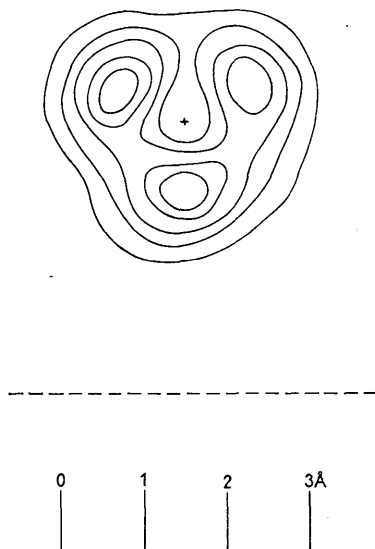

Fig. 2. A section, through the methyl hydrogen positions, of the three-dimensional difference synthesis. Contours are drawn at intervals of 0·1 e.Å⁻³, the lowest being at 0·1 e.Å⁻³. The small cross is the trace of the line containing the positions of C(4) and C(9). The broken line is the trace of the plane containing the positions of C(3)', C(5)', C(6)', and C(8)'.

Table 1. *Parameters used in ultimate structure-factor calculation*

Atom	x	y	z	B	ΔB_1	ΔB_2
C(1)	0·1638	0·2921	0·2056	2·53	0·83	1·30
	0·1417	0·2814	0·1960			
	0·1537	0·2699	0·2019			
	0·1518	0·3037	0·1997			
C(2)	0·1153	0·4047	0·1154	2·65	0·67	1·26
	0·0983	0·3953	0·0980			
	0·1023	0·3861	0·1114			
	0·1114	0·4139	0·1020			
C(3)	0·3197	0·0631	−0·0205	2·19	0·52	0·85
	0·3057	0·0568	−0·0049			
	0·3064	0·0518	−0·0185			
	0·3191	0·0680	−0·0070			
C(4)	0·3024	0·1575	0·0827	1·90	0·54	0·64
	0·2860	0·1485	0·0894			
	0·2922	0·1631	0·0921			
	0·2962	0·1429	0·0800			
C(5)	0·2016	0·1445	0·1335	2·12	0·66	0·99
	0·1846	0·1606	0·1420			
	0·1982	0·1648	0·1422			
	0·1881	0·1403	0·1333			
C(6)	0·1342	0·0254	0·1106	2·60	0·53	1·46
	0·1165	0·0470	0·1154			
	0·1263	0·0458	0·1242			
	0·1244	0·0265	0·1019			
C(7)	0·1657	−0·0794	0·0311	2·82	0·65	1·88
	0·1408	−0·0651	0·0346			
	0·1490	−0·0676	0·0471			
	0·1575	−0·0768	0·0185			
C(8)	0·2549	−0·0540	−0·0343	2·65	0·50	1·35
	0·2317	−0·0552	−0·0364			
	0·2372	−0·0560	−0·0240			
	0·2494	−0·0532	−0·0467			
C(9)	0·3876	0·2511	0·1260	2·35	0·65	1·10
	0·3738	0·2489	0·1465			
	0·3768	0·2644	0·1382			
	0·3845	0·2357	0·1344			
H(1a)	0·212	0·333	0·252	3·0	—	—
H(1b)	0·095	0·247	0·258	3·0	—	—
H(2a)	0·083	0·497	0·160	3·0	—	—
H(2b)	0·042	0·353	0·070	3·0	—	—
H(6)	0·055	0·040	0·158	3·0	—	—
H(7)	0·100	−0·167	0·020	3·0	—	—
H(8)	0·263	−0·125	−0·108	3·0	—	—
H(9a)	0·450	0·203	0·127	3·0	—	—
H(9b)	0·377	0·247	0·237	3·0	—	—
H(9c)	0·387	0·347	0·097	3·0	—	—

sequent structure-factor calculations, assuming (for simplicity) isotropic thermal motion with $B = 3\cdot0$ Å². (However, for Bragg angles exceeding 45°, the contributions of the hydrogen atoms were reckoned to be very small, and were omitted. Similarly, coefficients corresponding to Bragg angles exceeding 45° were omitted from the difference synthesis mentioned above, and from subsequent hydrogen-fixing syntheses. These innocuous abridgements conserved computation.) Three further cycles of refinement of the carbon positions were completed, with finite summation corrections estimated at each stage by comparison of F_o and F_c differential syntheses. The hydrogen positions were refined by means of one differential

Table 2. *Peak heights and curvatures*

Values in italics are from F_c differential synthesis

Atom	ϱ (e.Å^{-3})	ϱ_{xx} (e.Å^{-5})	ϱ_{yy} (e.Å^{-5})	ϱ_{zz} (e.Å^{-5})	ϱ_{xy} (e.Å^{-5})	ϱ_{yz} (e.Å^{-5})	ϱ_{xz} (e.Å^{-5})
C(1)	8·41	−75·3	−67·5	−86·0	0·3	0·9	6·9
	8·47	*−75·4*	*−69·9*	*−84·1*	*−0·7*	*0·8*	*5·2*
C(2)	8·35	−76·5	−77·0	−76·7	7·9	−3·6	5·8
	8·46	*−76·8*	*−78·5*	*−77·7*	*5·4*	*−3·3*	*4·8*
C(3)	9·29	−84·4	−87·1	−87·8	6·4	1·1	−3·1
	9·37	*−87·0*	*−87·2*	*−88·9*	*4·9*	*0·7*	*−2·5*
C(4)	9·9	−92·2	−93·8	−100·7	3·6	8·9	−2·5
	10·1	*−94·9*	*−96·2*	*−103·0*	*3·3*	*7·6*	*−1·5*
C(5)	9·28	−84·5	−80·6	−93·2	1·3	6·4	−2·9
	9·30	*−85·8*	*−81·8*	*−92·3*	*1·1*	*5·0*	*−3·1*
C(6)	8·35	−76·6	−73·9	−76·3	−3·6	9·5	1·0
	8·51	*−77·7*	*−76·1*	*−79·0*	*−2·2*	*6·9*	*0·8*
C(7)	7·97	−66·8	−79·1	−67·1	−5·0	4·8	−5·6
	8·00	*−67·4*	*−77·3*	*−68·9*	*−3·0*	*3·1*	*−4·0*
C(8)	8·41	−68·9	−83·9	−77·3	4·5	0·3	−2·7
	8·58	*−74·0*	*−83·1*	*−79·5*	*4·4*	*0·7*	*−0·6*
C(9)	8·97	−84·9	−82·3	−85·9	1·8	4·1	−2·4
	9·07	*−85·3*	*−84·2*	*−87·0*	*1·2*	*3·6*	*−0·7*
H(1a)	0·65	−3·2	−3·2	−3·0	−0·6	−0·2	0·0
H(1b)	0·57	−3·0	−2·4	−2·5	−0·1	0·2	0·2
H(2a)	0·55	−2·2	−3·1	−2·8	0·2	−0·1	0·2
H(2b)	0·67	−3·5	−3·2	−3·3	−0·3	−0·3	0·3
H(6)	0·54	−3·2	−2·0	−2·8	0·4	0·1	0·8
H(7)	0·55	−3·2	−3·1	−2·4	0·9	0·1	−0·1
H(8)	0·59	−2·8	−3·0	−3·4	−0·3	0·3	0·6
H(9a)	0·54	−3·3	−2·9	−2·0	0·3	−0·6	0·2
H(9b)	0·46	−2·0	−1·7	−2·7	−0·4	−0·2	0·5
H(9c)	0·54	−2·4	−3·2	−2·0	−0·3	0·3	−0·6

synthesis, the coefficients of which were the differences between F_o and the carbon contribution to F_c. A small portion of the corresponding Fourier synthesis has been computed also, in order to demonstrate the apparent non-rotation of the methyl group. A section through the methyl hydrogens is shown in Fig. 2.

At a late stage in the refinement, the more intense reflections were corrected for extinction in the manner described by Pinnock, Taylor & Lipson (1956). None of the corrections exceeded 20% of F_o.

The coordinates and temperature factors used in the final round of structure-factor calculations are given in Table 1. The quantities ΔB_1 and ΔB_2, however, do not appear in the calculations; they merely indicate the magnitude of the anisotropy represented by the corresponding rectangular distributions of quarter-atoms. Peak heights and curvatures are compared in Table 2; fair agreement between observed and calculated quantities appears to justify the treatment of thermal anisotropy. Much of this anisotropy can reasonably be interpreted as a libration of the molecule, of r.m.s. amplitude 3·0°, about its centre. Appropriate corrections to the atomic positions from the last refinement cycle have therefore been applied (Cruickshank, 1956). (The correction does not exceed 0·004 Å for any atom, and is therefore hardly significant.) The final atomic positions are given in Table 3.

Table 3. *Final atomic positions*

Atom	x	y	z
C(1)	0·1527	0·2868	0·2011
C(2)	0·1065	0·4000	0·1067
C(3)	0·3127	0·0597	−0·0128
C(4)	0·2941	0·1529	0·0864
C(5)	0·1930	0·1524	0·1378
C(6)	0·1249	0·0360	0·1133
C(7)	0·1530	−0·0725	0·0330
C(8)	0·2432	−0·0550	−0·0352
C(9)	0·3806	0·2501	0·1366
H(1a)	0·208	0·335	0·248
H(1b)	0·092	0·252	0·258
H(2a)	0·082	0·493	0·156
H(2b)	0·042	0·356	0·069
H(6)	0·055	0·039	0·154
H(7)	0·099	−0·161	0·016
H(8)	0·260	−0·121	−0·106
H(9a)	0·447	0·212	0·120
H(9b)	0·371	0·267	0·222
H(9c)	0·387	0·343	0·100

Assessment of results

Agreement between observed and calculated structure amplitudes is reasonable, and there can be no doubt of the essential correctness of the proposed structure. A summary of the agreement is given in Table 4.

Table 4. *Agreement summary*

Observed reflections

Category	Number of reflections
1. ($|\Delta F| \leq \frac{1}{4}F_T$ or $|\Delta F| \leq 0.1F_o$)	1068
2. ($\frac{1}{4}F_T < |\Delta F| \leq F_T$ or $0.1F_o < |\Delta F| \leq 0.2F_o$)	170
3. ($F_T < |\Delta F| \leq \frac{3}{2}F_T$ or $0.2F_o < |\Delta F| \leq 0.3F_o$)	19
4. ($\frac{3}{2}F_T < |\Delta F| \leq 2F_T$)	1

Unobserved reflections

1. ($|F_c| \leq F_T$)	154
2. ($F_T < |F_c| \leq \frac{3}{2}F_T$)	7
3. ($\frac{3}{2}F_T < |F_c| \leq 2F_T$)	1

$\Delta F = |F_o| - |F_c|$

F_T = estimated minimum observable structure amplitude for reflection concerned

The observed structure amplitudes range from 1·1 to 143·5, and $F_c(000) = 848$. The agreement residual ($R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$) is 0·061, for observed reflections only. A complete list of F_o and F_c is available from the author, on request.

The standard deviation of atomic positions has been estimated by Cruickshank's method (Lipson & Cochran, 1953). For carbon atoms it varies from 0·0015 to 0·0029 Å, with average value 0·002 Å. For hydrogen atoms the average value is 0·05 Å.

Description of the structure

The details of the structure are summarized in the several sketches of Fig. 3. The two benzene rings are displaced stepwise, and are distorted to a boat shape
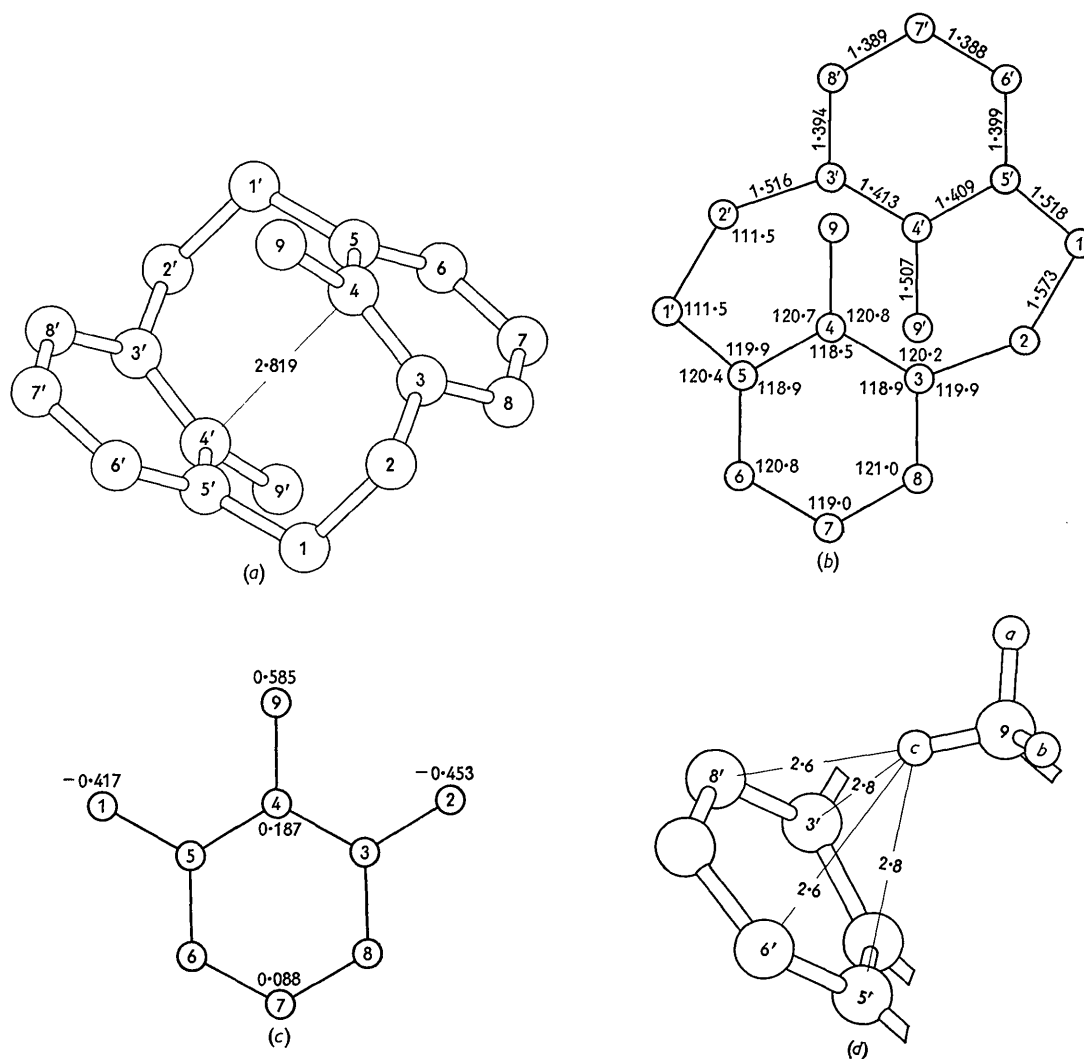

Fig. 3. Structural details; distances are given in Ångström units, and angles in degrees. (*a*) The carbon skeleton, viewed along **a**. The estimated standard deviation of the distance C(4)–C(4)' is 0·003 Å. (*b*) Bond lengths and angles. E.s.d. of bond lengths is 0·003 Å; of angles, 0·3°. (*c*) Distances of some atoms from the plane containing the positions of C(3), C(5), C(6), and C(8). (*d*) Juxtaposition of the methyl group and the opposing benzene ring. E.s.d. of distances is 0·05 Å.

in order to avoid too close mutual contact. The atoms C(3), C(5), C(6), and C(8) are precisely coplanar; the distances of adjacent atoms from this plane are shown in Fig. 3(c). A good indication of molecular strain is given by the length of the bond C(1)–C(2): 1·573 Å, with e.s.d. 0·003 Å. The distortions of the molecule are similar to, but greater than, those observed for the parent compound (2·2)metacyclophane, or di-m-xylylene (Brown, 1953b). The increased distortion undoubtedly results from the need to accommodate the methyl group, and it is therefore interesting to find that the methyl carbon (C(9)) is coplanar with the atoms C(3), C(4), and C(5), within the accuracy of the analysis.

The van der Waals contacts are normal; there are no intermolecular C–C distances less than 3·68 Å, but there are 17 per molecule in the range 3·68–4·00 Å.

In general the hydrogen atoms have not been located with sufficient accuracy to merit discussion. The positions are reasonable, and the mean C–H distance is 1·0 Å. The juxtaposition of the methyl group and the opposing benzene ring is illustrated in Fig. 3(d); the nearest hydrogen atom might be described as resting in the dimple of the π electron system.

The methyl group appears to be stationary, and this is not surprising when the proximity of other atoms is considered. Nevertheless, nuclear magnetic resonance studies have failed to distinguish the individual protons even at temperatures as low as −20 °C. The implied rotation need only be very slight, however; it is stated that 'due to tunneling, the barrier to the methyl group rotation would need to be of the order of 20 kcal. to affect the n.m.r. spectrum'

(Wilson, Boekelheide & Griffin, 1960). Moreover, the present work cannot very well distinguish between non-rotation and a state of strongly hindered rotation in which the observed configuration corresponds to a deep potential well. There is therefore no conflict between the n.m.r. study and the present work.

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Dimorphism in Methyl Ammonium Alum

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Dimorphism at room temperature in methyl ammonium alum has been induced by the repeated cooling of a single crystal of the alum to temperatures within the range 170 to 150 °K.; both structures have space group Pa3, the unit-cell edges being 12·50 and 12·17 Å respectively. Although the effect has been confined to single crystals from one particular batch, and to that extent appears to be fortuitous, it nevertheless confirms that the alum is dimorphous, the conclusion drawn by Lipson (1935a) from a study of the morphological features of a crystal of methyl ammonium alum deposited from solution on rubidium alum.

Introduction

It was shown by Lipson (1935a) that the alums, which had hitherto been considered to form an isomorphous series, were in fact polymorphous and could be classified as α, β and γ alums according to

which of three different types of structure they belonged. It was evident that the particular class of alum depended upon the size of the monovalent ion and Lipson (1935b) therefore considered the possibility of inducing one class of alum in another. Subsequently (Lipson, 1935a) he deposited from solution methyl