

The Crystal Structure of 4,12-Di(bromomethyl)[2,2]metacyclophane

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The crystal is monoclinic, $P2_1/c$, with $a = 7.84$, $b = 14.01$, $c = 7.50$ Å; $\beta = 114.71^\circ$; $Z = 2$; formula $C_{18}H_{18}Br_2$. The structure was determined from three-dimensional Patterson and Fourier syntheses and refined by least-squares procedures. The two benzene rings are displaced stepwise and slightly distorted to a boat shape to avoid too close mutual contacts.

Introduction

Crystallographic studies of [2,2]metacyclophane (Brown, 1953) and 4,12-dimethyl[2,2]metacyclophane (hereafter referred to as A) (Hanson, 1962) have shown that these molecules are considerably distorted by steric factors. A bromoderivative of A was prepared, with formula $C_{18}H_{18}Br_2$, in the expectation that it would be a simple substitution product in which a hydrogen atom in each of the methyl groups is replaced by bromine (Boekelheide, 1965). However, its properties are more consistent with that of a complex in which bromine ions stabilize a carbonium ion (Boekelheide, 1965). X-ray analysis was undertaken in order to investigate this possibility, but in fact the compound was found to be the expected substitution product.

Experimental

Crystal data

Monoclinic

$a = 7.84 \pm 0.01$, $b = 14.01 \pm 0.02$, $c = 7.50 \pm 0.01$ Å

$\beta = 114.71 \pm 0.05^\circ$

$V = 748.4$ Å³

Formula weight 394.16

$D_m = 1.76 + 0.01$ g.cm⁻³

$D_x = 1.749 + 0.004$ g.cm⁻³

$Z = 2$

$\mu = 75$ cm⁻¹ (Cu $K\alpha$)

Systematic absences: $h0l$ for l odd; $0k0$ for k odd

Space group $P2_1/c$ (from precession and Weissenberg photographs)

Molecular symmetry: centrosymmetric.

The compound crystallizes in thin plates. A small plate of thickness 0.05 mm was cut to a dimension of 0.10 mm \times 0.13 mm and this was used for the measurement of intensities.

The required goniostat settings were pre-computed. The moving-crystal moving-counter method of Furnas (1957) was used. Cu $K\alpha$ radiation was used and reasonable monochromatization was achieved by means of a $K\beta$ filter and pulse height analyser. Reflexions with $2\theta \leq 135^\circ$ were measured on a Picker manual diffractometer with full circle goniometer and those with $135^\circ < 2\theta \leq 164^\circ$ on the General Electric XRD 5 spectrogoniometer. Of the 1657 reflexions accessible to the spectrogoniometer ($2\theta \leq 164^\circ$ for Cu $K\alpha$) 1128 were observed. No absorption corrections were applied.

Structure determination

The structure determination was started with those reflexions for which 2θ was less than 135° . A three-

Table 1. Final parameters of the bromine and carbon atoms

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
	$\times 10^4$	$\times 10^4$	$\times 10^4$	$\times 10^5$	$\times 10^5$	$\times 10^5$	$\times 10^5$	$\times 10^5$	$\times 10^5$
Br	8934	3614	4254	3495	4158	7262	152	-1194	1991
C(1)	5121	3998	-2880	5586	4675	3459	217	-85	-1277
C(2)	5507	3328	-1079	4375	2845	5757	407	-631	-1218
C(3)	4592	3673	230	3536	2278	4150	46	-258	930
C(4)	5443	4410	1616	2911	2715	3211	-101	-235	808
C(5)	4332	4975	2243	4112	3750	2624	235	-533	-140
C(6)	2559	4649	1911	4269	5699	3724	1221	874	993
C(7)	1844	3825	849	3109	4725	6409	-28	544	2396
C(8)	2801	3373	-88	3366	3183	6198	-534	-822	1694
C(9)	7492	4602	2324	2716	2715	5263	-104	-849	809

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$$\text{T.F.} = \exp \left[-2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hk \cdot a^*b^* + 2U_{13}hl \cdot a^*c^* + 2U_{23}kl \cdot b^*c^*) \right]$$

dimensional Patterson synthesis was first computed and the positions of the bromine atoms were deduced. Structure factor calculations with bromine alone gave an R index of 0.31. A Fourier synthesis with the phases of the bromine contributions clearly showed all the carbon atoms. Their coordinates were refined by a second Fourier synthesis.

The refinement was completed by the least-squares method, with the program of Ahmed (1966). The program uses the block diagonal approximation with a 3×3 matrix for positional parameters and a 6×6

matrix for the thermal parameters of each atom. The scale factor of observed structure amplitudes and the overall isotropic temperature factor are refined by a 2×2 matrix (Cruickshank, 1961). Schomaker's correction (Hodgson & Rollett, 1963) is applied to the shifts of the thermal parameters. The weighting scheme used was $w = F_o^2/16F_T$ if $|F_o| \leq 4F_T$ or $w = 16F_T/F_o^2$ if $|F_o| > 4F_T$, where F_T is the nominal minimum value of F_o , in this case 2.2.

After three cycles of least-squares refinement with anisotropic thermal parameters for bromine and car-

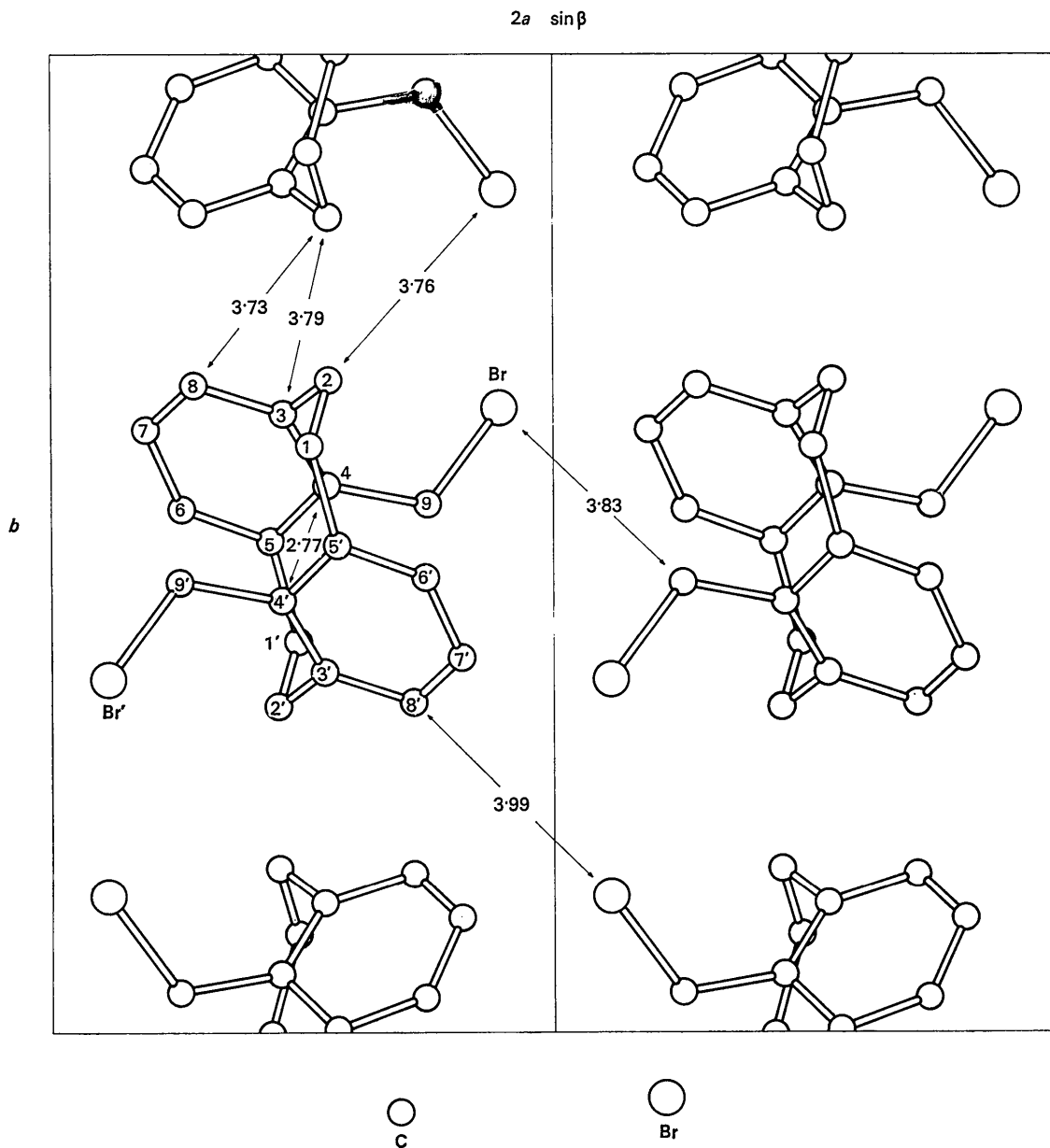


Fig. 1. Structural details; distances are given in Å and angles in degrees. (a) The structure viewed along c . The estimated standard deviation of the distance $C(4)-C(4')$ is 0.01 Å. Some of the short intermolecular distances are also given.

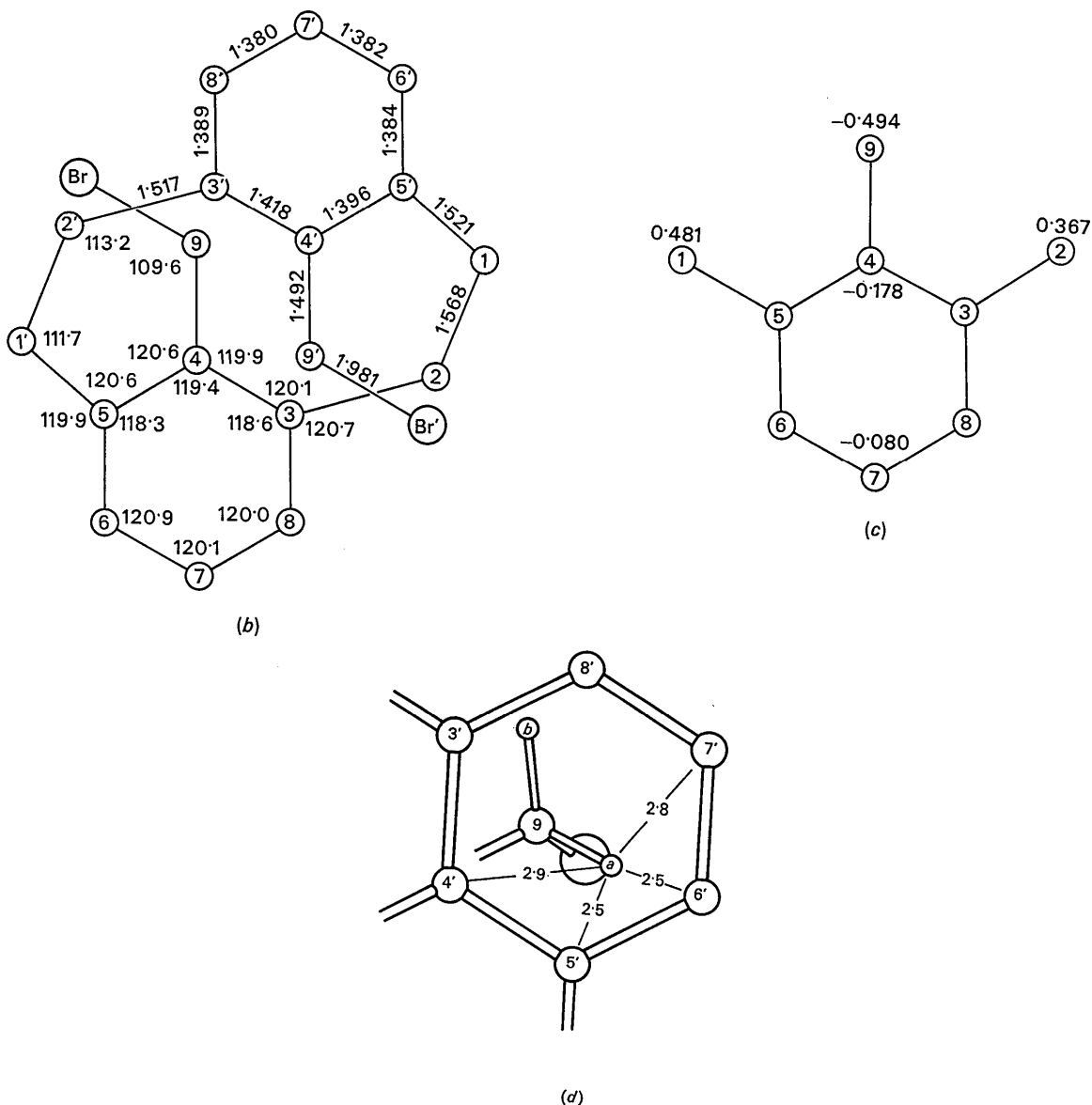


Fig. 1 (cont.) (b) A distorted view of the molecule showing bond lengths and angles. E.s.d. of bond lengths is 0.008 Å; of angles, 0.5° [0.4° for C(4)–C(9)–Br]. (c) Distances of adjacent atoms from the plane containing the positions of C(3), C(5), C(6), and C(8). (d) Projection of the opposing bromomethyl group on the plane containing positions C(3), C(5), C(6), and C(8). Some of the distances involving hydrogen atoms are also given.

bon atoms, the *R* index was 0.086. At this point a difference synthesis gave a fair indication of the positions of the hydrogen atoms and the contributions of the hydrogen atoms were included in subsequent calculations. The positions of the hydrogen atoms were, however, estimated from theoretical considerations and were not refined. Their thermal motion was assumed to be isotropic and they were given the average value for their bonded carbon atoms. Atomic scattering factors for bromine were taken from *International Tables for X-ray Crystallography* (1962, p. 206) and for carbon and hydrogen from Freeman (1959).

Table 2. Parameters of the hydrogen atoms

Atom	<i>x</i> × 10 ³	<i>y</i> × 10 ³	<i>z</i> × 10 ³	<i>B</i>
H(1a)	375	398	−377	3.69 Å ²
H(1b)	587	377	−359	3.69
H(2a)	690	330	−28	3.38
H(2b)	502	268	−158	3.38
H(6)	179	502	245	3.76
H(7)	63	356	77	3.86
H(8)	220	283	−100	2.96
H(9a)	784	459	119	2.70
H(9b)	778	524	297	2.70

Table 3. Observed and calculated structure factors

Table with multiple columns of numerical data representing observed and calculated structure factors for various h, k, l indices. The table is organized into several groups of columns, each representing a different set of indices (e.g., L FO FC, L FO FC, etc.).

Table 3 (cont.)

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC			
H _m 7, K _m 10																													
0 68 ^o -62	H _m 7, K _m 12	0 203 -203	-4 90 ^o 27			0 81 -103			-5 88 ^o 40			-2 80 ^o 61			-1 60 ^o 23			-6 104 -98			-4 78 ^o 40			-2 74 -64			-3 104 111		
1 62 -62		2 309 5	-6 84 ^o 23			-1 66 ^o 21			-7 88 ^o 30			-3 121 -104			-3 150 -155			H _m 9, K _m 1			-5 74 ^o 21			-3 74 ^o 53			-4 62 -64		
-1 82 -85		-2 67 74	-2 206 -209			-8 60 ^o -16			-2 126 120	H _m 8, K _m 6		-6 69 ^o -7			-4 65 ^o -12			-6 70 ^o 30			-4 97 89			-5 62 ^o 54			-6 84 -84		
-2 150 140		-3 639 -12	-4 91 ^o -75			-3 91 52			-7 55 ^o -44			-6 69 ^o -7			-6 57 54			-7 57 ^o -4			-5 72 ^o 38			-6 64 ^o 65			H _m 9, K _m 7		
-3 79 ^o -29		-4 60 62	-5 108 -101			0 140 -134			-5 85 ^o -54			0 71 45			-1 126 126			0 55 ^o -20			H _m 9, K _m 3			-2 182 126			H _m 9, K _m 5		
-4 115 99		-5 86 -109	-6 86 ^o 63			-1 119 -121			-6 98 113			-3 117 176			-2 182 126			-3 179 18			0 47 ^o 3			-1 56 ^o -40			-2 52 ^o 24		
-5 75 ^o 3		-6 63 ^o -45	H _m 8, K _m 0			-7 76 ^o -48			-8 52 ^o 15			-4 127 -120			-3 83 -64			-4 81 86			-2 122 -115			-3 59 ^o -32			-4 56 45		
H _m 7, K _m 11		0 146 135	H _m 8, K _m 2			-2 102 -118			-3 151 148	H _m 8, K _m 5		-5 80 ^o -16			-3 83 -64			-4 81 86			-5 52 ^o -18			-5 112 104			-5 77 85		
0 58 ^o -29		-2 156 165				-4 93 -80			-5 155 150			0 173 171			-6 75 ^o -9			-5 72 ^o 55			H _m 9, K _m 2			-6 87 ^o -48			-6 138 127		
-1 66 64		-4 222 -225				-7 155 150			0 173 171			-7 60 -51			-6 08 ^o -46			H _m 9, K _m 0			0 53 ^o -34			-7 53 ^o 44			-4 50 ^o -29		
-2 72 ^o -14		-8 96 -91				-6 83 ^o 50			1 79 -76			-1 79 -76			0 214 209			H _m 9, K _m 4			-1 151 -152			H _m 9, K _m 4			H _m 10, K _m 1		
-3 170 181		-8 63 ^o -40				-1 82 ^o -55			-2 253 245			-3 96 19			-2 75 ^o 34			H _m 8, K _m 7			-2 75 ^o -30			-1 63 86			-4 65 -68		
-4 71 ^o -13		-1 256 -245				-8 57 ^o 19			-2 253 245			-3 96 19			-4 91 -104			0 45 ^o -7			-4 91 -104			-3 147 -140					
-5 114 128		-2 91 ^o 44				-4 86 ^o 60			-1 80 68																				
-6 49 ^o -22		-3 183 -172																											

Data from the General Electric XRD 5 spectrogoniometer (*i.e.* reflexions for which $135^\circ < 2\theta \leq 164^\circ$) were combined with those from the Picker diffractometer at this stage and the refinement was continued. The reflexions 032, 1,17,2, and 22 $\bar{2}$, which appeared to be in error were given zero weight. After three more cycles, the indicated coordinate shifts were small (maximum 0.4σ) and so the refinement was considered to be complete. The final parameters are given in Tables 1 and 2. The numbers of the hydrogen atoms are those of the bonded carbon atoms.

Assessment of results

Agreement between observed and calculated structure amplitudes is reasonable and there can be no doubt about the essential correctness of the proposed structure. The observed and calculated structure amplitudes are given in Table 3 and a summary of the agreement in Table 4.

Table 4. Agreement summary

Category	Number of reflexions
Observed reflexions	
1. $ \Delta F \leq \frac{1}{2}F_T$ or $ \Delta F \leq 0.1F_0$	1081
2. $\frac{1}{2}F_T < \Delta F \leq F_T$ or $0.1F_0 < \Delta F \leq 0.2F_0$	39
3. $F_T < \Delta F \leq \frac{3}{2}F_T$ or $0.2F_0 < \Delta F \leq 0.3F_0$	8
Unobserved reflexions	
1. $ F_c \leq F_T$	426
2. $F_T < F_c \leq \frac{3}{2}F_T$	93
3. $\frac{3}{2}F_T < F_c \leq 2F_T$	10

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

F_T = estimated minimum observable structure amplitude for reflexion concerned.

$$R = (\sum ||F_o| - |F_c|| / \sum |F_o|) = 0.050 \text{ (observed reflexions only).}$$

The standard deviations of the coordinates, estimated from least squares results, are 0.001 \AA for the bromine atoms and 0.006 \AA (mean) for the carbon atoms.

Description of the structure

The details of the structure are summarized in the several sketches of Fig. 1. The C-Br bond length ($1.981 \pm 0.005 \text{ \AA}$) is slightly larger than the value of 1.937 \AA quoted as the mean for aliphatic compounds (*International Tables for X-ray Crystallography*, 1962). This may result from strain due to crowding, but there is

no doubt about the covalent nature of the C-Br bond.

The benzene rings are displaced stepwise and are slightly distorted to a boat shape as in the parent compound 4,12-dimethyl[2.2]metacyclophane (A) in order to avoid too close mutual contacts (Hanson, 1962). The distortions of the molecule are quite similar to, and of the same magnitude as, those in A. The present study extends additional evidence for the stretching of the C(1)-C(2) bond ($C(1)-C(2) = 1.568 \pm 0.008 \text{ \AA}$, compared with $1.573 \pm 0.003 \text{ \AA}$ in A) indicative of the molecular strain.

The atoms C(3), C(5), C(6), and C(8) are coplanar within the accuracy of the analysis. The distances of adjacent atoms from this plane are shown in Fig. 1(c).

The van der Waals contacts are normal. There are no intermolecular C-C distances less than 3.68 \AA .

The disposition of the bromomethyl group and the opposing benzene ring is illustrated in Fig. 1(d). The arrangement is a compromise between the packing tendencies of the bromine atom (as far away from the opposing ring as possible) and the nearer hydrogen atom (in the cavity of the π electron system). It must be remembered, however, that the positions of the hydrogen atoms have merely been deduced from theoretical considerations.

The problem was suggested and the specimen material supplied by Prof. V. Boekelheide. Computations were carried out on the IBM/360 model 50 computer using programs by Dr F. R. Ahmed and Mrs M. E. Pippy. Their assistance, and the continued encouragement of Dr W. H. Barnes and Dr A. W. Hanson, is gratefully acknowledged.

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