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X-ray Structure and Crystal Packing Analysis of Triphenylbromomethane,* C₁₉H₁₅Br

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Abstract

$M_r = 323.2$, trigonal, $P\bar{3}$, $a = 13.933(3)$, $c = 13.438(4)$ Å, $V = 2266.7$ Å³, $Z = 6$, $D_m = 1.42$, $D_x = 1.421$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.866$ mm⁻¹, $F(000) = 984$, room temperature, final $R = 0.049$ for 976 observed reflections. The molecules lie in special positions on the crystallographic three-fold axes. They are associated in pairs and form two distinct Ph₃C–Br···Br–CPh₃ head-to-head arrangements characterized by long C–Br bonds and short Br···Br contacts. The shortest Br···Br distance (3.203 Å) is about 0.5 Å smaller than the sum of the van der Waals radii. The lattice energy was computed using two different sets of published Buckingham potential functions. These calculations account satisfactorily for all the salient features of the crystal packing. Analysis of the thermal motion showed that the rigid-body approximation holds reasonably well for the triphenylbromomethane molecule.

Introduction

The present study is a natural extension to our recent investigation of the crystal structure and crystal packing of triphenylchloromethane (Dunand & Gerdil, 1982). Triphenylchloromethane (TPCM) and triphenylbromomethane (TPBM) crystallize in isomorphous systems and both structures display linear head-to-head C–X···X–C arrangements with long C–X bonds and unusually short X···X contacts. Previous studies by Landais (1953) and Stora & Poyer (1966) had already revealed the occurrence

of short Br···Br intermolecular contacts in TPBM crystals.

Experimental

Colourless hexagonal prisms of TPBM (Merck) grown from dry petroleum ether, m.p. 421–422 K, D_m measured by flotation, hygroscopic crystal sealed under argon in Lindemann capillary, 0.22 × 0.30 × 0.32 mm; automatic four-circle Philips PW 1100 diffractometer, graphite-monochromated Mo $K\alpha$; 38 reflections within range $10 \leq 2\theta \leq 30^\circ$ used for measuring lattice parameters; 2585 independent reflections scanned in the ω – 2θ mode, scan width 1.0° , scan speed $0.02^\circ \text{ s}^{-1}$, $6.0 \leq 2\theta \leq 50^\circ$, range of hkl : $-14 \leq h \leq 14$, $0 \leq k \leq 14$, $0 \leq l \leq 16$; three standard reflections monitored at 60 min intervals showed insignificant intensity variations: $2\bar{1}\bar{3}$, 241 and $\bar{5}43$ had average count rates and e.s.d.'s of 27423(217), 65720(523) and 55068(365); absorption corrections according to CAMEL JOCKEY method (Flack, 1975), minimum and maximum corrections 0.935 and 1.065 applied on F_o ; 976 reflections considered observed at the $2\sigma(I)$ level and used in the structure analysis; no systematic absences; structure solved by heavy-atom method, H atoms located from difference synthesis; full-matrix least-squares refinement on F ; calculations carried out with anisotropic temperature factors for non-H atoms and isotropic factors for H; final $R = 0.049$, $wR = 0.032$, $S = 1.7$, $w = 1/\sigma^2(F_o)$; ratio of maximum least-squares shift-to-error = 0.4, average ratio = 0.1; no extinction correction; atomic scattering factors for C and Br from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965), anomalous-dispersion correction for Br from Cromer (1965); programs of the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

* (Bromo)triphenylmethane.

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Table 1. Fractional coordinates ($\times 10^4$) and isotropic thermal parameters ($\times 10^3$)

Thermal parameters for non-hydrogen atoms are given in the form

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \cdot a_j$$

	x	y	z	U_{eq}/U_{iso} (\AA^2)
Br(1)	0	0	1296 (1)	90 (1)
C(1)	0	0	2802 (7)	57 (5)
C(2)	1196 (6)	796 (7)	3121 (5)	55 (5)
C(3)	1749 (8)	1872 (8)	2748 (5)	72 (5)
C(4)	2815 (8)	2611 (7)	3085 (7)	84 (6)
C(5)	3335 (7)	2293 (9)	3779 (7)	86 (6)
C(6)	2778 (8)	1251 (9)	4142 (5)	75 (5)
C(7)	1721 (7)	502 (6)	3821 (5)	59 (5)
Br(2)	6667	3333	2443 (1)	112 (1)
C(8)	6667	3333	948 (7)	58 (5)
C(9)	5528 (7)	2398 (6)	633 (6)	62 (5)
C(10)	5412 (7)	1673 (8)	-103 (6)	69 (5)
C(11)	4369 (11)	867 (8)	-425 (6)	89 (7)
C(12)	3447 (9)	793 (9)	31 (9)	107 (7)
C(13)	3558 (10)	1507 (10)	753 (9)	103 (7)
C(14)	4590 (10)	2331 (7)	1066 (6)	77 (6)
Br(3)	3333	6667	5181 (1)	116 (1)
C(15)	3333	6667	3697 (8)	55 (5)
C(16)	2210 (6)	5709 (6)	3365 (6)	58 (5)
C(17)	2129 (7)	5037 (8)	2588 (6)	67 (5)
C(18)	1098 (10)	4226 (8)	2247 (6)	84 (6)
C(19)	155 (9)	4081 (8)	2692 (9)	97 (7)
C(20)	216 (9)	4726 (9)	3461 (8)	94 (7)
C(21)	1227 (10)	5560 (7)	3802 (5)	77 (5)
H(3)	1374 (37)	2061 (37)	2207 (28)	78 (16)
H(4)	3135 (39)	3313 (40)	2868 (32)	93 (18)
H(5)	4027 (35)	2854 (36)	3964 (28)	73 (16)
H(6)	3062 (46)	1016 (43)	4740 (34)	114 (20)
H(7)	1325 (32)	-217 (32)	4103 (24)	51 (13)
H(10)	6088 (32)	1751 (30)	-366 (23)	45 (13)
H(11)	4369 (40)	409 (40)	-975 (31)	94 (18)
H(12)	2783 (40)	312 (40)	-203 (32)	97 (18)
H(13)	3012 (47)	1507 (47)	1078 (35)	129 (21)
H(14)	4651 (39)	2855 (38)	1598 (29)	89 (18)
H(17)	2753 (39)	5129 (36)	2292 (28)	80 (16)
H(18)	1120 (42)	3743 (44)	1668 (33)	117 (20)
H(19)	-475 (41)	3584 (42)	2475 (35)	109 (20)
H(20)	-436 (46)	4688 (49)	3844 (35)	139 (22)
H(21)	1323 (32)	6099 (31)	4334 (25)	50 (14)

Discussion

Final atomic and thermal parameters are listed in Table 1.* The atom-numbering system is shown in Fig. 1. The bond lengths and angles are given in Tables 2 and 3. Weighted mean values were calculated over equivalent bonds and angles. The associated e.s.d.'s are $\sigma_m = [\sum_i w_i (x_i - \bar{x}_m)^2 / (N-1) \sum_i w_i]^{1/2}$ and $\sigma'_m = (\sum_i w_i)^{-1/2}$, where $w_i = \sigma_i^{-2}$.

Molecular geometry

Each of the three independent propeller-shaped TPBM molecules has its C-Br bond coincident with a crystallographic threefold axis and therefore

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP38763 (21pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

possesses C_3 symmetry. When listed, the salient structural parameters of the unique part of each independent molecule will refer, in sequence, to molecules (I), (II) and (III) respectively, as labelled in Fig. 1.

The C-Br bond lengths are longer than the standard value of 1.97 Å. However, values larger than 2.0 Å are by no means rare. Gopalakrishna, Cooper & Norton (1969) have reported nine compounds displaying C-Br bond-length values exceeding this magnitude. A structural survey of the aliphatic bromo compounds clearly indicates that the C-Br bond distances increase regularly with increasing C-C-Br angles (Dunand, 1977). The bond lengths range roughly from 1.90 to 2.08 Å whereas the bond angles decrease correspondingly from 120 to 102°. The geometries observed for the three TPBM molecules fit into this scheme. Crystallographically equivalent TPBM and TPCM molecules have very similar overall geometries; in particular, the distortions from tetrahedral angular symmetry at the central C_c atom are equal within experimental error (average C-C-C and C-C-C-X angle values 112.3 and 106.5°, respectively). The internal steric interactions already detailed for TPCM (Dunand & Gerdil, 1982) are equally operative in TPBM. The dihedral angles between the phenyl mean planes and the plane through the C-C-Br fragment are 51.1, 46.6 and 44.0°, respectively.

Crystal packing analysis

Owing to the TPBM molecules being positioned on the crystallographic threefold axes the molecular

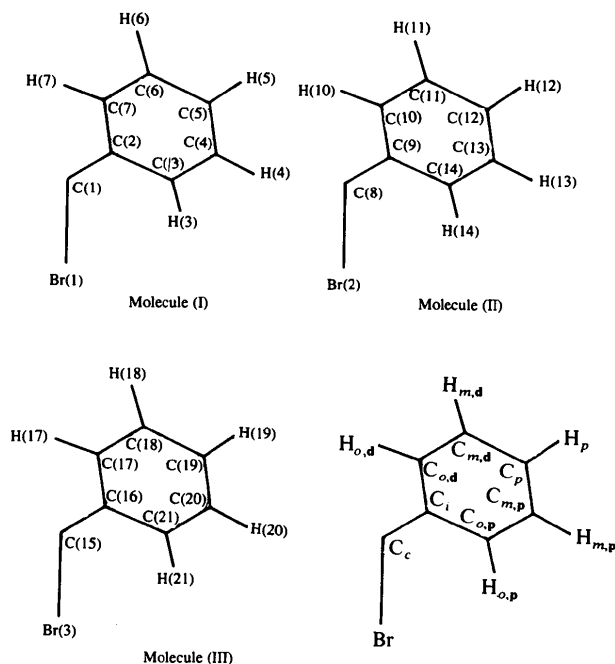


Fig. 1. The atom-numbering system and labelling scheme. $i = ipso$, $o = ortho$, $m = meta$, $p = para$; $p = proximal$, $d = distal$.

Table 2. Bond lengths (Å) with *e.s.d.*'s

\bar{d} is the weighted mean value calculated over the three molecules. σ'_m and σ_m are defined in the text ($\times 10^3$ for C-C, $\times 10^2$ for C-H bonds).

Molecule (I)	Molecule (II)	Molecule (III)	\bar{d}	σ'_m	σ_m			
C(1)-Br(1)	2.031 (10)	C(8)-Br(2)	2.016 (10)	C(15)-Br(3)	2.002 (11)	2.016	6	8
C(1)-C(2)	1.531 (7)	C(8)-C(9)	1.526 (7)	C(15)-C(16)	1.530 (7)	1.529	4	2
C(2)-C(3)	1.393 (13)	C(9)-C(14)	1.391 (17)	C(16)-C(21)	1.408 (16)	1.397	8	5
C(3)-C(4)	1.393 (12)	C(13)-C(14)	1.383 (14)	C(20)-C(21)	1.381 (13)	1.386	7	4
C(4)-C(5)	1.386 (16)	C(12)-C(13)	1.345 (19)	C(19)-C(20)	1.347 (17)	1.360	10	14
C(5)-C(6)	1.349 (14)	C(11)-C(12)	1.381 (20)	C(18)-C(19)	1.364 (18)	1.361	10	9
C(6)-C(7)	1.382 (11)	C(10)-C(11)	1.390 (13)	C(17)-C(18)	1.388 (12)	1.386	7	3
C(2)-C(7)	1.375 (13)	C(9)-C(10)	1.366 (13)	C(16)-C(17)	1.371 (13)	1.371	7	3
C(3)-H(3)	1.01 (5)	C(14)-H(14)	1.00 (5)	C(21)-H(21)	1.00 (4)	1.00	3	0
C(4)-H(4)	0.90 (5)	C(13)-H(13)	0.88 (7)	C(20)-H(20)	1.02 (7)	0.93	3	4
C(5)-H(5)	0.92 (5)	C(12)-H(12)	0.89 (4)	C(19)-H(19)	0.85 (4)	0.89	2	2
C(6)-H(6)	1.02 (6)	C(11)-H(11)	0.98 (5)	C(18)-H(18)	1.04 (6)	1.01	3	2
C(7)-H(7)	0.95 (4)	C(10)-H(10)	0.96 (5)	C(17)-H(17)	0.91 (6)	0.94	3	1

Table 3. Bond angles (°) with *e.s.d.*'s

$\bar{\theta}$ is the weighted mean value calculated over the three molecules (σ'_m and $\sigma_m \times 10$).

Molecule (I)	Molecule (II)	Molecule (III)	$\bar{\theta}$	σ'_m	σ_m			
Br(1)-C(1)-C(2)	106.3 (4)	Br(2)-C(8)-C(9)	106.2 (5)	Br(3)-C(15)-C(16)	107.0 (5)	106.5	3	4
C(2)-C(1)-C(2)	112.4 (5)	C(9)-C(8)-C(9)	112.6 (5)	C(16)-C(15)-C(16)	111.8 (5)	112.3	3	4
C(1)-C(2)-C(3)	119.7 (8)	C(8)-C(9)-C(14)	118.8 (7)	C(15)-C(16)-C(21)	120.1 (7)	119.5	4	4
C(1)-C(2)-C(7)	121.7 (7)	C(8)-C(9)-C(10)	121.4 (8)	C(15)-C(16)-C(17)	121.2 (8)	121.5	4	1
C(3)-C(2)-C(7)	118.5 (7)	C(10)-C(9)-C(14)	119.6 (7)	C(17)-C(16)-C(21)	118.5 (7)	118.8	4	4
C(2)-C(3)-C(4)	119.3 (9)	C(9)-C(14)-C(13)	118.7 (10)	C(16)-C(21)-C(20)	119.5 (9)	119.2	5	2
C(3)-C(4)-C(5)	121.2 (8)	C(12)-C(13)-C(14)	121.5 (13)	C(19)-C(20)-C(21)	121.0 (11)	121.2	6	1
C(4)-C(5)-C(6)	118.5 (8)	C(11)-C(12)-C(13)	120.6 (10)	C(18)-C(19)-C(20)	120.3 (9)	119.7	5	7
C(5)-C(6)-C(7)	121.4 (10)	C(10)-C(11)-C(12)	118.6 (10)	C(17)-C(18)-C(19)	120.2 (9)	120.0	6	8
C(2)-C(7)-C(6)	121.0 (8)	C(9)-C(10)-C(11)	121.0 (10)	C(16)-C(17)-C(18)	120.5 (9)	120.8	5	2
C(2)-C(3)-H(3)	118 (2)	C(9)-C(14)-H(14)	121 (3)	C(16)-C(21)-H(21)	116 (2)	117	1	1
C(4)-C(3)-H(3)	123 (2)	C(13)-C(14)-H(14)	120 (3)	C(20)-C(21)-H(21)	125 (3)	123	2	1
C(3)-C(4)-H(4)	118 (4)	C(14)-C(13)-H(13)	113 (3)	C(21)-C(20)-H(20)	112 (3)	114	2	2
C(5)-C(4)-H(4)	121 (3)	C(12)-C(13)-H(13)	126 (3)	C(19)-C(20)-H(20)	127 (3)	125	2	2
C(4)-C(5)-H(5)	114 (3)	C(13)-C(12)-H(12)	121 (4)	C(20)-C(19)-H(19)	120 (4)	117	2	2
C(6)-C(5)-H(5)	128 (3)	C(11)-C(12)-H(12)	119 (4)	C(18)-C(19)-H(19)	120 (4)	123	2	3
C(5)-C(6)-H(6)	122 (3)	C(12)-C(11)-H(11)	126 (3)	C(19)-C(18)-H(18)	125 (3)	124	2	1
C(7)-C(6)-H(6)	116 (3)	C(10)-C(11)-H(11)	115 (3)	C(17)-C(18)-H(18)	115 (3)	116	2	0
C(2)-C(7)-H(7)	121 (3)	C(9)-C(10)-H(10)	123 (2)	C(16)-C(17)-H(17)	120 (3)	122	1	1
C(6)-C(7)-H(7)	118 (3)	C(11)-C(10)-H(10)	116 (2)	C(18)-C(17)-H(17)	120 (3)	118	1	1

packing can be described in terms of two distinct head-to-head arrangements of pairs of molecules (see Fig. 2). Molecule (I) lies on the rotatory-inversion axis and is coupled with its enantiomer (I'). The molecular pair (II)-(III'), and its equivalent (II')-(III), are located on the proper threefold axes, and have their components interrelated by 'pseudo' symmetry centres at about $\frac{2}{3}, \frac{1}{3}, \frac{4}{11}$ and $\frac{1}{3}, \frac{2}{3}, \frac{7}{11}$ respectively. In the first C-Br...Br'-C' collinear arrangement, the halogen separation Br(1)...Br'(1) is 3.496(2) Å, 0.2 Å shorter than the sum of the van der Waals radii (3.70 Å) as proposed by Bondi (1964). The other intermolecular contact Br(2)...Br'(3) = 3.203(2) Å is 0.5 Å shorter than the van der Waals distance (Fig. 2) and 0.9 Å longer than the Br-Br bond (2.28 Å). It is the shortest Br...Br contact ever observed in the solid state. Another short Br...Br distance (3.3 Å) is observed in solid Br₂ with the Br-Br bonds lying at an angle (Vonnegut & Warren, 1936). Intermolecular C...H and H...H contacts behave normally.

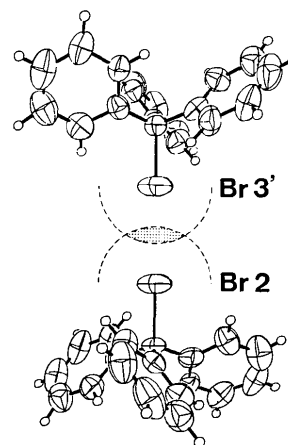


Fig. 2. Head-to-head pairing of two crystallographic independent TPBM molecules in the unit cell. The proper threefold axis is coincident with the C-Br bonds. The dashed lines outline the 'shape' of the Br atoms (van der Waals radius 1.85 Å). The intermolecular overlap region is represented by the dotted area.

Table 4. *Molecular packing analysis*

The results were calculated: in columns (a), with the torques of the phenyl rings fixed at their experimental values (*); in columns (b), with optimized rotation of the rings about the C_i-C_c bond.

Potential field	W-BB I		W-BB II	
	(a)	(b)	(a)	(b)
Lattice energy (kJ mol ⁻¹)	-414.5	-415.7	-412.5	-415.0
Calculated <i>a</i> (Å)	13.318	13.283	13.339	13.308
Calculated <i>c</i> (Å)	13.232	13.267	13.216	13.247
Br(1)···Br'(1) (Å)	3.530	3.541	3.518	3.528
Attractive term (kJ mol ⁻¹)	-5.0	-4.9	-8.6	-8.5
Repulsive term (kJ mol ⁻¹)	4.8	4.6	7.6	7.4
Non-bonding potential (kJ mol ⁻¹)	-0.2	-0.2	-1.0	-1.1
Br(2)···Br'(3) (Å)	3.361	3.399	3.353	3.388
Attractive term (kJ mol ⁻¹)	-13.3	-12.4	-23.1	-21.7
Repulsive term (kJ mol ⁻¹)	16.3	14.4	24.1	21.9
Non-bonding potential (kJ mol ⁻¹)	3.0	2.0	1.0	0.2
Br(1)-C(1)-C(2)-C(3) (°)	53.2*	51.0	53.2*	51.1
Br(2)-C(8)-C(9)-C(14) (°)	48.9*	47.0	48.9*	47.2
Br(3)-C(15)-C(16)-C(21) (°)	46.9*	49.7	46.9*	49.7

A minimization of the crystal lattice energy with respect to the lattice constants, molecular translations and rotations were performed by means of the program *PCK6* (Williams, 1972, 1974), following a procedure similar to that described for TPCM. Two sets of values were used as adjustable parameters in the function $U(r) = -Ar^{-6} + B \exp(-Cr)$ representing the non-bonded interatomic potential energy. These sets included the parameters as fitted by Williams (1966) for C···C and C···H interactions, together with the alternative groups of parameters I and II of Burgos & Bonadeo (1977) for the Br···Br, Br···C and Br···H interactions (hereafter W-BB I and W-BB II). The major difference between the two groups of potential functions lies in the Br···Br interaction, which in W-BB II has a deeper minimum and is softer than in W-BB I. Representative energy results are given in Table 4. Two runs were carried out for each set of potentials: in the first, the X-ray structure of TPBM was retained; in the second, the phenyl-ring rotations were relaxed. Nonetheless, all the optimized structures remain very similar, in particular with regard to the cell parameters, the Br···Br contact distances and the torques of the phenyl groups. The effects of including Coulombic terms in the potential energy were also estimated using the same approach as for TPCM. They were seen to involve similar variations, such as minor contractions of about 0.4% of the cell parameters and of the Br···Br distances.

The crystal did not withstand cooling below 150 K. At that temperature the unit-cell dimensions were $a = 13.875(7)$ and $c = 13.362(7)$ Å, thus undergoing respective contractions of 0.058 and 0.121 Å against the room-temperature values. The calculated structures lead to more pronounced contraction, especially along *a* (Table 4). The averaged calculated contacts Br(1)···Br'(1) = 3.53(1) and Br(2)···Br'(3) = 3.38(2) Å show a slight expansion of 0.03 and 0.15 Å

compared to the experimental distances. Since the Br(2)···Br'(3) contact is shorter than the separation at which the potential energy is zero (3.51 Å for W-BB I, 3.40 Å for W-BB II), the present models involve a net repulsion at the location of that pair of atoms. The observed small shortening of the C-Br(2) and C-Br(3) bonds relative to C-Br(1) might be a direct consequence of the steric compression occurring along the bond axis direction. A similar situation arises in TPCM, where the calculated Cl···Cl interaction energies take comparable values.

Thermal-motion analysis

The Br atoms display a strongly anisotropic thermal motion (Fig. 2). The r.m.s. displacements normal to and along the molecular threefold axis direction are, respectively, 0.336 and 0.212 Å for Br(1), 0.382 and 0.215 Å for Br(2), and 0.387 and 0.217 Å for Br(3) (e.s.d. 0.002 Å). The respective values for the central C atoms are: 0.216 and 0.183 Å for C(1), 0.270 and 0.169 Å for C(8), and 0.245 and 0.214 Å for C(15). These fairly large atomic displacements normal to the threefold axes might suggest that the C-Br bonds are tilted away from the crystallographic axes. Such an occurrence would of course imply somewhat longer Br···Br separations than those of the head-to-head arrangements if the C-Br bonds of a pair are permanently bent from each other. In the latter case, two extreme, mutually exclusive, cases could contribute to the apparent strong Br thermal motion. In the first case a dynamic process would allow the C-Br bonds to move 'freely' around the symmetry axes. The second case would be characterized by a disordered static arrangement consisting of three alternative molecular orientations consistent with the local threefold symmetry. Neither of these events can be ruled out on the sole basis of the present crystallographic information.

Table 5. Rigid-body-motion analysis

Shown are eigenvalues of the L and T tensors referred to a Cartesian coordinate system with z coaxial with the molecular C_3 axis. The T components are given in their reduced form (Schomaker & Trueblood, 1968).

Molecule	(I)	(II)	(III)
L_1^* (deg ²)	12.0 (6)	22.5 (8)	20.7 (1.0)
L_{33}	8.5 (1.6)	0.4 (2.0)	0.3 (2.3)
T_{11} (Å ²)	0.053 (2)	0.070 (2)	0.063 (3)
T_{33}	0.045 (1)	0.045 (1)	0.047 (1)
$\langle \Delta^2 U_{ij} \rangle^{1/2}$	0.0034	0.0040	0.0053
$\langle \sigma^2 U_{ij} \rangle^{1/2}$	0.0059	0.0069	0.0066
$\langle \Delta^2 U_{ij}(\text{Br}) \rangle^{1/2}$	0.0004	0.0007	0.0006
$\langle \Delta^2 U_{ij}(\text{C}_c) \rangle^{1/2}$	0.0056	0.0095	0.0106
R†	0.066	0.066	0.104

$$* L_{11} = L_{22}; T_{11} = T_{22}.$$

$$\dagger R = \sum w |\Delta U_{ij}| / \sum w |U_{ij}|.$$

A rigid-body-motion analysis carried out with the THMB program (Trueblood, 1978) indicates, for each unique molecule, that the thermal motion of the C–Br group is not independent from that of the whole molecule. This is evidenced, in particular, by the fair agreement between the observed and calculated U_{ij} 's for the Br and C_c atoms and, as a whole, by the satisfactory R values (Table 5). However, the agreement might be fortuitous in part, for the rigid-body approach is liable to be an oversimplified model with regard to the system studied. For molecules (I), (II) and (III), the thermal motion is described in a coordinate system in which the libration axes intersect on the C_3 molecular axis, in the central region of the molecule, respectively at distances 2.000, 1.290 and 1.684 Å from the C_c atom. It can further be calculated from the magnitude of the relevant tensor elements that the large motional displacement of the Br atom perpendicular to the C_3 axis is due to translation and libration in approximately equal proportions. As a whole, the magnitude of the thermal motion in TPBM is equivalent to that in TPCM.

In general, the main structural effect of reduced thermal motion is a slight concomitant contraction, which may be largely anisotropic, as was observed for TPBM at lower temperature. The force-field parameters used in our packing analysis are derived mostly from low-temperature structure data: e.g. the mean-square displacements implicit in the parameters associated with H and C are about three times smaller than those in the TPBM and TPCM structures. In accordance with a simple approximate treatment by Williams (1966, 1981) a decrease of the thermal displacement will lessen the repulsive coefficient and shift the non-bonded potential minimum by the amount of the displacement. Consequently, as is the case here, the neglect of thermal effects might contribute to the apparent contraction of the calculated cell parameters relative to the experimental room-temperature values.

Intermolecular partial covalent bonding

As pointed out for its congener TPCM, consideration of partial covalent bonding between pairs of coaxial TPBM molecules seems attractive in view of the very short Br(2) ··· Br'(3) distance. Comprehensive studies of partial covalent intermolecular bonding are still unavailable, except for a few recent extensive analyses of the packing forces in the chlorine crystal (Price & Stone, 1982; Burgos, Murthy & Righini, 1982). Both studies demonstrate that it is possible to achieve a satisfactory quantitative fit of several properties of the solid without involving any charge-transfer term. This is in agreement with the X-ray determination of the deformation density in solid Cl₂ (Stevens, 1979) which fails to disclose any significant intermolecular feature consistent with bonding interaction. On the other hand, NQR measurements predict significant intermolecular bonding in solid halogens, increasing on going from Cl₂ to I₂ (Nakamura & Chihara, 1967).

It is not pretended that no charge-transfer bonding is present at the sites of the Br atoms in the TPBM structure, particularly in view of the NQR results mentioned above. However, it is noteworthy that the present simple Buckingham potential reproduces, within reasonable limits, all the particular features of the experimental crystal packing while demonstrating the occurrence of an intermolecular repulsive interaction at the sites of the Br atoms. The still overestimated Br(2) ··· Br'(3) separation might be attributed to the growing inaccuracy of the dispersion term as the overlap between the Br atoms increases. In regard to 'fitting' the experimental data this discrepancy could probably be lessened by consideration of a potential-energy term to allow for partial bonding (Hsu & Williams, 1979), but in view of the complexity of the structure and of the approximations inherent in the models, a conclusive interpretation of the 'corrections' brought about by this latter approach would seem hazardous.

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The Geometry of Small Rings. VI. Geometry and Bonding in Cyclobutane and Cyclobutene

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Abstract

The molecular geometry, obtained by X-ray methods ($R \leq 0.10$) for 202 derivatives of cyclobutane and 21 derivatives of cyclobutene, has been analysed *via* the Cambridge Structural Database. For cyclobutane a mean ring bond length (d) of 1.554 (1) Å is obtained, but the range (1.521–1.606 Å) is wide; this is attributable to the numbers (n_1, n_2) of exocyclic non-H substituents on a ring bond C(1)–C(2). For n_1 or $n_2 = 0$, $d = 1.547$ (2) Å, but d increases to 1.575 (3) Å for $n_1 = n_2 = 2$. Puckered conformations are preferred in the range $20 < \varphi < 35^\circ$, although a complete range to 67.2° is represented. Whilst d is marginally longer for planar rings at 1.558 (3) Å, a constant d of 1.553 (1) Å is observed as φ increases from 5° and the ring valence angle (θ) decreases from 90° . Thus the transannular C–C distance must decrease and is 2.205 (4) Å at $\varphi = 0^\circ$, $\theta = 90^\circ$, and 2.107 (13) Å at $\varphi = 45^\circ$, $\theta = 85.5^\circ$. Increased transannular non-bonded repulsions are balanced by a decrease in these forces between vicinal 1,2-substituents. The substituent–substituent torsion angle must increase from 0° (eclipsed) as φ increases, and the effect is enhanced by inward rocking of the methylene groups by $\sim 0.12 \varphi$. Each ring C atom uses hybrids of $\sim 27\%$ s character for exocyclic bond formation and of $\sim 23\%$ s character to form the ring σ framework. Ring bonds are bent by *ca* 9° , compared with 22° in cyclopropane. Results for cyclobutene are restricted by the small data set. The C–C bonds, at 1.514 (2) and 1.573 (4) Å, are comparable with gas-phase results, but an unconjugated double bond of 1.323 (4) Å is relatively short.

Introduction

The highly strained cyclopropane (III) and cyclopropane (VI) exhibit properties which are atypical of higher cycloalkanes and cycloalkenes. The protons in (III) are markedly vinylic, while 1,2 protons in (VI) are acetylenic, as indicated by the $^1J_{\text{CH}}$ coupling constants. (III) also participates in conformation-dependent conjugative interactions with π -acceptor substituents which are analogous to those for ethylenic links. These anomalies are well explained by a variety of equivalent (Bernett, 1967) bonding models: the bent-bond model (Coulson & Moffitt, 1947, 1949), the trigonally hybridized model (Walsh, 1947, 1949; Sugden, 1947) and the MO approach of Hoffmann (1964). For (III) the models indicate rehybridization at C involving a pair of $\sim sp^2$ hybrids directed towards exocyclic substituents, and a pair of $\sim sp^5$ hybrids contributing to the ring σ framework. For (VI) the exocyclic C(1, 2) hybrids are $\sim sp^1$ while C(3) remains $\sim sp^2/sp^5$ as in (III). Conjugative orbital interactions between (III) and π acceptors were predicted to cause bond-length variations within the ring (Hoffmann, 1964, 1970).

Mean X-ray geometries of fragments containing (III) and (VI) determined by use of the Cambridge Structural Database (Allen *et al.*, 1979) have been examined in some detail in this series. The conjugative ability of (III) has been confirmed and quantified (Allen, 1980) in terms of substituent-induced bond-length asymmetry. It has also been possible to examine C hybridization in (III) (Allen, 1981*a*) and (VI) (Allen, 1982*a*) by a comparison of exocyclic C(ring)–C(sp^3) distances with the C(sp^n)–C(sp^3)