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The Crystal Structure of Monobromodehydrobispulegone

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Crystals of monobromodehydrobispulegone, $C_{20}H_{27}BrO$, are orthorhombic, space group $P2_12_12_1$, with four molecules per unit cell. The lattice constants are: $a=11·656$ (2), $b=11·669$ (2), $c=12·766$ (2) Å. The crystal structure has been solved by the heavy-atom technique and refined by the full-matrix least-squares method. The final R index for 692 independent observed reflexions is 0·107. The molecule shows stress in the pentagonal ring. In the cyclohexane ring the oxygen and bromine substituents appear to be coplanar and the methyl substituent is in an axial position. The molecular packing shows no remarkable directional features.

Introduction

The study of the crystal structure of monobromodehydrobispulegone, whose chemical formula appears in Fig. 1, was undertaken in order to determine some conformational aspects of the substances obtained from the reductive dimerization of the pulegone, and continues the work begun with the X-ray structure determination of the analogous compound, dibromodehydrobispulegone (Perales, Martínez-Carrera & García-Blanco, 1969). Extensive chemical studies of such a dimerization have already appeared in the literature (Camps, Esquefa, Ferrer, Magrans, Pascual & Sust, 1961; Bartual, Ferrer, Pascual & Vendrell, 1966; Bartual, Camps, Pares & Pascual, 1968; Bartual & Pascal, 1970; Bartual, Camps, Ferrer, Pascual & Roque, 1970; Font-Cistero, 1972). It was thought convenient to study the present compound by X-ray techniques in order to determine the cause of the stress on the C(8) atom (Fig. 1) and the conformation of the cyclohexane substituents.

Experimental

Crystals of monobromodehydrobispulegone were kindly made available to us by Dr J. Pascual Vila (Departamento de Química Orgánica, Universidad de Barcelona). The crystals are colourless prisms elongated along the c axis. The density was measured by flotation in aqueous potassium iodide solution. The lattice constants were determined by means of a four-circle automatic diffractometer and are shown in Table 1 with other physical constants.

Table 1. *Crystal data for monobromodehydrobispulegone*

Standard deviations, given in parentheses, refer to the least significant digits.

Formula	$C_{20}H_{27}BrO$
Molecular weight	362·91
Wavelength (Cu $K\bar{\alpha}$)	1·5418 Å
a	11·656 (2) Å
b	11·669 (2)
c	12·766 (2)
V	1737·64 Å^3
Z	4
D_{obs}(flotation)	1·33 g cm^{-3}
D_{cal}	1·39
μ(Cu $K\alpha$)	32·66 cm^{-1}
$F(000)$	760
Space group	$P2_12_12_1$

Intensity data were collected at room temperature with Ni-filtered Cu $K\alpha$ radiation from multiple-film integrated equi-inclination Weissenberg photographs of five layers along [100] and eight layers along [001]. The photographs had very few spots at $\theta > 65°$ and showed signs of crystal decay.

The 692 independent observed reflexions were measured by means of a double-beam microdensitometer Joyce–Loebl Mark III*C*. Geometrical corrections were applied, and all the intensities were converted into structure amplitudes and placed on a common scale by the least-squares method described by Rollett & Sparks (1960). Unobserved reflexions were included by taking one half of the minimum observed intensity. Because of the crystal size (the crystal selected had the dimensions $0{\cdot}010 \times 0{\cdot}017 \times 0{\cdot}019$ cm) no absorption corrections were applied.

Determination of the structure and refinement

The heavy-atom technique was used for the structure determination. The positional parameters for the bromine atom were obtained from the Harker sections in a three-dimensional Patterson map, calculated using $|F|^2$ for all observed reflexions. A set of structure factors, calculated from the coordinates of the bromine atom and isotropic temperature factor $B=3{\cdot}8$ (obtained from a Wilson plot) produced an R value of 0·375. The positional and isotropic thermal parameters of the bromine atom were refined by three-dimensional differential synthesis and, with the resulting values, the phases for all reflexions were calculated in order to compute successive three-dimensional Fourier syntheses. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). In the two first syntheses, reflexions with either $|F_c| < 5{\cdot}00$ or $\sin\theta > 0{\cdot}70$ were omitted. The peaks in the Fourier map were investigated as possible locations of atoms, and in each case the Patterson map was checked for appropriate bromine–light atom vectors. All the non-hydrogen atoms were identified in two cycles of Fourier synthesis, and by successive cycles the positions of the atoms were refined, reducing R to 0·185. Fig. 2 shows the last electron-density map viewed along the a axis.

The positional and thermal parameters for all non-hydrogen atoms were refined by successive cycles of full-matrix least-squares calculations. The program *ORFLS* (Busing, Martin & Levy, 1962) modified by R. Shiono was used to minimize the function $\sum w(\Delta F_{\rm obs})^2$ with a weight $w=1{\cdot}0$ for all observed reflexions. Together with these calculations, inter- and intramolecular distances and bond angles were obtained as a test of the improvement in the structure refinement. The final R values are 0·161 and 0·107 for the isotropic and anisotropic refinement respectively.

The observed and calculated structure factors are

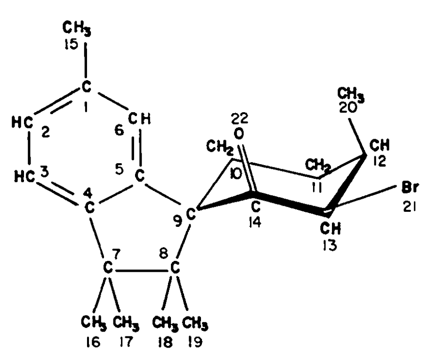


Fig. 1. Molecular structure for monobromodehydrobispulegone.

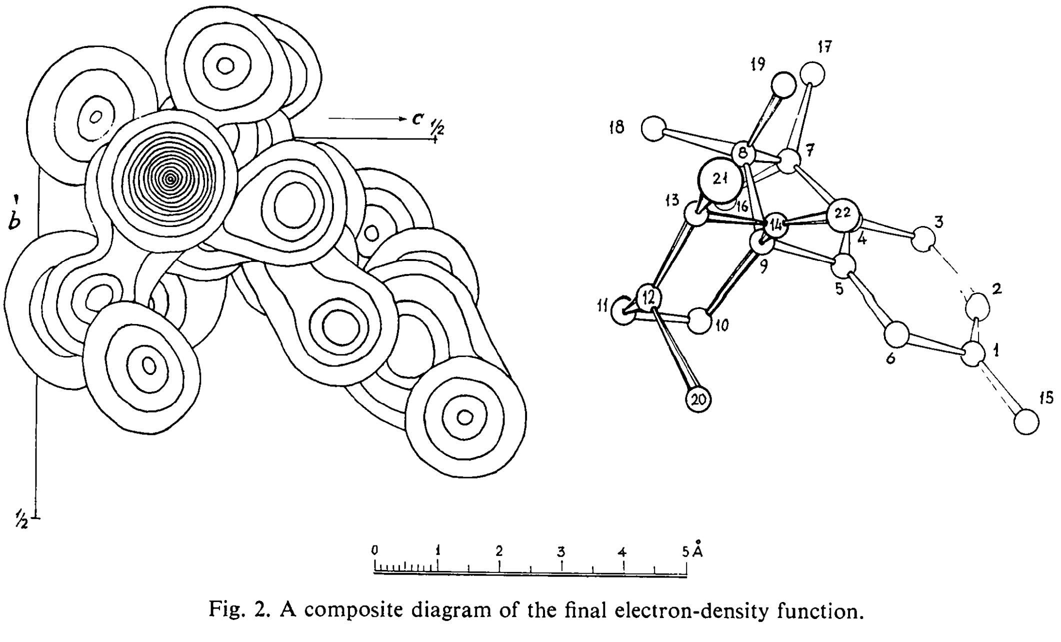
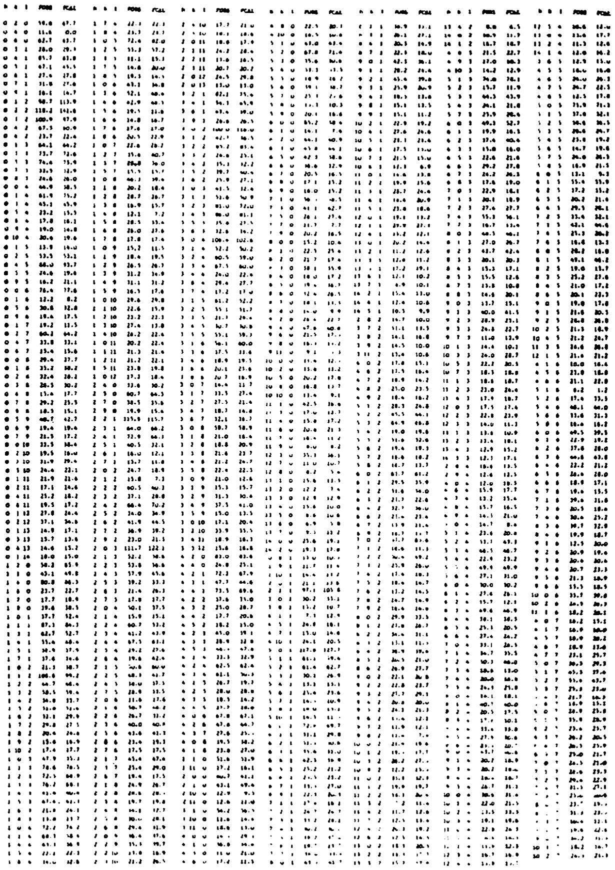


Fig. 2. A composite diagram of the final electron-density function.

shown in Table 2. The final fractional atomic coordinates and the anisotropic thermal parameters with their standard deviations are given in Table 3.

Table 2. *Observed and calculated structure factors*



Structural results

The molecular structure

Bond lengths and angles are shown in Tables 4 and 5; the mean standard deviations are 0·03 Å and 1·83° respectively. These values are uncorrected for thermal motion.

Table 4. *Bond lengths with e.s.d.'s in parentheses*

C(1)—C(2)	1·345 (26) Å
C(2)—C(3)	1·384 (32)
C(3)—C(4)	1·421 (28)
C(4)—C(5)	1·331 (26)
C(5)—C(6)	1·341 (30)
C(6)—C(1)	1·435 (27)
C(7)—C(4)	1·421 (33)
C(7)—C(8)	1·634 (29)
C(8)—C(9)	1·688 (33)
C(9)—C(5)	1·509 (29)
C(9)—C(10)	1·581 (33)
C(10) -C(11)	1·612 (27)
C(11) -C(12)	1·528 (27)
C(12) -C(13)	1·519 (39)
C(13) -C(14)	1·525 (35)
C(14) -C(9)	1·451 (29)
C(15) -C(1)	1·623 (33)
C(16) -C(7)	1·504 (32)
C(17) -C(7)	1·567 (36)
C(18) -C(8)	1·618 (32)
C(19) -C(8)	1·564 (32)
C(20) -C(12)	1·503 (38)
Br(21)-C(13)	1·955 (23)
O(22)-C(14)	1·188 (27)

In the aromatic ring the mean C–C distance is 1·376 Å before the correction for librational movement (Cox, Cruickshank & Smith, 1958) and the mean bond angle is 119·9°, in accordance with the accepted mean.

Table 3. *Atomic fractional coordinates* (× 10^4) *and thermal parameters* (× 10^3) *for non-hydrogen atoms*

Thermal factors are exp $(-2\pi^2 \sum U_{ij} a_i^* a_j^* h_i h_j \times 10^{-3})$. Standard deviations, given in parentheses, refer to the least significant digits.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	6521 (13)	2691 (18)	4664 (16)	18 (6)	29 (12)	27 (9)	0 (7)	−0 (9)	23 (9)
C(2)	5544 (16)	2105 (19)	4826 (16)	36 (9)	36 (14)	29 (10)	2 (9)	−2 (11)	5 (10)
C(3)	5183 (16)	1258 (23)	4143 (15)	30 (8)	58 (18)	26 (9)	−2 (10)	−8 (10)	30 (11)
C(4)	5888 (14)	1022 (20)	3261 (18)	19 (7)	52 (15)	19 (10)	−7 (8)	−1 (10)	3 (11)
C(5)	6858 (15)	1606 (19)	3132 (17)	27 (8)	43 (13)	34 (11)	−9 (8)	13 (10)	4 (10)
C(6)	7230 (16)	2436 (19)	3775 (16)	20 (8)	44 (13)	29 (10)	3 (8)	7 (10)	9 (9)
C(7)	5594 (15)	242 (20)	2449 (20)	24 (8)	36 (16)	47 (13)	−1 (8)	−9 (11)	11 (12)
C(8)	6828 (19)	55 (19)	1867 (18)	56 (11)	20 (12)	33 (12)	−5 (10)	23 (13)	15 (10)
C(9)	7509 (16)	1294 (23)	2151 (16)	30 (8)	66 (16)	33 (10)	−7 (10)	−20 (10)	16 (11)
C(10)	7300 (18)	2292 (21)	1335 (16)	35 (10)	58 (15)	18 (10)	−10 (10)	20 (12)	−17 (10)
C(11)	8145 (15)	2220 (22)	338 (14)	30 (8)	81 (16)	11 (7)	11 (9)	13 (9)	20 (9)
C(12)	9385 (19)	2083 (23)	705 (13)	49 (11)	63 (17)	2 (7)	−20 (11)	3 (10)	−10 (9)
C(13)	9460 (19)	972 (27)	1321 (22)	42 (10)	77 (21)	63 (17)	8 (11)	−28 (13)	−9 (15)
C(14)	8728 (18)	1101 (21)	2304 (18)	45 (11)	42 (15)	15 (11)	−0 (11)	−21 (13)	−14 (11)
C(15)	6923 (23)	3697 (24)	5461 (18)	65 (14)	57 (18)	33 (11)	−17 (13)	24 (14)	−33 (12)
C(16)	4721 (16)	728 (25)	1704 (21)	32 (8)	110 (20)	70 (14)	−13 (11)	−32 (12)	65 (17)
C(17)	5104 (19)	−964 (24)	2752 (26)	36 (10)	61 (18)	98 (24)	−14 (10)	−19 (13)	18 (16)
C(18)	6682 (19)	−169 (18)	624 (18)	61 (12)	27 (13)	44 (12)	−12 (9)	−29 (13)	−17 (10)
C(19)	7544 (21)	−922 (19)	2394 (20)	62 (13)	24 (12)	48 (13)	−1 (9)	−12 (15)	9 (10)
C(20)	9836 (19)	3097 (27)	1303 (23)	42 (10)	77 (20)	76 (19)	−18 (12)	7 (14)	−0 (16)
Br(21)	11045 (2)	533 (3)	1616 (3)	40 (1)	99 (2)	66 (2)	11 (2)	5 (2)	−10 (2)
O(22)	9161 (12)	979 (15)	3139 (13)	35 (7)	68 (12)	46 (10)	10 (7)	10 (9)	−4 (9)

Table 5. *Bond angles with e.s.d.'s in parentheses*

C(1)—C(2)—C(3)	121·6 (1·9)°
C(2)—C(3)—C(4)	117·5 (1·9)
C(3)—C(4)—C(5)	119·3 (1·9)
C(4)—C(5)—C(6)	124·7 (2·0)
C(5)—C(6)—C(1)	116·6 (1·8)
C(6)—C(1)—C(2)	120·2 (1·8)
C(4)—C(7)—C(8)	101·8 (1·7)
C(7)—C(8)—C(9)	101·7 (1·6)
C(8)—C(9)—C(5)	98·5 (1·6)
C(9)—C(5)—C(4)	113·9 (1·8)
C(5)—C(4)—C(7)	116·3 (1·9)
C(9)—C(10)-C(11)	112·8 (1·7)
C(10)—C(11)-C(12)	109·9 (1·6)
C(11)—C(12)-C(13)	107·6 (1·8)
C(12)—C(13)-C(14)	108·1 (2·0)
C(13)—C(14)-C(9)	116·9 (2·0)
C(15)—C(1)—C(2)	121·1 (1·8)
C(15)—C(1)—C(6)	118·7 (1·7)
C(16)—C(7)—C(17)	104·4 (1·9)
C(18)—C(8)—C(19)	111·1 (1·8)
C(20)—C(12)-C(11)	113·8 (1·9)
C(20)—C(12)-C(13)	112·9 (2·0)
Br(21)-C(13)-C(12)	112·2 (1·7)
Br(21)-C(13)-C(14)	113·3 (1·7)
O(22) -C(14)-C(13)	119·3 (2·1)
O(22) -C(14)-C(9)	123·7 (2·1)

The pentagonal ring shows rather long distances for the bonds C(7)–C(8) and C(8)–C(9). This agrees with the chemical evidence for stress at C(8), which was the last atom located from the successive Fourier syntheses. Stress would occur in this ring because it is fused to the benzene ring (Baeyer stress) but it also exhibits Pitzer stress due to the gem-dimethyl groups on both C(7) and C(8) and the cyclohexane ring on C(9). Fig. 3 shows the Newman projections along the bond C(7)–C(8) [Fig. 3(*a*)] and along the bond C(8)–C(9) [Fig. 3(*b*)] which give a qualitative idea about this interaction. The angle C(8)–C(9)–C(5) appears too small as in dibromodehydrobispulegone (Perales, Martínez-Carrera & García-Blanco, 1969). This fact is in agreement with some studies of analogous substitued pentagonal rings (Goaman & Grant, 1963).

In the cyclohexane ring the distances and angles agree with those expected for a ring with an exocyclic carbonyl group. The C=O and C–Br distances are normal.

Equations for the more important conformational least-squares planes in the molecule were calculated by the method of Schomaker, Waser, March & Bergman (1969) and the results obtained are as follows:

Benzene ring:

$$-0{\cdot}4980X+0{\cdot}6815Y-0{\cdot}5362Z=-4{\cdot}8430\,.$$

Pentagonal ring:

$$-0{\cdot}4600X+0{\cdot}6302Y-0{\cdot}6255Z=-4{\cdot}9374\,.$$

Cyclohexane ring:

$$0{\cdot}3119X+0{\cdot}7983Y+0{\cdot}5152Z=5{\cdot}5021\,,$$

where X, Y, Z are in fractional coordinates.

Table 6 shows the deviations of atoms from the least-squares planes.

Table 6. *Displacements* (Å) *of the atoms from the various planes*

(i) Plane through benzene ring.
(ii) Plane through pentagonal ring.
(iii) Plane through cyclohexane ring.

	(i)		(ii)		(iii)
C(1)	0·005	C(4)	−0·072	C(9)	−0·153
C(2)	−0·004	C(5)	−0·060	C(10)	0·165
C(3)	−0·001	C(7)	0·160	C(11)	−0·250
C(4)	0·005	C(8)	−0·174	C(12)	0·314
C(5)	−0·005	C(9)	0·145	C(13)	−0·289
C(6)	−0·001	C(16)	1·581	C(14)	0·212
C(15)	0·027	C(17)	−0·706	C(20)	1·816
		C(18)	0·733	O	0·805
		C(19)	−1·696	Br	0·073

In the pentagonal ring a best least-squares plane analysis of the various possible combinations of four atoms, shows that the plane formed by C(4), C(5), C(7) and C(9) has the smallest deviations (Table 7). This ring has an envelope conformation with an angle of 27·5° between the planes corresponding to C(7), C(8), C(9) and to C(4), C(5), C(7), C(9). The atom C(8) is 0·49 Å from the plane formed by C(4), C(5), C(7), C(9), in agreement with the theoretical calculations for minimum energy (Pitzer & Donath, 1959; Brutcher, Roberts, Barr & Pearson, 1959) and other crystal structure determinations (Allen, Rogers & Troughton, 1971).

Table 7. *Four-membered planes*

Atoms	$\sum_{i=1}^{4}(\Delta^2)$ atoms in plane
C(4),C(7),C(8),C(9)	0·08
C(7),C(8),C(9),C(5)	0·07
C(8),C(9),C(5),C(4)	0·02
C(9),C(5),C(4),C(7)	0·00
C(5),C(4),C(7),C(8)	0·03

The cyclohexane ring has a chair conformation corresponding to its multisubstitution and its least-squares plane forms an angle of 95·3° with that corresponding to the benzene-cyclopentane system; the Br atom is in

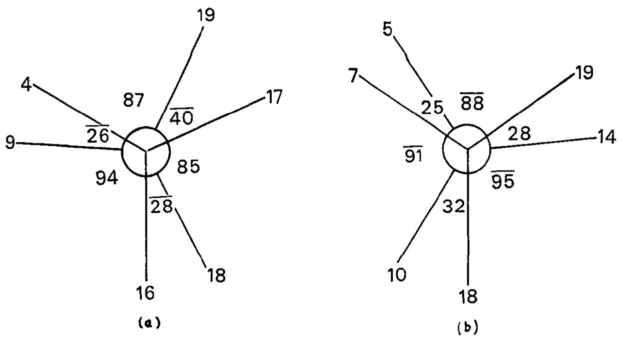


Fig. 3. Newman projections.

an equatorial position and the C(20) methyl group is axial.

Although the Bijvoet test was performed, the data were not good enough for determining the absolute configuration, but from chemical grounds we think it is that shown in Figs. 1 and 2.

Crystal structure

Intermolecular distances less than 4 Å are shown in Table 8. Figs. 4 and 5 depict the projections of the structure along the *c* and *b* axes respectively. Molecular packing is determined mainly by non-directed van der Waals forces. The projection along **c** shows the C(17) methyl group roughly directed towards the centre of the benzene ring. The projection along **b** shows a stacking of the mean planes through C=O and C–Br bonds as found in other structures (Craven & Mascarenhas, 1964; Craven, Martínez-Carrera & Jeffrey, 1964; Klug, 1965) but here the distance between successive planes is longer and the atoms involved have more pronounced anisotropic thermal vibrations along the *b* axis, suggesting no interaction.

The numerical calculations were carried out on a IBM 7090 Computer (Centro de Calculo de la Universidad de Madrid, Spain) and on a UNIVAC 1108 Computer (Centro de Proceso de Datos del Ministerio de Educación y Ciencia). The present work is part of a Doctoral Thesis by one of us (J.M.F.).

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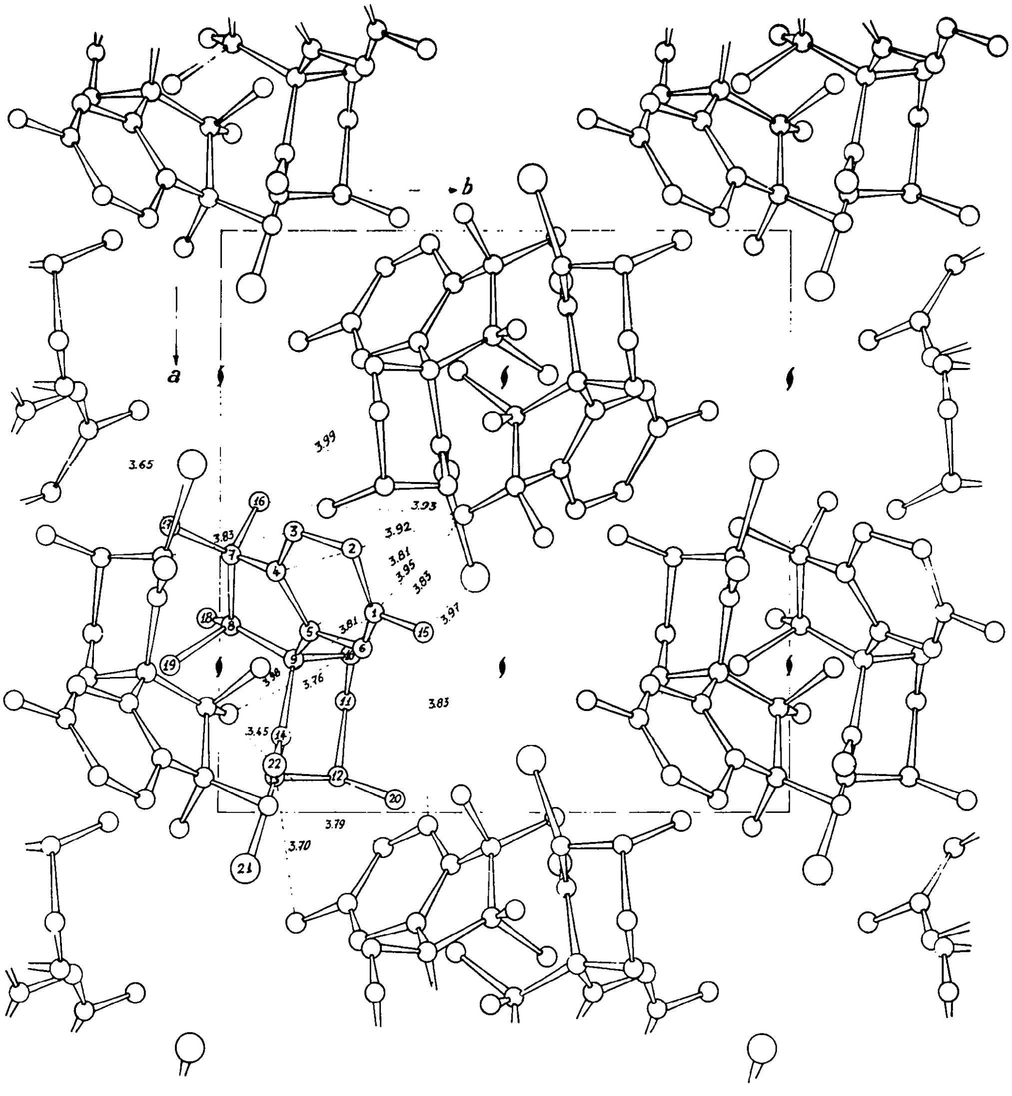

Fig. 4. Packing diagram projected along [001]. Some intermolecular distances less than 4·0 Å are shown.

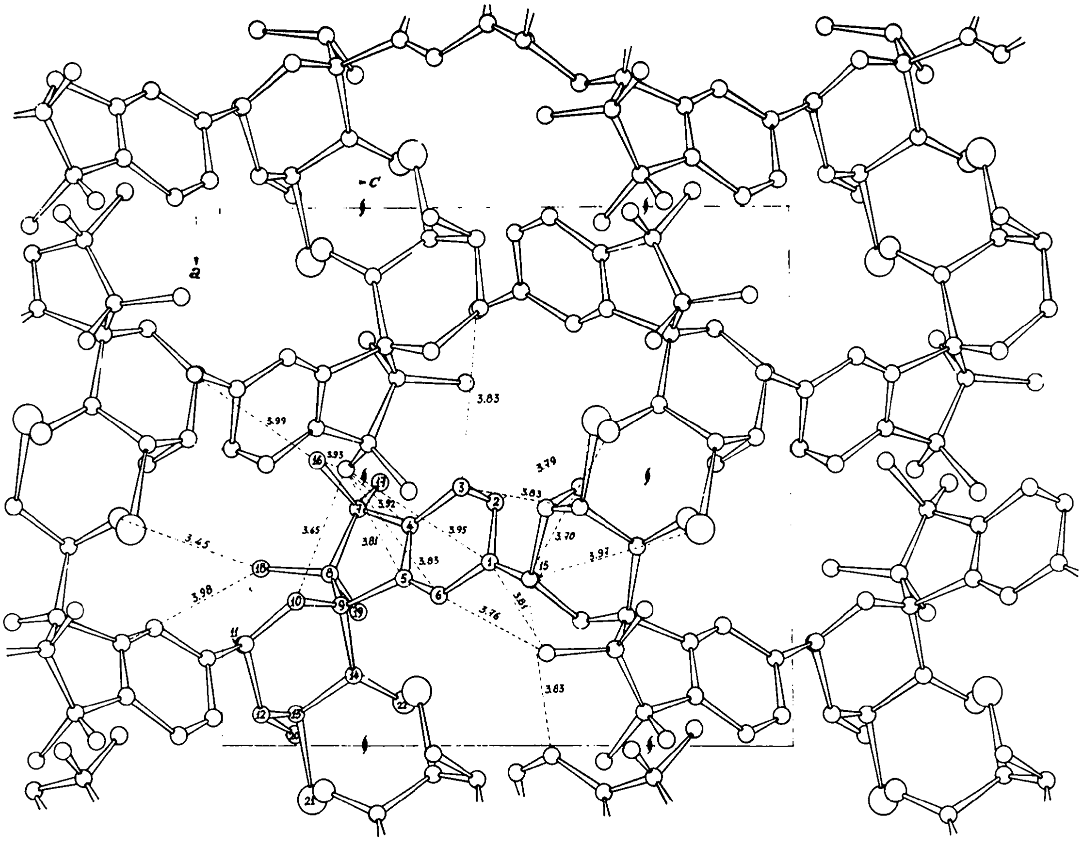

Fig. 5. Packing diagram projected along [010].

Table 8. *Intermolecular distances less than* 4 Å

The following roman numbers give the symmetry relationship of the atoms concerned.

I	(x	y	z)
II	($1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$)
III	($\frac{1}{2}+x$	$\frac{1}{2}-y$	$-z$)
IV	($-\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$)
V	($\frac{3}{2}-x$	$-y$	$\frac{1}{2}+z$)
VI	($\frac{3}{2}-x$	$-y$	$-\frac{1}{2}+z$)

C(1) (I)$\cdots$C(17) (II)	3·945
C(1) (I)$\cdots$C(18) (V)	3·814
C(2) (I)$\cdots$O(22) (IV)	3·788
C(3) (I)$\cdots$C(13) (V)	3·831
C(3) (I)$\cdots$C(15) (IV)	3·834
C(4) (I)$\cdots$C(17) (II)	3·922
C(5) (I)$\cdots$C(17) (II)	3·814
C(5) (I)$\cdots$C(18) (V)	3·978
C(6) (I)$\cdots$C(17) (II)	3·832
C(6) (I)$\cdots$C(18) (V)	3·765
C(10) (I)$\cdots$C(17) (II)	3·654
C(11) (I)$\cdots$C(16) (III)	3·987
C(15) (I)$\cdots$Br(21) (IV)	3·972
C(15) (I)$\cdots$O(22) (IV)	3·701
C(16) (I)$\cdots$C(17) (II)	3·927
C(18) (I)$\cdots$O(22) (VI)	3·453

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