The Conformations of Tetracyclic Diterpenes. II. The Crystal and Molecular Structure of a Product of the Acetolysis of Methyl 12α-Toluene-*p*-sulphonyloxy-*ent*-beyeran-19-oate

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Crystals of the acetolysis product are orthorhombic with $a = 7\cdot360$ (1), $b = 9\cdot221$ (1), $c = 37\cdot957$ (6) Å, $Z = 4$, space group $P2_12_12_1$. The structure was solved by direct methods and refined by least-squares procedures to $R = 0\cdot046$ for 1592 reflexions. Rings A and B have chair conformations while within the bicyclo[3,2,1]octane moiety rings C and D have half-chair and chair conformations respectively. Short intramolecular contacts appear to have little effect on the observed ring conformations.
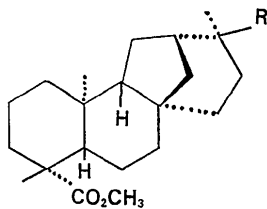
Introduction

We have previously described (Ferguson & Marsh, 1975) the structure of a tetracyclic diterpene containing a bicyclo[3,2,1]octane moiety, 3-acetoxy-9-hydroxy-17-norkauran-16-one (I).
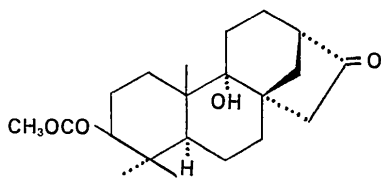
(I)
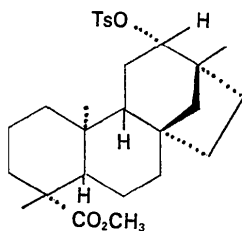
(II)

(III)

The carbonium ion rearrangements in the bicyclooctane moiety of tetracyclic diterpenoids have been the subject of extensive study (McAlees, McCrindle & Murphy, 1975) and a series of experiments involving the solvolysis of the tosylate of 12α-beyeranol (II)

under conditions of kinetic control was carried out. A tertiary acetate (III, $R = OCOCH_3$) was the only product from the solvolysis of (II) in buffered acetic acid and was the major product (53%) from the solvolysis of (II) in buffered trifluoroacetic acid.

The elucidation of the stereochemistry of (III) by chemical means is difficult and, as details of the overall molecular conformation play an important role in predicting the extent and probability of its reactions, the X-ray analysis of the *p*-bromobenzoate (III, $R = OCOC_6H_4Br$) was undertaken.

Experimental

The heavy-atom derivative of the solvolysis product (III, $R = OCOC_6H_4Br$) crystallized as irregular colourless prisms. Preliminary cell parameters and space-group data were determined from rotation, Weissenberg and precession photographs; accurate cell parameters and orientation matrix were obtained by a least-squares procedure applied to 12 reflexions with non-zero Miller indices measured on a Hilger and Watts diffractometer.

Crystal data

$C_{28}H_{37}BrO_4$, $M = 517\cdot51$. Orthorhombic, $a = 7\cdot360(1)$, $b = 9\cdot221(1)$, $c = 37\cdot957(6)$ Å, $U = 2576\cdot0$ Å^3, $D_c = 1\cdot33$ gcm^{-3}, $Z = 4$, $F(000) = 1088$. λ(Mo $K\alpha$) $= 0\cdot71069$ Å, μ(Mo $K\alpha$) $= 17\cdot2$ cm^{-1}. Systematic absences $h00$, h odd; $0k0$, k odd; $00l$, l odd. Space group $P2_12_12_1(D_2^4)$.

The intensities of all reflexions with 2θ(Mo $K\alpha$) $< 50°$ were measured on a PDP8-I-controlled Hilger and Watts four-circle diffractometer with a scintillation counter and graphite monochromator. A θ/ω step scan was employed with $0\cdot01°$ steps, 1 s per step counting time, and a scan width of $0\cdot7°$ in θ. Background counts of $17\cdot5$ s were made at the beginning and end of each scan. The intensities of three standard reflexions, well separated in reciprocal space, were measured after every 100 reflexions; the maximum variation was $\pm 1\cdot3\%$. Lorentz and polarization factors

were applied and the structure amplitudes derived. Of the 2627 unique data, 1035 reflexions had a net count of less than 3σ above background $\{\sigma(I) = [S + 4(B_1 + B_2) + (0.02S)^2]^{1/2}$ with S the scan count and B_1 and B_2 the background counts$\}$ and were excluded from subsequent refinement.

Structure analysis

The data were placed on an absolute scale (Wilson, 1942) and normalized structure amplitudes, E, derived. The 330 largest E's were subsequently used as input into *MULTAN* (Germain, Main & Woolfson, 1971) and yielded an E map which revealed the positions of 28 of the 33 non-hydrogen atoms. The remaining five atoms were located from an $(F_o - F_c)$ synthesis. The initial arbitrary choice of enantiomorph corresponded to the known absolute configuration (McAlees, McCrindle & Murphy, 1975).

Isotropic full-matrix least-squares followed by anisotropic block-diagonal refinement gave $R = 0.090$. Inclusion of the 37 H atoms in calculated positions with an isotropic B of 7.0 $Å^2$ lowered R to 0.070. Further refinement, with the H atoms included in the structure-factor claculation only, converged to a final R of 0.046 for the 1592 observed reflexions and 0.073 for all 2627 reflexions.

The scattering factors for Br, O, and C, including corrections for the anomalous scattering of Br, were taken from *International Tables for X-ray Crystallography* (1962), and those for H from Stewart, Davidson & Simpson (1965). The weighting scheme was $\omega = 0$ for the unobserved and $\omega = 1/[\sigma^2(F) + 0.5F + 0.001F^2]$ for the observed reflexions. The relative validity of the weighting scheme, judged by the variation of $\omega\Delta^2$ over ranges of $\sin\theta/\lambda$ and $|F_o|$, was satisfactory. The final weighted R $([\sum\omega(F_o - F_c)^2/\sum\omega F_o^2]^{1/2})$ was 0.061. A final difference synthesis showed maximum fluctuations of ± 0.2 e $Å^{-3}$ except in the neighbourhood of the Br atom where ripples of ± 0.5 e $Å^{-3}$ were present. The final coordinates and anisotropic thermal parameters are listed in Table 1 while Table 2 gives the final bond lengths and angles.* A stereo view of the molecule produced by *ORTEP* (Johnson, 1965) illustrating the ellipsoids of thermal motion is shown in Fig. 1. The thermal motion was analysed in terms of the rigid-body modes of translation, libration, and screw motion (Schomaker & Trueblood, 1968). It was found that the fused ring skeleton, C(1)–C(16) (Fig. 1), was a good approximation to a. rigid body; the r.m.s. standard deviation in the temperature factors, U_{ij} (Table 1), was 0.0045 $Å^2$ while the r.m.s. ΔU_{ij} was 0.0040 $Å^2$. The appropriate bond distances and angles in the molecule were corrected for libration (Cruickshank, 1956, 1961); however there were no significant changes to those values listed in Table 2, and the corrected values are not given.
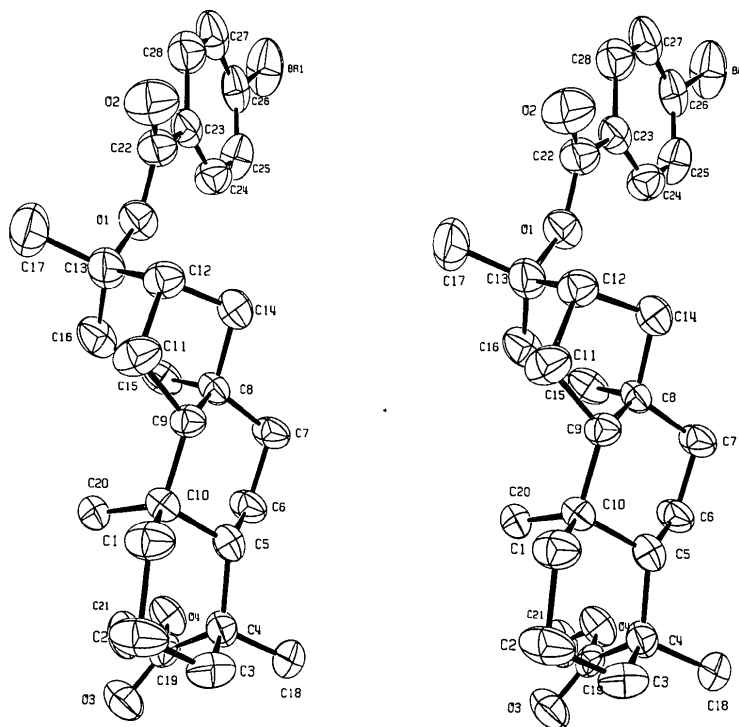
Fig. 1. Stereo view of (III), R = $OCOC_6H_4Br$; the thermal ellipsoids shown are at the 50% probability level.

Discussion

The detailed conformations of the various rings in the molecule are defined by the intra-annular torsion angles given in Table 3. The conformation of ring A is a normal chair with a mean puckering angle, 56·4°, very similar to that found for cyclohexane, 55·9° (Geise, Buys & Mijlhoff, 1971). Indeed, examination of the individual values reveals a maximum deviation of 1·3° from the mean, a difference of less than 2σ, indicating virtually no deformation of the ring. This is somewhat surprising in view of the short transannular contact between O(4) and C(20) [3·277(9) Å]. In other similar situations some flattening of ring A at the junction to ring B has been observed (Ferguson, Macauley, Midgley, Robertson & Whalley, 1970; Rendle, 1972; Ferguson & Marsh, 1975) and attributed to relief of this transannular interaction.

Ring B also has a chair conformation but here the chair is puckered to a somewhat greater degree at the C(6) end. There is a short [3·313(10) Å] contact across this ring between C(20) and C(15) and the slight de-

Table 1. Atomic coordinates and thermal parameters

(a) Fractional coordinates ($\times 10^4$) with estimated standard deviations in parentheses

	x	y	z		x	y	z
Br	741 (2)	−1445 (1)	2638 (1)	C(13)	6148 (12)	5744 (8)	3373 (2)
O(1)	5252 (8)	4427 (5)	3220 (1)	C(14)	4892 (10)	4934 (8)	3959 (2)
O(2)	7580 (8)	2854 (6)	3284 (2)	C(15)	3185 (11)	6745 (8)	3619 (2)
O(3)	2596 (8)	12699 (5)	4482 (2)	C(16)	4716 (13)	6897 (8)	3346 (2)
O(4)	747 (8)	11050 (5)	4255 (1)	C(17)	7831 (15)	6119 (10)	3158 (2)
C(1)	6563 (10)	9444 (8)	4477 (2)	C(18)	1288 (12)	9983 (9)	4977 (2)
C(2)	6165 (10)	10903 (9)	4660 (2)	C(19)	2073 (9)	11462 (8)	4466 (2)
C(3)	4503 (12)	10753 (8)	4894 (2)	C(20)	4622 (11)	9886 (7)	3938 (2)
C(4)	2791 (10)	10244 (7)	4701 (2)	C(21)	−39 (13)	12154 (11)	4035 (3)
C(5)	3265 (9)	8769 (7)	4507 (2)	C(22)	6082 (12)	3143 (8)	3202 (2)
C(6)	1657 (11)	7944 (8)	4342 (2)	C(23)	4707 (11)	2084 (8)	3056 (2)
C(7)	2243 (10)	6377 (8)	4255 (2)	C(24)	2881 (12)	2240 (9)	3101 (2)
C(8)	3827 (9)	6379 (7)	3997 (2)	C(25)	1654 (13)	1197 (11)	2978 (2)
C(9)	5363 (9)	7301 (7)	4156 (2)	C(26)	2386 (13)	−13 (8)	2807 (2)
C(10)	4932 (9)	8891 (7)	4257 (2)	C(27)	4210 (14)	−210 (8)	2759 (2)
C(11)	7085 (10)	6921 (9)	3949 (2)	C(28)	5379 (13)	843 (9)	2891 (2)
C(12)	6622 (10)	5434 (8)	3765 (2)				

(b) Anisotropic thermal parameters ($\text{Å}^2 \times 10^2$) in the expression $[-2\pi^2(h^2a^{*2}U_{11}+k^2b^*U_{22}+l^2c^*U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})]$ with estimated standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	12·57 (9)	8·98 (7)	8·97 (6)	−5·83 (7)	−0·09 (7)	−0·70 (6)
O(1)	6·9 (4)	4·8 (3)	4·5 (3)	−0·3 (3)	0·9 (3)	−0·7 (2)
O(2)	5·4 (3)	7·1 (4)	8·6 (4)	0·6 (3)	−0·5 (3)	−2·0 (3)
O(3)	7·4 (4)	3·6 (3)	8·6 (4)	−0·7 (3)	0·2 (3)	0·1 (3)
O(4)	5·9 (3)	4·7 (3)	7·9 (4)	0·1 (3)	−1·3 (3)	1·3 (3)
C(1)	3·9 (4)	5·1 (4)	6·7 (5)	0·1 (3)	0·0 (4)	−1·6 (4)
C(2)	3·7 (4)	5·7 (5)	8·7 (6)	−0·7 (4)	−1·1 (4)	−3·3 (4)
C(3)	5·9 (5)	5·4 (4)	5·1 (4)	0·6 (4)	−0·8 (4)	−1·8 (4)
C(4)	4·5 (4)	3·6 (4)	4·6 (4)	−0·1 (3)	0·4 (3)	0·6 (3)
C(5)	3·5 (4)	3·7 (4)	4·7 (4)	−0·1 (3)	−0·6 (3)	0·7 (3)
C(6)	4·6 (4)	3·8 (4)	8·1 (5)	−0·9 (3)	1·2 (4)	−0·8 (4)
C(7)	4·4 (4)	3·6 (3)	7·5 (5)	−1·0 (4)	0·8 (4)	−0·7 (4)
C(8)	3·7 (4)	2·9 (3)	5·0 (4)	−0·3 (3)	−0·1 (3)	0·3 (3)
C(9)	3·5 (4)	3·9 (3)	4·4 (4)	0·1 (3)	0·0 (3)	−0·4 (3)
C(10)	3·8 (4)	3·2 (3)	4·5 (4)	−0·0 (3)	0·2 (3)	0·1 (3)
C(11)	4·1 (4)	6·1 (5)	5·8 (4)	−0·4 (4)	0·1 (4)	−2·1 (4)
C(12)	4·6 (4)	4·4 (4)	4·9 (4)	−0·3 (4)	−0·2 (4)	−1·2 (3)
C(13)	7·2 (6)	4·6 (4)	4·7 (4)	−1·1 (4)	0·3 (4)	−0·8 (4)
C(14)	4·7 (4)	4·3 (4)	5·0 (4)	−0·1 (3)	−0·7 (4)	0·6 (3)
C(15)	6·1 (5)	4·1 (4)	7·0 (5)	−0·2 (4)	−2·2 (4)	−0·3 (4)
C(16)	9·3 (6)	5·0 (4)	4·4 (4)	0·2 (4)	−1·8 (5)	0·8 (4)
C(17)	10·9 (8)	7·2 (6)	6·9 (6)	−3·5 (6)	4·1 (6)	−1·8 (5)
C(18)	7·5 (6)	5·3 (5)	4·9 (4)	−0·4 (4)	2·1 (4)	0·1 (4)
C(19)	3·4 (4)	4·5 (4)	4·1 (4)	0·5 (3)	1·1 (3)	0·0 (3)
C(20)	5·9 (5)	3·9 (4)	4·7 (4)	−1·1 (4)	0·8 (4)	−0·1 (3)
C(21)	7·2 (6)	7·4 (6)	8·5 (6)	0·8 (5)	−1·4 (5)	3·5 (5)
C(22)	7·7 (6)	4·4 (4)	4·7 (4)	0·3 (4)	0·7 (4)	−1·4 (3)
C(23)	6·5 (5)	4·0 (4)	3·8 (3)	−0·2 (4)	−0·3 (4)	0·0 (3)
C(24)	7·0 (6)	5·8 (5)	5·6 (5)	0·5 (5)	0·2 (4)	−0·9 (4)
C(25)	7·1 (6)	8·7 (7)	5·8 (5)	−1·6 (6)	0·1 (5)	0·1 (5)
C(26)	8·1 (6)	5·2 (5)	5·3 (4)	−2·3 (5)	−1·0 (5)	1·0 (4)
C(27)	9·8 (7)	4·4 (4)	5·6 (5)	−1·6 (5)	0·0 (5)	0·3 (4)
C(28)	7·4 (5)	5·3 (4)	5·7 (4)	0·3 (5)	0·4 (5)	−0·5 (4)

Table 2. *Bond lengths* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

Br——C(26)	1·903 (9)	C(12)–C(13)	1·554 (10)
C(1)—C(2)	1·543 (11)	C(12)–C(14)	1·542 (10)
C(1)—C(10)	1·547 (10)	C(13)–O(1)	1·498 (9)
C(2)—C(3)	1·517 (11)	C(13)–C(16)	1·501 (12)
C(3)—C(4)	1·532 (11)	C(13)–C(17)	1·524 (13)
C(4)—C(5)	1·584 (9)	C(15)–C(16)	1·537 (12)
C(4)—C(18)	1·545 (11)	C(19)–O(3)	1·205 (9)
C(4)—C(19)	1·526 (10)	C(19)–O(4)	1·319 (8)
C(5)—C(6)	1·540 (10)	C(21)–O(4)	1·438 (11)
C(5)—C(10)	1·554 (9)	C(22)–O(1)	1·334 (9)
C(6)—C(7)	1·543 (10)	C(22)–O(2)	1·176 (10)
C(7)—C(8)	1·522 (10)	C(22)–C(23)	1·512 (11)
C(8)—C(9)	1·538 (9)	C(23)–C(24)	1·362 (12)
C(8)—C(14)	1·552 (10)	C(23)–C(28)	1·394 (11)
C(8)—C(15)	1·548 (11)	C(24)–C(25)	1·399 (13)
C(9)—C(10)	1·549 (9)	C(25)–C(26)	1·398 (13)
C(9)—C(11)	1·531 (10)	C(26)–C(27)	1·367 (14)
C(10)-C(20)	1·537 (9)	C(27)–C(28)	1·391 (12)
C(11)-C(12)	1·578 (11)		

C(13)O(1)C(22)	122·5 (6)	C(9)C(10)C(20)	113·5 (5)
C(19)O(4)C(21)	116·5 (6)	C(9)C(11)C(12)	104·3 (6)
C(2)C(1)C(10)	112·5 (6)	C(11)C(12)C(13)	108·3 (6)
C(1)C(2)C(3)	109·7 (6)	C(11)C(12)C(14)	103·1 (6)
C(2)C(3)C(4)	114·3 (6)	C(13)C(12)C(14)	109·1 (6)
C(3)C(4)C(5)	107·6 (6)	O(1)C(13)C(12)	108·7 (5)
C(3)C(4)C(18)	108·1 (6)	O(1)C(13)C(16)	103·8 (6)
C(3)C(4)C(19)	109·8 (5)	O(1)C(13)C(17)	109·5 (6)
C(5)C(4)C(18)	109·8 (5)	C(12)C(13)C(16)	110·8 (6)
C(5)C(4)C(19)	116·0 (5)	C(12)C(13)C(17)	111·9 (7)
C(18)C(4)C(19)	105·3 (6)	C(16)C(13)C(17)	111·9 (7)
C(4)C(5)C(6)	116·3 (6)	C(8)C(14)C(12)	101·8 (5)
C(4)C(5)C(10)	113·2 (5)	C(8)C(15)C(16)	114·9 (7)
C(6)C(5)C(10)	113·2 (6)	C(13)C(16)C(15)	113·8 (6)
C(5)C(6)C(7)	109·6 (6)	O(3)C(19)O(4)	122·6 (6)
C(6)C(7)C(8)	110·6 (6)	O(3)C(19)C(4)	123·9 (6)
C(7)C(8)C(9)	108·1 (5)	O(4)C(19)C(4)	113·4 (5)
C(7)C(8)C(14)	116·4 (6)	O(1)C(22)O(2)	128·1 (7)
C(7)C(8)C(15)	111·3 (6)	O(1)C(22)C(23)	106·6 (7)
C(9)C(8)C(14)	98·0 (5)	O(2)C(22)C(23)	125·3 (7)
C(9)C(8)C(15)	117·9 (5)	C(22)C(23)C(24)	123·1 (7)
C(14)C(8)C(15)	104·8 (5)	C(22)C(23)C(28)	117·2 (7)
C(8)C(9)C(10)	118·0 (5)	C(24)C(23)C(28)	119·5 (7)
C(8)C(9)C(11)	106·3 (5)	C(23)C(24)C(25)	121·5 (8)
C(10)C(9)C(11)	120·9 (6)	C(24)C(25)C(26)	117·0 (9)
C(1)C(10)C(5)	108·0 (5)	C(25)C(26)C(27)	123·2 (8)
C(1)C(10)C(9)	106·6 (5)	C(25)C(26)Br	117·7 (7)
C(1)C(10)C(20)	110·0 (6)	C(27)C(26)Br	119·1 (6)
C(5)C(10)C(9)	104·1 (5)	C(26)C(27)C(28)	117·7 (7)
C(5)C(10)C(20)	114·0 (6)	C(23)C(28)C(27)	121·0 (8)

formation of the chair may be attributed to this steric interaction. In the tetracyclic diterpene (I) (Ferguson & Marsh, 1975), ring *B* is deformed in a similar manner, although to a greater extent, the distortions being attributed to similar cross-ring steric interactions.

Within the bicyclo[3,2,1]octane system the *cis*-fused six-membered ring *D* possesses a chair conformation which is flattened at the C(16) end and increasingly puckered at the C(14) end. Similar deformations of the six-membered ring have been observed in other bicyclo-[3,2,1]octanes (Coggon & Sim, 1969; McPhail & Sim, 1966; Abrahamsson & Nilsson, 1966; McCapra, McPhail, Scott, Sim & Young, 1966; Iitaka & Natsume, 1966). The torsion angles within the five-membered ring *C* exhibit approximate C_s symmetry, such an arrangement being characteristic of a half-chair conformation. In the majority of the other bicyclo[3,2,1]octane derivatives this ring is intermediate between an envelope and a half-chair with conformations closer to the latter predominating. The valency angles within the bicyclic moiety reflect the strains inherent in such systems. The internal angles in the five-membered ring range from 98·0 to 106·3°, much less than the normal tetrahedral values, while in the six-membered ring the values at the flattened C(13)-C(16)C(15) end of the ring are all greater than tetrahedral (110·8, 113·8, 114·9° respectively) with a concomitant decrease at the C(8)C(14)C(12) end (104·8, 101·8, 109·1° respectively).

For the most part the bond lengths listed in Table 2 do not differ significantly from expected values (Sutton, 1965). The mean values are C_{sp3}–C_{sp3} = 1·542, C–C (aromatic) = 1·385, C_{sp3}–O_{sp3} = 1·468, and C_{sp2}–O_{sp2} = 1·191 Å. The relatively small overall effect of the intramolecular steric interactions is somewhat surprising, especially in view of the rather large distortions of the ring conformations in the tetracyclic diterpene (I).

The molecular packing is shown in Fig. 2. There are no unusual intermolecular contacts; those less than 3·7 Å are listed in Table 4 and correspond to van der Waals interactions.

Table 3. *cis Torsion angles* (°)

Ring *A*

C(10)C(1)–C(2)C(3)	57·2 (8)	C(3)C(4)–C(5)C(10)	−55·3 (7)
C(1)C(2)—C(3)C(4)	−57·1 (8)	C(4)C(5)–C(10)C(1)	56·5 (7)
C(2)C(3)—C(4)C(5)	55·3 (8)	C(2)C(1)–C(10)C(5)	−56·9 (8)

Ring *B*

C(6)C(5)–C(10)C(9)	−55·3 (6)	C(6)C(7)—C(8)C(9)	55·4 (7)
C(8)C(9)–C(10)C(5)	54·6 (7)	C(5)C(6)—C(7)C(8)	−59·7 (8)
C(7)C(8)–C(9)C(10)	−56·6 (7)	C(10)C(5)–C(6)C(7)	61·3 (8)

Ring *C*

C(14)C(8)–C(9)C(11)	42·5 (6)	C(11)C(12)–C(14)C(8)	40·5 (7)
C(8)C(9)—C(11)C(12)	−18·3 (7)	C(9)C(8)——C(14)C(12)	−50·8 (6)
C(9)C(11)–C(12)C(14)	−13·8 (7)		

Ring *D*

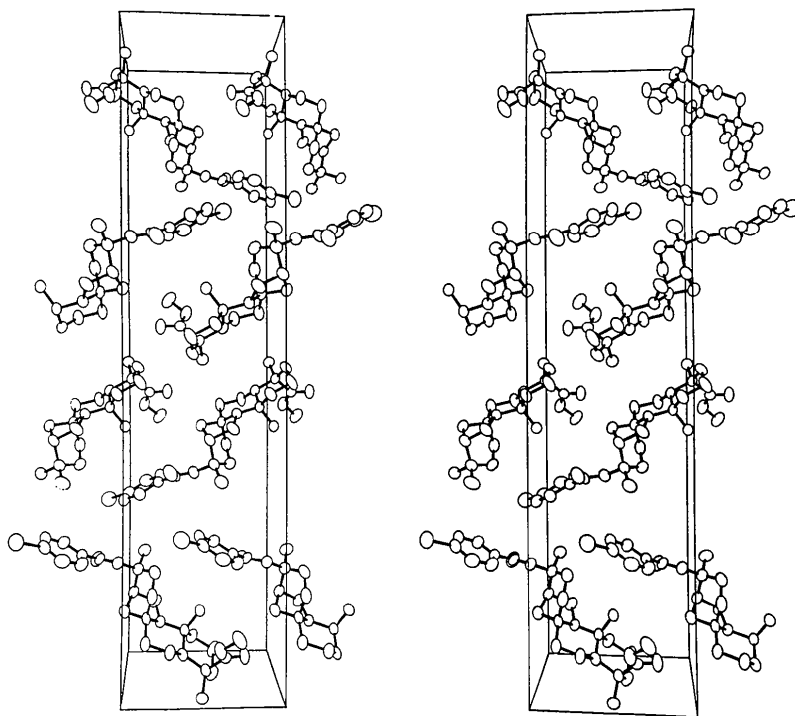|			
C(14)C(8)—C(15)C(16)	−58·3 (8)	C(14)C(12)–C(13)C(16)	59·3 (8)
C(8)C(15)—C(16)C(13)	43·3 (9)	C(13)C(12)–C(14)C(8)	−74·4 (7)
C(12)C(13)–C(16)C(15)	−41·6 (9)	C(15)C(8)—C(14)C(12)	71·0 (6)

Fig. 2. Stereo view of the molecular packing. The origin is at the bottom left-hand corner with the x axis pointing towards the viewer, $y \to$, and $z \uparrow$.

Table 4. *Intermolecular distances* (Å) *less than* $3 \cdot 7$ Å

Br·····C(17^i)	3·677	O(3)····C(3^v)	3·582
Br·····C(25^{ii})	3·648	O(3)····C(7^{vi})	3·510
O(2)···C(21^{iii})	3·410	O(3)····C(14^{vi})	3·324
O(2)···C(25^{iv})	3·560	O(4)····C(1^{vii})	3·519
O(3)···C(2^v)	3·656	C(16)···C(27^{vi})	3·496

Superscripts refer to atoms at

i	$(x-1, y-1, z)$	v	$(x-\frac{1}{2}, \frac{5}{2}-y, 1-z)$
ii	$(-x, y-\frac{1}{2}, \frac{1}{2}-z)$	vi	$(x, y+1, z)$
iii	$(x+1, y-1, z)$	vii	$(x-1, y, z)$
iv	$(x+1, y, z)$		

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