Table 2. *Hydrogen-bond radii*

(Less-well-established values in parentheses)

Donor groups	(Å)	Acceptor groups	(Å)		(Å)		(Å)
NH_n	1·55	N^-	(1·52)	O^-	1·43	F^-	(1·35)
NH_n^+	1·41	N	1·51	O	1·40	Cl^-	1·79
OH_n	1·30	NH_n	1·59	OH_n	1·48	Br^-	1·98
		NH_n^+	(1·68)				

of oxygen was assumed to be the same as the van der Waals radius, it may be seen that the other acceptor radii for atoms not attached to hydrogen follow the van der Waals radii very closely. This fact may be used to predict the acceptor radii for other atoms, e.g. sulphur might be expected to have a value of about 1·85 Å, or possibly less in view of shorter van der Waals radii for sulphur adopted by some authors. Eighteen $NH_n \cdots S$ contacts which might be hydrogen bonds have been found in the literature. They range in length from 3·23 to 3·51 Å and have a mean value of 3·40 Å, which is the distance expected for hydrogen bonds of this type if the acceptor radius for sulphur is 1·85 Å. Five of these distances—3·26 (Penfold, 1953), 3·42 (Nardelli, Braibanti & Fava, 1957), 3·23 (Cavalca, Nardelli & Branchi, 1960), 3·44 and 3·50 (Dvoryankin & Vainshtein, 1960)—were described as hydrogen bonds by the authors who reported them. A distance $OH \cdots S$ of 3·246 Å for which a hydrogen bond is suggested (Nardelli, Fava & Giraldi, 1962) is also consistent with an acceptor radius for sulphur of approximately 1·85 Å.

The short hydrogen bonds of lengths about 2·6 Å in carboxylic acids, although not included in Table 1, may nevertheless be brought into the suggested scheme if they are imagined as being formed from a OH_n^+ donor, with a not unreasonable hydrogen bond radius of about 1·2 Å, and a O^- acceptor.

The chief limitation in the prediction of hydrogen-bond lengths by the addition of hydrogen-bond radii is the rather large variation in length found for any one type of hydrogen bond. One reason for this variation is the fact that each crystal structure must be the result of a compromise between a number of different attractive and repulsive intermolecular forces which may be of similar magnitude, and the way in which the compromise is reached affects the observed hydrogen-bond lengths. Another reason, which the present analysis of the data brings out clearly, is that the lengths of hydrogen bonds are very sensitive to the electron distribution in the Y–H donor groups. It is hoped that the establishment of typical average hydrogen-bond distances may serve as a basis for more detailed discussion of individual distances in terms of the electron distributions within the donor groups.

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The Crystal Structure of Shellolic Bromolactone Hydrate

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Shellolic bromolactone hydrate is orthorhombic ($P2_12_12_1$, $a = 7·07$, $b = 14·80$, $c = 15·56$ Å and $Z = 4$). The structure was determined by the application of the 'heavy atom' technique to the three-dimensional data and refined by differential syntheses. The structure found is in complete agreement with that proposed for shellolic acid by Yates & Field on chemical grounds, and confirms that the carbon skeleton is that of cedrene. The six-membered ring is in the chair form and the Br atom is *trans* to O_3, the oxygen atom of the γ-lactone ring.

Introduction

Shellolic acid $C_{15}H_{17}O_2$ is a component of shellac, a resin originating from the lac insect (Tschirch &

Stock, 1936). Earlier work on the acid (Nagel & Mertens, 1937, 1939) failed to establish the skeleton to which the functional groups are attached, and the present analysis was undertaken to assist recent chemical work. It was known at the outset that the

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bromolactone (SBL) was a γ-lactone with three carbo-cyclic rings, one ether ring and the lactone ring (Cookson, 1958). No use was made, however, of these facts in the actual structure solution.

The first part of the work was carried out at the Viriamu Jones Laboratory, Cardiff and the three-dimensional solution and refinement of the structure at the National Research Council, Ottawa.

Experimental details

The crystals of SBL ($C_{15}H_{17}O_5Br.H_2O$, Fig. 1) were prepared by Prof. R. C. Cookson. They are long thin needles, approximately 0.04×0.04 mm. cross-section, and tabular on (011). The space group is determined uniquely by systematic absences as $P2_12_12_1$, with cell dimensions (from precession photographs)

$$a = 7.07, \quad b = 14.80, \quad c = 15.56 \text{ Å}.$$

These values give a calculated density of 1.53 g.cm.$^{-3}$, if $Z = 4$, and that measured by flotation in a mixture of carbon tetrachloride and ether is 1.54 g.cm.$^{-3}$. The corresponding chlorine derivative (SCL) was also prepared and examined. Its cell dimensions

$$a = 7.07, \quad b = 14.32, \quad c = 15.60 \text{ Å}$$

are close to those of SBL, though the structural isomorphism has not been established. The observed and calculated densities for SCL are both 1.39 g.cm.$^{-3}$.
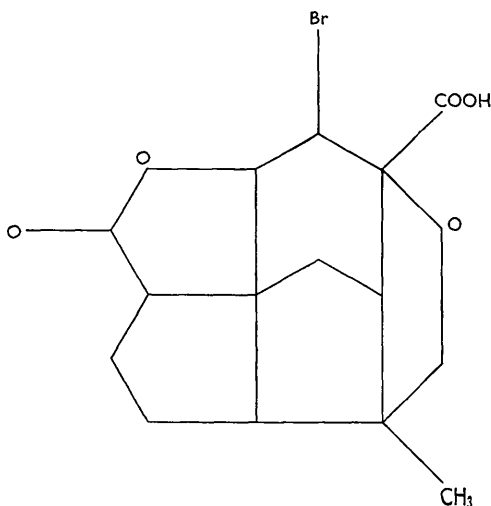

Fig. 1. The molecule of shellolic bromo-lactone.

The intensities of the three sets of zero-level reflections were collected for both substances, using the multiple-film Weissenberg technique. The levels $1kl$ to $6kl$ were collected on equi-inclination Weissenberg photographs for SBL alone. The intensities were measured visually and, where appropriate, correction was made for distortion of the spots (Phillips, 1954). Lorentz and polarization factors were applied (Cochran, 1948), but no correction was made for

absorption, because of the small size of the crystals. If they are considered to be cylinders of radius 0.03 mm., $\mu R = 0.13$ ($\mu = 43$ cm.$^{-1}$), for which the value of A^*, the absorption factor, does not change over the whole θ range (Bond, 1959).

The crystals decompose under the action of X-rays in about 80 hr. and, because of their small size, exposure times of the order of 50 hr. were needed to obtain a reasonable percentage of the data for each level. Hence a new crystal was required for each level and these were chosen to be of approximately the same dimensions. Errors introduced in this way are not thought to be serious because of the low value of μR. In this way 1450 reflections were observed out of a possible 1927 for the 7 levels collected. No attempt was made to collect the 247 reflections in the levels $7kl$ to $9kl$ within the Cu $K\alpha$ sphere. The necessary scaling of the levels was accomplished initially by comparison of each level with common lines on the $h0l$ and $hk0$ levels. The results obtained in this way agreed very closely with each other. In spite of this agreement, however, it was necessary to apply large corrections to the scaling factor during the analysis. The actual amount of the correction increased with h and in the case of the $6kl$ level the final scale factor was 2.1 times its initial value.

Structure determination

Normal projections

The work on electron-density projections was done at Cardiff and the necessary calculations were performed on Ferranti Pegasus computers, with the programs written by Dr H. J. Milledge.

The data for the three zero levels of both SBL and SCL were brought to an approximately absolute scale (Wilson, 1942), and Patterson syntheses were computed using F^2_{oBr} and $F^2_{oBr} - F^2_{oCl}$ (Kartha & Rama-chandran, 1955) as coefficients. These gave the halogen position unambiguously and, with the coordinates obtained, Br and Cl structure factors were computed for the three zones. Signs were given to about 70% of the terms of each zone using isomorphous replacement, and the three Fourier syntheses were computed with these terms for the SCL data. Numerous attempts were made to fit a tentative model to these maps but it was impossible to reduce the R value below about 0.30.

Three-dimensional refinement

Because of the failure of the projection methods, the three-dimensional data for SBL were collected and measured, with the intention of using the conventional 'heavy-atom' technique for the structure determination. The levels were scaled as described above and the coefficients F^2_{oBr} were sharpened by applying the function $1/(\bar{f})^2 \exp(-4\pi^2 \sin^2 \theta / 7.5\lambda^2)$ (Lipson & Cochran, 1953). A Patterson synthesis was computed with these sharpened coefficients, at

intervals $u/16$, $v/32$, $w/32$ over the unique volume, i.e., 0 to $\frac{1}{2}$ in each direction. This confirmed the Br position as 0·144, 0·152, and 0·238. The maps were used to construct a vector-convergence map, using only the positive regions. As the Br atom was assumed to lie at $z=\frac{1}{4}$ for the purposes of this construction, a mirror plane was produced at $z=\frac{1}{4}$ in the resulting map. The resolution of this map was poor, and it could not be interpreted in any detail beyond the general molecular position.

The work at Cardiff was concluded at this stage and resumed later in Ottawa. All the subsequent calculations were performed either on TRANSFER or on an IBM 650, with the programs described by Ahmed (1957, 1961).

A set of Br structure factors was calculated using the position quoted above and $B=2\cdot5$ Å²; an analysis of the results indicated a correction $\Delta B=+2\cdot0$ Å². Terms for which the ratio $||F_o|-|F_{cBr}||/|F_o| \leq 0\cdot50$ were included in a Fourier summation, with the phase of F_{cBr}, computed at intervals $x/15$, $y/30$, $z/30$ over the ranges $0 \leq x \leq 1$ and $0 \leq \{y/z\} \leq \frac{1}{2}$.

In spite of the fact that the Br atom is near a special position, there was very little evidence of the artificial mirror plane in the resulting synthesis and 13 of the 21 light atoms could be seen quite clearly, and these were included in the next round of calculations. Another Fourier synthesis was calculated with the new phases and all light atoms were identified. The interpretation of these Fourier syntheses was greatly facilitated by drawing the contours on perspex sheets (Przybylska & Ahmed, 1958). Of the 13 light atoms identified in the first map, 3 were included in the subsequent structure-factor calculation as oxygen atoms; the choice, which was based on peak height, proved to be correct. Molecular geometry was calculated with the 22 positions from the second map, and was sufficiently good to enable the two doubly-bonded oxygen atoms to be distinguished. The atoms made up a molecule close to that shown in the perspective drawing Fig. 2, in which the final parameters were used, and the molecule is viewed down a line parallel to the xy plane and $-30°$ from the x-axis. $R=0\cdot22$ for the first set of structure factors with all atoms.

Refinement was carried out in three cycles of differential synthesis. The first cycle used the F_o data only and 1·6 times the indicated shifts were applied to give the coordinates for the next set of structure factors, with an overall $B=4\cdot7$ Å². The next cycle of differential synthesis was performed with both F_o and F_c values. By comparing the results, individual isotropic temperature factors were assigned to the light atoms and an anisotropic temperature factor was given to the Br atom. The direction of minimum thermal motion for the Br atom was found to be along the bond joining it to the molecule, as would be expected. With these temperature factors and 1·6 times the indicated shifts the next set of structure

factors gave $R=0\cdot15_7$. The calculations necessitated by the anisotropic motion of the Br atom were performed using the approximation of Kartha & Ahmed (1960). In this set of structure factors, terms with high l index gave $F_c > F_o$, and the next differential cycle showed that B_z for the Br atom needed to be increased substantially. The value of B_z used was 5·5 Å², and in order to find out how much to increase B_z, the 65 terms with $l \geq 12$, in the reflection group $h+k=2n$, $k+l=2n$, were calculated with $B_z=6\cdot0$, 6·5, 7·0 Å². With $B_z=5\cdot5$ Å² the R value for these terms was 0·27$_6$, and the new values were 0·19, 0·15, and 0·14, respectively.

The average shifts shown in this cycle of F_c differential synthesis were 0·0073, 0·0069, and 0·0070 Å

Table 1. *Final atomic coordinates*

	x/a	y/b	z/c
Br	0·1498	0·1498	0·2350
C_1	0·1925	0·2722	0·1941
C_2	0·0576	0·2941	0·1208
C_3	0·0856	0·3928	0·0926
C_4	−0·0137	0·4494	0·1611
C_5	0·1347	0·4434	0·2323
C_6	0·1841	0·3452	0·2640
C_7	0·4748	0·4151	0·2391
C_8	0·3288	0·4647	0·1881
C_9	0·2956	0·4300	0·0957
C_{10}	0·2935	0·4966	0·0197
C_{11}	0·1665	0·4593	−0·0491
C_{12}	0·0353	0·3905	−0·0015
C_{13}	0·0887	0·2939	−0·0258
C_{14}	0·0549	0·3195	0·3390
C_{15}	0·3684	0·5700	0·1885
O_1	−0·1262	0·3171	0·3162
O_2	0·1098	0·2995	0·4104
O_3	0·3637	0·3588	0·2988
O_4	0·1126	0·2433	0·0430
O_5	0·1084	0·2629	−0·0978
H_2O	0·6115	0·2956	0·4330

Table 2. *Final observed and calculated peak heights and mean principal curvatures*

	ϱ_o (e.Å⁻³)	ϱ_c (e.Å⁻³)	ϱ_o'' (e.Å⁻⁵)	ϱ_c'' (e.Å⁻⁵)	B (Å²)
Br	52·7	53·3	412·0	423·0	—
C_1	7·1	6·8	61·9	57·7	3·8
C_2	6·8	6·5	54·6	53·4	4·1
C_3	7·0	6·5	55·8	50·1	4·1
C_4	7·0	6·5	56·6	52·2	4·1
C_5	8·0	7·2	65·4	64·6	3·5
C_6	7·5	7·2	62·2	62·2	4·1
C_7	6·6	6·3	49·7	50·1	4·1
C_8	6·9	6·3	52·7	49·6	4·1
C_9	6·2	6·0	47·7	46·0	4·4
C_{10}	5·8	5·7	43·3	43·7	4·7
C_{11}	5·8	6·0	41·5	46·9	5·0
C_{12}	6·1	6·2	47·6	48·2	4·7
C_{13}	6·8	6·7	54·4	54·6	4·4
C_{14}	6·9	6·6	54·7	53·9	4·4
C_{15}	6·0	6·0	47·8	50·2	4·7
O_1	9·6	9·8	67·6	74·2	4·7
O_2	9·1	9·8	68·3	75·5	4·7
O_3	10·8	10·9	82·5	86·9	4·1
O_4	9·4	9·7	68·7	70·9	4·7
O_5	8·8	9·1	62·7	67·8	4·7
H_2O	8·0	9·0	55·1	65·9	5·3

Table 3. *Agreement summary*

1450 observed reflections $|F_o|_{min.} \simeq 3 \cdot 0$

Category	No. of reflections
1. $|\varDelta F| \leq 3$ or $|\varDelta F| \leq 0 \cdot 2 |F_o|$	1231
2. $|\varDelta F| \leq 6$ or $|\varDelta F| \leq 0 \cdot 4 |F_o|$	185
3. $|\varDelta F| \leq 9$ or $|\varDelta F| \leq 0 \cdot 6 |F_o|$	29
4. $|\varDelta F| \leq 12$ or $|\varDelta F| \leq 0 \cdot 8 |F_o|$	5

102 unobserved reflections $(\sin^2 \theta \leq 0 \cdot 6)$

Category	No. of reflections
1. $3 > |F_c|$	37
2. $6 > |F_c| \geq 3$	41
3. $9 > |F_c| \geq 6$	20
4. $|F_c| \geq 9$	4

refinement cycle preceding the final set of structure factors, and the agreement would have been improved if another cycle had been calculated. The list of structure factors is not presented (it may be obtained from the author), but a summary of agreement is given in Table 3, similar to that of Hanson & Ahmed (1958). Of the 34 observed reflections in categories 3 and 4 (Table 3), none has $|F_o| > 20$ and 18 have $|F_o| \leq 12$ ($|F_o|_{max.} = 180$). 373 possible reflections were not observed in the part of the Cu $K\alpha$ sphere investigated, and of these 102 have $\sin^2 \theta \leq 0 \cdot 6$. These were calculated and the results are summarized in the second part of Table 3. The disagreement in categories 3 and 4 of both parts of Table 3 must be due in some measure to the 76 hydrogen atoms in the cell, for which no allowance was made in the calculations.

in the three directions, and it seems that the x-direction is not significantly more affected by finite summation errors than the other two directions. The F_o shifts were corrected for finite summation and the geometry was calculated using coordinates given by applying 1 times the shift and $1 \cdot 6$ times the shift. The latter set of coordinates, shown in Table 1, gave a small but distinct improvement of bond lengths and angles and these were used to calculate a final set of structure factors, for which $R = 0 \cdot 12_9$. The temperature factors adopted for the Br atom were $B_x = 5 \cdot 5$, $B_y = 4 \cdot 8$ and $B_z = 7 \cdot 0$ Å^2. A list of observed and calculated peak heights, mean principal curvatures and temperature factors is given in Table 2. The peak heights and curvatures have been taken from the
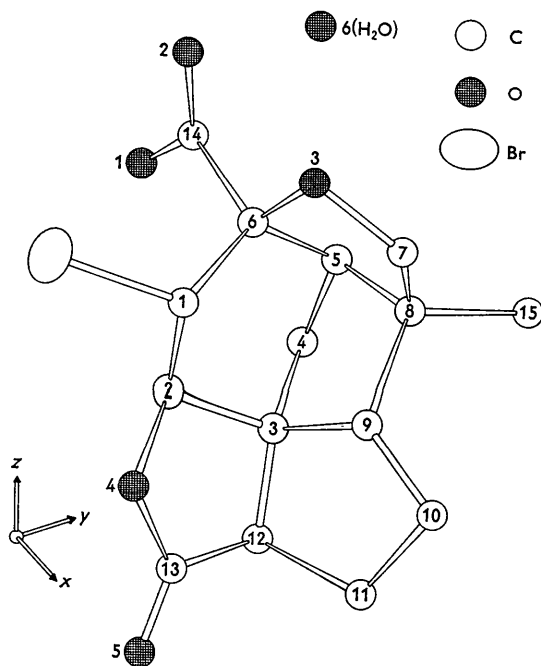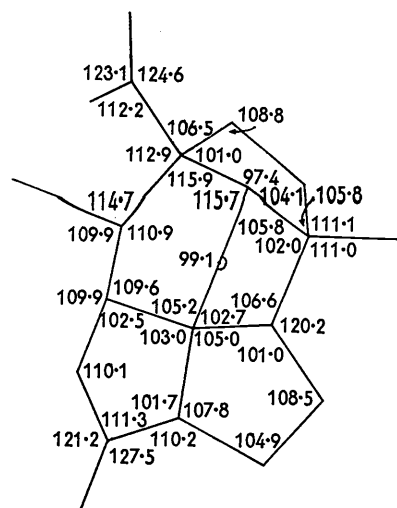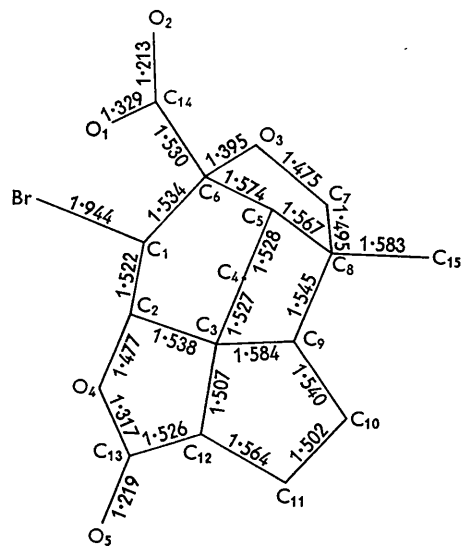

Fig. 2. Perspective view of the molecule of shellolic bromo-lactone hydrate.

Fig. 3. Intramolecular bond lengths and angles.

(a)

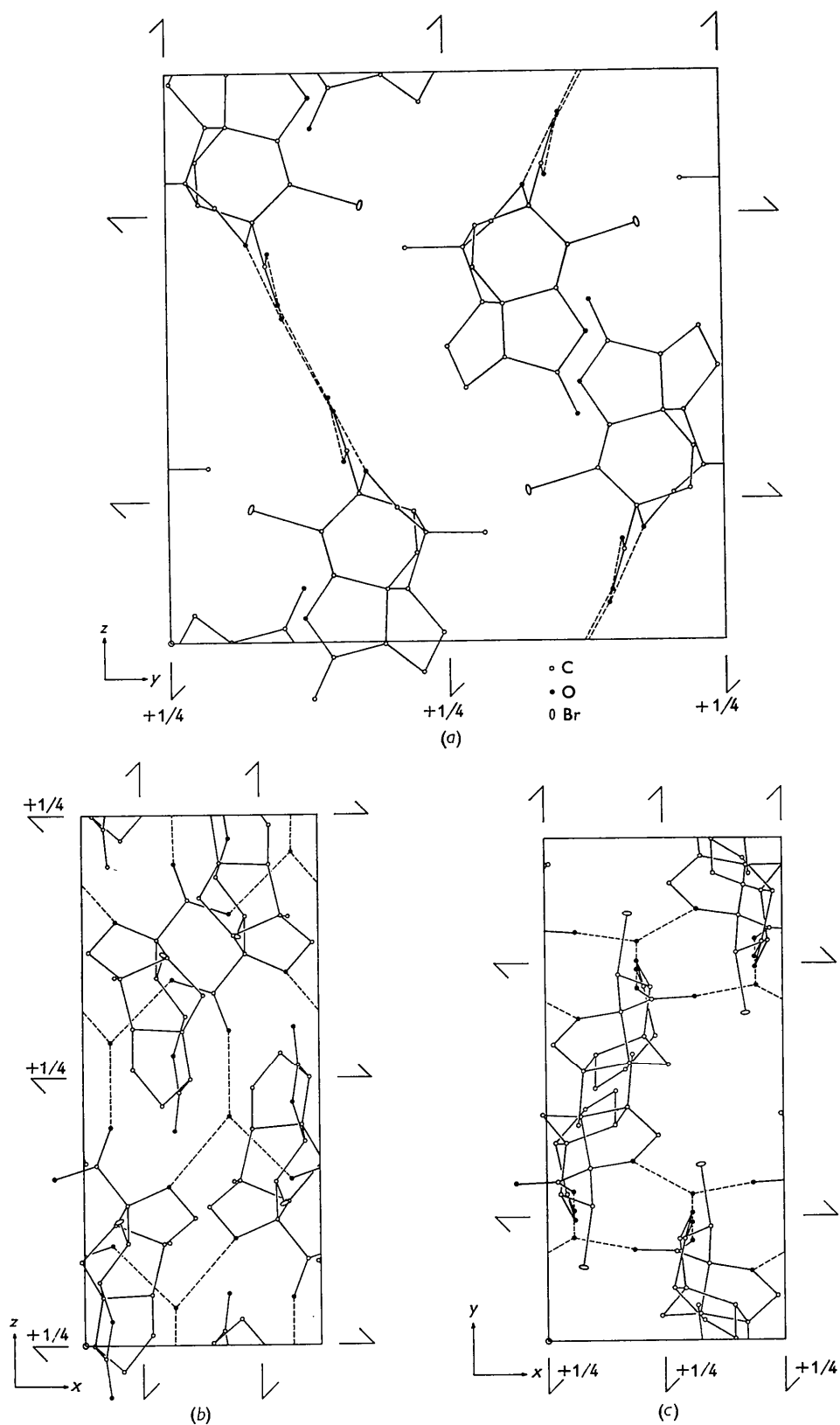(b)   (c)

Fig. 4(a), (b), (c). Projections of the structure along the three axes, showing the hydrogen bond scheme.

Results and discussion

The structure found in the analysis is in complete agreement with that found by Yates & Field (1960), on chemical evidence alone.

The final bond lengths and angles within the molecule are shown in Fig. 3. The following angles were also calculated: C_1-C_6-O_3 = 110·0°, C_5-C_6-C_{14} = 109·6°, C_7-C_8-C_9 = 115·8°, C_5-C_8-C_{15} = 110·6°, C_2-C_3-C_9 = 116·2° and C_4-C_3-C_{12} = 125·6°. Standard deviations were calculated by Cruickshank's method (Lipson & Cochran, 1953), the r.m.s. values being 0·0153 Å for the carbon atoms, 0·0120 Å for the oxygen atoms, and 0·0019 Å for the bromine atom. The mean standard deviations of bond lengths and angles, therefore, are 0·02 Å and 1·3°, respectively. Using Cruickshank's significance criterion (Lipson & Cochran, 1953), differences between observed and accepted values greater than 0·047 Å in bond lengths, and 3·0° in angles, are to be considered significant. On this basis, however, there are no significant differences of C–C bonds from normal, and the C–O distances, although varied, are all close to the expected values for particular bonds. It is interesting, for example, to note the inequality of bond lengths about both the cyclic oxygen atoms, which has been observed in other structures (Przybylska & Ahmed, 1958; Kartha, Ahmed & Barnes, 1960; Kartha, Ahmed & Barnes, 1961). It seems probable that the double bond C_{13} = O_5 appreciably shortens the bond C_{13}–O_4, and the shortening of this bond to 1·317 Å must be considered significant.

Many of the tetrahedral angles are very different from the theoretical value of 109·5°, and no attempt is made to explain these distortions in detail. The molecule is rather strained, however, and it would appear that these strains are compensated to some extent by a distortion of the angles. The angles around C_{13} and C_{14} are of interest because, although the sum of the three angles is 360°, one angle is significantly different from the other two, and for both this is the angle which does not contain the double bond. The effect has also been observed previously (see latter references above).

A complete scan of all the distances between one molecule and its 8 nearest neighbours showed three O–H_2O distances less than 2·9 Å. The oxygen atoms involved are O_1, O_2 and O_3 in different adjacent molecules. The distances are H_2O–O_1 = 2·61₆, H_2O–O_2 = 2·81₄, and H_2O–O_3 = 2·88₂ Å. Projections of the structure down the three axes are shown in Fig.

4(a), (b), and (c). Two flat chains of molecules, roughly perpendicular to the b axis, are formed. Unfortunately the angle O_3 · · · H–O–H · · · O_2, as shown in Fig. 4(b), is 142·9°, which is rather a high value for the H–O–H angle necessary if the two distances involved are hydrogen bonds. The distances are also rather long for hydrogen bonds, though not unreasonably so, and probably they are weak hydrogen bonds which have been distorted in the structure. The angle C_{14}–O_1 · · · H_2O is 119·6°, which is nearer the accepted value of 105°, between the two bonds from an oxygen atom. In this case the H-bond distance is 2·616 Å, and it seems probable that this is a normal H-bond.

I wish to thank Prof. R. C. Cookson for suggesting the problem and supplying the crystals, Dr D. F. Grant of Cardiff for much helpful advice during the early stages of the work, Dr W. H. Barnes of this laboratory for permission to continue the work, and Dr F. R. Ahmed and Mrs M. E. Pippy for considerable help with the computations.

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