The Crystal Structure of 5-Bromo-austdiol, C₁₁H₁₁O₄Br

By D. W. Engel

Physics Department, University of the Orange Free State, Bloemfontein, South Africa

and G. J. Kruger

*National Physical Research Laboratory, Pretoria, South Africa*

$C_{11}H_{11}O_4Br$ has space group $P1$ with $a=13\cdot762$, $b=10\cdot960$, $c=8\cdot320$ Å, $\alpha=109\cdot1$, $\beta=103\cdot2$, $\gamma=91\cdot9°$ and $Z=4$. Data were collected on a four-circle diffractometer with Mo $K\alpha$ radiation and the structure was refined to $R=0\cdot059$. The molecules pack in layers. In one type of layer the molecules form H-bonded dimers, in the other they form bands along c. The different packing environments distort the molecules significantly from their equilibrium configuration.

Introduction

Austdiol is a gastro-intestinal toxin isolated from mouldy maize meal (Steyn, 1973). The crystal structure analysis of 5-bromo-austdiol was undertaken in order to verify the conformation and absolute configuration deduced by Vleggaar, Steyn & Nagel (1974) from NMR measurements on austdiol and derived compounds and by the partial resolution method of Horeau (1961). The systematic name of the compound is 5-bromo-8-hydro-7,8-hydroxy-3,7-dimethyl-2-benzopyran-6-one (I).

(I)
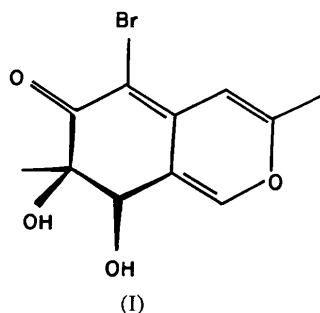
Experimental

5-Bromo-austdiol crystallizes from benzene–*n*-hexane as transparent yellow-brown needles. Crystal data are given in Table 1. Intensities were collected on a Philips 1100 four-circle diffractometer with Mo $K\alpha$ radiation and a graphite monochromator. 2117 reflexions were measured with h positive and of these, 1931 had $I>2\sigma$. No absorption correction was applied.

Structure determination

A Patterson synthesis was calculated and the six strongest peaks were interpreted as vectors between four unrelated heavy atoms. This confirmed the choice of the non-centrosymmetric space group $P1$. The structure solution was completed by Fourier methods and refined isotropically to a residual of $R=0\cdot15$ without H atoms. The scattering factors for C and O were taken from Cromer & Mann (1968) and for Br from Hanson, Herman, Lea & Skillman (1964). The real part of the anomalous scattering factor for Br was included from the outset with $f'=-0\cdot37$ (Cromer & Liberman, 1970).

At this stage the absolute configuration was determined. For this determination and all subsequent refinement the imaginary part of the Br scattering factor was included ($f''=2\cdot46$, Cromer & Liberman, 1970). As f' had already been applied to the Br scattering factor table, it was entered explicitly as zero in the refinement. Structure factors were calculated for both enantiomers with dispersion correction. Reflexions were then selected for which (*a*) $F_o>10$ and (*b*) the magnitude of the (calculated) Bijvoet difference defined as $\{|F(hkl)|-|F(\bar{h}\bar{k}\bar{l})|\}/\frac{1}{2}\{|F(hkl)|+|F(\bar{h}\bar{k}\bar{l})|\}$ was $>0\cdot05$. Residuals were calculated for the two enantiomers for the 761 reflexions selected. Values of $R^+=0\cdot179$ and $R^-=0\cdot169$ were obtained indicating that the mirror image had the correct (absolute) configuration. This was confirmed by direct measurement of 10 Bijvoet differences.

The refinement was continued with the correct configuration taking dispersion into account with the X-RAY system (1972). First, all light-atom parameters were held constant and the four Br atoms re-

Table 1. *Crystal data*

C₁₁H₁₁O₄Br	M.W. 287·13
Space group $P1$	$V=1146\cdot4$ Å³
$a=13\cdot762$ (10) Å	λ(Mo $K\bar{\alpha}$)$=0\cdot7107$ Å
$b=10\cdot960$ (10)	$Z=4$
$c=8\cdot320$ (8)	$D_c=1\cdot664$ g cm⁻³
$\alpha=109\cdot1$ (1)°	μ(Mo $K\alpha$)$=38\cdot0$ cm⁻¹
$\beta=103\cdot2$ (1)	
$\gamma=91\cdot9$ (1)	
Crystal size $0\cdot30\times0\cdot25\times0\cdot15$ mm	

Table 2. Fractional coordinates and thermal parameters

(a) Fractional coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{Å}^2 \times 10^{-3}$) with e.s.d.'s in parentheses. The atoms are numbered so that the first digit refers to the molecule and further digits to the position in the molecule. For Br(1) x, y and z were kept constant to fix the origin.

	x	y	z	U
Br(1)	−19	−8	−10	–
Br(2)	4709 (2)	7253 (3)	8401 (4)	–
Br(3)	5591 (2)	5461 (3)	2642 (4)	–
Br(4)	6758 (2)	8679 (3)	3238 (5)	–
C(11)	7841 (13)	8701 (18)	3823 (24)	33 (5)
C(12)	9483 (14)	7504 (18)	4333 (25)	40 (5)
C(13)	8725 (15)	6277 (20)	3439 (26)	44 (5)
C(14)	9650 (13)	8311 (17)	5962 (22)	31 (4)
C(15)	741 (12)	127 (16)	8388 (22)	26 (4)
C(16)	1634 (14)	1034 (18)	9120 (25)	34 (5)
C(17)	2347 (12)	980 (16)	7940 (22)	28 (4)
C(18)	1178 (13)	666 (17)	6045 (23)	35 (5)
C(19)	975 (12)	9493 (16)	5454 (22)	28 (4)
C(110)	465 (12)	9338 (17)	6716 (23)	27 (4)
C(111)	3097 (14)	10001 (18)	8170 (25)	40 (5)
O(11)	10 (10)	7631 (12)	3181 (17)	45 (3)
O(12)	1876 (11)	1799 (13)	628 (18)	53 (4)
O(13)	2887 (9)	2259 (12)	8445 (16)	41 (3)
O(14)	2413 (10)	376 (13)	4844 (18)	50 (4)
C(21)	1729 (17)	5714 (21)	2802 (30)	55 (6)
C(22)	3095 (17)	7262 (22)	3135 (31)	64 (6)
C(23)	3442 (20)	8190 (26)	2231 (35)	75 (8)
C(24)	3531 (17)	7216 (22)	4672 (31)	61 (6)
C(25)	3434 (15)	6326 (20)	7007 (27)	50 (6)
C(26)	2941 (14)	5590 (18)	7746 (24)	33 (5)
C(27)	1824 (13)	5124 (17)	6820 (24)	36 (5)
C(28)	1677 (15)	4610 (20)	4872 (27)	51 (6)
C(29)	2128 (15)	5648 (19)	4258 (27)	45 (5)
C(210)	3073 (14)	6411 (19)	5446 (26)	43 (5)
C(211)	1203 (17)	6293 (21)	7530 (29)	57 (6)
O(21)	2155 (12)	6581 (16)	2093 (22)	74 (5)
O(22)	3320 (11)	5298 (14)	9033 (18)	56 (4)
O(23)	1508 (10)	4071 (13)	7379 (17)	49 (4)
O(24)	621 (10)	4348 (13)	3958 (18)	49 (4)
C(31)	6278 (14)	4358 (18)	8440 (25)	37 (5)
C(32)	7381 (17)	5938 (21)	8085 (29)	57 (6)
C(33)	8339 (19)	6871 (25)	9049 (34)	70 (7)
C(34)	6816 (15)	5763 (19)	6565 (26)	41 (5)
C(35)	5363 (13)	4567 (17)	4155 (23)	31 (5)
C(36)	4543 (15)	3518 (19)	3383 (27)	41 (5)
C(37)	4436 (13)	2621 (17)	4388 (23)	31 (5)
C(38)	4682 (13)	3394 (17)	6318 (23)	31 (5)
C(39)	5697 (12)	4158 (16)	6900 (22)	24 (4)
C(310)	5942 (13)	4816 (16)	5752 (22)	27 (4)
C(311)	5007 (17)	1504 (21)	3879 (29)	55 (6)
O(31)	7170 (12)	5249 (15)	9124 (21)	64 (4)
O(32)	3978 (12)	3272 (16)	1894 (22)	70 (5)
O(33)	3352 (10)	2158 (12)	3900 (17)	43 (4)
O(34)	4690 (9)	2550 (12)	7354 (17)	45 (3)
C(41)	8304 (15)	2575 (20)	9045 (28)	47 (5)
C(42)	6894 (18)	1196 (24)	8806 (33)	64 (7)
C(43)	6139 (20)	1015 (26)	9897 (35)	82 (8)
C(44)	6889 (17)	470 (22)	7204 (30)	59 (6)
C(45)	7630 (15)	220 (20)	4681 (26)	43 (5)
C(46)	8296 (15)	710 (19)	3850 (26)	40 (5)
C(47)	8817 (15)	2060 (20)	4813 (27)	47 (6)
C(48)	9199 (14)	2264 (19)	6756 (25)	38 (5)
C(49)	8344 (13)	1955 (17)	7468 (23)	32 (5)
C(410)	7601 (15)	807 (19)	6315 (26)	41 (5)
C(411)	8106 (15)	3046 (19)	4423 (26)	47 (5)
O(41)	7559 (12)	2276 (15)	9792 (20)	65 (4)
O(42)	8417 (12)	87 (16)	2397 (21)	68 (5)
O(43)	9684 (10)	2150 (13)	4135 (18)	49 (4)
O(44)	9614 (10)	3573 (13)	7777 (18)	52 (4)

Table 2 (cont.)

(b) Anisotropic thermal parameters ($\text{Å}^2 \times 10^{-3}$) for the Br atoms, defined by $\exp\{-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}hka^*b^* + \ldots)\}$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	61 (2)	65 (2)	54 (1)	−17 (1)	27 (1)	17 (1)
Br(2)	45 (1)	54 (2)	109 (2)	−9 (1)	25 (1)	14 (1)
Br(3)	85 (2)	73 (2)	69 (2)	−24 (1)	22 (1)	42 (1)
Br(4)	68 (2)	44 (2)	130 (3)	−24 (1)	27 (2)	6 (2)

fined isotropically. This resulted in an average shift of these atoms of 0·029 Å in the negative **a** direction. From an expression given by Cruickshank & McDonald (1967) for polar space groups a shift of 0·036 Å is predicted in this case. All parameters except the positional parameters of Br(1) were then refined further, the Br atoms anisotropically, to a final residual of $R = 0·059$. The final parameters for the four molecules are given in Table 2.*

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31714 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
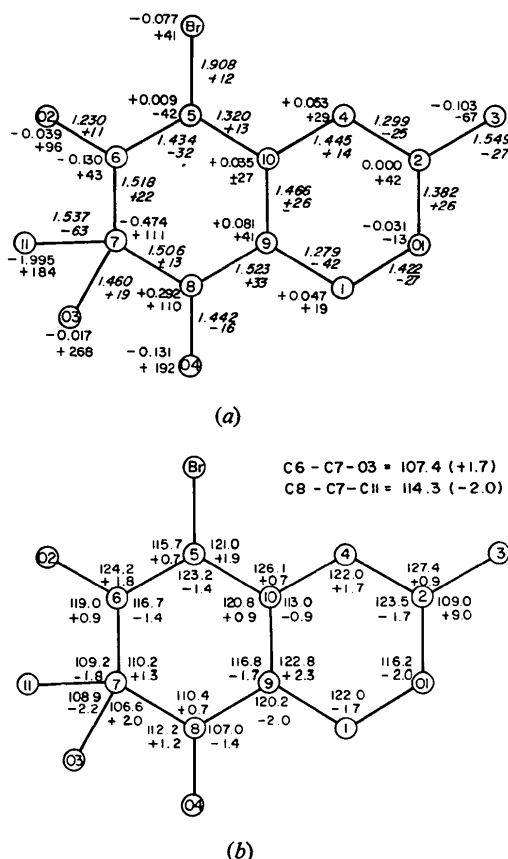

(a)

(b)

Fig. 1. (a) Bond lengths and atomic distances from the plane defined by all atoms except C7, C8, C11, O3 and O4. The values shown are means for the four molecules with the largest deviation from the mean for any one molecule in parentheses. (b) Bond angles, means and largest deviations.

For the 44 H atoms in the cell, 40 peaks were located in a difference synthesis at chemically reasonable positions. The peak heights were, however, poor and there were many large spurious peaks. The H positional and thermal parameters were refined but only 20 atoms retained low temperature factors. More reflexions and an absorption correction would be required to determine all the H positions. Two H atoms of interest to the bonding structure could, however, be placed with reasonable certainty and these are indicated as small dashed circles in Fig. 2(b).
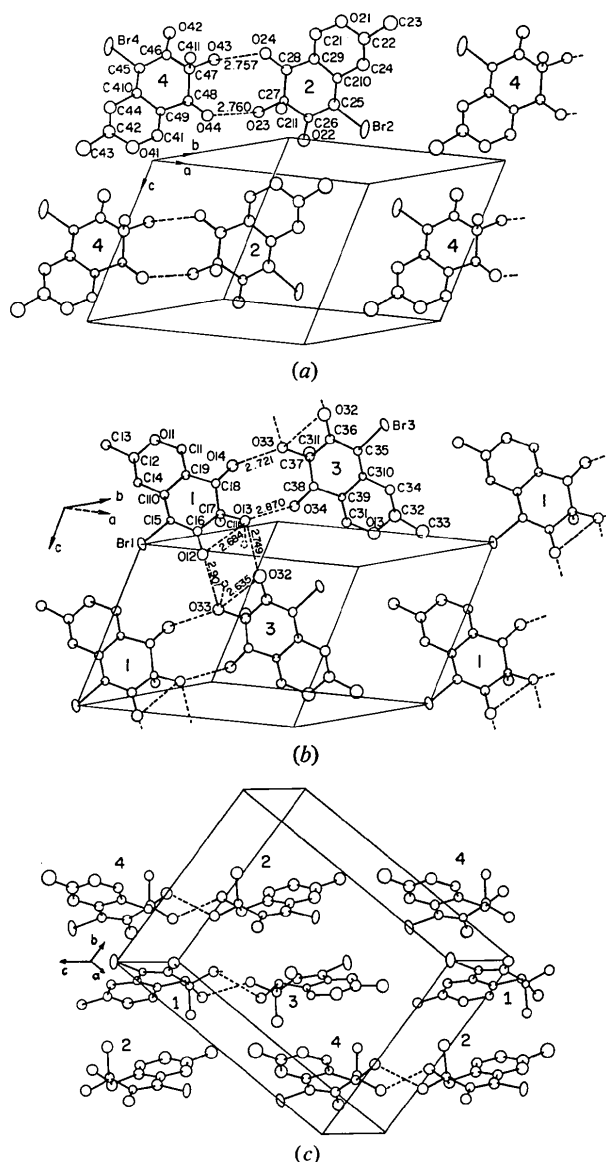

(a)

(b)

(c)

Fig. 2. (a) Projection of layer containing molecules 2 and 4 perpendicular to the (1T0) plane. The molecules in this layer form dimers. (b) Projection of layer containing molecules 1 and 3 perpendicular to the (1T0) plane. The molecules in this layer are H-bonded in bands along c. (c) Projection parallel to the (1T0) plane at right angles to the [110] direction.

Molecular structure

The conformation and absolute configuration of the molecule deduced by Vleggaar, Steyn & Nagel (1974) is confirmed, the two –OH groups being *trans*-diequatorial. The bond lengths and angles, and the distances out of a plane defined by all atoms except C7, C8, C11, O3 and O4 are shown in Fig. 1. The values given are means for the four molecules and, in parentheses, the largest deviation for any one molecule from the mean. The molecules will be compared in greater detail below. For the present we note that the average e.s.d.'s excluding Br atoms are 0·020 Å for atomic coordinates, 0·028 Å for bond lengths and 1·8° for bond angles.

Hydrogen bonding and molecular packing

The occurrence of four molecules in the asymmetric unit is unusual and the hydrogen-bond structure associated with the molecular packing is interesting. The molecules are arranged in layers parallel to the (1T0) plane. One layer contains molecules 2 and 4 which form dimers connected by pairs of hydrogen bonds between O3 and O4; O(23)···O(44) is 2·760 and O(43)···O(24) 2·757 Å. Fig. 2(a) shows a projection of this layer normal to the (1T0) plane.

Alternating with these layers are layers containing molecules 1 and 3. These molecules are upside down with respect to molecules 2 and 4 of the first layer. Molecules 1 and 3 are again connected as in the case of the dimers across O3 and O4; O(14)···O(33) is 2·721 and O(13)···O(34) 2·870 Å. There is, however, a further pair of short intermolecular contacts from O2 and O3 to the equivalent atoms in the next molecule; O(12)···O(33) is 2·901 and O(13)···O(32) 2·749 Å. In this layer the molecules are thus hydrogen bonded in bands along c [Fig. 2(b)].

Fig. 2(b) also shows the probable positions of the two H atoms which are responsible for the formation of the bands of molecules 1 and 3. The positions of these H atoms seem to indicate that the short intramolecular distances between O2 and O3 [O(12)···O(13) is 2·684 and O(32)···O(33) 2·635 Å] are intramolecular H bonds. If this is indeed the case O(13) and O(33) are H-bonded to three other O atoms.

It could not be ascertained whether intramolecular H bonds are formed between O2 and O3 of molecules 2 or 4.

The effect on molecular vibrations of the firmer binding in the layer containing bands is quite noticeable. The average U's of the C and O atoms in molecules 1 and 3 of the band layer are 0·037 and 0·045 Å² while in molecules 2 and 4 of the dimer layer the values are 0·053 and 0·051 Å² respectively. The average e.s.d.'s of bond lengths amongst C and O atoms are 0·024 and 0·025 Å for molecules 1 and 3, and 0·031 and 0·030 Å for molecules 2 and 4 in the more loosely bound layer.

Within each layer the molecules are related by a pseudo twofold rotation axis perpendicular to the layer. In two successive layers the pseudo axes are nearly coincident (0·4 Å apart). The C11 methyl groups stick out into the space between these two layers [Fig. 2(c)]. Going to the next layer the pseudo axis is displaced by 2·1 Å. The angles between the defining planes of the four molecules were calculated. Molecules 2 and 4, which are H-bonded as dimers, are inclined at 44·6° to one another, molecules 1 and 3 at 36·7°. Molecules 2 and 3, which lie above one another in successive layers [Fig. 2(c)], are virtually parallel, being at an angle of 5·1°, and molecules 1 and 4 at 4·9°. Molecules 1 and 2 lie above one another in the following pair of layers but have methyl groups pointing into the space between the layers. The planes are inclined at 39·7° to one another, those of molecules 3 and 4 at 41·5°.

Comparison of the four molecules

The occurrence of four molecules in the asymmetric unit provides an opportunity for determining a mean molecular configuration and for investigating whether the molecules differ appreciably from the mean due to different packing environments. We can consider this mean configuration as a good representation of the equilibrium configuration undistorted by packing. The molecular parameters are shown in Fig. 1. By

Table 3. *Distances* (Å × 10⁻³) *of atoms from the mean plane defined by the atoms in the upper part of the table*

Distances are given for the individual molecules as well as mean distances for equivalent atoms. δ is the maximum deviation from the mean and the relevant molecule is marked with an asterisk.

	Mol. 1	Mol. 2	Mol. 3	Mol. 4	Mean	δ
Br	+118*	+39	+66	+87	+77	+41
C1	+54	+33	+37	+66*	+47	+19
C2	−12	+42*	−23	−9	0	+42
C3	−170*	−73	−70	−100	−103	−67
C4	+82*	+46	+37	+48	+53	+29
C5	+37	−33*	+33	0	+9	−42
C6	−144	−140	−87*	−150	−130	+43
C9	+115	+40*	+89	+79	+81	−41
C10	+62*	+8*	+30	+41	+35	±27
O1	−27	−20	−44*	−35	−31	−13
O2	−115	+57*	−70	−27	−39	+96
C7	−462	−545	−361*	−527	−474	+113
C8	+273	+221	+402*	+273	+292	+110
C11	−1987	−2127	−1811*	−2056	−1995	+184
O3	+31	−220	+251*	−129	−17	+268
O4	−173	−280	−61*	−134	−131	+192

comparing the deviations from the means with the e.s.d.'s for the particular parameters we can deduce whether the molecules are significantly distorted by their environment.

The bond lengths have e.s.d.'s of about 0·028 Å. The largest individual deviation from the mean is 0·063 Å for C7–C11 in molecule 3. The other deviations are less than 0·042 Å. The bond angles have e.s.d.'s of about 1·8°. The largest observed deviation is 2·2°. These deviations do not appear to be significant.

The atomic positional parameters have e.s.d.'s of about 0·020 Å. The deviations of individual distances from the mean distances from the plane are generally large (see Table 3). The deviations are the smallest and do not show any particular trend in the flat part of the molecule. However, the positions of the five atoms in the 'non-planar' part of the molecule (C7, C8, C11, O3 and O4) differ considerably. In molecule 3 the distances of these five atoms from the plane are all significantly more positive, in molecule 2 all more negative, than the mean distances for corresponding atoms. For molecule 3 the deviations are consistent with a bending of the molecule by 5° away from its undistorted configuration about a line through C6 and C9. Molecule 2 is bent by 3° in the opposite sense about a similar line.

These results suggest that packing forces including H bonding can distort a stiff molecule quite considerably in directions normal to the bonds while leaving bond lengths and angles fairly constant.

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