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The Crystal Structure of the Condensation Product of Alloxan Hydrate and the Bromo Derivative of *o*-Aminodiethylaniline

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The product formed by the condensation of alloxan hydrate and the bromo derivative of *o*-aminodiethylaniline can be described as 5-(6′-bromo-3′-ethyl-2′-methylbenzimidazolium) barbiturate, although this configuration was not thought likely on chemical grounds. The crystals have the composition $C_{14}N_4O_4H_{15}Br$ and are monoclinic with space group $P2_1/n$. There are 8 molecules in the unit cell, which has the dimensions

$$a=8\cdot687,\ b=14\cdot995,\ c=23\cdot730\ \text{Å};\ \beta=95°\ 5'.$$

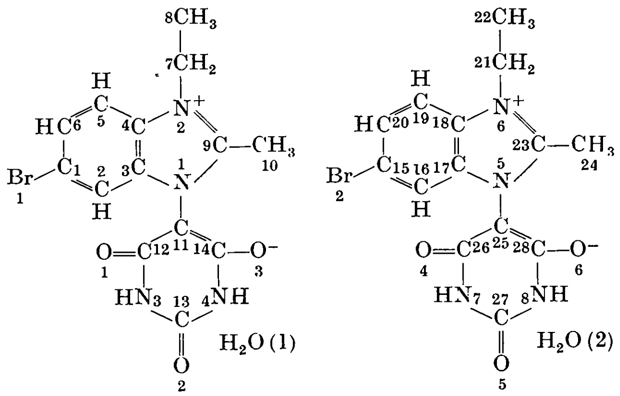
The positions of the two bromine atoms were found by the combined use of Harker sections and general line sections through the three-dimensional Patterson function. The remainder of the structure was found by the application of Woolfson's (1956) improved 'heavy atom' technique. Structure refinement, using isotropic temperature factors, was by the 'differential difference' Fourier method. The final R index for the 4804 observed reflexions was 17·3%.

The dimensions of the two crystallographically independent molecules are similar, and all bond lengths are within normal limits. In each molecule both the benzimidazole and barbiturate ring atoms are close to coplanar; in one molecule the dihedral angle between these planes is 66·7°, and in the other, 69·8°. The molecular arrangement implies an extensive array of hydrogen bonds in which the water molecules play an important part.

Introduction

From the structural viewpoint, the condensations of *o*-phenylenediamines with alloxan are very interesting, for they involve a type of ring formation unique in the literature (King & Clark-Lewis, 1951*a*, *b*). Furthermore, the products formed in these condensations also take part in some unusual reactions. The condensation products have subsequently been studied extensively by chemical methods, but in several cases the molecular structures have remained in doubt (King & Clark-Lewis, 1953; Thompson, 1957; Clark-Lewis, 1962). One such condensation product, $C_{14}N_4O_4H_{16}$, is formed by the reaction between *o*-aminodiethylaniline and alloxan hydrate; in this case it was not possible to differentiate chemically between plausible 5- or 6-membered ring structures. This X-ray analysis of the bromo analogue $C_{14}N_4O_4H_{15}Br$ was therefore undertaken with the hope that it would provide a starting point from which a knowledge of this series of related compounds and reactions would follow. The analysis has in fact shown $C_{14}N_4O_4H_{15}Br$ to have a structure not expected on chemical grounds and the implications of this result are discussed in more detail by Clark-Lewis, Edgar, Shannon & Thompson (1964).

The structure determined by X-ray diffraction, and the atom numbering used for the two molecules, are:



This configuration can be described systematically as 5-(6′-bromo-3′-ethyl-2′-methylbenzimidazolium) barbiturate hydrate.

Experimental

Crystals of the bromo condensation product (hereafter B.Br) were kindly supplied by Prof. Clark-Lewis of the Organic Chemistry Department of the University of Adelaide. The crystals were generally well formed, brittle, and tabular, elongated along [100], and with the (010) and (001) faces most prominent. Cleavage was possible parallel to the principal faces, and to (100).

From the systematically absent reflexions, *h*0*l* for

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$h+l$ odd and $0k0$ for k odd, the space group was determined unequivocally as $P2_1/n$. The unit-cell parameters were determined by a method similar to that described by Buerger (1958), and the results are summarized in Table 1. The density observed by flotation was 1·652 g.cm^{-3}. For two B.Br molecules plus two water molecules in the asymmetric unit the calculated density is 1·652 g.cm^{-3}.

Table 1. *Lattice constants and their standard deviations*

$a \sin \beta = 8{\cdot}6531 \pm 0{\cdot}0036$ Å	$a = 8{\cdot}687 \pm 0{\cdot}004$ Å
$c \sin \beta = 23{\cdot}6363 \pm 0{\cdot}0027$ Å	$c = 23{\cdot}730 \pm 0{\cdot}004$ Å
$\beta = 95° \; 5{\cdot}3' \pm 1{\cdot}5'$	$b = 14{\cdot}995 \pm 0{\cdot}003$ Å

The intensities were recorded photographically with the use of the equi-inclination Weissenberg technique, and were measured by visual comparison with a standard scale of spots. Two crystals were used; the first measured $1{\cdot}0 \times 0{\cdot}13 \times 0{\cdot}13$ mm and was used to record the layers ($0kl$) through ($7kl$); the second measured $0{\cdot}13 \times 0{\cdot}6 \times 0{\cdot}13$ mm and was used to record the layers ($h0l$) through ($h4l$). Within the limiting sphere for copper radiation, there were about 7010 independent reflexions; 6765 of these reflexions were recorded, and of these, 4804 observed to have a non-zero intensity. A correction was made for the spot shape of each reflexion. For the extended spots, the correction of Phillips (1956) was used; for the contracted spots, a semi-empirical correction was applied. A correction curve for each layer was constructed in part from the analytic expression of Phillips, and in part from direct measurements of spot lengths. By using all the intensities common to both a axis and b axis photographs, the individual layers of reflexions were brought to a common scale. Wilson's (1942) statistical method was then used to find the absolute scaling factor and overall temperature exponent.

Determination of the structure

Determination of the heavy atom positions

Instead of calculating the full three-dimensional Patterson function, the heavy atom positions were found by a combination of Harker (1936) sections and general line sections through the Patterson function. Before calculation, these sections were sharpened by modifying the coefficients in the manner suggested by Shoemaker, Barieau, Donohue & Lu (1953).

The actual modification used was of the form

$$(F_o^2)_{\text{sharp}} = F_o^2\,(\sin^2\theta/\lambda^2)^2\,(1/f_O^2)\,\exp\,[(2B-19{\cdot}4)\sin^2\theta/\lambda^2]$$

where f_O is the scattering factor for oxygen, and the other symbols have their usual meaning; $2B$ was equated to 7·0 Å^2, as determined statistically.

The $(x, \frac{1}{2}, z)$ Harker section, and $(\frac{1}{2}, y, \frac{1}{2})$ Harker line section are shown in Figs. 1 and 2(a) respectively. Although the two bromine–bromine vector interactions are quite prominent in each section there are two possible ambiguities in the determination of the two bromine coordinates (say (x_1, y_1, z_1) and (x_2, y_2, z_2)) from these two sections alone: First, the peaks in one section must be correctly correlated with the peaks in the other — a wrong correlation leading to bromine coordinates (x_1, y_2, z_1) and (x_2, y_1, z_2). Secondly, the coordinates of the two heavy atoms must be determined with respect to the same origin — a wrong choice of origin leading to coordinates of the form (x_1, y_1, z_1) and $(x_2+\frac{1}{2}, y_2, z_2)$. The first ambiguity mentioned above was removed by using appropriately chosen line sections to search for the 'Br(1)–Br(1)' heavy atom vector peak at $(2x_1, 2y_1, 2z_1)$, and the 'Br(2)–Br(2)' peak at $(2x_2, 2y_2, 2z_2)$. The values of $2x_1, 2z_1, 2x_2$ and $2z_2$ were found unambiguously from the Harker section $P(x, \frac{1}{2}, z)$, and the two corresponding line sections $P(2x_1, y, 2z_1)$ and $P(2x_2, y, 2z_2)$ are shown in Fig. 2(b) and (c). This enabled the coordinates of one of the bromine atoms to be fixed, after which the position of the other was found unambiguously by using the line sections shown in Fig. 2(d) and (e) to search for the 'Br(1)–Br(2)' interaction at $(x_1-x_2, y_1-y_2, z_1-z_2)$. The prominent peak in Fig. 2(d) shows this section to be $P(x_1-x_2, y, z_1-z_2)$, while Fig. 2(e), with no such peak, must be $P(x_1-x_2+\frac{1}{2}, y, z_1-z_2)$. To confirm the Br(1) and Br(2) coordinates the line section $P(x_1+x_2, y, z_1+z_2)$ was also calculated (Fig. 2(f)) and this does in fact show a strong 'Br(1)–Br(2)' interaction at the expected position of $(x_1+x_2, y_1+y_2, z_1+z_2)$. The final coordinates obtained for Br(1) and Br(2) were $x_1=0{\cdot}8784$, $y_1=0{\cdot}4347$, $z_1=0{\cdot}2107$, and $x_2=0{\cdot}4952$, $y_2=0{\cdot}2032$, $z_2=0{\cdot}1750$. These values of y_1 and y_2 are the ones used in drawing the vertical lines in Fig. 2(a) to (f). It may also be noted that the vector peaks shown in Fig. 2(b) and (c) are expected to be approximately half the height of the peaks shown in (a), (d) and (f) as is observed.

The agreement index R for structure factors calculated from the two bromine atoms alone was 57%.

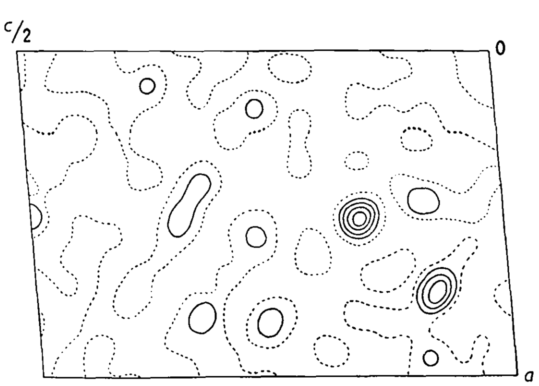

Fig. 1. Harker section $P(x, \frac{1}{2}, z)$. Zero contours are dashed, and positive contours drawn at arbitrary equal intervals.

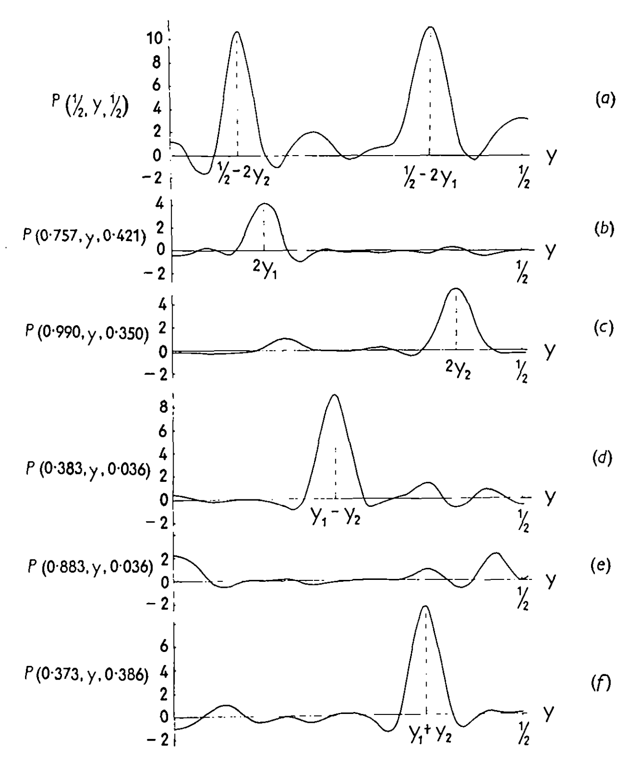

Fig. 2. Patterson line sections. The sections are parallel to b and are shown from $y=0$ to $y=\frac{1}{2}$ on an equal but arbitrary scale.

Determination of the light atom positions

The approximate coordinates of the remaining non-hydrogen atoms were found from a three-dimensional 'heavy atom' Fourier synthesis. In this synthesis, the method of Woolfson (1956) was used to weight each coefficient according to the probability that its sign was correct. In addition, as recommended by Woolfson, the contribution of the heavy atoms to each structure factor was subtracted from F_o. The more prominent peaks of the resultant synthesis were represented by stringing appropriately coloured corks on thin wire stretched parallel to one of the unit cell edges (*cf.* Wood, Geith, Pan Liang & Dockrill, 1961). From this model, the molecular structure was immediately apparent; the two independent molecules appeared to be very similar, and the system of intermolecular hydrogen bonding could be seen. As a final confirmation of the general correctness of the structure, which was not thought likely from chemical evidence at this stage, structure factors were calculated and gave an agreement index of 33%.

In this application, the weighting system of Woolfson proved most successful, for, except in the immediate vicinity of the bromine positions, the background density only occasionally approached the value of 3·6 e.Å^{-3}, this being the lowest peak density corresponding to a real atom.

To improve the atomic coordinates as known at this stage, a second Fourier synthesis was calculated. In this synthesis, the coefficients were not weighted; also the calculated contribution of the bromine atoms was not subtracted from the observed structure amplitudes, as done before. After this synthesis, all the intramolecular bond lengths were compatible with the proposed structure, and the R value for all observed reflexions had fallen to 21%.

Refinement of the structure

Structure refinement was by the 'differential difference' Fourier method (Cochran, 1951; Cruickshank, 1952). Throughout refinement, individual isotropic temperature factors were used for each atom. The coefficients $\Delta F = w(F_o - F_c)$ were weighted in a manner similar to that of Hughes (1941); *i.e.* $w=1$ if $F_o < 4F_m$, and $w = 1/F_o$ if $F_o > 4F_m$, F_m being the observable threshold of F_o. For those F_o's observed as zero, but having $|F_m| < |F_c| < 2|F_m|$, the coefficient $\Delta F = (F_m - F_c)$ was included; for $|F_o| < |F_m|$, or $|F_c| > 2|F_m|$, ΔF was equated to zero.

During the first two cycles of refinement, R was reduced to 18·3%. Generally the overall coordinate shifts were not large, averaging about 0·01 Å; the greatest shift was 0·09 Å for C(6), an atom close to a bromine atom.

At this stage, the 14 reflexions observed to have $F_o > 200$ were corrected for secondary extinction. The correction applied was of the form described by James (1958), *i.e.*

$$(F_o^2)_{\text{corr.}} = F_o^2/(1-2gF_o^2)\ .$$

By plotting $(1-F_o^2/F_c^2)$ against F_o^2, $2g$ was found to be $2{\cdot}8 \times 10^{-6}$.

After three further cycles, the refinement was concluded. During the final cycle, the maximum shift was 0·013 Å for C(1) (adjacent to Br(1)) and just exceeded the corresponding coordinate standard deviation of 0·011 Å. Mean shifts for the x, y and z coordinates were 0·0044, 0·0016 and 0·0026 Å respectively. The final value of the residual R was 17·3% for the observed reflexions.

The list of the 6470 final non-zero structure factors is not presented (it may be obtained from the author).

Table 2. *Structure factor agreement summary*

$|F_o|_{\max} = 357{\cdot}7, \quad |F_o|_{\min} \simeq 9{\cdot}0$

4804 observed reflexions

	$0 \le r < 0{\cdot}2$	$0{\cdot}2 \le r < 0{\cdot}4$	$0{\cdot}4 \le r < 0{\cdot}6$	$0{\cdot}6 \le r$
$\Delta F < 10$	2508	1009	373	379
$10 \le \Delta F < 20$	72	176	88	145
$20 \le \Delta F < 30$	9	13	9	12
$30 \le \Delta F < 46$	3	4	1	3

1666 unobserved reflexions excluding systematic absences

$\lvert F_c\rvert \le 10$	$10 < \lvert F_c\rvert \le 20$	$20 < \lvert F_c\rvert < 22$
1496	168	2

Instead, Table 2 summarizes the relative and absolute values of the discrepancies $\Delta F = ||F_o| - |F_c||$. The 4804 experimentally observed reflexions were categorized according to both the absolute magnitude of F, and to the relative value r of ΔF, defined by $r = 2\Delta F/(|F_o| + |F_c|)$. (The categories are similar to those of Hanson & Ahmed, 1958). Presumably the larger discrepancies are due to the 120 hydrogen atoms in the unit cell, none of which has been taken into account.

The final positional and thermal parameters are given in Table 3. The coordinate standard deviations were found by using the formulae of Cruickshank (1949), *e.g.*

$$\sigma(x_n) = \frac{2\pi}{aV_c} \{\Sigma h^2(F_o - F_c)^2\}^{\frac{1}{2}} \Big/ \left(\frac{\partial^2 \varrho_c}{\partial x^2}\right)_n .$$

Table 3. *Final atomic parameters*

Atom	x/a	y/b	z/c	$\sigma(x)$ Å)	B (Å^2)
Br(1)	0·8792	0·4362	0·2111	0·0013	4·7
Br(2)	0·4957	0·2031	0·1750	0·0012	4·2
O(1)	0·9362	0·2387	0·1003	0·008	3·9
O(2)	0·4923	0·7586	0·0247	0·007	3·6
O(3)	0·6589	0·9766	0·0542	0·006	3·1
O(4)	0·2407	0·4049	0·1350	0·007	3·8
O(5)	0·7771	0·4318	0·0320	0·006	3·7
O(6)	0·0425	0·6866	0·0811	0·008	4·1
(H_2O)(1)	0·2745	0·3335	0·0215	0·013	7·2
(H_2O)(2)	0·9525	0·8657	0·0727	0·008	4·9
N(1)	0·9207	0·0545	0·1164	0·007	2·4
N(2)	0·1485	0·0031	0·1499	0·007	3·2
N(3)	0·7204	0·2393	0·0389	0·007	2·9
N(4)	0·5846	0·1104	0·0159	0·007	2·9
N(5)	0·2730	0·5930	0·1438	0·007	2·6
N(6)	0·5065	0·6394	0·1729	0·007	2·9
N(7)	0·0081	0·4210	0·0829	0·007	2·7
N(8)	0·9111	0·5590	0·0544	0·007	3·1
C(1)	0·7919	0·9592	0·2470	0·011	3·2
C(2)	0·7698	0·0015	0·1960	0·008	2·7
C(3)	0·9033	0·0141	0·1679	0·008	2·2
C(4)	0·0405	0·9816	0·1885	0·008	2·9
C(5)	0·0653	0·9387	0·2404	0·010	3·6
C(6)	0·5634	0·4278	0·2309	0·010	4·7
C(7)	0·3042	0·9705	0·1534	0·013	4·6
C(8)	0·3159	0·8754	0·1337	0·016	5·7
C(9)	0·0679	0·0453	0·1062	0·009	3·2
C(10)	0·1378	0·0784	0·0557	0·011	4·3
C(11)	0·8077	0·1034	0·0807	0·008	2·7
C(12)	0·8276	0·1958	0·0755	0·008	2·5
C(13)	0·6019	0·1997	0·0088	0·008	2·9
C(14)	0·6857	0·0564	0·0518	0·008	2·3
C(15)	0·3318	0·1883	0·2224	0·009	2·9
C(16)	0·1344	0·6461	0·2263	0·008	2·8
C(17)	0·2678	0·6358	0·1951	0·008	2·4
C(18)	0·4129	0·6651	0·2137	0·008	2·7
C(19)	0·0567	0·2068	0·2335	0·010	3·3
C(20)	0·1867	0·2209	0·2031	0·010	3·4
C(21)	0·6745	0·6578	0·1764	0·010	3·7
C(22)	0·7083	0·7513	0·1583	0·013	5·0
C(23)	0·4258	0·5958	0·1302	0·008	2·8
C(24)	0·4758	0·5552	0·0797	0·009	3·6
C(25)	0·1487	0·5502	0·1113	0·009	2·5
C(26)	0·1434	0·4577	0·1121	0·008	2·3
C(27)	0·8937	0·4688	0·0550	0·007	2·5
C(28)	0·0386	0·6059	0·0823	0·008	2·9

Standard deviations of the x, y and z coordinates of any given atom were found to be nearly equal, and the quoted deviations are the average of these three.

Computations were done with the aid of IBM 1620 and IBM 7090 computers with programs written by the author. The atomic scattering factor curves of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) were used for oxygen, nitrogen and carbon; the curve of Freeman & Watson (1961), modified by the anomalous dispersion correction of Dauben & Templeton (1955), was used for bromine.

Discussion of the stucture

The molecular structure

In the following discussion, molecule A will refer to the molecule containing the atoms Br(1), C(1), C(2), *etc.*; molecule B will refer to that containing Br(2), C(15), C(16), *etc.* The dimensions of both molecules are given in Tables 4 and 5 and are illustrated dia-

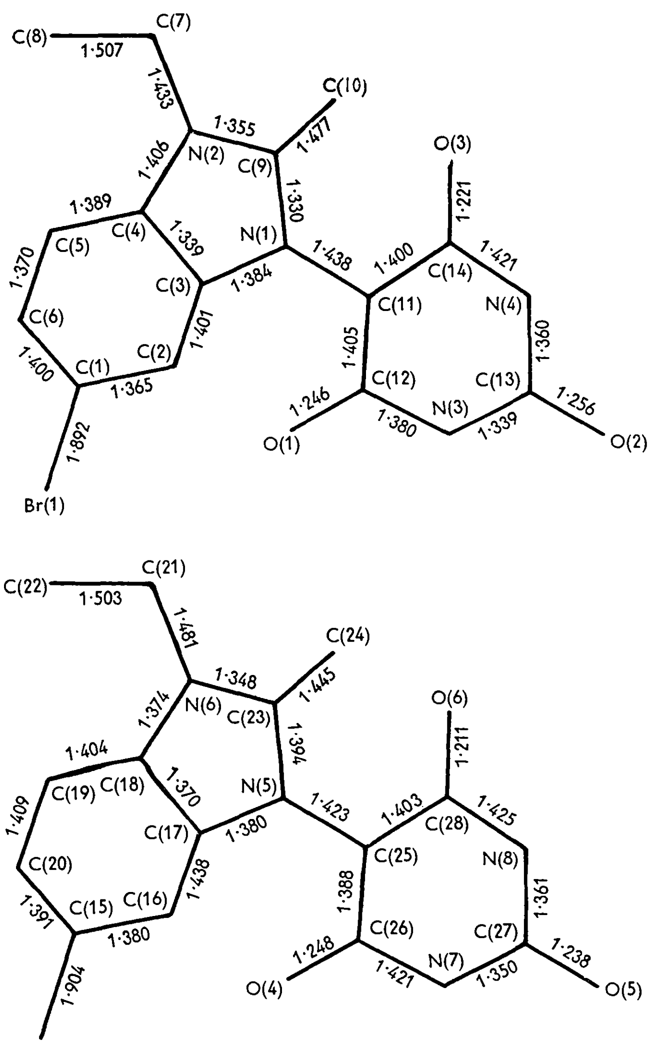

Fig. 3. Intramolecular bond lengths (Å).

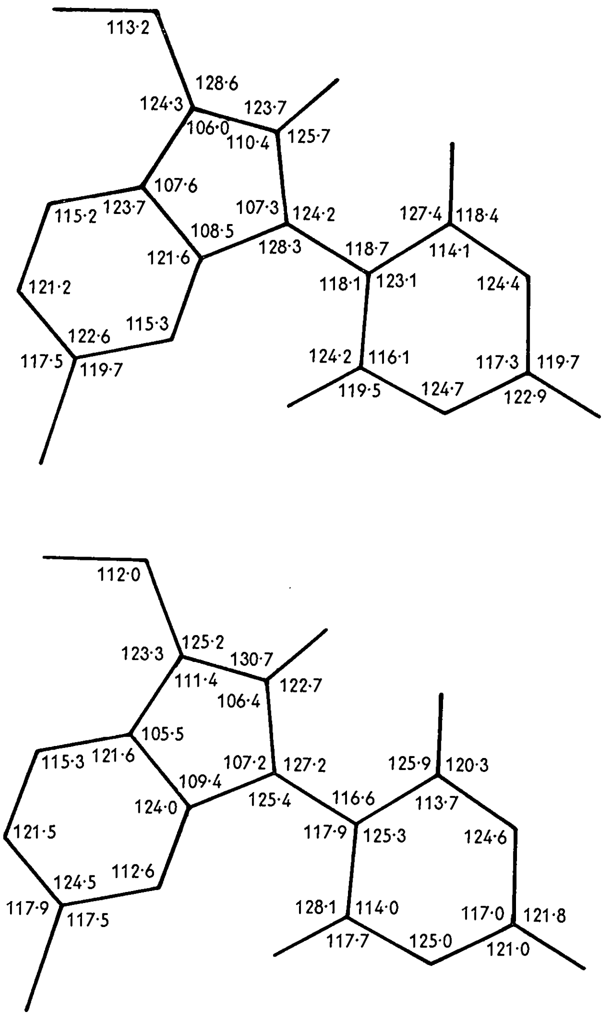

Fig. 4. Intramolecular bond angles (°). The atoms are arranged as in Fig. 3.

grammatically in Figs. 3 and 4. Generally the two molecules are similar, the greatest differences being in the vicinity of the imidazole rings. In three cases the individual molecules differ significantly from the 'average' molecule. First for the N(1)–C(9) (and N(5)–C(23)) bonds the difference is significant; secondly for the C(4)–N(2)–C(9) (and C(18)–N(6)–C(23)) angles the difference is possibly significant, and thirdly there is also a possibly significant difference for the N(2)–C(9)–C(10) (and N(6)–C(23)–C(24)) angles. (The levels of significance used are those suggested by Cruickshank & Robertson, 1953). The two instances of significantly different angles mentioned above can be regarded as a consequence of the difference in bond length between N(1)–C(9) (1·330 Å) and N(5)–C(23) (1·394 Å). The 'expected' lengths for carbon–nitrogen single and double bonds are respectively 1·472 Å and 1·322 Å (*International Tables for X-ray Crystallography*, 1962). Since both C–N bonds lie within these limits, the difference between them could be explained by

Table 4. *Final bond lengths and their standard deviations*

Corresponding bonds from the two molecules are listed side by side

Bond	Length (Å)	Bond	Length (Å)
C(1)–C(2)	1·365±0·014	C(15)–C(16)	1·380±0·012
C(2)–C(3)	1·401±0·011	C(16)–C(17)	1·438±0·011
C(3)–C(4)	1·339±0·011	C(17)–C(18)	1·370±0·011
C(4)–C(5)	1·389±0·013	C(18)–C(19)	1·404±0·013
C(5)–C(6)	1·370±0·014	C(19)–C(20)	1·409±0·014
C(6)–C(1)	1·400±0·015	C(20)–C(15)	1·391±0·013
C(7)–C(8)	1·507±0·021	C(21)–C(22)	1·503±0·016
C(9)–C(10)	1·477±0·014	C(23)–C(24)	1·445±0·012
C(11)–C(12)	1·405±0·011	C(25)–C(26)	1·388±0·012
C(11)–C(14)	1·400±0·011	C(25)–C(28)	1·403±0·012
N(1)–C(3)	1·384±0·011	N(5)–C(17)	1·380±0·011
N(1)–C(9)	1·330±0·011	N(5)–C(23)	1·394±0·011
N(1)–C(11)	1·438±0·011	N(5)–C(25)	1·423±0·011
N(2)–C(4)	1·406±0·011	N(6)–C(18)	1·374±0·011
N(2)–C(9)	1·355±0·011	N(6)–C(23)	1·348±0·011
N(2)–C(7)	1·433±0·015	N(6)–C(21)	1·481±0·012
N(3)–C(12)	1·380±0·011	N(7)–C(26)	1·421±0·011
N(3)–C(13)	1·339±0·011	N(7)–C(27)	1·350±0·010
N(4)–C(13)	1·360±0·011	N(8)–C(27)	1·361±0·010
N(4)–C(14)	1·421±0·011	N(8)–C(28)	1·425±0·011
O(1)–C(12)	1·246±0·011	O(4)–C(26)	1·248±0·011
O(2)–C(13)	1·256±0·011	O(5)–C(27)	1·238±0·010
O(3)–C(14)	1·221±0·010	O(6)–C(28)	1·211±0·011
Br(1)–C(1)	1·892±0·011	Br(2)–C(15)	1·904±0·009

Table 5. *Final bond angles and their standard deviations*

Corresponding angles from the two molecules are listed side by side

Atoms	Angle (°)	Atoms	Angle (°)
C(1)–C(2)–C(3)	115·3±1·4	C(15)–C(16)–C(17)	112·6±1·3
C(2)–C(3)–C(4)	121·6±1·3	C(16)–C(17)–C(18)	124·0±1·3
C(3)–C(4)–C(5)	123·7±1·4	C(17)–C(18)–C(19)	121·6±1·4
C(4)–C(5)–C(6)	115·2±1·5	C(18)–C(19)–C(20)	115·3±1·5
C(5)–C(6)–C(1)	121·2±1·6	C(19)–C(20)–C(15)	121·5±1·6
C(6)–C(1)–C(2)	122·6±1·7	C(20)–C(15)–C(16)	124·5±1·5
C(4)–C(3)–N(1)	108·5±1·2	C(18)–C(17)–N(5)	109·4±1·2
C(3)–N(1)–C(9)	107·3±1·2	C(17)–N(5)–C(23)	107·2±1·1
N(1)–C(9)–N(2)	110·4±1·3	N(5)–C(23)–N(6)	106·4±1·2
C(9)–N(2)–C(4)	106·0±1·2	C(23)–N(6)–C(18)	111·4±1·2
N(2)–C(4)–C(3)	107·6±1·2	N(6)–C(18)–C(17)	105·5±1·2
C(11)–C(12)–N(3)	116·1±1·2	C(25)–C(26)–N(7)	114·0±1·2
C(12)–N(3)–C(13)	124·7±1·2	C(26)–N(7)–C(27)	125·0±1·2
N(3)–C(13)–N(4)	117·3±1·2	N(7)–C(27)–N(8)	117·0±1·1
C(13)–N(4)–C(14)	124·4±1·2	C(27)–N(8)–C(28)	124·6±1·2
N(4)–C(14)–C(11)	114·1±1·2	N(8)–C(28)–C(25)	113·7±1·2
C(14)–C(11)–C(12)	123·1±1·3	C(28)–C(25)–C(26)	125·3±1·4
Br(1)–C(1)–C(2)	119·7±1·3	Br(2)–C(15)–C(16)	117·5±1·1
Br(1)–C(1)–C(6)	117·5±1·4	Br(2)–C(15)–C(20)	117·9±1·2
C(8)–C(7)–N(2)	113·2±1·9	C(22)–C(21)–N(6)	112·0±1·5
C(7)–N(2)–C(4)	124·3±1·4	C(21)–N(6)–C(18)	123·3±1·2
C(7)–N(2)–C(9)	128·6±1·4	C(21)–N(6)–C(23)	125·2±1·2
C(10)–C(9)–N(2)	123·7±1·4	C(24)–C(23)–N(6)	130·7±1·3
C(10)–C(9)–N(1)	125·7±1·5	C(24)–C(23)–N(5)	122·7±1·3
C(11)–N(1)–C(9)	124·2±1·2	C(25)–N(5)–C(17)	125·4±1·2
C(11)–N(1)–C(3)	128·3±1·2	C(25)–N(5)–C(23)	127·2±1·2
N(1)–C(11)–C(14)	118·7±1·2	N(5)–C(25)–C(28)	116·6±1·3
N(1)–C(11)–C(12)	118·1±1·2	N(5)–C(25)–C(26)	117·9±1·3
O(1)–C(12)–C(11)	124·2±1·4	O(4)–C(26)–C(25)	128·1±1·4
O(1)–C(12)–N(3)	119·5±1·3	O(4)–C(26)–N(7)	117·7±1·3
O(2)–C(13)–N(3)	112·9±1·3	O(5)–C(27)–N(7)	121·0±1·2
O(2)–C(13)–N(4)	119·7±1·3	O(5)–C(27)–N(8)	121·8±1·2
O(3)–C(14)–N(4)	118·4±1·3	O(6)–C(28)–N(8)	120·3±1·4
O(3)–C(14)–C(11)	127·4±1·2	O(6)–C(28)–C(25)	125·9±1·3

Table 6. *Deviations from planarity*

Plane *PA*1		Plane *PB*1		Plane *PA*2		Plane *PB*2	
Atom	Deviation	Atom	Deviation	Atom	Deviation	Atom	Deviation
C(1)	−0·002 Å	C(15)	0·028 Å	C(11)	0·008 Å	C(25)	−0·022 Å
C(2)	−0·022	C(16)	−0·003	C(12)	−0·005	C(26)	0·014
C(3)	0·016	C(17)	−0·025	N(3)	−0·004	N(7)	0·001
N(1)	0·018	N(5)	0·003	C(13)	0·011	C(27)	−0·011
C(9)	−0·020	C(23)	0·019	N(4)	−0·006	N(8)	0·009
N(2)	−0·002	N(6)	0·002	C(14)	−0·002	C(28)	0·004
C(4)	−0·012	C(18)	−0·027				
C(5)	0·013	C(19)	0·021	O(1)	0·019	O(4)	0·052
C(6)	0·009	C(20)	−0·010	O(2)	0·029	O(5)	−0·063
				O(3)	−0·004	O(6)	−0·021
Br(1)	−0·079	Br(2)	0·124				
C(11)	0·130	C(25)	0·062				
C(10)	−0·036	C(24)	0·084				
C(7)	−0·190	C(21)	0·012				

a difference in double-bond character; however, it is thought that the analysis is not of sufficient accuracy to show that there is a real difference between the two independent molecules. In each molecule there is no bond length which departs significantly from its expected value.

The best fit planes through the benzimidazole and barbiturate rings of each molecule were found by the method of Schomaker, Waser, Marsh & Bergman (1959). The plane through the nine benzimidazole atoms of molecule *A* will be called *PA*1, that through the six barbiturate atoms, *PA*2. Corresponding planes for molecule *B* will be referred to as *PB*1 and *PB*2. The equations of these four planes are given below, where the constant on the right is the origin to plane perpendicular distance in Å.

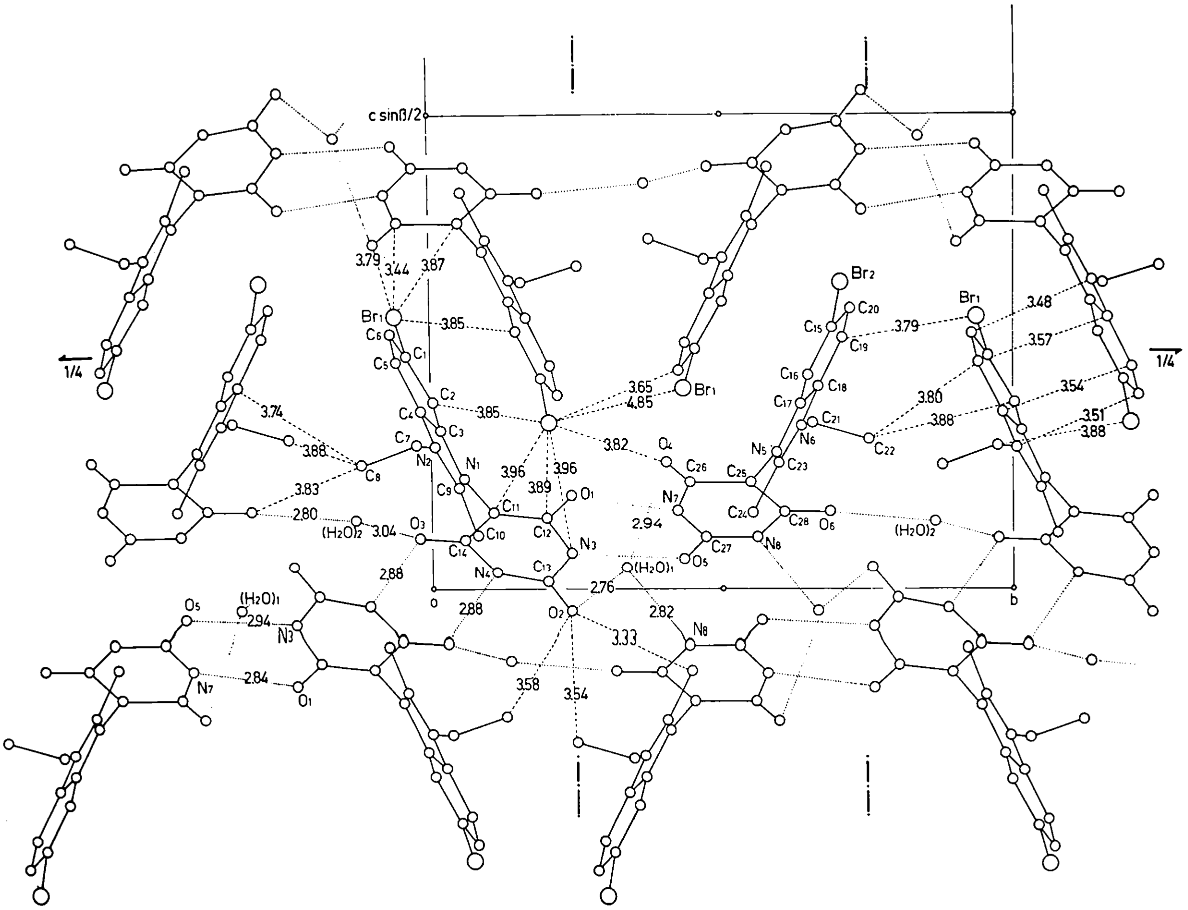

Fig. 5. The molecular arrangement. Intermolecular approaches less than 4·0 Å are shown dashed and hydrogen bonds dotted.

$PA1$: $1{\cdot}295x+13{\cdot}089y+10{\cdot}668z=-3{\cdot}129$
$PB1$: $1{\cdot}286x-13{\cdot}133y+10{\cdot}547z=5{\cdot}923$
$PA2$: $5{\cdot}545x-2{\cdot}410y-19{\cdot}138z=-2{\cdot}677$
$PB2$: $4{\cdot}818x-0{\cdot}847y-20{\cdot}791z=-2{\cdot}042$

The deviations of the ring and ring-substituent atoms from their respective planes are given in Table 6. In each case the atoms are close to coplanar. For molecule *A*, the dihedral angle between the benzimidazole and barbiturate planes is 66·7°; for molecule *B* this angle is 69·8°.

The molecular arrangement

The packing of the two molecules in the crystal is illustrated by Fig. 5. The orientations of the independent molecular planes are somewhat similar, this also being indicated by the similarity of the equations of these planes given in the previous section. The barbiturate planes of molecules *A* and *B* have a dihedral angle of 7·7°; also, after applying the $P2_1/n$ screw operation to molecule *B*, its benzimidazole plane is only 1·1° from parallel with the corresponding plane of molecule *A*.

Although no attempt was made to locate the hydrogen atoms, the probable pattern of hydrogen bonding is implied by the molecular packing. Two hydrogen bonds of the type N–H ⋯ O are formed between the independent barbiturate rings of molecules *A* and *B*, the N(7)–O(1) and N(3)–O(5) distances being 2·84 Å and 2·94 Å respectively. There are also pairs of N(4)–H ⋯ O(3) bonds across the centre of symmetry (N(4)–O(3) = 2·88 Å). The only remaining barbiturate nitrogen atom is N(8), and this is hydrogen bonded to the oxygen atom O(*W*1) of $H_2O(1)$ (N(8)–O(*W*1) = 2·82 Å). In addition, O(*W*1) is hydrogen bonded to O(2) and O(4), the interatomic distances and angle involved being O(2)–O(*W*1) = 2·76 Å, O(*W*1)–O(4) = 2·94 Å and O(2)–O(*W*1)–O(4) = 133°. The oxygen atom O(*W*2) of the second water molecule also takes part in hydrogen bonding, in this case with O(3) and O(6); here the distances and angle of bonding are O(3)–O(*W*2) = 3·04 Å, O(*W*2)–O(6) = 2·80 Å and O(3)–O(*W*2)–O(6) = 90°. The hydrogen bonding is therefore extensive, molecule *A* being involved in six bonds and molecule *B* in five, and all potential hydrogen bonding atoms are satisfied. The hydrogen bonds described above are shown in Fig. 5 as dotted lines; the dashed lines show the intermolecular approaches less than 4 Å.

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