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THE CRYSTAL AND MOLECULAR STRUCTURE OF 2-METHOXY-4-HYDROXY-5-OXO-BENZ[f]AZEPINE

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Abstract—Crystals of 2-methoxy-4-hydroxy-5-oxo-benz[f]azepine belong to the orthorhombic space group $P2_12_12_1$, with $a = 14{\cdot}107$, $b = 16{\cdot}924$, $c = 3{\cdot}982$ Å and four molecules per unit cell. The structure was solved by direct methods and refined to an R index of 0·033 using 876 independent terms. The molecular skeleton is planar within ± 0·04 Å and the only atoms lying out of the plane are two hydrogens of the methyl group. Bond alternation is observed in the 7-membered ring indicating little π-electron delocalization. In the crystal structure the hydroxyl group forms a bifurcated hydrogen bond, one branch of which links the molecules into infinite spirals extending down the twofold screw axes parallel to *c*.

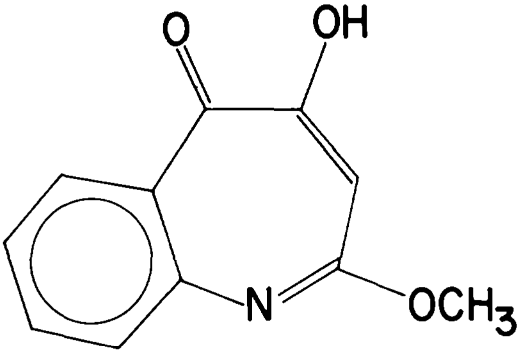
IN RECENT years much interest has been shown in the extent of π-electron delocalization in unsaturated 7-membered ring systems, such as occur in tropolone, tropone and heptafulvene derivatives.[1,2] As yet, however, the bonding in azepine systems has been studied to a somewhat lesser degree. An X-ray analysis of a 1H-azepine derivative[3] has shown that the azepine ring has a conformation similar to the true polyene, cycloheptatriene,[4] and the results of X-ray studies of dibenz[b,f]azepine[5] and the related diketone, 5H-10,11-dioxodihydrodibenzo[b,f]azepine,[6] have shown the 7-membered ring in both compounds to be non-planar, and indicated little delocalization in the azepine ring of the diketone other than could be attributed to the associated functional groups. To investigate the extent of delocalization in the molecule, 2-methoxy-4-hydroxy-5-oxo-benz[f]azepine (I), its X-ray structure has been determined. The chemistry and chemical formulation[7] of this azepine had suggested that it should be planar with an alternation of formal single and double bonds around the 7-membered ring. This planarity would therefore appear to provide an ideal configuration for delocalization of the π-electrons.

Structural detail and discussion

A conventional representation of the molecule is given in I. The molecular skeleton is planar within ± 0·04 Å and the plane through the eleven atoms comprising the fused ring system and the three associated oxygen atoms is defined by the equation,

$$0{\cdot}4165X + 0{\cdot}2967Y - 0{\cdot}8594Z - 0{\cdot}6852 = 0.$$

The deviation of all atoms in the molecule from this plane are given in Fig 1c.



I

In the benzene ring the carbon atoms are planar within ± 0·01 Å; the C—C lengths range from 1·370 to 1·420 Å (Fig. 1a), but the average length of 1·394 Å agrees with the standard value, 1·395 Å.[8] The seven atoms forming the azepine ring are planar within ± 0·005 Å, but 0 (3) and 0 (2) lie 0·027 Å above and 0·020 Å below the plane respectively. This no doubt is the result of some dipolar repulsion between the two oxygen atoms. The benzene and tropolone rings are inclined at a small angle, 1·2°.

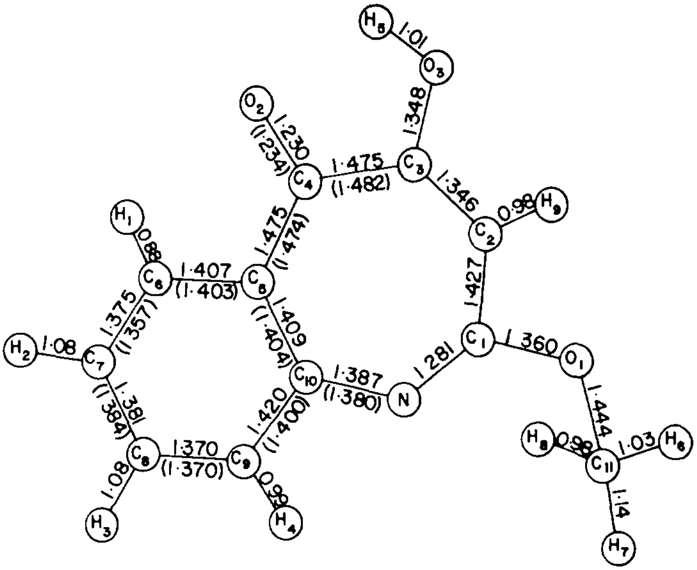
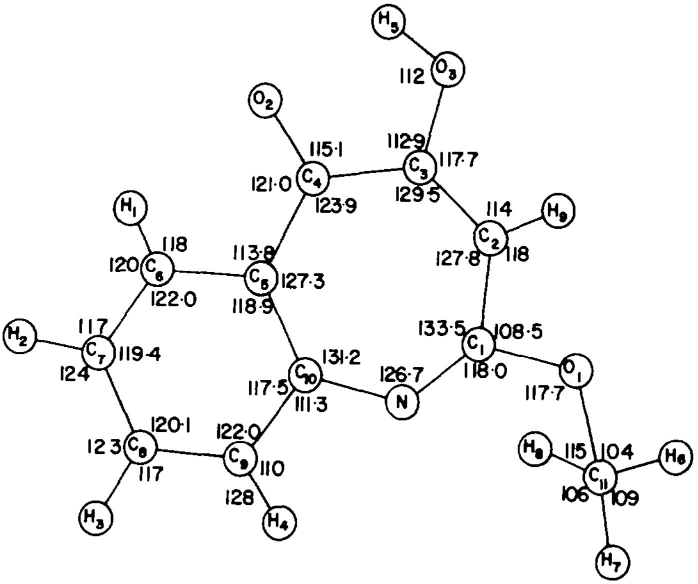
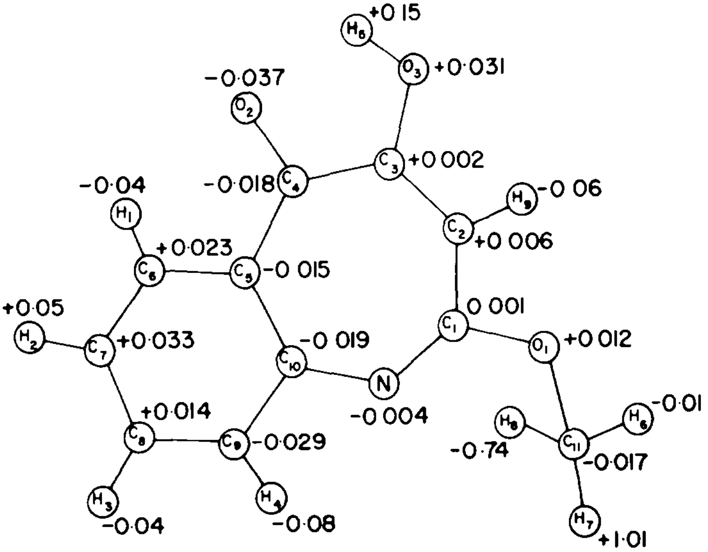


FIG 1a Bond lengths. The e.s.d.s. for lengths involving H were 0·04 Å and for all others 0·006 Å. Some bond lengths for 5H-10,11-dioxodihydrodibenzo[b,f]-azepine have been included in parenthesis.[6]



b Bond angles. The e.s.d.s. for angles involving H were 4·0° and for all others 0·6°.



c Deviations of the atoms from the mean molecular plane. The e.s.d.s. for the H atoms were 0·04 Å and for all others 0·004 Å.

This apparent small deviation from planarity could be due to librational effects, for which the atomic parameters were not corrected. The oxygen and carbon atoms of the OMe group are coplanar with the ring skeleton and the C (1)—O (1) and C (11)—O (1) bonds of 1·360 and 1·444 Å respectively agree with the values of 1·358 and 1·430 Å found for the comparable lengths in thiathiaphthene.[9] The average bond angle in the ring is 128·6° which is the value for a regular heptagon. The C (1)—N bond of 1·281 Å lies close to values reported for pure C—N double bonds which range from 1·255–1·270 Å,[10] whereas the C (10)—N bond of 1·387 Å is comparable with the value of 1·411 Å found for a single C (aromatic)—N bond in dibenz[b,f]azepine.[5] The average value for the essentially single C—C bonds in the azepine ring (C (1)—C (2), C (3)—C (4) and C (4)—C (5)) of 1·459 Å, and the bond length for C (2)—C (3) of 1·346 Å agree with the mean values for other nominal single and double bond lengths (1·46 and 1·35 Å respectively) observed in conjugated cyclic systems.[11] It is apparent, therefore, that there is a considerable bond alternation in the ring, and hence little evidence of π-electron delocalization. This is also in accord with molecular orbital bond length calculations for 6,7-benzotropolone,[2] but contrasts with the situation noted in the X-ray study of free tropolone[12] where delocalization around most of the ring is indicated.

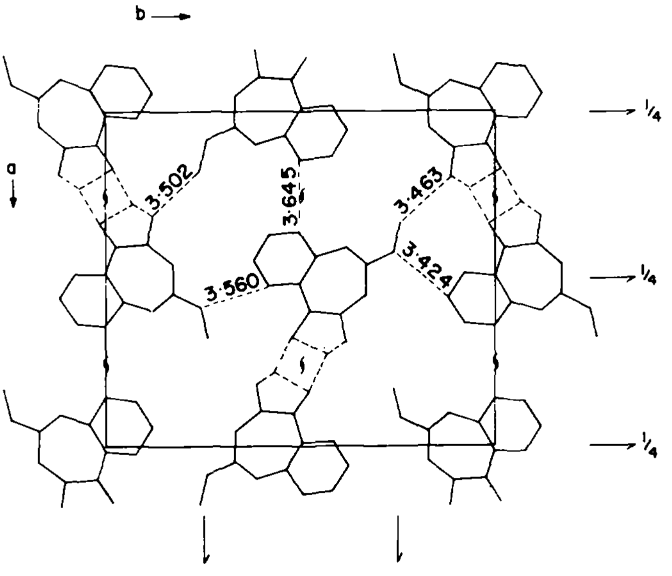


Fig 2. A projection of the structure down 001 illustrating the molecular packing.

All the H atoms were clearly located; H (1) to H (4) were coplanar with the benzene ring to within experimental error (a mean deviation of ± 0·05 Å) and H (9) which is bonded to C (2) is coplanar with the azepine ring. The C—O bond lengths of 1·230 and 1·348 Å for the bonds C (4)—O (2) and C (3)—O (3) respectively, suggested that the former was a carbonyl group whereas the latter formed part of a hydroxyl group.

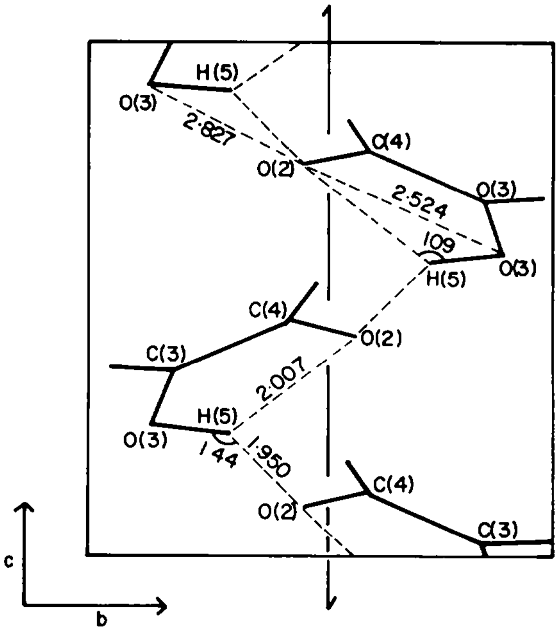


FIG 3. Part of the structure projected onto 001 showing the H-bonding system.

This was confirmed when H (5) was located 1·01 Å from O (3). The hydrogen being bonded to O (3) and not to the nitrogen results in the molecule assuming a tropolone-like configuration. This contrasts with the molecule of 5H-10,11-dioxodihydrodibenzo[b,f]azepine which has the tautomeric diketo structure;[6] some bond lengths determined for this molecule are given (in parenthesis) in Fig. 1a. The Me hydrogens are fixed, and H (6) is coplanar with the azepine ring and *trans* to C (1), whereas H (7) and H (8) are staggered above and below the plane of the ring.

In the crystal the azepine molecules lie with their mean molecular plane inclined at 30·8° to the 001 plane. Hydrogen bonds of 2·827 Å between the ketonic oxygen and hydroxyl group of an adjacent molecule, symmetry-related by the twofold screw axis parallel to the *c* axis, link the molecules into infinite spirals (Figs. 2 and 3). The molecule also has an intramolecular hydrogen bond between the hydroxyl hydrogen, H (5), and adjacent carbonyl oxygen atom, O (2). Atom O (3), therefore, acts as a donor in a bifurcated hydrogen bond to O (2) and O′ (2), where the prime indicates an atom in a symmetry related molecule. The dimensions for the hydrogen bonding system are given in Fig. 3. The inter- and intramolecular lengths are in accord with other reported values,[13] but the angle, O (2)—H (5)—O (3) of 109° is rather low for hydrogen bond formation although the two oxygen atoms are at an appropriate distance, 2·524 Å, with H (5) being located 2·007 Å from O (2). However, an intramolecular angle of 119° in a bifurcated system was found in methyl α-D-altropyranoside.[14]

The intermolecular approach distances are normal and closest contacts are listed in Table 2—see also Fig. 2. Most of the clse contacts are between the atoms of mole-

TABLE 1. FINAL ATOMIC CO-ORDINATES AND THERMAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESIS. ALL VALUES HAVE BEEN MULTIPLIED BY 10^4. THE THERMAL PARAMETERS ARE IN THE FORM GIVEN BY THE EXPRESSION $\exp-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33})$

	X	Y	Z	β_{11}	β_{22}	β_{33}
C (1)	0460 (2)	3309 (2)	3642 (10)	0042 (2)	0021 (1)	0601 (25)
C (2)	4584 (2)	1670 (2)	7908 (10)	0048 (2)	0026 (1)	0703 (30)
C (3)	3939 (2)	1059 (2)	8046 (10)	0043 (2)	0033 (1)	0610 (26)
C (4)	4032 (2)	0256 (2)	6649 (10)	0038 (2)	0029 (1)	0667 (27)
C (5)	0126 (2)	0025 (2)	9801 (9)	0039 (2)	0025 (1)	0537 (23)
C (6)	0179 (2)	0823 (2)	8831 (10)	0053 (2)	0027 (1)	0705 (29)
C (7)	4460 (3)	3812 (2)	2910 (11)	0071 (2)	0027 (1)	0736 (31)
C (8)	3656 (3)	4236 (2)	3724 (11)	0059 (2)	0031 (1)	0686 (31)
C (9)	1418 (2)	4985 (2)	7832 (10)	0044 (2)	0031 (1)	0599 (28)
C (10)	0697 (2)	4592 (2)	5989 (9)	0039 (2)	0024 (1)	0567 (27)
C (11)	1758 (3)	2421 (2)	4619 (14)	0059 (2)	0036 (2)	1010 (40)
N	0953 (2)	3820 (1)	5251 (8)	0037 (1)	0025 (1)	0641 (21)
0 (1)	0837 (2)	2577 (1)	3182 (7)	0051 (1)	0025 (1)	0863 (21)
O (2)	1652 (2)	0181 (1)	2128 (8)	0042 (1)	0041 (1)	1114 (27)
O (3)	3116 (2)	1168 (1)	9704 (9)	0042 (1)	0040 (1)	1119 (27)
H (1)	0717 (25)	1078 (21)	9183 (113)			
H (2)	4569 (24)	3197 (22)	3572 (119)			
H (3)	3089 (25)	3991 (20)	5225 (122)			
H (4)	1936 (24)	4618 (20)	8343 (111)	These atoms were given the same β_{ij} values as the heavier atoms to which they were attached.		
H (5)	2745 (26)	0664 (21)	−0052 (117)			
H (6)	1889 (25)	1840 (21)	3967 (123)			
H (7)	2228 (26)	2821 (21)	3018 (119)			
H (8)	1844 (27)	2612 (23)	7160 (116)			
H (9)	4300 (27)	2161 (20)	8874 (112)			

cules which are related by a c lattice translation (*cf.* dibenzazepine diketo derivative).[6] The separation of the molecular planes is 3·421 Å which corresponds to the normal van der Waals contact between layers of benzenoid rings.

TABLE 2. INTERMOLECULAR APPROACH DISTANCES LESS THAN 3·75 Å

C (1)......N	3·521 Å	C (5)......C (9)	3·655 Å
C (1)......C (2)	3·603	C (6)......0 (1)	3·560
C (2)......C(10)	3·618	C (6)......O (2)	3·553
C (2)......N	3·469	C (6)......C (7)	3·496
C (3)......C (4)	3·688	C (6)......C (8)	3·663
C (3)......O (3)	3·524	C (7)......O (1)	3·424
C (3)......C (5)	3·513	C (8)......C (10)	3·625
C (3)......O (3)	3·569	C (9)......C (10)	3·468
C (3)......C (10)	3·606	C (9)......N	3·612
C (4)......O (3)	3·421	C (9)......C′ (9)	3·645
C (4)......C (5)	3·489	C (11)......O (1)	3·658
C (4)......C (6)	3·571	C (11).. ...O (3)	3·502
C (5)......O (2)	3·746	C (11)......O′(3)	3·463
C (5)......C (7)	3·630	O (2)......O (3)	2·827
C (5)......C (8)	3·538	O (2)......O′ (2)	3·173

EXPERIMENTAL

The pale yellow needles of the azepine, $C_{11}H_9NO_3$ (from petroleum ether), were found from Weissenberg photographs to belong to the non-centrosymmetric space group $P2_12_12_1$. The unit cell parameters, determined from diffractometer settings, were $a = 14{\cdot}107\ (8)$, $b = 16{\cdot}924\ (8)$, $c = 3{\cdot}982\ (5)$ Å, $U = 950{\cdot}7$ Å^3. The density, $D_x = 1{\cdot}37$, was calculated on the basis of four molecules in the unit cell (measurement by flotation was not carried out owing to the high solubility of the crystals in the available liquids). A set of non-equivalent 3-dimensional intensity data out to 0·87 Å was recorded with CuKα radiation on a Picker automatic diffractometer. Of the 882 measured terms, 795 had values significantly greater than the background scatter. No absorption corrections were applied to the intensity data in view of the reasonably constant and short X-ray path length through the crystal (a crystal of approximately 0·15 × 0·15 mm cross-section was aligned about the needle axis), and the low absorption coefficient ($\mu = 22{\cdot}1$ cm^{-1}) for CuKα radiation. All scattering factors used in the analysis were taken from *International Tables for X-ray Crystallography.*[15]

The structure was solved by direct methods.[16] Successive application of the tangent formula gave phases for 102 terms in which the normalized structure factor $|E|$ was greater than 1·50. The resultant 3-dimensional E-map displayed a distribution of well-defined peaks corresponding to the sites of the C, N and O atoms, and after least-squares refinement* with isotropic temperature factors for these heavy atoms an R index of 0·103 was obtained where $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$. A difference synthesis then revealed the H atoms which were then included in the model: further refinement of the heavy atoms with anisotropic temperature factors, reduced R to 0·057. In order to refine the hydrogen coordinates with the limited size of matrix available, the cross-product terms in the temperature factor expression, β_{12}, β_{23}, β_{13}, were omitted from subsequent calculations, as they were all found to be insignificant. At this stage it was observed that a very large proportion of $\Sigma||F_0| - |F_c||^2$ was due to six large, low angle terms. The discrepancy in the latter was consistent with the presence of extinction, and on this assumption these terms were omitted from the final refinement cycles. A final R of 0·033 was attained for 876 terms in which the H atoms were given the same thermal parameters as the heavier atom to which they were attached.

The final atomic parameters with their estimated standard deviations are given in Table 1, while bond lengths and deviations of the atoms from the mean molecular plane are shown in Fig. 1. A line diagram of the structure projected down the c axis is given in Fig. 2, and intermolecular approach distances < 3·75 Å are listed in Table 2—see also Fig. 2. A table listing a comparison of measured and calculated structure amplitudes has not been included but is available on request from the authors.

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* All least-squares refinements were carried out using the Busing and Levy programme ORFLS, with unit weight being given to all terms.

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