THE CRYSTAL AND MOLECULAR STRUCTURE OF 5H-10,11-DIOXODIHYDRODIBENZO-[*b*,*f*]AZEPINE

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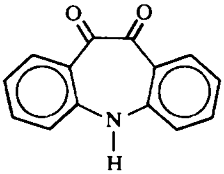
Abstract—Crystals of 5*H*-10,11-dioxodihydrodibenzo[*b*,*f*]azepine were found to belong to the orthorhombic space group *Pccn*, with $a = 5{\cdot}07$, $b = 14{\cdot}50$, $c = 13{\cdot}78$Å. The molecules had two-fold symmetry and there were four in the unit cell. The structure was solved by direct methods and refined to an R index of 0·053. The molecule is not quite planar but propeller-like in shape, with the atoms other than the oxygens lying in two planes inclined at 8·4° to each other about the molecular two-fold axis. Dimensions associated with the 7-membered ring indicated some π-electron delocalization in the latter. It was concluded, however, that this could be attributed to the vinylogous amide grouping rather than to aromatic character in the azepine ring. The structure exhibits a bifurcated hydrogen-bond which links the molecules head-to-tail, forming chains running throughout the crystal parallel to *c*.

CONTROVERSY concerning the degree of aromaticity that should be attributed to unsaturated 7-membered ring compounds has led to considerable interest in the molecular detail of tropolone,[1–3] tropone[4–7] and heptafulvene[8,9] derivatives. Recently, Bertelli and Andrews[10] concluded that the aromatic character of these compounds and their derivatives has been overestimated and similar conclusions regarding tropones have been reached by Cook and Forbes.[11]

The chemistry of 5*H*-10,11-dioxodihydrodibenzo-[*b*,*f*]azepine (I) has been studied by Cooke and Russel[12] and, although it is formally an azadibenzotropolone, its chemical properties were quite uncharacteristic of such a system; however these authors did not exclude the possibility of tautomerism. An X-ray analysis of crystals of the diketone was undertaken in an attempt to define the precise structural detail. It was hoped that the molecular dimensions would reveal whether in this compound the 7-membered ring did in fact possess any appreciable aromatic character.



I

Structural detail and discussion

A view of the molecule is shown in Fig 1 and a more conventional representation in I. It is virtually planar, but the deviations give it a slightly propeller-like shape with the nitrogen and mid-point of the C(1)—C′(1) bond lying on a two-fold axis.

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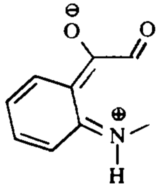
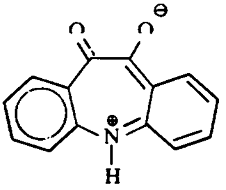
Although the closeness to planarity implies that the azepine ring may display a certain level of aromaticity, more detailed study shows it is better viewed as two vinylogous amides, linked to form the 7-membered ring.

The C(1), C(2), O, C(1′) groupings and the benzene rings are both completely planar to within experimental error (mean deviation of ±0·005Å), though the former are inclined to each other at 21·9° and the latter at 9·6°. The C(1) and N deviate from the plane of the associated benzene ring by −0·065Å and +0·035Å respectively, and the oxygen deviates by +0·200Å from the C(1), C(2), C(7) plane, this being equivalent to a 10·6° rotation about the C(1)—C(2) bond. The N—C(7)—C(2)—C(1)=O chain, which comprises a vinylogous amide grouping, may therefore be sufficiently planar to be quite highly conjugated. The resonance contributors (I, II and III) indicate that if this is the case, there should be a strengthening of the N—C(7) and C(1)—C(2) bonds together with bond fixation in the benzene ring, C(3)—C(4), C(5)—C(6) having more double bond character and C(4)—C(5), C(2)—C(3), C(6)—C(7) having more single bond character. This in fact appears to be reflected in the observed bond lengths and angles. Bonds C(3)—C(4) and C(5)—C(6) are 1·357 and 1·370Å respectively both of which are significantly less than the standard value 1·395Å,[13] whereas C(3)—C(2), C(2)—C(7) and C(7)—C(6) have the slightly larger values, 1·403, 1·404 and 1·400Å respectively. The distortion of bond angles within the benzene ring are in accord with the symmetrical expansion of one side of the ring together with contraction of the other.


II


III

The C(7)—N bond of 1·380Å which, as predicted, is rather less than the C(aromatic)—N length of 1·413Å in N-acetanilide;[14] the C(1)—C(2) bond has also decreased, in this case from 1·52Å given by *Interatomic Distances*[13] to 1·474Å. The CO bond appears to have lengthened very little; as no libration corrections were applied however, this may have been obscured by the anisotropic vibration of the oxygen. The C(1)—C′(1) bond is not significantly shorter than anticipated (1·482Å compared with an average for C—C in O=C—C=O groupings of 1·49Å[13]) therefore delocalization along this bond seems very unlikely, and the azepine ring would be better described as a combination of two vinylogous amides rather than as an aromatic system. Lending support to this interpretation, the azepine ring in two non-condensed azepine derivatives[15] was found to be in the boat conformation similar to the true polyene, cycloheptatriene,[16] and bond lengths so far reported for tropones,[4,5] heptafulvenes[8] and azepines[15] have indicated considerable bond alternation in their 7-membered rings. On the other hand, however, dimensions available for the tropolones[1-3] indicate that these compounds do have true aromatic character.[17]

On examination of a Dreiding model of the molecule of the diketone, it was found that preserving normal bond lengths and angles both vinylogous systems could be simultaneously planar only if the molecule is planar or approximately so and propeller-like in shape. All other conformations allow only one such system to be planar unless an impossibly large ring strain is introduced. Even so, the strain resulting from the observed configuration must be rather high judging by the extraordinary facility of the benzilic acid arrangement which reduces the azepine ring to a strain free aromatic 6-membered ring.[12] The slight propeller-like distortion from planarity of the molecule is most likely enhanced by the steric interaction between each of the oxygen atoms and its closest respective hydrogen, H(1), H(1′) and dipolar repulsion between the oxygen atoms. This results in a dihedral angle between the two carbonyl groups of 21·9°.

It is of interest that even though there is a great deal of ring strain and no aromaticity, the vinylogous systems constrain the azepine ring to an almost planar conformation (maximum deviation 0·20Å). The average bond angle in the azepine ring is 0·4° lower than the value of 128·2° for a regular heptagon because of the slight ring puckering. The individual values however are considerably different, the C(7)—N—C(7′) angle being 135·2° and the rest 127 ± 0·2°. The much larger deviation of the C(7)—N—C(7′) angle may be due to the relative ease with which the nitrogen may take up partial sp hybridisation since it is only strongly bonded to two other atoms.

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 ±0·14Å). The H atom associated with the N atom was clearly 0·98Å distant, showing conclusively that in the solid state at least there is no tautomerism to produce the corresponding azatropolone.

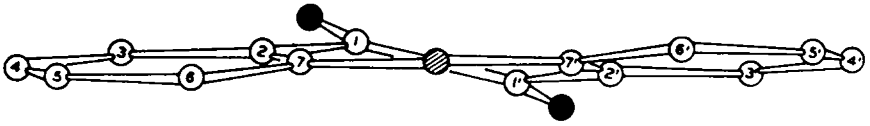


FIG 1. Molecular skeleton viewed down the two-fold axis.

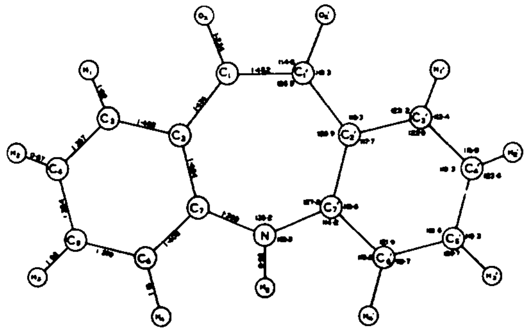


FIG 2. Bond lengths and angles. The e.s.d.s. for lengths and angles involving H were 0·06Å and 4° and for all others 0·004Å and 0·3° respectively. Thermal parameters indicated that libration in the molecule was negligible and thus corrections have not been applied.

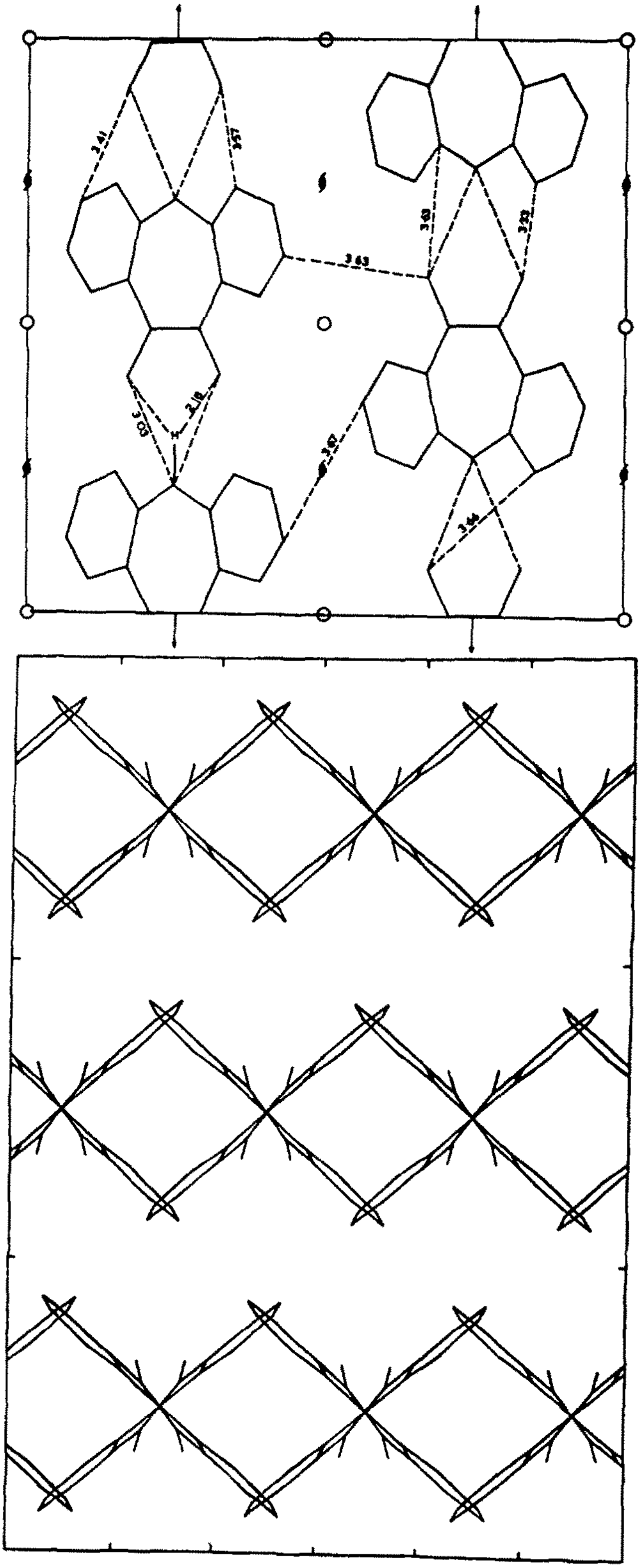


FIG 3. Line diagram of the structure viewed (a) down the *a* axis and (b) down the *c* axis.

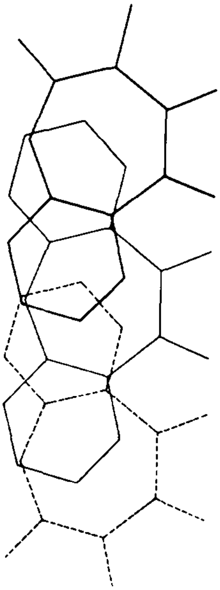


FIG 4. Partial projection of the structure on the (130) plane.

In the crystal the diketone molecules are lying parallel to the **130** and **1$\bar{3}$0** planes—see Fig 3(b). They are linked head-to-tail by bifurcated H-bonds between the N and both O atoms of an adjacent molecule, forming chains running throughout the crystal parallel to the *c* axis—see Fig 3(a). The H-bond dimensions, N..... 0, 3·03Å, H..... O, 2·18Å, N—H—O, 144·2Å are in accord with the values observed by neutron diffraction for bifurcated H-bonds.[18] The intermolecular approach distances are normal and closest contacts are listed in Table 2—see also Fig 3(a)—of which there are relatively few between atoms in symmetry related molecules in the unit cell. Most of the close contacts are between the atoms of the almost planar molecules which are related by an *a* lattice translation, with the overlap of the π-bonding system occurring only between such molecules. This is illustrated in the partial projection of the structure on the **130** plane (Fig 4). The separation of these molecular planes is 3·48Å which corresponds to the normal van der Waals contact between layers of benzenoid rings.

The thermal stability of this compound (m.p. > 360°) and its insolubility in all easily available solvents are rather curious. However, the structure is composed of almost planar molecules arrayed in two independent planes extending throughout the crystal (cf. ellagic acid[19]), and the resulting π–π interactions in the *a* and *b* directions, including those associated with the CO groups, together with dipole coupling in the *c* direction must give the lattice great stability.

EXPERIMENTAL

The red plate-like orthorhombic needles of the diketone, $C_{14}H_9NO_2$, were found from Weissenberg photographs to belong to the centrosymmetric space group *Pccn*. The unit cell parameters, determined from diffractometer settings, were $a = 5·07$, $b = 14·50$, $c = 13·78$Å, $U = 1014$Å^3. The density, $D_m = 1·44$,

TABLE 1. FINAL ATOMIC CO-ORDINATES AND THERMAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESIS. THE EXPRESSION USED FOR THE TEMPERATURE FACTOR WAS EXP-$(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$. HYDROGEN COORDINATES HAVE BEEN MULTIPLIED BY 10^3 AND ALL OTHER PARAMETERS BY 10^4

	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	3370(7)	2089(2)	5044(2)	0391(18)	0067(2)	0032(2)	0007(5)	−0003(4)	0003(2)
C(2)	4762(6)	1691(2)	4204(2)	0293(14)	0044(2)	0035(2)	−0013(4)	−0002(4)	0002(1)
C(3)	6767(8)	1059(3)	4430(2)	0412(19)	0059(2)	0046(2)	0005(6)	−0018(6)	0006(2)
C(4)	8302(8)	0655(3)	3745(3)	0390(19)	0049(2)	0066(2)	0024(5)	−0008(6)	0002(2)
C(5)	7913(8)	0874(3)	2777(3)	0380(18)	0059(2)	0054(2)	0001(6)	0020(5)	−0004(2)
C(6)	6006(7)	1500(2)	2528(2)	0344(15)	0047(2)	0045(2)	−0004(5)	0009(5)	−0004(2)
C(7)	4372(6)	1912(2)	3222(2)	0256(14)	0047(2)	0035(2)	−0020(4)	0001(4)	−0005(1)
N	2500	2500	2841(2)	0326(18)	0045(2)	0025(2)	0014(6)	0000	0000
O	3670(7)	1722(2)	5845(2)	1001(22)	0103(2)	0035(1)	0130(6)	0021(4)	0013(1)
H(1)	693(9)	075(3)	509(3)	These atoms were given the same βij values as the heavier atoms to which they were attached.					
H(2)	973(9)	039(3)	396(3)						
H(3)	900(9)	054(3)	225(3)						
H(4)	559(8)	165(3)	171(3)						
H(5)	250	250	213(4)						

measured by flotation in a bromoform/xylene mixture, is in accord with the value $D_x = 1{\cdot}46$, calculated on the basis of four molecules per unit cell. It was thus assumed that the molecule had a two-fold symmetry axis. A complete set of 3-dimensional intensity data out to 0·85Å was recorded with CuKα radiation on a Picker automatic diffractometer from a crystal of dimensions 0·22 × 0·36 × 0·04 mm.[3] Absorption corrections were applied to the measured intensities by the method of Busing and Levy,[20] employing a linear absorption coefficient for CuKα radiation of $8{\cdot}2\ \mathrm{cm}^{-1}$. Of the 812 measured terms, 554 had values significantly greater than the incoherent background. Measurement of the intensity of the strongest reflexion (130), with different orientations about the scattering vector, indicated that extinction was not a serious source of error for this crystal; however in the final least-squares refinement cycles the two strongest reflexions (130) and (020) were omitted. All scattering factors used in the analysis were taken from *International Tables for X-ray Crystallography.*[21]

Space group requirements necessitated the molecular 2-fold axis to be coincidental with the 2-fold axis in the unit cell at $x = \frac{1}{4}$, $y = \frac{1}{4}$, while the high intensity of the (130) reflexion relative to any other indicated that the molecule was lying approximately in this plane. The structure however was essentially solved by direct methods. By the symbolic addition method,[22] phases for 12 terms were correctly assigned, and then refinement by successive application of the tangent formula[23] gave phases for 98 terms in which the normalized structure factor $|E|$ was greater than 1·55. 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 anisotropic least-squares refinement* of these heavy atoms an R index of 0·099 was obtained for $R = \Sigma||F_o| - F_c||/\Sigma|F_o|$. A difference synthesis then revealed the H atom sites and a final R of 0·053 was attained for the 552 observed terms.

In the final refinements the H atoms were given the same anisotropic thermal parameters as the heavy atom to which they were attached. The N and C atoms displayed little anisotropy of thermal vibration and all were vibrating with an approximate isotropic temp factor of $B \sim 4{\cdot}0\text{Å}^2$. The oxygens, on the other hand, displayed marked thermal anisotropy and were vibrating in the direction perpendicular to the molecular plane (Table 1).

The final atomic parameters with their estimated standard deviations are given in Table 1, while bond lengths and angles are shown in Fig 2. Line diagrams of the structure projected down the *a* and *c* axes are given in Fig 3 while a partial projection of the structure on the (130) plane is shown in Fig 4. Some short intermolecular approach distances are listed in Table 2—see also Fig 3(a). Tables listing a comparison of measured and calculated structure amplitudes have not been included but are available on request from the authors.

TABLE 2. INTERMOLECULAR APPROACH DISTANCES LESS THAN 3·80Å

C(1).......C(3)	3·76Å	C(5).......N	3·31Å
C(1).......C(4)	3·76	C(5).......C′(7)	3·55
C(1).......C′(3)	3·74	C(5).......C(5)	3·67
C(2).......C(4)	3·66	C(5).......O	3·41
C(2).......C′(1)	3·64	C(6).......N	3·62
C(2).......C′(3)	3·72	C(6).......O	3·33
C(3).......N	3·72	C(6).......O	3·57
C(4).......C(7)	3·65	C(6).......O	3·66
C(4).......N	3·64	C(7).......C′(6)	3·42
C(4).......C′(7)	3·79	C(7).......C′(7)	3·60
C(4).......O	3·63	C(7).......O	3·63
C(5).......C(7)	3·66	N ....O	3·03

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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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