

The Crystal and Molecular Structure of 5-Keto-1,5-dihydrobenz[*cd*]indole*

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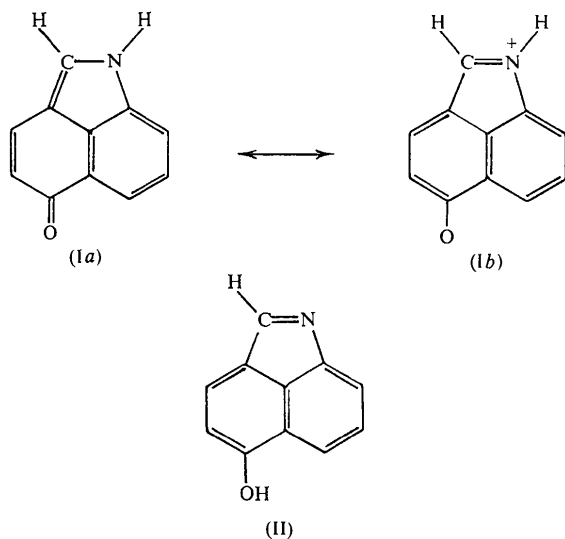
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5-Keto-1,5-dihydrobenz[*cd*]indole, $C_{11}H_7NO$, forms monoclinic needles, space group $P2_1/c$, with $a_0 = 3.893$, $b_0 = 13.39$, $c_0 = 15.37$ Å, $\beta = 90^\circ 40'$, and four molecules in the unit cell. Intensity data were collected photographically. The structure was solved with the help of a Patterson projection and a molecular search program, and was refined by least-squares methods to $R = 0.071$. The bond distances indicate that the molecule exists predominantly in the quinonoid form, in agreement with other chemical evidence. The strain induced by the exocyclic bridge distorts the molecule and buckles it slightly, the angle between the normals to the planes of the fused six-membered rings being about 1.4° . The molecules are packed in herringbone fashion and are linked in infinite chains by $N-H \cdots O$ hydrogen bonds parallel to c . The molecular motion in the crystal is small.

Introduction

Grob & Hofer (1953) concluded that the dehydrogenation product of 5-oxybenz[*cd*]indolin existed as a resonance hybrid, 5-keto-1,5-dihydrobenz[*cd*]indole (Ia, Ib) rather than as the tautomeric form (II).



This conclusion was based on a study of the reactions of (I), and a comparison of its ultraviolet and infrared spectra with those of its *N*-methyl derivative to unambiguous structure. Our analysis has confirmed that (I) is the correct structure, with (Ia) the principal contributor. We were interested in the molecule as part of a study of strained organic systems; the exocyclic

C-N bridge introduces appreciable distortion of the naphthalene moiety, since this bond length is about 1 Å shorter than the normal distance of 2.4 Å between the 1 and 8-positions of a naphthalene nucleus.

Experimental

A sample of (I) was supplied by C. A. Grob. Yellow needle-like crystals, elongated along **a**, were obtained by slow evaporation of a methanol solution. Rotation and Weissenberg photographs with unfiltered $Cu K\alpha$ radiation showed the crystals to be monoclinic. The systematic extinctions, $0k0$ absent with k odd and $h0l$ absent with l odd, indicated the space group to be $P2_1/c$. Unit-cell dimensions were determined from zero-layer Weissenberg photographs about **a** and **b** which had been calibrated with superimposed sodium chloride ($a_0 = 5.639$ Å) and ceric oxide ($a_0 = 5.411$ Å) powder photographs, $\lambda(Cu K\alpha) = 1.5418$ Å: $a_0 = 3.893$, $b_0 = 13.39$, $c_0 = 15.37$ Å, $\beta = 90^\circ 40'$. The estimated standard deviations are about 0.1% and 0.1° . The density measured by flotation in a mixture of bromoform and *n*-octane is 1.414 g.cm^{-3} ; that calculated for four molecules in the unit cell is 1.403 g.cm^{-3} .

Intensity data were obtained from multiple-film equi-inclination Weissenberg photographs taken around **a** and **c** with unfiltered $Cu K\alpha$ radiation. Intensities were estimated visually by comparison with a calibrated intensity strip. The crystal mounted around **a** was a needle of dimensions $3 \times 0.28 \times 0.22$ mm; that mounted around **c** was a small chunk about $0.2 \times 0.24 \times 0.15$ mm. The absorption coefficient for $Cu K\alpha$ is 0.88 mm^{-1} and the dimensions of both crystals were such that the variation in absorption was at most 5%; consequently, no absorption corrections were made.

The intensities were converted to relative values of F^2 , which were placed on a single scale by comparison of 372 common reflections. Of the 1808 independent reflections within the copper sphere, 1207 were observed, 367 were too weak to be measured and the rest

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The atomic scattering factors used were those of McWeeny (1951) for hydrogen and (1954) for graphite carbon, and Hoerni & Ibers (1954) for neutral nitrogen and oxygen. All calculations were done on IBM 709 and 7090 computers.

Determination and refinement of the structure

The structure was first solved in projection down the short *a* axis, with the help of a sharpened Patterson projection. This two-dimensional function suggested three possible orientations of the molecule in the plane, but attempts to determine the translational parameters from packing considerations were not immediately fruitful, because the molecule could be tilted as much as 30° relative to this plane. A search program was

then written for the computer, based on a method described by C. A. Taylor (1957), and Taylor & Morley (1959). This program used as input variables the cell dimensions, a set of approximate relative positional parameters consistent with a reasonable model of the molecule, and three angles describing the orientation of the molecule within and relative to the plane. For each specific orientation of the molecule, the function $X(y, z) = [(F_o - |F_c|)/\sigma(F_o)]^2$ was evaluated over the area of the projection, with *y* and *z* being the positional parameters of some arbitrary reference point of the molecule. Only those reflections with $(\sin \theta)/\lambda$ less than 0.4 Å⁻¹ were used. Approximate translational parameters were quickly found from the lowest minimum in the maps corresponding to the orientations consistent with the Patterson function. Inspection of

Table 2. *Final positional and thermal parameters*

All values $\times 10^4$ for C, N, and O atoms; for H, position parameters $\times 10^3$. E.s.d.'s in parentheses are in units of least significant digit. Isotropic *B*'s for H atoms in Å²; for other atoms, the expression is:

$$\exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)].$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>b</i> ₁₁ or <i>B</i>	<i>b</i> ₂₂	<i>b</i> ₃₃	<i>b</i> ₁₂	<i>b</i> ₁₃	<i>b</i> ₂₃
C(1)	-1481 (7)	2573 (2)	909 (2)	603 (17)	43 (1)	30 (1)	30 (7)	9 (7)	-4 (2)
C(2)	78 (7)	3409 (2)	544 (2)	673 (19)	56 (2)	29 (1)	29 (8)	56 (7)	9 (2)
C(3)	820 (7)	4211 (2)	1094 (2)	611 (18)	50 (1)	39 (1)	-45 (8)	22 (8)	18 (2)
C(4)	110 (7)	4205 (2)	1985 (2)	552 (17)	45 (1)	36 (1)	5 (7)	-5 (7)	5 (2)
C(5)	-2487 (7)	3241 (2)	3269 (2)	617 (17)	47 (1)	27 (1)	54 (8)	34 (7)	1 (2)
C(6)	-4241 (7)	2294 (2)	3478 (2)	673 (19)	55 (2)	29 (1)	14 (8)	50 (7)	14 (2)
C(7)	-4867 (7)	1551 (2)	2901 (2)	616 (18)	48 (1)	37 (1)	-8 (8)	16 (8)	21 (2)
C(8)	-3828 (7)	1668 (2)	2015 (2)	578 (16)	39 (1)	35 (1)	8 (7)	-9 (7)	6 (2)
C(9)	-2214 (6)	2579 (2)	1802 (2)	530 (15)	37 (1)	28 (1)	31 (7)	9 (6)	2 (2)
C(10)	-1517 (6)	3373 (2)	2356 (2)	536 (16)	38 (1)	28 (1)	25 (7)	6 (7)	6 (2)
C(11)	-3985 (8)	1121 (2)	1252 (2)	812 (21)	46 (1)	38 (1)	-9 (9)	-14 (9)	-3 (2)
N	-2580 (7)	1654 (2)	587 (1)	886 (19)	47 (1)	33 (1)	-2 (7)	5 (7)	-11 (2)
O	-1937 (6)	3892 (2)	3834 (1)	1107 (19)	55 (1)	29 (1)	0 (7)	40 (6)	-8 (1)
H(2)	58 (8)	341 (2)	-10 (2)	1.5 (6)					
H(3)	215 (9)	470 (3)	87 (2)	2.0 (7)					
H(4)	76 (9)	477 (3)	239 (2)	2.0 (7)					
H(6)	-495 (9)	223 (3)	406 (2)	2.3 (7)					
H(7)	-600 (8)	103 (2)	307 (2)	2.0 (5)					
H(11)	-499 (10)	44 (3)	108 (3)	3.4 (8)					
H(N)	-223 (10)	139 (3)	-4 (3)	3.1 (9)					

Table 3. *Rigid-body motion parameters*

Values are for the molecule of Table 2. The tensors are referred to axes parallel to **a**, **b**, and **c***.

L [σ(L)]	[(°) ²]	7.1 (0.6)	1.5 (0.6)	0.9 (0.6)
			11.9 (0.8)	-3.9 (0.5)
				10.7 (1.1)
T [σ(T)]	[Å ² × 10 ⁻⁴]	352 (11)	44 (8)	16 (7)
			347 (8)	24 (6)
				335 (7)
S [σ(S)]	[(°) - Å × 10 ⁻²]	3 (2)	0 (1)	-3 (1)
		0 (1)	5 (3)	0 (2)
		3 (1)	1 (2)	-8
			Direction cosines	
Principal axes: L	15.2 (°) ²	-0.071	-0.769	0.636
	8.9	0.671	0.435	0.600
	5.5	-0.738	0.469	0.485
	T	0.0405 Å ²	0.658	0.654
		0.0326	0.462	0.040
		0.0304	0.594	-0.880
			-0.756	0.278
$[\sum (\Delta U_{ij})^2 / (m-s)]^{1/2}$		0.0020 Å ²		

the upper level data suggested that the molecule must lie approximately parallel to (121), which led to reasonable values for the other two orientation angles. The corresponding R value for the $0kl$ data was 0.35. Least-squares refinement of the three angular and two

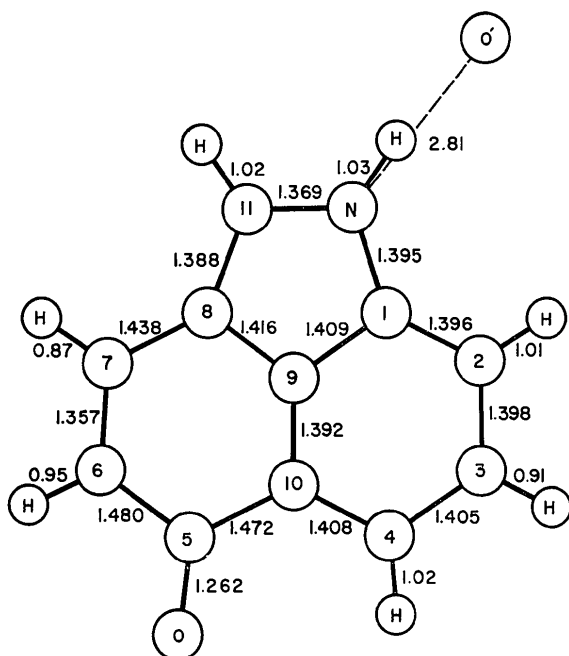


Fig. 1. Bond distances, including librational corrections. The e.s.d.'s are about 0.004 Å for the C-C and C-N distances, about 0.01 Å for the C-O and N...O distances, and about 0.04 Å for the C-H and N-H distances.

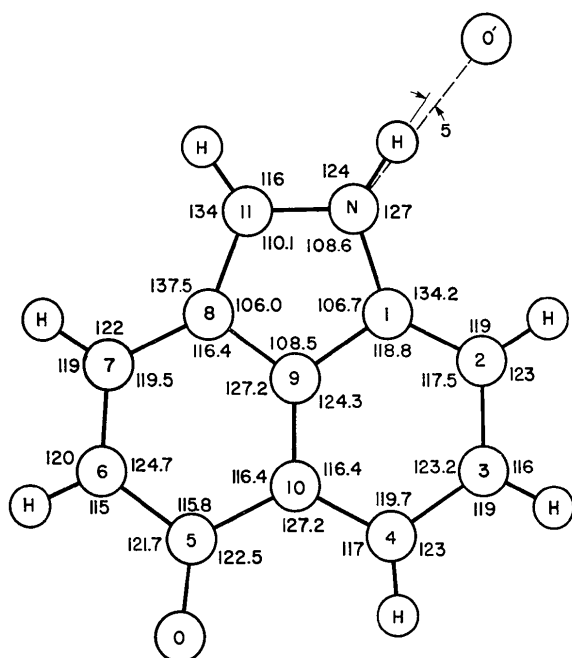


Fig. 2. Bond angles, including librational corrections. The e.s.d.'s of angles involving only C, N, and O atoms are about 0.3°; those for angles involving H atoms are about 3°.

positional parameters reduced this to 0.20, and conventional least-squares refinement of the individual atoms reduced R further to 0.13. All seven hydrogen atoms were then found in a two-dimensional difference map.

Approximate values of the x parameters were found by applying the search program to the $hk0$ data, and then three-dimensional full-matrix least-squares refinement of the positional and anisotropic thermal parameters of the C, N, and O atoms was begun. R fell from 0.29 to 0.11. The program was that of Gantzel, Sparks & Trueblood (ACA old no. 317), which minimizes $\sum \omega(F_o - |F_c|)^2$; Hughes's (1941) weighting scheme was used. The positions and isotropic temperature factors for the seven hydrogen atoms were next refined by two cycles of least squares; the resulting parameters were used in the final refinement of the heavy atoms but were not themselves further refined. After several indexing and scaling errors had been corrected and seven reflections suffering from apparent extinction effects removed, four final cycles of least squares, the first three without and the last with the 367 unobserved reflections, gave R values of 0.071 and 0.090 respectively. The structure factor amplitudes of the unobserved reflections were given the value $0.58F_{\min}$ (Hamilton, 1955). In the final structure-factor calculation, only fifteen of the 367 corresponding $|F_c|$ values were larger than $2F_{\min}$; none was greater than $3.1F_{\min}$.

Table 1 lists the observed and calculated structure factors for the final parameters ($R=0.090$). The corresponding atomic positional and thermal parameters with their estimated standard deviations, obtained from the diagonal elements of the inverse of the matrix of the normal equations for the final least-squares cycle, are given in Table 2. A final difference map was computed from the 1200 observed reflections, not including the seven believed to suffer from extinction (marked with an E in Table 1). No peak or trough in this map had a value exceeding $0.25 \text{ e.}\text{\AA}^{-3}$, which is about twice the e.s.d. of the electron density (Cruickshank, 1949).

The anisotropic thermal parameters of the C, N, and O atoms were used in an analysis of the possible rigid-body motion of the molecule (Schomaker & Trueblood 1968). The fit (Table 3) was quite good. The cross-tensor S is so small that the results are very nearly the same as those obtained by the method of Cruickshank (1956a); the reduced T (Schomaker & Trueblood, 1968) is essentially identical to T evaluated relative to the centroid of the molecule (Table 3) and the displacements of the non-intersecting axes are negligible.

The translational motion of the molecule is small and almost isotropic. The librational motion is also rather small; the principal libration, with an r.m.s. amplitude of 3.9° , makes an angle of 25° with the normal to the least-squares plane of the molecule, and the next principal librational motion, with an amplitude of 3.0° , is about an axis that lies essentially in the molecular plane. The corrections to the apparent bond

distances for the rigid-body motion (Cruickshank, 1956*b*) are minor, the largest being 0.004 Å. However, the oxygen atom is vibrating especially anisotropically, the principal component of its motion being normal to the molecular plane, as is common for comparable doubly-bonded oxygen atoms. The C–O bond distance has been corrected for this non-rigid motion, by about 0.015 Å; this correction is at best only an approximation, and hence the e.s.d. of the C–O bond distance is larger than those for the other bond distances.

Molecular and crystal structure

The bond distances and bond angles, after correction for libration, are given in Figs. 1 and 2, with their estimated standard deviations. In terms of a valence bond picture, the quinonoid form (*Ia*) predominates over form (*Ib*) in a ratio of about 2:1 in these crystals, a proportion estimated by interpolation of relevant distances, notably C(6)–C(7), C(11)–N and C(5)–O, between appropriate standard values. The fact that the C–O bond does not have the properties of a normal carbonyl linkage has been verified by chemical experiments. Cohen, Heath-Brown & Rees (1953) tried to build up the remainder of the lysergic acid molecule, which contains the skeleton of (*I*), through reactions at the keto group of (*I*) and its simple *N*-derivatives. All such attempts failed, presumably because of the non-ketonic character of these compounds.

The observed C(11)–N bond distance accords well with the valence bond description of the molecule, as deduced from the other distances mentioned. This fact suggests that this bridge bond is not significantly stretched by the molecular distortion. The strain is relieved primarily by distortion of bond angles, as is evident in Fig. 2, and to a small extent by buckling of the molecule. Whereas the C(1)⋯C(8) and C(4)⋯C(5) distances are identical in naphthalene, these non-bonded distances in the present molecule are 2.29 and 2.57 Å, respectively, and the corresponding external angles at C(9) and C(10) differ by 19°.

Least-squares planes were calculated for all thirteen heavy-atoms in the molecule, and for each of the three fused rings separately (Table 4). The naphthalene ring system is bowed to a small but significant extent. This bowing is illustrated in an exaggerated form in Fig. 3, in which the scale perpendicular to the plane of the ring

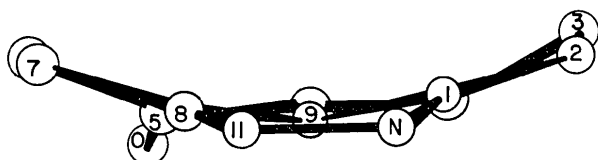


Fig. 3. A view of the bowing of the molecule, with the deviations from the plane exaggerated by a factor of thirty. The radii of the circles representing the atoms are three times the e.s.d. of the atomic positions; the bowing appears to be significant.

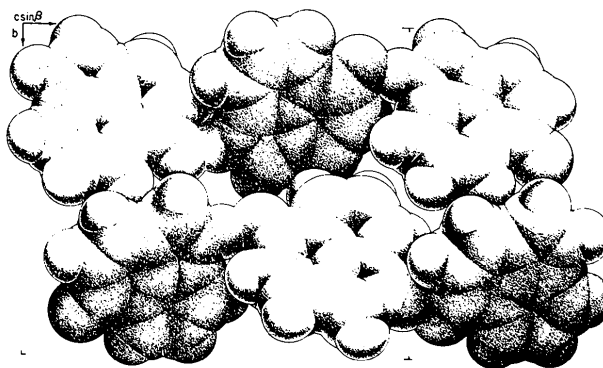


Fig. 4. A view of the structure down *a*. Note the chains of hydrogen-bonded molecules parallel to *c*. The planes of successive molecules in each chain are tilted relative to each other by about 43° (see also Fig. 5).

is thirty times that in the plane; the radius of the circle representing each atom is about three times the e.s.d. of an atomic position. The angle between the normals to the planes of the individual fused six-membered rings is 1.4°; these planes are inclined about equally to the overall plane of the molecule, which is also essentially the plane of the five-membered ring. The non-planarity makes the molecule chiral; both enantiomers are, of course, present in this centrosymmetric crystal.

Table 4. *Some least-squares planes*

Calculated by the method of Schomaker, Waser, Marsh & Bergman (1959). The equation of each plane is in the form $l_1X + l_2Y + l_3Z + D = 0$ with *X*, *Y*, and *Z* orthogonalized coordinates in Å parallel to *a*, *b*, and *c**. The deviations of atoms used to define the plane are shown in bold type.

	1	2	3	4
$l_1 \times 10^4$	8927	8969	8872	8935
$l_2 \times 10^4$	-3999	-3942	-4064	-3980
$l_3 \times 10^4$	2079	2006	2184	2080
<i>D</i> , Å	1.618	1.611	1.593	1.604
R.m.s. deviation, Å	0.016	0.007	0.010	0.005
Deviations (Å × 10 ³)				
C(1)	1	2	-28	-6
C(2)	-15	-2	-61	-20
C(3)	-20	-5	-65	-23
C(4)	7	11	-22	4
C(5)	10	-12	16	4
C(6)	-29	-64	-8	-38
C(7)	-24	-59	-4	-35
C(8)	6	-17	8	-5
C(9)	14	4	1	7
C(10)	-1	-10	-13	-6
C(11)	13	-6	7	1
N	14	9	-10	3
O	24	1	32	20
H(2)	-37			
H(3)	112			
H(4)	53			
H(6)	-64			
H(7)	-87			
H(11)	-24			
H(N)	52			

Although it is possible that the structure is disordered, with each enantiomer randomly occupying each molecular site in different unit cells, we believe it more likely that it is ordered. The least-squares refinement converged to the bowed configuration, rather than to an average one as might have been expected if random disorder were present, or if the bowing were dynamic rather than static. Furthermore, either of these effects would lead to appreciably higher apparent temperature factors normal to the molecular plane for atoms 2, 3, 6, and 7 than for the inner atoms of the naphthalene nucleus. Although there is a small trend in this direction, it is only about one-third as large as needed to account for the observed bowing, and seems more likely to result from a small molecular libration. As noted earlier, the fit of the thermal parameters to a rigid-body model is good.

Similar small deviations from planarity might be expected to be found in comparable molecules whose structures have been determined, such as acenaphthene (Ehrlich, 1957), pyracene (Simmons & Lingafelter, 1961), and various substituted acenaphthenes (Mak & Trotter, 1963, 1964; Trotter & Mak, 1963; Avoyan & Struchkov, 1961, 1963). Unfortunately the e.s.d.'s of the atomic positions in these structure determinations are too large to permit meaningful discussion of any small deviations from planarity. The study of the *cis* dimer of acenaphthylene (Welberry, 1971) seems nearly precise enough; the e.s.d.'s are two to three times as great as those in the present work. In one half of the dimer, the angle between the normals to the planes of the fused six-membered rings that comprise the naphthalene nucleus is 1.4° ; in the other half of the

molecule, this angle is 2.1° . In each residue, the six-membered rings are inclined unequally to the five-membered ring to which they are fused. The significance of all these deviations from planarity is, however, marginal.

A recent study of the structure of 1,8-dinitros-naphthalene (Prout, Cameron, Dunn, Hodder & Viterbo, 1971) does provide sufficiently precise data on a comparable molecule. The nitrogen atoms of the nitroso groups are bonded together in this compound; a five-membered ring is thus fused to the naphthalene nucleus across the 1 and 8 positions, as in the present structure. The molecule is significantly non-planar; the angle between the two fused six-membered rings is 3.3° and the bond angle distortions are very similar to those found in the present study.

The bowing in the present molecule, evident in Fig. 3, seems a direct consequence of the strain introduced by the exocyclic bridge. However, a comparable bending of a naphthalene residue has been reported (Drew, 1969) in a structure in which there is no obvious cause for the bending; it does not seem to be a consequence either of packing forces or of the molecular conformation. Each of the component six-membered rings of the naphthalene residue is planar within experimental error, but the angle between their normals is 1.8° , and this non-planarity seems significant. The residue occurs as a side-chain in a substituted mandelamide, and Drew reports that there are no short inter or intra-molecular contacts.

Figs. 4 and 5 illustrate the packing in the present structure. The molecules are linked by nearly linear $N-H \cdots O$ hydrogen bonds of length 2.81 \AA (Figs. 1 and 2, Table 5) into infinite chains parallel to *c*. Each molecule is tilted by 27° relative to the (100) plane;

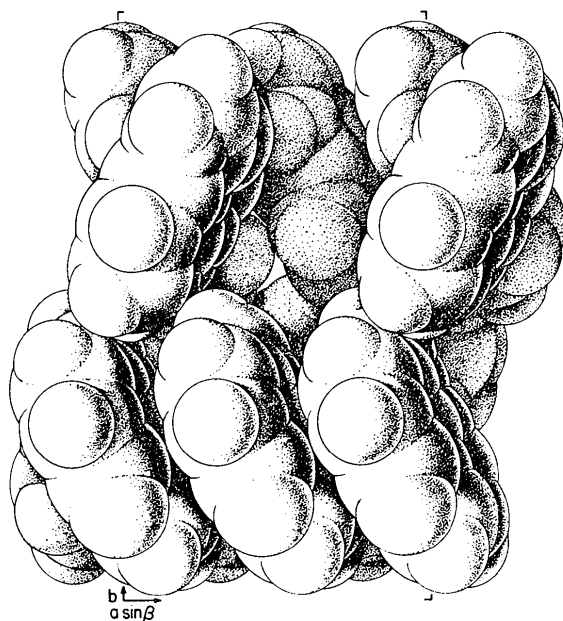


Fig. 5. A view of the structure down *c*. One molecule in the front layer has been omitted to permit a better view of the packing.

Table 5. *Some intermolecular distances*

All heavy-atom distances less than 3.50 , all $C \cdots H$, $N \cdots H$, and $O \cdots H$ distances less than 3.00 , and all $H \cdots H$ distances less than 2.60 \AA are shown.

From atom at x, y, z	To atom*	Distance
N	O, IV(00 $\bar{1}$)	2.81 \AA
H(N)	O, IV(00 $\bar{1}$)	1.78
C(11)	O, III($\bar{1}10$)	3.38
H(11)	O, III($\bar{1}10$)	2.40
H(2)	H(6), IV(10 $\bar{1}$)	2.34
H(N)	H(6), IV(00 $\bar{1}$)	2.52
H(4)	H(7), III	2.59
H(N)	C(5), IV(00 $\bar{1}$)	2.65
H(4)	C(7), III	2.90
N	H(6), IV(00 $\bar{1}$)	2.92
C(4)	H(7), III	2.92
H(4)	C(8), III	2.94
H(N)	C(6), IV(00 $\bar{1}$)	3.00
C(5)	C(6), I(100)	3.46
C(4)	C(10), I(100)	3.48

* The different equivalent positions are identified as follows: I, x, y, z ; II, $-x, -y, -z$; III, $-x, \frac{1}{2} + y, \frac{1}{2} - z$; IV, $x, \frac{1}{2} - y, \frac{1}{2} + z$. The three numbers in parentheses represent translations parallel to *a*, *b*, and *c* respectively.

adjoining molecules in each chain are tipped 43° relative to one another (Figs. 4 and 5). The shortest distances between atoms in different molecules are listed in Table 5; none is unusually short. The C(11)···O and H(11)···O intermolecular distances of 3.38 and 2.40 Å might be taken as evidence for a very weak C–H···O hydrogen bond between neighboring molecules. These distances, and the corresponding angles, fit with Sutor's (1963) examples of possible C–H···O bonds. However, we are inclined to share Donohue's (1968) skepticism about the classification of such interactions as hydrogen bonds, and feel that the present example is more likely an accidental consequence of other requirements for efficient packing.

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References

- AVOYAN, G. L. & STRUCHKOV, T. Y. (1961). *Zh. Strukt. Khim.* **2**, 719.
 AVOYAN, G. L. & STRUCHKOV, T. Y. (1963). *Zh. Strukt. Khim.* **4**, 631.
 COHEN, A., HEATH-BROWN, B. & REES, A. H. (1953). *Chem. Ind.* p. 1179.
 CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
 CRUICKSHANK, D. W. J. (1956a). *Acta Cryst.* **9**, 754.
 CRUICKSHANK, D. W. J. (1956b). *Acta Cryst.* **9**, 757.
 DONOHUE, J. (1968). *Structural Chemistry and Molecular Biology*, edited by A. RICH and N. DAVIDSON, p. 443. San Francisco: W. H. Freeman.
 DREW, M. G. B. (1969). *Acta Cryst.* **B25**, 1320.
 EHRLICH, H. W. W. (1957). *Acta Cryst.* **10**, 699.
 GROB, C. A. & HOFER, B. (1953). *Helv. Chim. Acta*, **36**, 847.
 HAMILTON, W. C. (1955). *Acta Cryst.* **8**, 185.
 HOERNI, J. A. & IBERS, J. A. (1954). *Acta Cryst.* **7**, 744.
 HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
 MAK, T. C. W. & TROTTER, J. (1963). *Acta Cryst.* **16**, 811.
 MAK, T. C. W. & TROTTER, J. (1964). *Acta Cryst.* **17**, 367.
 MCWEENEY, R. (1951). *Acta Cryst.* **4**, 513.
 MCWEENEY, R. (1954). *Acta Cryst.* **7**, 180.
 PROUT, C. K., CAMERON, T. S., DUNN, R. M. A., HODDER, O. J. R. & VITERBO, D. (1971). *Acta Cryst.* **B27**, 1310.
 SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63.
 SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.
 SIMMONS, G. L. & LINGAFELTER, E. C. (1961). *Acta Cryst.* **14**, 872.
 SUTOR, D. J. (1963). *J. Chem. Soc.* p. 1105.
 TAYLOR, C. A. (1957). *Acta Cryst.* **10**, 749.
 TAYLOR, C. A. & MORLEY, K. A. (1959). *Acta Cryst.* **12**, 101.
 TROTTER, J. & MAK, T. C. W. (1963). *Acta Cryst.* **16**, 1032.
 WELBERRY, T. R. (1971). *Acta Cryst.* **B27**, 360.

Acta Cryst. (1972). **B28**, 1926

Structure Cristalline du Complexe Moléculaire 1:1 Trinitrobenzène Formyl-3 Benzothiophène

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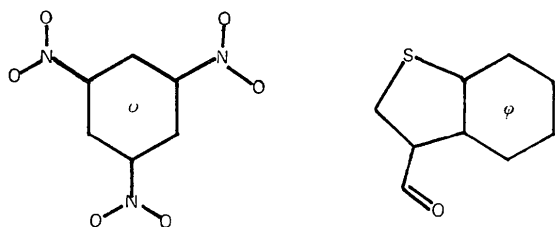
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The crystals of the 1:1 molecular complex formed between *sym*-trinitrobenzene and 3-formylbenzothiophene belong to the monoclinic space group $P2_1/c$, with cell dimensions $a=8.00$, $b=7.708$, $c=25.50$ Å; $\beta=90^\circ$. The sulphur atom coordinates have been found by sharpened Patterson analysis, and the light atoms were localized on *E* maps. The structure was refined to a final *R* value of 0.083. The complex molecules are stacked alternately in infinite columns, parallel to the *a* axis, with which they make an angle of 60° .

Introduction

La résolution de la structure du complexe moléculaire 1:1 trinitrobenzène symétrique (TNB)–formyl-3 benzothiophène (BTCHO)



est présentée dans le cadre d'une étude générale des propriétés en phase solide de complexes du même type: l'accepteur d'électrons est maintenu constant (TNB), tandis que le donneur est constitué de molécules variées, appartenant à la série du naphtalène, ou d'hétérocycles d'encombrement stérique analogue. Entrent dans cette catégorie, les complexes TNB–indole et TNB–scatole (Hanson, 1964), TNB–azulène (Hanson, 1965), dont la structure a déjà été déterminée.

Une étude systématique de ces complexes a été entreprise, utilisant l'analyse cristallographique et l'analyse thermique différentielle (Pascard, 1972). Un apport important concernant les mouvements moléculaires au sein de ces complexes à l'état solide a été fourni par