The Oxime of (5,5-Dideuterio)-6,7-dihydro-6,6-dimethylbenzofurazan-4(5*H*)-one 1-Oxide

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Abstract. $C_8H_9D_2N_3O_3$, monoclinic, $P2_1/n$, $a = 12.275$ (7), $b = 12.925$ (8), $c = 6.002$ (7) Å; $\beta = 95.12$ (5)°; $Z = 4$, $D_c = 1.39$ g cm^{-3}; m.p. 132–135 °C. Crystal dimensions: $0.15 \times 0.20 \times 0.40$ mm. The furoxan moiety is very distorted; π-delocalization occurs through a large molecular fragment.

Introduction. The title fused-ring furoxan derivative was prepared by Ackrell & Boulton (1973) from the corresponding ketone which, according to NMR results, has the keto group *trans* to the N → O group. The brown needles obtained by Ackrell & Boulton proved to be suitable for X-ray investigation; the crystals soften at 125°C, below the melting point.

Weissenberg photographs showed the systematic extinctions of space group $P2_1/n$; approximate values of the cell parameters were obtained from the photographs (Cu $K\alpha$) and were refined by least squares from diffractometer data (Mo $K\alpha$). The intensities of 1340 independent reflexions were measured on a Hilger & Watts four-circle automated diffractometer with the θ–2θ step-scanning technique (β-filtered Mo $K\alpha$ radiation); only 629 reflexions had $I \geq 2.5\sigma(I)$ and were used in the analysis. The solution was found with *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). With 217 E's ($E_{min} = 1.3$) and 2000 $\sum_2$ relationships, 32 sets of phases were generated; the E map from the most consistent set showed all 14 non-hydrogen atoms. The refinement was by full-matrix least squares; the non-hydrogen atoms were refined anisotropically; the H atoms were located on a difference map and refined isotropically. A secondary extinction parameter was also refined (Larson, 1970). The weighting scheme was: $w = P/\{A|F_o|^2 + B|F_o| + C\}$, if $|F_o| \geq 2|F_{min}|$ ($2|F_{min}| = 30.0$; $|F_o|$ on absolute scale), or $w = D|F_o|^2 + E|F_o| + G$, if $|F_o| < 2|F_{min}|$. The coefficients were: $P = 33.0$, $A = 0.030$, $B = -1.80$, $C = 60.0$, $D = -0.0011$, $E = 0.067$,

Table 1. *Atomic coordinates and temperature factors*

Standard deviations are in parentheses. The anisotropic temperature factors are the coefficients of the expression:
$$\exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)\right].$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	0.2835 (6)	0.4985 (5)	0.4764 (14)	8.7 (5)	5.1 (3)	10.1 (5)	−0.1 (4)	−0.9 (4)	−0.5 (4)
O(2)	0.3257 (9)	0.4028 (7)	0.2034 (17)	16.0 (9)	9.0 (6)	13.4 (7)	0.6 (6)	0.7 (6)	0.9 (5)
O(3)	−0.0829 (6)	0.4046 (5)	0.8800 (10)	8.1 (4)	5.3 (3)	5.1 (3)	1.5 (3)	1.6 (3)	−0.7 (2)
N(1)	0.2640 (9)	0.4135 (10)	0.3332 (16)	8.0 (7)	12.0 (9)	7.5 (6)	4.9 (6)	4.6 (5)	2.8 (6)
N(2)	0.2020 (7)	0.4980 (7)	0.6122 (12)	4.6 (4)	8.6 (5)	6.8 (5)	0.2 (4)	1.5 (4)	1.6 (4)
N(3)	0.0171 (6)	0.4369 (5)	0.8026 (11)	6.5 (4)	5.0 (3)	4.3 (4)	1.1 (3)	0.8 (3)	0.1 (3)
C(1)	0.1779 (8)	0.3619 (7)	0.3662 (15)	3.6 (4)	6.2 (5)	5.7 (5)	0.2 (4)	1.4 (4)	2.0 (4)
C(2)	0.1401 (7)	0.4164 (7)	0.5437 (13)	4.2 (4)	4.7 (4)	4.4 (4)	0.8 (4)	0.0	0.6 (4)
C(3)	0.0430 (7)	0.3844 (6)	0.6332 (13)	5.4 (5)	4.1 (4)	4.0 (4)	0.6 (4)	0.2 (4)	0.1 (3)
C(4)	−0.0203 (7)	0.2995 (7)	0.5110 (15)	5.0 (5)	5.2 (5)	5.1 (5)	−0.3 (4)	0.0	0.1 (4)
C(5)	0.0520 (7)	0.2189 (6)	0.4093 (14)	7.0 (5)	3.7 (4)	4.9 (4)	1.7 (4)	0.8 (4)	−0.4 (4)
C(6)	0.1297 (8)	0.2697 (8)	0.2523 (15)	5.7 (6)	5.9 (6)	4.2 (5)	1.2 (4)	0.2 (4)	0.1 (4)
C(7)	−0.0243 (13)	0.1441 (8)	0.2700 (22)	11.0 (9)	5.0 (6)	8.3 (9)	0.2 (6)	0.1 (6)	−1.9 (6)
C(8)	0.1195 (9)	0.1612 (7)	0.5919 (9)	9.8 (9)	4.1 (5)	6.0 (6)	1.3 (5)	2.2 (5)	1.1 (4)

	x	y	z	B		x	y	z	B
H(3)	−0.097 (7)	0.450 (6)	0.953 (15)	3.5 (10)	D(41)	−0.067 (6)	0.326 (6)	0.401 (13)	3.5 (10)
D(42)	−0.066 (6)	0.268 (6)	0.604 (12)	3.5 (10)	H(61)	0.193 (7)	0.224 (6)	0.221 (14)	5.5 (10)
H(62)	0.064 (7)	0.293 (7)	0.135 (15)	5.5 (9)	H(71)	0.020 (6)	0.088 (6)	0.238 (10)	3.3 (10)
H(72)	−0.057 (7)	0.100 (7)	0.368 (15)	4.9 (10)	H(73)	−0.060 (8)	0.183 (7)	0.188 (16)	5.3 (10)
H(81)	0.169 (8)	0.206 (7)	0.652 (16)	6.2 (9)	H(82)	0.070 (7)	0.130 (7)	0.672 (14)	5.3 (10)
H(83)	0.160 (7)	0.101 (7)	0.539 (14)	5.8 (10)					

$G = 0.020$. At convergence R was 0.081 ($wR = 0.079$).*

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31792 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *with standard deviations in parentheses*

1	1·39 (1)	10	0·76 (8)	19	1·51 (1)
2	1·34 (1)	11	1·50 (1)	20	0·90 (9)
3	1·35 (1)	12	0·90 (8)	21	0·90 (9)
4	1·40 (1)	13	0·92 (8)	22	0·99 (9)
5	1·14 (1)	14	1·53 (1)	23	1·55 (1)
6	1·28 (1)	15	1·54 (1)	24	1·01 (8)
7	1·41 (1)	16	0·94 (8)	25	1·07 (9)
8	1·29 (1)	17	0·93 (9)	26	1·47 (1)
9	1·41 (1)	18	0·80 (9)		

| 1,2	114·5 (8)	12,13	104 (7)	19,22	115 (5)
2,3	104·5 (7)	12,14	109 (5)	20,21	123 (6)
3,4	105·7 (7)	13,14	110 (5)	20,22	108 (5)
4,5	115·2 (7)	14,11	113·6 (7)	21,22	101 (8)
4,6	114·4 (9)	14,15	107·3 (8)	23,15	108·3 (8)
5,6	130·4 (9)	14,19	110·3 (7)	23,19	108·9 (3)
6,1	101·0 (9)	14,23	111·3 (7)	23,24	113 (5)
7,1	119·6 (8)	15,16	105 (5)	23,25	93 (5)
7,2	126·0 (8)	15,17	108 (6)	23,26	107·8 (8)
7,8	115·0 (7)	15,18	102 (7)	24,25	126 (7)
8,9	112·8 (6)	16,17	87 (7)	24,26	106 (5)
9,10	102 (6)	16,18	131 (9)	25,26	109 (5)
11,7	116·5 (7)	17,18	122 (9)	26,1	128·2 (8)
11,8	128·3 (8)	19,15	110·7 (8)	26,6	130·8 (9)
11,12	110 (5)	19,20	106 (6)		
11,13	110 (5)	19,21	105 (6)		
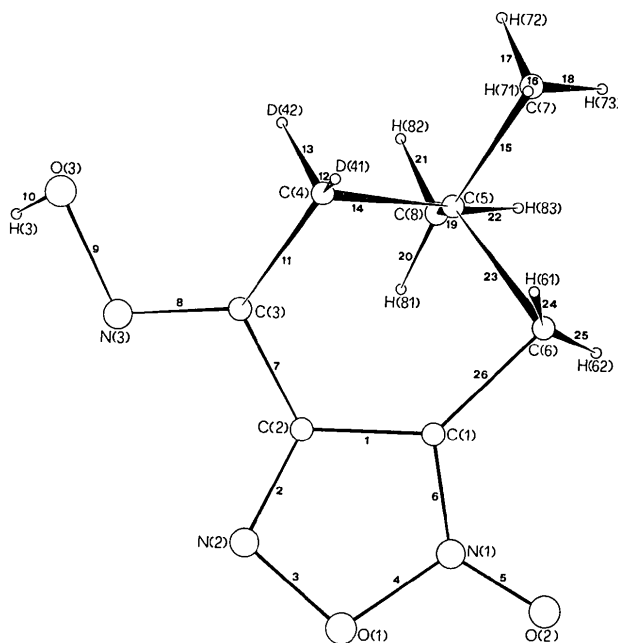
Fig. 1. Projection of the molecule onto the mean plane through the furazan ring.

The atomic coordinates and temperature factors are given in Table 1, bond distances and angles in Table 2. The thermal motion is very marked and as a consequence the number of reflexions with intensity significantly greater than the background is small; hence the errors in the bond distances and angles are relatively large. Fig. 1 shows the projection of the molecule onto the mean plane through the furazan ring and the numbering scheme which follows that already adopted (*e.g.* Calleri & Viterbo, 1976).

Discussion. The relative position of the oxime and N → O groups (Fig. 1) is that predicted by Ackrell & Boulton (1973). The furazan ring is planar, the average deviation being 0·002 Å, with O(2) at 0·012 Å. The ring shows a number of peculiarities. The difference between bonds 3 and 4 is one of the smallest found so far among the furoxan derivatives, excluding the special case of dinitrobenzofuroxan (Prout, Hodder & Viterbo, 1972); both the bonds are shorter than the expected N–O single-bond length, 1·44 Å (Pauling, 1960). The lengths of bonds 2 and 6 are not unusual, but their difference is the largest so far found. Bond 6 is consistently longer than 2 in disubstituted furoxans (Calleri, Chiari, Villa, Manfredotti, Guastini & Viterbo, 1976), while it may be equal to, or even less than 2 in the fused-ring derivatives (*e.g.* Britton & Noland, 1972; Calleri, Chiari & Viterbo, 1973). Bond 1 is among the shortest both here and in the corresponding keto derivative with the N → O group *cis* to the keto group (Calleri & Viterbo, 1976); bond 5 is here by far the shortest found in the furoxans. N(1) and O(2) have large thermal motion (Table 1); the analysis of their ellipsoids has shown that the motion of N(1) is very anisotropic with a general orientation of the ellipsoid whilst O(2) shows a more rounded ellipsoid with a large vibrational component in the xy plane, almost orthogonal to the N → O bond. The thermal behaviour of the N → O group might be related to the softening below the melting point (Ackrell & Boulton, 1973).

The endocyclic angles of the furazan ring also show an unusual trend (Table 2): 1,6 is significantly less than the average for the other furoxans ($\sim 107°$); 4,6 is here larger than 2,3 whilst the two angles are usually similar; 3,4 is less than the average (107–108°) which is unexpected since bonds 3 and 4 are shorter than the average as noted above (*cf.* Calleri, Chiari, Villa, Manfredotti, Guastini & Viterbo, 1975; Calleri, Viterbo, Villa & Guastini, 1975). The overall effect of these unusual features is to cause a very distorted furoxan ring (Fig. 1).

The conformation of the oxime moiety is typical (*e.g.* Calleri, Ferraris & Viterbo, 1966); bond 8 is longer than the ideal N=C bond, 1·247 Å (Pauling, 1960). The group C(2)C(3)N(3)O(3)C(4) is not strictly planar (average deviation 0·012 Å) and makes an angle of 5·7° with the furazan ring.

The analysis shows an extended π-delocalization throughout the system N(3)C(3)C(2)C(1)N(2) involving

also the fragment C(6)C(1)N(1)O(1)N(2), but to a lesser extent.

The contacts shorter than the sum of the van der Waals radii are: O(3)$\cdots$D(42) 2·44 (8), N(3) $(\bar{x},1-y,1-z)\cdots$H(3) 2·24 (8), N(3) $(\bar{x},1-y,1-z)\cdots$ O(3) 2·864 (9) Å, N(3) $(\bar{x},1-y,1-z,)\cdots$H(3)$\cdots$O(3) 140 (4)°.

We intend to proceed with the analysis of the other isomer in order to compare the effect of the relative position of the N-oxide and the oxime groups on the geometry of the furoxan moiety.

References

ACKRELL, J. & BOULTON, A. J. (1973). *J. Chem. Soc. Perkin* I, pp. 351–355.

BRITTON, D. & NOLAND, W. E. (1972). *Acta Cryst.* B28, 1116–1121.

CALLERI, M., CHIARI, G., VILLA, A. C., MANFREDOTTI, A. G., GUASTINI, C. & VITERBO, D. (1975). *Acta Cryst.* B31, 2384–2389.

CALLERI, M., CHIARI, G., VILLA, A. C., MANFREDOTTI, A. G., GUASTINI, C. & VITERBO, D. (1976). *Acta Cryst.* B32, 1032–1038.

CALLERI, M., CHIARI, G. & VITERBO, D. (1973). *Cryst. Struct. Commun.* 2, 335–338.

CALLERI, M., FERRARIS, G. & VITERBO, D. (1966). *Acta Cryst.* 20, 73–80.

CALLERI, M. & VITERBO, D. (1976). *Acta Cryst.* B32, 2236–2237.

CALLERI, M., VITERBO, D., VILLA, A. C. & GUASTINI, C. (1975). *Cryst. Struct. Commun.* 4, 13–16.

DECLERCQ, J. P., GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1973). *Acta Cryst.* A29, 231–234.

LARSON, A. C. (1970). *Crystallographic Computing*, pp. 291–294. Copenhagen: Munksgaard.

PAULING, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.

PROUT, C. K., HODDER, O. J. R. & VITERBO, D. (1972). *Acta Cryst.* B28, 1523–1526.

Phenylmercury(II) Cyanide

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Abstract. Tetragonal, $P4_2/n$ (No. 86), $a=15\cdot161$ (3), $c=6\cdot146$ (1) Å, formula C_7H_5NHg, $Z=8$, $D_c=2\cdot87$ g cm^{-3}, μ(Mo $K\bar{\alpha}$)$=222\cdot4$ cm^{-1}. The structure consists of discrete molecular units. The C–Hg–C–N group is approximately linear, with Hg–C(phenyl) and Hg–C(cyanide) bond distances of 2·05 and 2·09 Å respectively. An upper limit of 1·50 Å is suggested for the van der Waals radius of the Hg atom.

Introduction. $Hg(CN)_2$, Ph–Hg–CN and Ph_2Hg (Ph= C_6H_5) are known to form 1:1 adducts with neutral bidentate ligands whose stability decreases with the decreasing electronegativity of the R groups in the R_2Hg molecule. The adducts of $Hg(CN)_2$ with phen (1,10-phenanthroline) and DMP (2,9-dimethyl-1,10-phenanthroline) have been recently studied by Cano & Santos (1976). The crystal structures of two crystalline adducts of $HgPh_2$ with phen and TMP (2,4,7,9-tetramethyl-1,10-phenanthroline) have been previously reported (Canty & Gatehouse, 1972) and more recently the formation of the adducts of Ph–Hg–CN with phen and DMP has been proved (Santos & Cano, 1975).

A first stage in the elucidation of the stereochemistry of these adducts is the determination of the molecular structure of the acceptors. The molecular structure of $Hg(CN)_2$ has been determined three times both by X-ray and neutron diffraction, the most accurate structure having been reported by Seccombe & Kennard (1969) (by neutron diffraction). Also the geometry of the Ph_2Hg group is known as several structures containing this group have been determined. To date the best data of its geometry are possibly those obtained by Mathew & Kunchur (1969) for di-p-tolylmercury. The structure of Ph–Hg–CN is not known and the present paper deals with its determination.

Crystals of Ph–Hg–CN were prepared by reaction of $Hg(CN)_2$ and Ph_2Hg in ethanol in a sealed tube and recrystallization from ethanol.

A crystal of dimension 0·09 × 0·10 × 0·40 mm, sharply delimited by the faces $\{110\}$ and $\{001\}$, was mounted along the c axis. Intensity data were collected on an automatic Philips PW 1100 four-circle diffractometer using monochromated Mo $K\bar{\alpha}$ radiation and the $\omega/2\theta$ scan technique. Out of the 2056 reflexions measured ($\theta \leq 30°$), 996 were unobserved, a reflexion being con-