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6,7-Dihydro-6,6-dimethylbenzofurazan-4(5*H*)-one 3-Oxide

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Abstract. $C_8H_{10}N_2O_3$, triclinic, $P\bar{1}$; $a=10·625$ (8), $b=6·393$ (7), $c=6·863$ (7) Å, $\alpha=102·32$ (5), $\beta=85·07$ (5), $\gamma=105·71$ (5)°; $Z=2$, $D_c=1·38$ g cm^{-3}; m.p. 85–86°. Crystal dimensions: 0·45 × 0·65 × 0·70 mm. The structural assignment proposed on the grounds of spectrophotometric results has been confirmed: the *N*-oxide group is adjacent to the keto group; the furoxan ring is planar; and little or no conjugation takes place between the *N*-oxide and the keto group.

Introduction. The title fused-ring furoxan derivative was synthesized by Ackrell & Boulton (1973) as part of a study of furoxans with electron-withdrawing substituents. The yellow prismatic crystals proved suitable for X-ray analysis. Weissenberg photographs showed no systematic absences and $P\bar{1}$ was tentatively chosen. Approximate cell dimensions were obtained from the Weissenberg photographs (Cu *Kα*) and refined by least squares from diffractometer measurements (Mo *Kα*). The intensities of 2050 independent reflexions were collected on a Hilger & Watts four-circle automated diffractometer by the θ–2θ step-scanning technique (Mo *Kα*, *β*-filtered radiation); 410 reflexions with $I \leq 2·5\sigma(I)$ were treated as unobserved. The structure was solved with *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). The statistics of the normalized structure factors confirmed the presence of the inversion centre. With 232 *E*'s ($E_{\rm min}=1·6$) and 1534 $\sum_2$ relationships, 16 sets of phases were generated. The map computed with the most consistent set showed all 13 non-hydrogen atoms. The least-squares refinement was by full-matrix methods, refining anisotropically the non-hydrogen atoms; all H atoms were located on a difference map and refined isotropically. With a secondary extinction parameter (Larson, 1970) *R* was 0·068 at convergence ($R=0·080$ for all 2050 reflexions).* The weighting scheme in the final stage was: $w=P/[A|F_o|^2+B|F_o|+C]$ if $|F_o| \geq 2|F_{\rm min}|$ ($2|F_{\rm min}|=9·0$, $|F_o|$ on absolute scale) or $w=D|F_o|^2+E|F_o|+G$ if $|F_o|<2|F_{\rm min}|$. The coefficients were: $A=0·0142$, $B=-0·050$, $C=0·280$, $D=-0·0309$, $E=0·483$, $G=0·206$, $P=2·06$.

The atomic coordinates and temperature factors are given in Table 1 and the bond distances and angles in Table 2. Fig. 1 shows the numbering scheme on a projection of the molecule onto the mean plane

Table 1. *Atomic coordinates and temperature factors*

Standard deviations are shown in parentheses. The anisotropic temperature factors are the coefficients of the expression:

$$\exp\,[-\tfrac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)].$$

	x	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	0·6946 (2)	0·5708 (3)	0·7957 (3)	6·21 (3)	6·07 (11)	3·91 (9)	1·49 (9)	−0·66 (8)	−0·75 (8)
O(2)	0·4796 (2)	0·3741 (4)	0·7697 (3)	5·64 (11)	6·35 (11)	4·51 (10)	1·89 (9)	1·39 (8)	0·77 (8)
O(3)	0·4463 (2)	0·1049 (3)	0·3431 (3)	3·53 (8)	5·79 (10)	4·51 (9)	0·65 (7)	0·00	0·79 (7)
N(1)	0·8037 (2)	0·5945 (4)	0·6679 (4)	5·11 (12)	5·65 (13)	5·08 (12)	0·91 (10)	−0·62 (10)	−0·71 (10)
N(2)	0·5846 (2)	0·4144 (4)	0·6828 (3)	4·58 (10)	4·72 (11)	3·63 (9)	1·28 (8)	0·13 (8)	0·45 (8)
C(1)	0·7655 (2)	0·4680 (4)	0·4945 (4)	3·95 (11)	3·99 (11)	4·15 (12)	0·87 (9)	−0·39 (9)	0·07 (9)
C(2)	0·6329 (2)	0·3564 (4)	0·5004 (3)	3·86 (10)	4·06 (11)	3·13 (10)	1·28 (9)	0·11 (8)	0·39 (8)
C(3)	0·5618 (2)	0·1948 (4)	0·3325 (4)	3·58 (11)	4·04 (11)	3·44 (10)	1·09 (9)	−0·16 (8)	0·75 (8)
C(4)	0·6491 (3)	0·1640 (5)	0·1490 (4)	4·10 (12)	4·46 (13)	3·45 (11)	1·12 (10)	0·01 (9)	0·16 (10)
C(5)	0·7952 (2)	0·2070 (4)	0·1832 (4)	3·58 (10)	3·65 (11)	4·00 (11)	1·02 (8)	0·45 (8)	0·60 (9)
C(6)	0·8475 (3)	0·4399 (5)	0·3096 (4)	3·74 (12)	3·88 (12)	5·16 (14)	0·67 (10)	0·21 (10)	0·70 (10)
C(7)	0·8688 (4)	0·1936 (7)	−0·0193 (5)	5·20 (17)	6·13 (19)	5·18 (16)	1·45 (14)	1·66 (13)	0·79 (15)
C(8)	0·8185 (3)	0·0336 (6)	0·2873 (6)	4·72 (15)	5·00 (16)	6·50 (18)	1·95 (12)	0·85 (13)	1·59 (14)

	x	*y*	*z*	*B*		*x*	*y*	*z*	*B*
H(41)	0·636 (3)	0·256 (5)	0·073 (5)	3·0 (7)	H(42)	0·620 (2)	0·018 (5)	0·090 (4)	2·0 (6)
H(61)	0·839 (2)	0·547 (5)	0·235 (4)	2·0 (6)	H(62)	0·937 (3)	0·453 (4)	0·333 (4)	2·0 (5)
H(71)	0·858 (3)	0·288 (6)	−0·089 (5)	3·9 (9)	H(72)	0·837 (4)	0·053 (7)	−0·094 (6)	5·1 (9)
H(73)	0·959 (4)	0·217 (6)	−0·003 (5)	4·5 (8)	H(81)	0·777 (3)	0·019 (5)	0·413 (5)	4·0 (8)
H(82)	0·791 (3)	−0·120 (6)	0·210 (5)	3·5 (7)	H(83)	0·910 (3)	0·049 (5)	0·310 (4)	3·3 (7)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31729 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

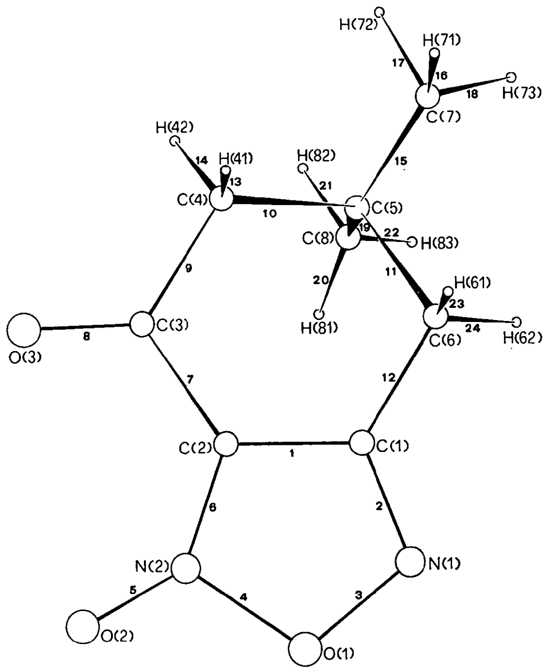

Fig. 1. Projection of the molecule onto the mean plane through the furazan ring: numbering scheme.

through the furazan ring; this unconventional numbering scheme follows that adopted for several other furoxan derivatives (*e.g.* Calleri, Chiari, Chiesi Villa, Gaetani Manfredotti, Guastini & Viterbo, 1975).

Discussion. On oxidation of 5,5-dimethylcyclohexane-1,2,3-trione 1,2-dioxime, Ackrell & Boulton (1973) obtained one keto derivative which, on heating in light petroleum and toluene, was isomerized almost quantitatively to the title compound. The structural assignments of these authors, based on NMR spectra, have been confirmed by the present analysis; of the two positional isomers, the more stable is the one with the *N*-oxide next to the keto function (Fig. 1).

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

1	1·398 (4)	9	1·509 (4)	17	0·92 (4)
2	1·315 (4)	10	1·531 (4)	18	0·95 (4)
3	1·387 (3)	11	1·537 (4)	19	1·523 (4)
4	1·470 (3)	12	1·483 (4)	20	0·94 (4)
5	1·210 (3)	13	0·91 (3)	21	0·99 (4)
6	1·328 (3)	14	0·92 (3)	22	0·97 (4)
7	1·478 (3)	15	1·533 (5)	23	0·97 (3)
8	1·210 (3)	16	0·88 (4)	24	0·96 (3)
1,2	111·8 (2)	10,11	110·1 (2)	15,16	114 (2)
2,3	106·6 (2)	10,13	111 (2)	15,17	108 (2)
3,4	107·6 (2)	10,14	107 (2)	15,18	111 (2)
4,5	117·3 (2)	10,15	108·8 (2)	15,19	109·0 (2)
4,6	105·6 (2)	10,19	110·3 (2)	16,17	107 (3)
5,6	137·1 (2)	11,12	109·7 (2)	16,18	109 (3)
6,1	108·4 (2)	11,15	108·6 (2)	17,18	108 (3)
6,7	126·5 (2)	11,19	109·9 (2)	19,20	119 (3)
7,1	125·0 (2)	11,23	108 (2)	19,21	114 (3)
7,8	122·8 (2)	11,24	106 (2)	19,22	115 (2)
7,9	112·0 (2)	12,1	121·6 (2)	20,21	102 (3)
8,9	125·1 (2)	12,2	126·7 (3)	20,22	103 (3)
9,10	116·7 (2)	12,23	107 (2)	21,22	102 (3)
9,13	105 (2)	12,24	114 (2)	23,24	112 (2)
9,14	105 (2)	13,14	112 (2)		

The furoxan moiety is planar since none of the atoms is more than 0·006 Å from the mean plane. The endocyclic angles fit the trend found for disubstituted and fused-ring furoxans (*e.g.* Calleri, Chiari, Chiesi Villa, Gaetani Manfredotti, Guastini & Viterbo, 1975; Calleri, Viterbo, Chiesi Villa & Guastini, 1975). The length of bond (6) (Table 2) is not among the longest in fused-ring furoxans (*e.g.* Britton & Noland, 1972), but is significantly longer than the expected N=C length, 1·247 Å (Pauling, 1960). Bond (5) is one of the shortest found in furoxans so far and its length, 1·210 Å, compares well with the ideal N=O length, 1·200 Å (Pauling, 1960); the length of bond (8), 1·210 Å, is typical of C=O. Therefore the X-ray results do not reveal the appreciable degree of conjugation of the *N*-oxide with the keto group deduced by Ackrell & Boulton (1973) from spectrophotometric results. Bond (7) is actually shorter than the C_{sp2}–C_{sp2} length, 1·52 Å (Sutton, 1965), but so are bonds (12) and (1). Hence we may note an appreciable degree of π-delocalization throughout the large molecular fragment C(3), C(2), C(1), C(6), N(1), N(2) which is, in fact, approximately planar with only C(3) appreciably out of the mean plane. This may account for the fact that the present isomer is largely favoured at the equilibrium. Unfortunately we did not succeed in growing suitable crystals for the other positional isomer.

No abnormal intra- or intermolecular contacts occur.

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