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

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Abstract. $C_8H_{11}N_3O_3$, monoclinic, $P2_1/c$, a = 8·478 (1), b = 5·855 (2), c = 18·721 (1) Å; β = 92·86 (1)°; Z = 4, D_c = 1·41 g cm^{-3}; m.p. 210–213 °C; crystal dimensions 0·18 × 0·38 × 0·75 mm; elongation axis [010]. The furoxan moiety is planar and shows the usual trend of bond distances and angles; the oxime group is *anti* to the furoxan ring as in the 1-oxide isomer.

Introduction. The compound was prepared by A. J. Boulton as transparent, slightly pleochroic, yellowish prisms suitable for X-ray investigation. The present analysis confirmed that the oxime function is *cis* to the N → O group according to the NMR results of Ackrell & Boulton (1973). The structure of the 1-oxide isomer has been described (Calleri, Chawdhury & Viterbo, 1976).

Approximate cell parameters were determined from Weissenberg photographs and refined by least squares from diffractometer observations (Cu $K\alpha$). The intensities of 1565 independent reflexions were measured, at room temperature, on a Philips PW 1100 four-circle diffractometer (graphite-monochromatized Cu $K\alpha$ radiation): θ–2θ step scanning, rate of scanning 0·02° s^{-1}, scan range 1·40°; 1435 reflexions had $I \geq 2{\cdot}5\sigma(I)$ and were used for the refinement. The solution was found with *MULTAN* (Declercq, Germain, Main & Woolfson, 1973): with 200 E's ($E_{\rm min}$ = 1·49) and 1725 Σ_2 relationships, eight sets of phases were generated one of which had decidedly better figures of merit. The corresponding E map revealed all 14 non-hydrogen atoms whose parameters were initially refined by block-diagonal least squares. The H atoms were located on a difference synthesis and the refinement was completed by full-matrix least squares, refining isotropically the H and anisotropically the non-hydrogen atoms. No correction for secondary extinction was required. The weighting scheme was: $w = P/(A|F_o|^2 + B|F_o| + C)$ with P = 12·5, A = 0·085, B = 1, C = 12·2. At convergence R was 0·050 (wR = 0·074).

The atomic parameters are given in Table 1;* Fig. 1 shows the projection of the molecule on the mean plane through the furazan ring and some bond angles and distances; the remaining lengths and angles appear in Table 2. The overall thermal motion is modest;

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32820 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atomic coordinates* (×10^4; *for* H ×10^3), *with standard deviations in parentheses*

	x	y	z		x	y	z	B (Å^2)
O(1)	6626 (2)	4306 (3)	8066 (1)	H(3)	363 (4)	957 (6)	1036 (2)	2 (1)
O(2)	7086 (2)	7397 (3)	8799 (1)	H(42)	147 (3)	609 (5)	958 (1)	2 (1)
O(3)	3257 (2)	8659 (3)	10185 (1)	H(62)	297 (3)	91 (5)	878 (2)	2 (1)
N(1)	5402 (2)	2758 (4)	7939 (1)	H(72)	46 (4)	131 (6)	931 (2)	3 (1)
N(2)	6151 (2)	5870 (3)	8611 (1)	H(81)	57 (3)	472 (5)	773 (2)	3 (1)
N(3)	4301 (2)	7940 (3)	9679 (1)	H(83)	22 (3)	663 (5)	835 (2)	4 (1)
C(1)	4303 (3)	3296 (4)	8370 (1)	H(41)	234 (3)	395 (5)	981 (2)	2 (1)
C(2)	4737 (2)	5225 (4)	8791 (1)	H(61)	241 (3)	144 (5)	796 (2)	2 (1)
C(3)	3756 (2)	6212 (4)	9324 (1)	H(71)	−40 (3)	163 (5)	852 (2)	2 (1)
C(4)	2208 (3)	5009 (4)	9412 (1)	H(73)	−74 (4)	336 (6)	912 (2)	3 (1)
C(5)	1538 (2)	3761 (4)	8738 (1)	H(82)	201 (3)	626 (5)	798 (2)	3 (1)
C(6)	2766 (3)	2119 (4)	8451 (1)					
C(7)	104 (3)	2366 (5)	8944 (2)					
C(8)	1031 (3)	5499 (5)	8163 (1)					

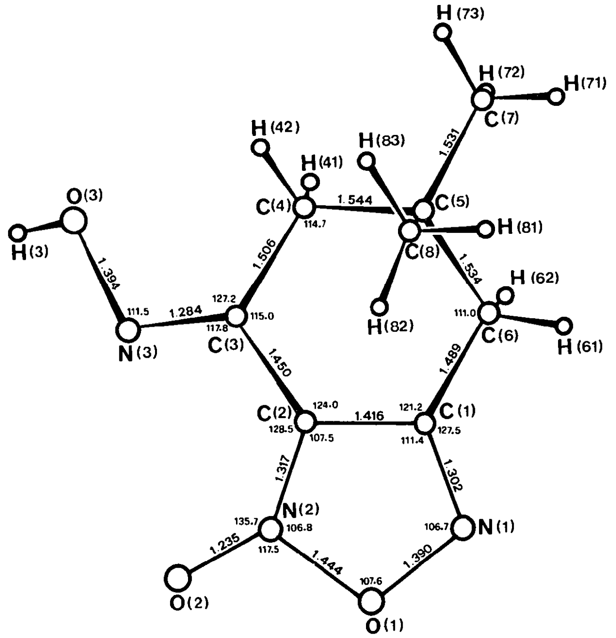

Fig. 1. Projection of the molecule on the furazan-ring plane showing the unconventional numbering scheme and some bond distances and angles. Standard deviations: 0·003 Å for the bonds, 0·2° for the angles.

Table 2. *Bond lengths* (Å) *and angles* (°) *not displayed in Fig.* 1, *with standard deviations in parentheses*

O(3)–H(3)	0·70 (3)	C(4)–H(41)	0·97 (3)
C(4)–H(42)	0·95 (3)	C(7)–H(71)	0·98 (3)
C(7)–H(72)	0·96 (3)	C(7)–H(73)	0·99 (3)
C(5)–C(8)	1·528 (3)	C(8)–H(81)	0·99 (3)
C(8)–H(82)	1·01 (3)	C(8)–H(83)	1·03 (3)
C(6)–H(61)	1·03 (3)	C(6)–H(62)	0·95 (3)
C(3)–C(4)–H(41)	108 (2)	C(3)–C(4)–H(42)	108 (2)
H(41)–C(4)–H(42)	103 (2)	C(5)–C(4)–H(41)	110 (2)
C(5)–C(4)–H(42)	111 (2)	C(4)–C(5)–C(6)	110·8 (2)
C(4)–C(5)–C(7)	108·1 (2)	C(4)–C(5)–C(8)	109·9 (2)
C(6)–C(5)–C(7)	108·4 (2)	C(6)–C(5)–C(8)	110·1 (2)
C(7)–C(5)–C(8)	109·5 (2)	C(5)–C(7)–H(71)	110 (2)
C(5)–C(7)–H(72)	107 (2)	C(5)–C(7)–H(73)	112 (2)
H(71)–C(7)–H(72)	113 (3)	H(71)–C(7)–H(73)	103 (2)
H(72)–C(7)–H(73)	111 (3)	H(81)–C(8)–H(82)	103 (2)
H(81)–C(8)–H(83)	109 (2)	H(82)–C(8)–H(83)	114 (2)
C(5)–C(6)–H(61)	112 (1)	C(5)–C(6)–H(62)	110 (2)
C(1)–C(6)–H(61)	108 (1)	C(1)–C(6)–H(62)	106 (2)
H(61)–C(6)–H(62)	109 (2)	N(3)–O(3)–H(3)	84 (1)

however, all the atoms of the 1-oxide had much greater B_{ij} parameters and greater standard deviations (Calleri, Chawdhury & Viterbo, 1976). The two isomers show a large difference in melting points: 210–213 and 132–135 °C respectively.

Discussion. The dimensions of the furoxan group compare well with the average values found for disubstituted and fused-ring furoxans (*e.g.* Calleri, Chiari, Chiesi, Gaetani, Guastini & Viterbo, 1975, 1976). The moiety is planar, the mean deviation being 0·003 Å, as for the corresponding keto derivative (Calleri & Viterbo, 1976), whilst in most other derivatives only the furazan ring can be considered strictly planar. The oxime function too shows the usual trend (*e.g.* Calleri, Ferraris & Viterbo, 1966) with C(3)–N(3) longer than the ideal N=C bond, ~1·24 Å (Pauling, 1960; Gillespie, 1972). The group C(2)C(3)N(3)O(3)C(4) is not strictly planar, mean deviation 0·01 Å, and makes an angle of 1·6° with the furazan ring; this angle is 5·7° for the 1-oxide. The only intermolecular contact worth noting occurs between N(3) and the OH group of the approaching molecule: N(3)···H(3)($\bar{x}$, $1-y$, $1-z$) 2·28 (3), N(3)···O(3) ($\bar{x}$, $1-y$, $1-z$) 2·875 (3) Å, N(3)···H(3)–O(3) 112 (1)°. The packing is, therefore, very similar to that of the other isomer (Calleri, Chawdhury & Viterbo, 1976), which, however, showed unusual trends for the bond angles and distances of the furoxan group. A slight difference between the two isomers is the distance apart of the oxime and furazan groups. The N(3)···N(2) distance is here 2·870 (3) Å whilst it is 2·747 (11) Å in the 1-oxide; the angles N(2)–C(2)–C(3) and C(2)–C(3)–N(3) are 2·5° larger in the present isomer. These steric effects may be related to the necessity of accommodating the extranuclear O(2) adjacent to the oxime group.

In both isomers the oxime group is *anti* with respect to the furoxan ring and there is no possibility of intramolecular hydrogen bonding. Although we need not expect a strict correspondence of behaviour in the solid state and in solution, this supports the conclusions of Boulton (1973) about the interconversion mechanism *via* the dinitroso intermediate, since the *anti* position found for both isomers makes unlikely other types of rearrangement.

The X-ray results offer no clear evidence as to why, at equilibrium, the 3-oxide is favoured [though not so strongly as the corresponding keto derivatives (Boulton, 1973; Ackrell & Boulton, 1973)]. All we may conclude is that the bonds involved in the fragment from O(3) to O(2), Fig. 1, suggest here the existence of a limited donation from the oxime to the N → O group contrasting with the back-donation from O(2) which is apparent in the 1-oxide and possibly responsible, there, for the unusual trend in bonds and angles.

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2,4,4,*trans*-6,8,8-Hexachloro-2,6-bis(*N*-methylanilino)-*cyclo*-tetraphosphazatetraene

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Abstract. $N_4P_4Cl_6[N(CH_3)(C_6H_5)]_2$, $M_r = 605$, monoclinic, $P2_1/n$, $a = 12{\cdot}35$ (2), $b = 16{\cdot}59$ (2), $c = 6{\cdot}08$ (1) Å, $\beta = 93{\cdot}23$ (30)°, $V = 1244$ Å^3, $D_c = 1{\cdot}615$ g cm^{-3}, $Z = 2$, μ(Cu $K\alpha$) = 0·85 cm^{-1}. The compound (m.p. 145 °C) is the 2,*trans*-6 isomer. The P—N ring has a chair conformation. The final R was 0·084 for 1102 visually estimated reflections.

Introduction. The crystals were needles elongated along **c**. A crystal of radius 0·14 mm was used to collect intensities for reflections 0–7*kl* by the multiple-film Weissenberg technique with Cu $K\alpha$ radiation. 1102 intensities were estimated visually and corrected for absorption. The structure was solved by direct methods with *MULTAN* (Main, Woolfson & Germain, 1971) adapted for the IBM 360/44 system by M. R. Narasimha Murthy and S. Rama Kumar. The parameters were refined first isotropically and later anisotropically by block-diagonal least squares. A difference map failed to reveal the positions of the H atoms. Five H atoms of the phenyl ring were included at calculated positions but were not refined. The final R [$= \Sigma||F_o| - |F_c||/\Sigma |F_o|$] for the observed reflections is 0·084. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/(a + |F_o| + c|F_o|^2)$ with $a = 9{\cdot}0$ and $c = 0{\cdot}035$ (Cruickshank, Bujosa, Lovell & Truter, 1961). Scattering factors were from Cromer & Waber (1965). The final atomic coordinates of the non-hydrogen atoms are given in Table 1.*

Table 1. *Final fractional atomic coordinates* (×10^4) *with e.s.d.'s in parentheses*

	x	*y*	*z*
Cl(1)	7936 (4)	647 (4)	5351 (13)
Cl(2)	6768 (5)	895 (4)	9635 (12)
Cl(3)	3896 (5)	1119 (4)	7819 (12)
P(1)	6478 (4)	488 (3)	6457 (11)
P(2)	4415 (4)	1108 (3)	4691 (10)
N(1)	5699 (13)	1074 (10)	5013 (32)
N(2)	3762 (16)	417 (10)	3323 (40)
N(3)	4047 (13)	1959 (9)	3487 (34)
C(1)	2921 (19)	2105 (14)	2655 (54)
C(2)	4720 (17)	2680 (12)	3878 (44)
C(3)	4633 (19)	3157 (13)	5755 (43)
C(4)	5243 (23)	3886 (15)	5965 (54)
C(5)	5872 (22)	4086 (15)	4304 (58)
C(6)	5949 (20)	3624 (16)	2502 (51)
C(7)	5372 (19)	2899 (14)	2260 (50)

Discussion. The reaction of octachloro-*cyclo*-tetraphosphazatetraene, $N_4P_4Cl_8$, with *N*-methylaniline was studied by John, Moeller & Audrieth (1960), and a bis-*N*-methylanilinohexachloro derivative, $N_4P_4Cl_6$-$(NMePh)_2$ (m.p. 145°C), isolated. A reinvestigation of the reaction showed it to be far more complex and two isomers having m.p.'s of 145 and 105°C were obtained in comparable yields (Keat *et al.*, 1974). The

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