charges as the minimum energy calculated corresponds to a structure some 100 kcal mol^{-1} more stable than the separated ions. The addition of the methyl group has the effect of making most atoms less positively charged, except at C(1) where the atom becomes more positively charged. This conceivably accounts for the short halide–C(1) distance as the attractive force is intensified.

The X-ray result is somewhat in agreement with the calculation in that a short halide–C(1) distance was obtained; however, this distance was not the shortest halide–ring contact. The current investigation is more in accord with the findings of Rérat (1962) on pyridine hydrochloride, with halide–N distances representing short contacts. It should be pointed out that the distances of 3·76 and 3·90 Å, while significantly different, are not different enough to conclude that any single interaction dictates the cation–anion relationship. The I^- to ring distances correspond approximately to the mean ionic radius calculated from the thermodynamic data (*ca* 4–5 Å, Hemmes *et al.*, 1978). As nucleophilic substitution in the gas phase is more favored than in solution, the short Cl^- to ring distances found by theory (Jordan, 1975) perhaps approximate the structure of an intermediate for nucleophilic substitution rather than a ground-state ion pair.

Programs used were of local origin and also included the following: refinement of cell dimensions, Syntex program; Fourier synthesis, Zalkin's (1962) *FORDAP*; hydrogen calculations, Shiono's *GENATM*; lengths and angles, the Busing, Martin & Levy (1964) program *ORFFE*; plotting, Johnston's (1970) *ORTEP* II thermal ellipsoid plotting program.

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

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Abstract. $C_8H_{11}N_3O_2$, monoclinic, $P2_1/n$, $a = 6{\cdot}048$ (2), $b = 12{\cdot}934$ (1), $c = 11{\cdot}565$ (1) Å, $\beta = 92{\cdot}59$ (2)°, $Z = 4$, $D_c = 1{\cdot}33$ g cm^{-3}, m.p. 193–194 °C. The furazan ring is planar and nearly coplanar with the oxime group which is *anti* to the ring, as in the two related furoxan isomers.

Introduction. The present investigation follows those on the 1-oxide and 3-oxide furoxan analogues and dihydrodimethylbenzofurazan-4(5*H*)-one 3-oxide (Calleri, Chawdhury & Viterbo, 1976; Calleri, Bonaccorti & Viterbo, 1977*a*; Calleri & Viterbo, 1976). All four compounds were prepared by A. J. Boulton and coworkers with the aim of investigating the tautomerism and possible rearrangement mechanisms (Ackrell & Boulton, 1973; Boulton, 1973).

The compound synthesized by Ackrell (personal communication) was recrystallized from toluene as transparent colourless prisms. Approximate cell parameters, derived from Weissenberg photographs, were refined by least squares from diffractometer observations (Cu $K\alpha$). The intensities of 1345 independent reflexions were measured on a Philips PW 1100 four-circle diffractometer (graphite-monochromatized Cu $K\alpha$ radiation) with θ–2θ step scanning at 0·10° s^{-1}, and a scan range of 1·5°. For all the computations use was made of the *SHELX* suite of programs (Sheldrick, 1976). The solution was found using 228 E's ($E_{\min}$ = 1·30) and 1964 $\sum_2$ relationships; four sets of phases were generated and the E map corresponding to the set with the best figures of merit revealed all 13 non-hydrogen atoms. The least-squares refinement was based on the 1013 reflexions with $I \geq 3\sigma(I)$. The H atoms, located on a difference map, were tentatively refined with no constraint; since they showed a tendency to 'collapse' onto the bonding C atoms, the C—H distances were constrained to remain at 1·00 ± 0·05 Å. In the initial stages use was made of the weights from counting statistics; the final cycles were with unit weights, refining all the non-hydrogen atoms anisotropically, and the H atoms isotropically to R = 0·062. The thermal parameters of the H atoms were grouped into two sets (Table 1). The three strongest reflexions were given zero weight because they were manifestly affected by secondary extinction. The atomic parameters are in Table 1* and the bond

Table 1. *Atomic coordinates* (×10⁴, *for* H ×10³) *with standard deviations in parentheses*

	x	y	z	B (Å^2)
O(1)	802 (6)	9852 (3)	1976 (3)	
O(2)	6076 (5)	9058 (3)	5867 (3)	
N(1)	2198 (7)	8998 (3)	2163 (3)	
N(2)	9289 (7)	9913 (3)	2836 (3)	
N(3)	6956 (6)	9376 (3)	4821 (3)	
C(1)	1566 (7)	8570 (3)	3106 (4)	
C(2)	9743 (7)	9137 (3)	3521 (4)	
C(3)	8673 (7)	8846 (3)	4571 (4)	
C(4)	9757 (8)	7993 (4)	5253 (4)	
C(5)	823 (7)	7154 (4)	4498 (4)	
C(6)	2520 (8)	7644 (4)	3701 (4)	
C(7)	2030 (9)	6393 (5)	5303 (5)	
C(8)	9033 (9)	6599 (5)	3761 (5)	
H(2)	495 (7)	949 (3)	597 (4)	4·9 (5)
H(41)	879 (8)	766 (4)	580 (4)	4·9 (5)
H(42)	87 (8)	830 (4)	584 (4)	4·9 (5)
H(61)	294 (8)	712 (3)	309 (4)	4·9 (5)
H(62)	374 (7)	781 (4)	424 (4)	4·9 (5)
H(71)	319 (8)	673 (4)	578 (4)	5·3 (5)
H(72)	108 (8)	605 (4)	582 (4)	5·3 (5)
H(73)	271 (8)	581 (3)	487 (4)	5·3 (5)
H(81)	827 (8)	705 (4)	316 (4)	5·3 (5)
H(82)	963 (9)	602 (3)	329 (4)	5·3 (5)
H(83)	796 (8)	627 (4)	429 (4)	5·3 (5)

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

See Fig. 1 for bond numbering.

1	1·426 (6)	11	1·490 (6)	19	1·526 (7)
2	1·296 (6)	12	0·98 (4)	20	1·01 (4)
3	1·401 (5)	13	1·02 (4)	21	1·00 (4)
4	1·384 (5)	14	1·551 (6)	22	1·00 (4)
6	1·300 (6)	15	1·518 (7)	23	1·546 (6)
7	1·451 (6)	16	0·98 (4)	24	1·02 (4)
8	1·288 (5)	17	0·96 (4)	25	0·97 (4)
9	1·405 (5)	18	1·00 (4)	26	1·485 (7)
10	0·89 (4)				
1,2	109·0 (4)	12,13	98 (4)	19,22	109 (3)
2,3	105·6 (4)	12,14	109 (4)	19,23	109·4 (4)
3,4	110·3 (3)	13,14	112 (3)	20,21	103 (4)
4,6	105·4 (4)	14,15	108·0 (4)	20,22	112 (5)
6,1	109·7 (4)	15,16	112 (3)	21,22	106 (4)
6,7	128·4 (4)	15,17	113 (3)	23,14	110·7 (4)
7,1	121·9 (4)	15,18	112 (3)	23,24	109 (3)
7,8	116·4 (4)	15,23	108·5 (4)	23,25	102 (3)
8,9	112·3 (3)	16,17	107 (4)	23,26	110·6 (4)
9,10	105 (3)	16,18	109 (4)	24,25	113 (4)
11,7	115·6 (4)	17,18	103 (4)	24,26	109 (3)
11,8	128·0 (4)	19,14	109·9 (4)	25,26	112 (3)
11,12	114 (3)	19,15	110·3 (4)	26,1	123·3 (4)
11,13	109 (3)	19,20	114 (3)	26,2	127·7 (4)
11,14	113·8 (4)	19,21	113 (3)		

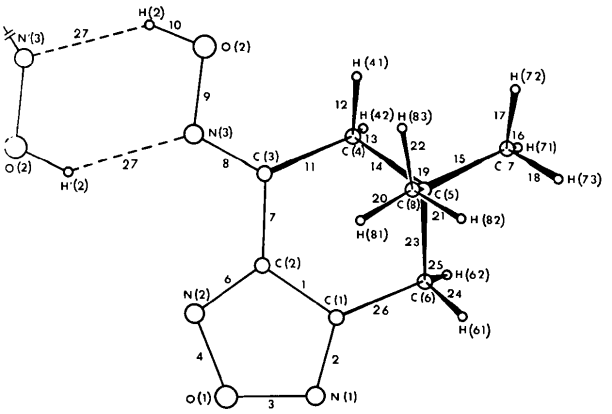

Fig. 1. Projection of the molecule onto the plane of the furazan ring. The numbering scheme is shown.

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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 33650 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

distances and angles in Table 2; Fig. 1 shows the numbering scheme, already adopted for other furazan derivatives (Gaetani, Guastini, Calleri & Viterbo, 1976).

Discussion. The bond distances and angles of the furazan ring, except bond 3, are identical within one standard deviation to those of furazan itself (Table 2; Saegebarth & Cox, 1965). From the results available in the literature, it can be assumed that the percentage of π-bond order is about 70 for bonds 2 and 6 and over 40 for bond 1; bonds 3 and 4 are both shorter than the expected N—O value of 1·43 Å (*e.g.* Cameron & Prout, 1969; Shefter, Evans & Taylor, 1971). The degree of electron delocalization found in several disubstituted furoxans is slightly less marked in the present furazan where, however, it seems to involve the whole ring smoothly (Calleri, Chiari, Chiesi, Gaetani, Guastini & Viterbo, 1975, 1976). The furazan ring is planar, the mean deviation from the plane being 0·003 Å. Also, C(3) and C(6) are nearly coplanar with the ring, their deviations being 0·009 and 0·023 Å respectively. This is consistent with the bond trend of the six-membered ring – common to the present molecule, to its two furoxan analogues and to the 3-oxide isomer of dihydrodimethylbenzofurazan-4(5*H*)-one. In fact, for these four structures, whilst the $\langle$C—C$\rangle$ value for bonds 14,23 is 1·54 Å, those for bonds 11,26 and 1,7 are 1·49 and 1·43 Å respectively; that is, significantly smaller than the commonly accepted C_{sp^2}—C_{sp^3} or C_{sp^2}—C_{sp^2} single-bond values of 1·52 and 1·50 Å respectively. Since the effect is neatly shown by furoxan and furazan derivatives, it may be ascribed to the electron-withdrawing power of the N—O—N group of the penta-atomic ring. In the 3-oxide oxime derivative (Calleri, Bonaccorti & Viterbo, 1977*a*) this 'inductive' effect is accompanied by a limited conjugation between the oxime and the N → O functions, while in the 1-oxide isomer (Calleri, Chawdhury & Viterbo, 1976) it is accompanied by a back-donation effect from the extranuclear O atom. The induction appears less marked in the 3-oxide ketone derivative (Calleri & Viterbo, 1976) where the X-ray results alone do not indicate the appreciable presence of any other effect.

In all three oxime derivatives the oxime group is nearly coplanar (the dihedral angle is 6° in the present molecule) and *anti* with respect to the penta-atomic ring and forms 'dimers' centred on symmetry centres as shown in Fig. 1. The N(3)···H′(2) distance here is 2·05 (4) Å, but the narrowness of the O(2)—H(2)···N′(3) angle, 111 (3)°, indicates the weakness of these interactions; the same obtains with the two furoxan analogues. That notwithstanding, the 3-oxide ketone derivative, in which no such interaction takes place, has a much lower melting point (85–86 °C). The intramolecular N(3)···N(2) distance here is 2·835 (6) Å; that is, intermediate between those of the related furoxan isomers. The packing and conformation are therefore very similar in all three oximes – except for the angle between the extensions of bonds 2 and 6 (*cf.* Boulton & Middleton, 1974; Calleri, Bonaccorti & Viterbo, 1977*b*). This angle varies between 37·2 and 40° (mean 38·5°) for the unfused furoxans and furazans; one may assume that deviations from 38·5° are an index of strain with respect to the unfused derivatives and that the differences from 60° represent the angular deformation for the fusion to a six-membered ring. The angle is between 39 and 40° in the present furazan, in the 3-oxide analogue and in the 3-oxide ketone derivative, whilst it is only 35·5° in the 1-oxide analogue. The difference is not very large, though statistically significant, but it may be related to the fact that the 1-oxide is the form which is unfavoured at equilibrium (Boulton, 1973), which has a melting point (132–135 °C) lower than that of the other two oximes, and which has larger thermal parameters (Calleri, Chawdhury & Viterbo, 1976).

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