

## Isopropyl 4-Methyl-3-furazancarbamate

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**Abstract.** C<sub>7</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub>, monoclinic,  $P2_1/c$ ,  $a = 9.14$  (4),  $b = 11.91$  (2),  $c = 8.92$  (3) Å,  $\beta = 91.3$  (1)°,  $V = 970.8$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.27$  Mg m<sup>-3</sup>; m.p. 385–386 K;  $R = 0.048$  for 1543 independent reflexions. The furazan and carbamate moieties are planar, the two mean planes making an angle of 7.3 (2)°. The former is slightly asymmetric because of a difference between the two N–O bonds. A comparison is given of the dimensions of the furazan ring in disubstituted derivatives.

**Introduction.** This structural analysis was undertaken as part of an investigation of disubstituted furazans and furoxans; it is comparable in particular to the structures of the two isomers of isopropyl methylfuroxancarbamate (Calleri, Chiari, Chiesi Villa, Gaetani Manfredotti, Guastini & Viterbo, 1977). The compound prepared by Gasco, Ruà, Menziani, Mortarini & Fundaro' (1971) was recrystallized from ethanol–water to yield prismatic transparent crystals suitable for

X-ray measurements. The space group was determined from Weissenberg photographs; the cell parameters and intensities were measured at room temperature by an automated Siemens AED diffractometer (Cu  $K\alpha$ ,  $\beta$ -filtered radiation) using  $\theta$ – $2\theta$  scans. The number of independent intensities measured within the interval  $6^\circ < 2\theta \leq 140^\circ$  was 1800; 1543 had  $I > 2\sigma(I)$  and were included in the analysis. The structure was solved with *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). The non-hydrogen atoms were refined anisotropically by block-diagonal least squares with unit weights. The H atoms, located from difference Fourier maps, were refined isotropically. At convergence  $R$  was 0.048 ( $R = 0.059$  for all the reflexions).\* The final atomic parameters are given in Table 1. Fig. 1 shows a view of the molecule,

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38011 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters ( $\times 10^4$ ;  $\times 10^3$  for H), equivalent isotropic thermal parameters for non-hydrogen atoms, and isotropic thermal parameters for H atoms, with e.s.d.'s in parentheses

$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* b_j^* a_i \cdot b_j$$

	x	y	z	$B_{eq}$ or $B$ (Å <sup>2</sup> )		x	y	z	$B_{eq}$ or $B$ (Å <sup>2</sup> )
C(1)	–452 (2)	939 (1)	6606 (2)	4.47 (6)	C(2)	473 (2)	1791 (1)	6015 (2)	3.79 (5)
C(3)	–283 (3)	303 (2)	8012 (2)	6.33 (9)	C(4)	2682 (2)	2930 (1)	6083 (2)	3.65 (5)
C(5)	4873 (2)	3955 (2)	6605 (2)	5.40 (8)	C(6)	6119 (3)	3308 (3)	6061 (4)	9.38 (16)
C(7)	5258 (3)	4665 (2)	7949 (3)	7.65 (8)	N(1)	–1517 (2)	770 (2)	5646 (2)	5.92 (7)
N(2)	–37 (2)	2127 (1)	4714 (2)	5.21 (7)	N(3)	1726 (1)	2190 (1)	6713 (1)	3.99 (5)
O(1)	–1295 (1)	1489 (1)	4464 (2)	6.32 (6)	O(3)	2569 (1)	3306 (1)	4835 (1)	4.58 (5)
O(4)	3730 (1)	3176 (1)	7083 (1)	5.04 (5)	H(3)	189 (2)	203 (1)	772 (2)	4.4 (3)
H(31)	–103 (2)	–4 (2)	826 (2)	8.2 (5)	H(32)	51 (2)	–6 (2)	799 (2)	8.1 (5)
H(33)	–31 (2)	73 (2)	891 (3)	9.2 (6)	H(5)	443 (2)	445 (2)	581 (2)	5.7 (4)
H(61)	643 (3)	278 (2)	673 (3)	8.8 (6)	H(62)	578 (3)	309 (2)	522 (3)	9.9 (7)
H(63)	693 (3)	389 (2)	575 (3)	9.4 (6)	H(71)	550 (3)	421 (2)	877 (3)	8.9 (6)
H(71)	606 (2)	523 (2)	757 (3)	8.5 (5)	H(73)	427 (3)	501 (2)	842 (3)	9.2 (6)

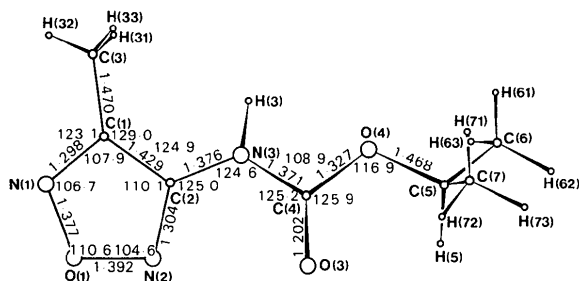


Fig. 1. Bond distances (Å) and angles (°). E.s.d.'s are 0.002–0.004 Å for bonds and 0.3–0.4° for angles.

Table 2. Bond distances (Å) and angles (°) involving non-hydrogen atoms, not displayed in Fig. 1

Standard deviations are in parentheses.

C(3)–H(31)	0.83 (2)	C(3)–H(32)	0.84 (2)
C(3)–H(33)	0.95 (3)	N(3)–H(3)	0.93 (2)
C(5)–H(5)	1.00 (2)	C(5)–C(6)	1.467 (4)
C(5)–C(7)	1.502 (4)	C(6)–H(61)	0.91 (3)
C(6)–H(62)	0.85 (3)	C(6)–H(63)	1.06 (3)
C(7)–H(71)	0.93 (3)	C(7)–H(72)	1.06 (2)
C(7)–H(73)	1.09 (3)		
O(4)–C(5)–C(6)	109.1 (4)	O(4)–C(5)–C(7)	106.2 (3)
C(6)–C(5)–C(7)	113.0 (4)		

the (unconventional) numbering scheme already adopted in several preceding articles (*e.g.* Chiari, Viterbo, Gaetani Manfredotti & Guastini, 1975) and the more relevant bond distances and angles; the values not displayed appear in Table 2.

**Discussion.** The furazan ring is strictly planar and also the group N(3)C(4)O(3)O(4)C(5) forms a plane with a maximum deviation of 0.007 (2) Å; the two mean planes make an angle of 7.3 (2)°. Atom N(3) is 0.012 (1) Å out of the furazan ring and C(2) is

–0.047 (2) Å below the carbamate-group plane. The mutual orientation of these two moieties would then be consistent with conjugation; however, the dimensions of the furazan ring do not reveal the presence of this effect despite bond C(2)–N(3), 1.376 (4) Å, being shorter than the normal  $C_{sp^2}$ –N single-bond value, 1.41–1.43 Å (*e.g.* Service d'Analyse, Bordeaux, 1976; Ganis, Avitabile, Migdal & Goodman, 1971). The shortening may be attributed to the marked withdrawing power of the N–O–N fragment of furazan, already noted (Messmer & Palenik, 1971; Calleri, Chiari & Viterbo, 1978). The fragment N(1)C(1)–C(2)N(2) shows the  $\pi$  delocalization characteristic of all the furazans (Table 3): the bond orders of the two C=N and of the C(1)–C(2) bonds are approximately 70 and 45% respectively (Cameron & Prout, 1969, and references therein). An appreciable degree of delocalization may be noted as well through the planar group C(2)N(3)C(4)O(4) where the N–C lengths are both shorter than the expected single-bond value and, moreover, closer to each other than in similar groups (Ganis *et al.*, 1971; Service d'Analyse, Bordeaux, 1976). The conformation of the carbamate function is altogether comparable with that of the isomers of isopropyl methylfuroxancarbamate and the same considerations apply to all three compounds (Calleri *et al.*, 1977). In the present furazan the intramolecular separation N(2)···O(3) is 2.765 (3) Å and therefore shorter than the sum of the van der Waals radii. The only intermolecular interaction worth noting is: N(3)( $x, \frac{1}{2} - y, \frac{1}{2} + z$ )···O(3) = 2.933 (3); H(3)( $x, \frac{1}{2} - y, \frac{1}{2} + z$ )···O(3) = 2.01 (2) Å. The packing is very reminiscent of that in the corresponding higher-melting furoxan isomer, but is more open here, as revealed by the lower density, 1.27 against 1.35 Mg m<sup>-3</sup>.

Table 3 shows the dimensions of the furazan rings of the disubstituted derivatives investigated so far. For 3-amino-4-methylfuroxan the averaged values are given

Table 3. Relevant bond distances (Å) and angles (°) of furazan and of CH<sub>3</sub>–(C<sub>2</sub>N<sub>2</sub>O)–R' derivatives

E.s.d.'s are 0.002–0.004 Å for bonds and 0.2–0.4° for angles.

	Furazan <sup>(1)</sup>	Amino <sup>(2)</sup>	Dimethyl-aminocarbonyl <sup>(3)</sup>	Carbo-hydrizide <sup>(4)</sup>	Isopropyl carbamate <sup>(5)</sup>	Tolyl-sulphonyl <sup>(6)</sup>
C(1)–C(2)	1.421	1.427	1.421	1.439	1.429	1.422
C(1)–N(1)	1.300	1.287	1.306	1.307	1.298	1.298
C(2)–N(2)	1.300	1.297	1.301	1.299	1.304	1.294
N(1)–O(1)	1.380	1.380	1.384	1.389	1.377	1.392
N(2)–O(1)	1.380	1.405	1.382	1.376	1.392	1.359
C(1)–C(3)	—	1.486	1.484	1.478	1.470	1.486
C(1)–C(2)–N(2)	109.0	109.7	110.0	109.9	110.1	110.6
C(2)–C(1)–N(1)	109.0	109.0	108.4	107.6	107.9	107.7
C(1)–N(1)–O(1)	105.6	106.5	105.6	106.2	106.7	105.5
C(2)–N(2)–O(1)	105.6	104.8	104.9	105.5	104.6	104.8
N(1)–O(1)–N(2)	110.4	110.0	111.0	110.8	110.6	111.3

References: (1) Sægebarth & Cox (1965); (2) Viterbo & Serafino (1978); (3) Chiari *et al.* (1975); (4) Gaetani Manfredotti, Guastini, Calleri & Viterbo (1976); (5) present work; (6) Calleri, Chiari, Chiesi Villa & Guastini (1976).

of the two independent molecules in the asymmetric unit (Viterbo & Serafino, 1978). It is clear that furazan itself and its derivatives are quite similar as regards the group N(1)C(1)C(2)N(2). Also, the angle C(1)–C(2)–N(2) takes a value close to  $110^\circ$  irrespective of the  $R'$  substituent; the angle C(1)–C(2)–N(2) too is nearly constant, but closer to  $108^\circ$ , the ideal value in a regular pentagon. The cause of this modest angular deformation is not apparent; it does not appear to correlate either with the asymmetry of the N–O bonds or with the C(1)–C(3) lengths. Cady, Larson & Cromer (1966), from the results for benzotrifuroxan, deduced that the length N–O = 1.384 (7) Å corresponds to a bond order of 1.03. Hence we may assume that most of the N–O bonds of Table 3 show the expected single-bond value; moreover, the mean value of the angle at O(1),  $110.7(2)^\circ$ , is close to that for  $O(sp^3)$ . Nonetheless the bonds are asymmetric, excepting the dimethylaminocarbonyl derivative; this is surprising in view of the absence of appreciable conjugation between the furazan ring and the  $R'$  substituents. Seemingly the N–O lengths are much more sensitive to their environment than the others, as noted also in several fused-ring furazans by Cameron & Prout (1969). In fact, as illustrated in the articles cited in Table 3, N(2) is involved in intra- and intermolecular interactions in the structures of the carbamate and sulphonyl derivatives which reduce to a weak intermolecular hydrogen interaction in the case of the nevertheless significantly asymmetric amino compound. Such interactions are absent in the much more symmetric molecules of the dimethylaminocarbonyl and carbonylhydrazide derivatives.

In the literature we found just one example of furazan disubstituted symmetrically which, in contrast, shows a most asymmetric ring as regards both the bonds and the angles: the diphenyl derivative (Mellini & Merlino, 1976). The authors attribute the effect to electron drift from the furazan ring towards one of the phenyl groups, the two rings making an angle of  $19^\circ$ . This would be very surprising because of the repeatedly noted electron-withdrawing power of furazan and, moreover, because the angles *and* the bonds do not

seem to comply entirely with the rules of Domenicano, Vaciego & Coulson (1975). Therefore we did not include in Table 3 the results for this structure, which seemed otherwise very interesting and worth an accurate redetermination.

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