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3-Amino-4-methylfurazan

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Abstract. $C_3H_5N_3O$, monoclinic, $P2_1/c$, a = 10·968 (2), b = 10·648 (2), c = 8·216 (1) Å, β = 92·72 (1)°; Z = 8, D_c = 1·37 g cm^{-3}; m.p. 72–73°C. The compound was prepared [Cusmano & Tiberio (1951). *Gazz. Chim. Ital.* **81**, 106–116] and crystallized from water as prismatic crystals. The two independent molecules do not show significant geometrical differences. The five-membered rings are asymmetrical as a consequence of a significant difference between the two N—O bonds.

Introduction. The present structural analysis was undertaken as part of an extensive study of the structural properties of disubstituted furoxans and furazans. In particular, after analyzing several compounds with electron-withdrawing substituents, we are now turning our attention to some electron-donor substituents such as the NH_2 group.

The cell parameters were determined and refined from diffractometer data. The systematic absence of reflexions $0k0$ with k odd and $h0l$ with l odd uniquely indicated the space group $P2_1/c$, with two independent molecules in the asymmetric part of the unit cell. The intensities of 1418 independent reflexions were measured at room temperature, on a Philips PW 1100 four-circle diffractometer (graphite-monochromatized Cu $K\alpha$ radiation) using the θ–2θ scanning technique; 423 reflexions with $I \leq 2\sigma(I)$ were considered as unobserved and not used for the refinement.

The solution was found using the program *MULTAN* (Declercq, Hull, Germain, Lessinger, Main & Woolfson, 1976); with 200 E's ($E_{\min}$ = 1·47) and 2000 $\sum_2$ relationships, 16 sets of phases were generated.

The E map computed with the set having the best figures of merit revealed all 14 non-hydrogen atoms, whose positions and individual isotropic temperature factors were initially refined by three full-matrix least-squares cycles. The H atoms were located on a difference map computed after three further anisotropic cycles. Attempts at isotropically refining the H atoms with no constraint caused them to drift from their stereochemically plausible positions. Using the *SHELX* system of programs (Sheldrick, 1976), the C—H, N—H and H—H distances were then constrained to their normal values; the final cycles with anisotropic temperature factors assigned to all non-hydrogen atoms converged to an R value of 0·053 (R value for all 1418 measured data: 0·078). The weighting scheme was $w = 1/[\sigma^2(F_o) + aF_o^2]$, where $\sigma(F_o)$ is the estimated standard deviation of the observed amplitudes as derived from counting statistics and a is a variable parameter to be adjusted after each cycle; its final value was a = 0·03 and the final weighted R factor was 0·061. The atomic parameters for both molecules in the asymmetric unit are given in Table 1.* Fig. 1 shows the projections of the molecules on their mean planes through the furazan rings, together with the unconventional numbering scheme already adopted in preceding articles (*e.g.* Calleri, Chiari, Chiesi Villa, Gaetani Manfredotti, Guastini & Viterbo, 1975, 1976), and some bond distances and angles; the bond angles not displayed appear in Table 2.

Discussion. In both molecules the five-membered ring is planar, the average distance from the two planes being 0·002 and 0·003 Å. On considering the two extranuclear O and N atoms, only molecule I remains significantly planar. In fact N(3′) is –0·039 Å out of the furazan plane of molecule II, where the amino group assumes a slightly pyramidal configuration. In both molecules the NH_2 group is rotated with respect to the furazan ring; the dihedral angles are 11·5 and 24° in molecules I and II respectively.

A comparison of bond distances and angles in the two independent molecules shows that there are no outstanding differences. The only possibly significant discrepancies concern bonds C(1)–N(1) and C(2)–N(3) and the two external angles at C(2). These and the above-mentioned conformational differences, may be explained by the rather different packing of the two molecules.

Fig. 2 shows that the molecules are packed in layers normal to the *x* axis. Each layer has a ‘sandwich’ structure with two sublayers of molecules I in the middle and one of molecules II above and below. The molecules within each ‘sandwich’ are connected by weak hydrogen interactions linking molecules I both to molecules I [N(3)–H(5)···O(1) = 3·045 Å] and to molecules II [N(3)–H(4)···N(2′) = 3·077 Å, N(3′)–H(5′)···N(2) = 3·133 Å, N(3′)–H(4′)···N(1) = 3·176 Å]. The interactions in which N(3) is involved are relatively stronger, and this may explain most of the differences between the two molecules. Along *x*, the layers are connected only by van der Waals interactions.

Table 1. *Final fractional atomic coordinates and isotropic temperature factors of the* H *atoms, with e.s.d.’s in parentheses*

Molecule I

	x	*y*	*z*	*U* (Å²)
C(1)	0·6955 (3)	0·5298 (2)	0·9537 (4)	
C(2)	0·6042 (3)	0·6041 (3)	0·8706 (4)	
C(3)	0·7968 (3)	0·5745 (3)	1·0659 (4)	
N(1)	0·6773 (2)	0·4140 (2)	0·9171 (3)	
N(2)	0·5311 (2)	0·5323 (3)	0·7832 (4)	
N(3)	0·5908 (3)	0·7288 (3)	0·8798 (5)	
O(1)	0·5762 (2)	0·4104 (2)	0·8106 (3)	
H(1)	0·849 (4)	0·512 (4)	1·113 (6)	0·123 (7)
H(2)	0·842 (4)	0·644 (4)	1·020 (5)	0·123 (7)
H(3)	0·764 (4)	0·613 (4)	1·163 (5)	0·123 (7)
H(4)	0·650 (3)	0·778 (3)	0·922 (4)	0·080 (6)
H(5)	0·530 (3)	0·770 (3)	0·834 (5)	0·080 (6)

Molecule II

	x	*y*	*z*	*U* (Å²)
C(1′)	0·8792 (2)	0·0886 (3)	0·1187 (4)	
C(2′)	0·7777 (2)	0·0452 (3)	0·0188 (3)	
C(3′)	0·0209 (4)	0·2202 (3)	0·1430 (5)	
N(1′)	0·9341 (2)	–0·0069 (2)	0·1863 (3)	
N(2′)	0·7712 (2)	–0·0762 (2)	0·0274 (3)	
N(3′)	0·7013 (3)	0·1168 (2)	–0·0752 (4)	
O(1′)	0·8691 (2)	–0·1117 (2)	0·1342 (3)	
H(1′)	0·991 (3)	0·226 (4)	0·215 (5)	0·123 (7)
H(2′)	0·936 (4)	0·252 (4)	0·030 (4)	0·123 (7)
H(3′)	0·862 (4)	0·276 (4)	0·194 (5)	0·123 (7)
H(4′)	0·702 (3)	0·196 (3)	–0·059 (4)	0·080 (6)
H(5′)	0·635 (3)	0·078 (3)	–0·113 (4)	0·080 (6)

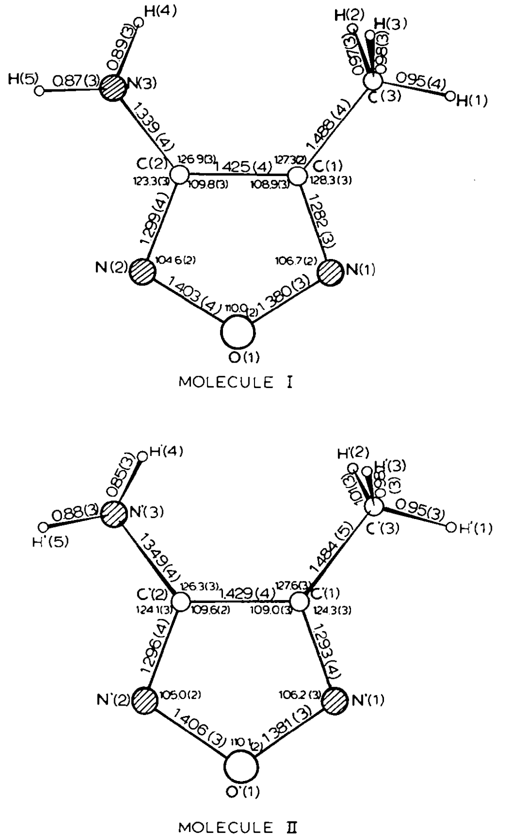

Fig. 1. Projection of the two independent molecules on the planes of their respective furazan rings, showing the unconventional numbering scheme and some bond distances and angles (standard deviations in parentheses).

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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 33744 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

Molecule I		Molecule II	
C(1)–C(3)–H(1)	117 (3)	C(1′)–C(3′)–H(1′)	113 (3)
C(1)–C(3)–H(2)	112 (3)	C(1′)–C(3′)–H(2′)	105 (3)
C(1)–C(3)–H(3)	110 (3)	C(1′)–C(3′)–H(3′)	115 (3)
H(1)–C(3)–H(2)	112 (4)	H(1′)–C(3′)–H(2′)	113 (4)
H(1)–C(3)–H(3)	102 (3)	H(1′)–C(3′)–H(3′)	103 (4)
H(2)–C(3)–H(3)	102 (3)	H(2′)–C(3′)–H(3′)	109 (4)
C(2)–N(3)–H(4)	122 (2)	C(2′)–N(3′)–H(4′)	118 (3)
C(2)–N(3)–H(5)	124 (2)	C(2′)–N(3′)–H(5′)	115 (3)
H(4)–N(3)–H(5)	113 (3)	H(4′)–N(3′)–H(5′)	122 (3)

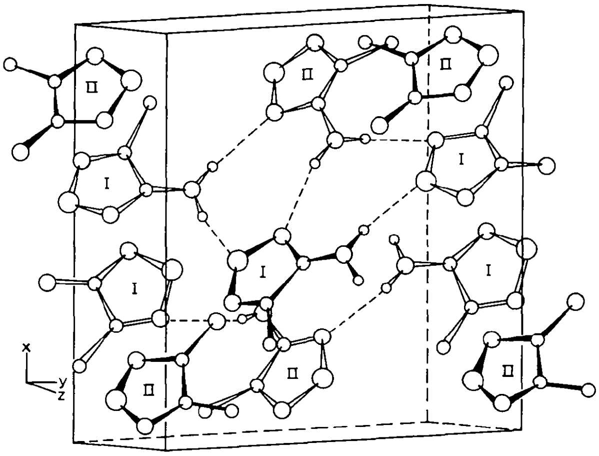

Fig. 2. Clinographic projection, along the *z* axis, of the content of a unit cell, showing the packing of the molecules.

As far as the five-membered ring is concerned, we notice that the geometry of the N(1)–C(1)–C(2)–N(2) fragment, where π-delocalization is present, is here, as in other furazans we have analyzed (Chiari, Viterbo, Gaetani Manfredotti & Guastini, 1975; Calleri, Chiari, Chiesi Villa & Guastini, 1976; Gaetani Manfredotti, Guastini, Calleri & Viterbo, 1976), very close to that of furazan itself (Cox & Saegebarth, 1965).

Bonds N(1)–O(1) and N(2)–O(1) differ significantly, the difference being 0·023 Å in molecule I and 0·025 Å in molecule II. The mirror symmetry of the five-membered rings is lost as a consequence of the lengthening of the N(2)–O(1) bond.

In both molecules the C(2)–N(3) bond is considerably shorter than C_{sp^2}–N and also shorter than the corresponding C–N bond in isopropyl *N*-(4-methyl-3-furazanyl)carbamate (results to be published) of 1·376 Å, and in the related furoxan isomers (Calleri, Chiari, Chiesi Villa, Gaetani Manfredotti, Guastini & Viterbo, 1977) (1·382 and 1·391 Å). The C–NH_2 bond is shorter in molecule I where the amino group forms a smaller angle with the furazan plane and does not assume a pyramidal configuration.

A comparison of the structures of all the furazan derivatives so far analysed will be given in a following paper on the structure of isopropyl *N*-(4-methyl-3-furazanyl)carbamate, with an attempt at correlating some of the results described above.

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