

## Crystal and Molecular Structure of 3-Methyl-4-nitrofuoxan, C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>O<sub>4</sub>

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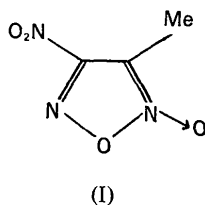
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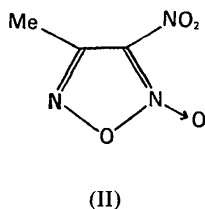
The structure of the title compound has been determined by single-crystal X-ray analysis. The crystals are orthorhombic, space group  $P2_12_12_1$ , with  $a = 7.010$  (1),  $b = 5.824$  (1),  $c = 14.225$  (2) Å,  $Z = 4$ . The structure was solved by direct methods from 471 independent data collected on a four-circle diffractometer, and has been refined by full-matrix least-squares calculations to  $R = 0.046$ . The ring system and its immediate neighbours are almost planar, with the nitro group twisted  $16.7^\circ$  about the C(4)–N(8) bond with respect to the ring plane. The N(2)–O(1) [1.479 (5) Å] is considerably longer than the N(5)–O(1) [1.367 (5) Å] bond, while the exocyclic N(2)–O(6) bond has a length of 1.220 (5) Å.

### Introduction

The preparation and properties of methylnitrofuoxan have been described by several groups of workers. A recent synthesis (Nikolaeva *et al.*, 1972) is based on the reaction between a dichloroethane solution of methacrylic acid and sodium nitrate dissolved in sulphuric acid. The product, obtained as colourless crystals, m.p.  $67\text{--}68^\circ$ , was formulated as 3-methyl-4-nitrofuoxan (I).



An earlier but somewhat similar synthetic route (Levy & Scaife, 1946), in which propylene is treated with dinitrogen trioxide, also results in colourless crystals, m.p.  $67\text{--}69^\circ$ , which were formulated as the isomeric product 4-methyl-3-nitrofuoxan (II).



The compounds resulting from both synthetic routes are identical, although in each case either isomer could plausibly have been produced. Moreover, it did not prove possible to distinguish unambiguously between the two structural possibilities by spectroscopic techniques.

We therefore undertook a single-crystal X-ray analysis of the crystalline material resulting from the syn-

thetic route devised by Nikolaeva and coworkers, and have shown unambiguously that the compound is 3-methyl-4-nitrofuoxan (I).

### Experimental

#### Crystal data

3-Methyl-4-nitrofuoxan, C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>O<sub>4</sub>,  $M = 145.1$ . Orthorhombic,  $a = 7.010$  (1),  $b = 5.824$  (1),  $c = 14.225$  (2) Å,  $U = 580.8$  Å<sup>3</sup>,  $D_m = 1.62$  g cm<sup>-3</sup> (by flotation),  $Z = 4$ ,  $D_c = 1.66$  g cm<sup>-3</sup>,  $F(000) = 296$ . Space group  $P2_12_12_1$  ( $D_2^4$ ). Mo  $K\alpha$  radiation,  $\lambda = 0.7170$  Å,  $\mu(\text{Mo } K\alpha) = 1.67$  cm<sup>-1</sup>.

#### Crystallographic measurements

The unit-cell parameters were initially determined photographically, and were subsequently refined by least-squares techniques prior to the diffractometer data collection. The systematic absences in the  $h00$ ,  $0k0$  and  $00l$  spectra uniquely define the space group as  $P2_12_12_1$ .

Intensity measurements were made on a Hilger and Watts Y 290 diffractometer. A small crystal, mounted about  $b$ , was exposed to Zr-filtered Mo  $K\alpha$  radiation, and 471 ( $I \geq 3\sigma_I$ ) independent reflexions were measured by the  $\theta\text{--}2\theta$  scan technique in the range  $2\theta = 0\text{--}50^\circ$ . The intensities were corrected for Lorentz and polarization effects, but absorption effects were considered small and were therefore ignored.

#### Structure determination and refinement

The structure was solved by the symbolic addition method with programs incorporated into the X-RAY 70 suite of programs. An initial  $E$  map based on 80 reflexions ( $E \geq 1.40$ ) completely revealed the structure, and a preliminary refinement was effected by two rounds of structure-factor and electron-density calculations in which an overall isotropic vibration parameter  $U_{\text{iso}} = 0.05$  Å<sup>2</sup> was assumed.

The positional, vibrational and overall-scale parameters were then refined by full-matrix least-squares calculations which converged after 10 cycles when  $R$  was

0.046. A difference synthesis had revealed the three methyl-hydrogen atoms. Positional and isotropic vibrational parameters for these were refined in subsequent cycles. Throughout the refinement it was not found necessary to apply weights other than unity.

On convergence of the least-squares refinement, the evaluation of electron-density and difference syntheses

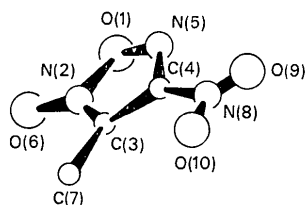


Fig. 1. A view of one molecule showing the atomic numbering.

revealed no errors in the structure, and the refinement was therefore considered complete.\* Full details of the least-squares strategy are given in Table 1. Final fractional coordinates and thermal parameters appear in Table 2, while Table 3 contains all bond lengths, inter-bond angles, and pertinent intra- and intermolecular non-bonded distances. The estimated standard deviations, given in parentheses in Tables 2 and 3, are derived from the inverse of the least-squares normal-equation matrix, and are best regarded as minimum values. Table 4 contains details of mean-plane calculations.

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30237 (3 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Course of refinement*

Cycles	Parameters refined	Final <i>R</i>
1—3	$x, y, z, U_{iso}$ for O, N, C, overall scale-factor. Full matrix, unit weights	0.098
4—6	$x, y, z, U_{ij}$ for O, N, C, overall scale-factor. Full matrix, unit weights, hydrogen atom contributions included but not refined	0.051
7—10	$x, y, z, U_{ij}$ for O, N, C, $x, y, z, U_{iso}$ for H, overall scale factor. Full matrix, unit weights	0.046

Table 2. *Atomic parameters*

(a) Fractional coordinates and isotropic thermal parameters ( $\text{\AA}^2$ ).

	$x/a$	$y/b$	$z/c$	$U_{iso}$
O(1)	-0.02967 (51)	0.57793 (63)	0.14057 (25)	
N(2)	0.13317 (56)	0.67483 (72)	0.19339 (28)	
C(3)	0.19312 (67)	0.85913 (77)	0.14649 (31)	
C(4)	0.07313 (68)	0.86699 (76)	0.06781 (30)	
N(5)	-0.05521 (62)	0.70933 (76)	0.06193 (28)	
O(6)	0.17988 (54)	0.57815 (67)	0.26593 (25)	
C(7)	0.35613 (94)	0.99605 (89)	0.18065 (43)	
N(8)	0.08039 (60)	1.03808 (74)	-0.00695 (27)	
O(9)	0.16997 (62)	1.21233 (65)	0.00907 (29)	
O(10)	-0.00206 (57)	0.99275 (70)	-0.08045 (23)	
H(1)	0.403 (8)	0.947 (11)	0.239 (4)	0.063 (24)
H(2)	0.457 (9)	0.994 (11)	0.146 (4)	0.045 (21)
H(3)	0.321 (10)	1.134 (11)	0.194 (4)	0.047 (22)

(b) Anisotropic thermal parameters for non-hydrogen atoms ( $\text{\AA}^2$ ).

	$U_{11}$	$U_{22}$	$U_{33}$	$2U_{12}$	$2U_{13}$	$2U_{23}$
O(1)	0.0549	0.0572	0.0708	-0.0205	0.0012	0.0025
N(2)	0.0385	0.0511	0.0524	0.0021	0.0039	0.0013
C(3)	0.0360	0.0384	0.0453	0.0003	0.0090	0.0008
C(4)	0.0369	0.0412	0.0393	0.0017	0.0014	-0.0035
N(5)	0.0521	0.0608	0.0527	-0.0089	-0.0036	-0.0016
O(6)	0.0684	0.0679	0.0563	-0.0015	0.0007	0.0253
C(7)	0.0507	0.0635	0.0510	-0.0133	-0.0080	0.0008
N(8)	0.0431	0.0526	0.0487	0.0110	-0.0002	-0.0015
O(9)	0.0839	0.0509	0.0636	-0.0072	-0.0139	0.0081
O(10)	0.0744	0.0752	0.0486	0.0053	-0.0180	0.0090

Average e.s.d.'s for anisotropic thermal parameters.

	$U_{11}$	$U_{22}$	$U_{33}$	$2U_{12}$	$2U_{13}$	$2U_{23}$
O	0.0025	0.0024	0.0021	0.0024	0.0021	0.0021
N	0.0025	0.0025	0.0023	0.0024	0.0021	0.0022
C	0.0029	0.0029	0.0026	0.0027	0.0025	0.0025

Table 3. Bonded distances (Å), interbond angles (°), and pertinent intra- and intermolecular non-bonded distances (Å)

(a) Bonded distances (Å)			
O(1)–N(2)	1.479 (5)	C(3)–C(7)	1.476 (8)
O(1)–N(5)	1.367 (5)	C(4)–N(5)	1.288 (6)
N(2)–C(3)	1.332 (6)	C(4)–N(8)	1.458 (6)
N(2)–O(6)	1.220 (5)	N(8)–O(9)	1.223 (5)
C(3)–C(4)	1.401 (6)	N(8)–O(10)	1.215 (6)
Average C–H distance 0.89 (6) Å			
(b) Interbond angles (°)			
N(2)O(1)N(5)	107.7 (3)	C(3)C(4)N(5)	116.6 (4)
O(1)N(2)C(3)	107.3 (4)	C(3)C(4)N(8)	125.7 (4)
O(1)N(2)O(6)	117.4 (4)	N(5)C(4)N(8)	117.7 (4)
C(3)N(2)O(6)	135.3 (4)	O(1)N(5)C(4)	104.7 (4)
N(2)C(3)C(4)	103.7 (4)	C(4)N(8)O(9)	117.3 (4)
N(2)C(3)C(7)	120.9 (4)	C(4)N(8)O(10)	116.9 (4)
C(4)C(3)C(7)	135.3 (5)	O(9)N(8)O(10)	125.8 (4)
Average C–C–H angle 113 (4)°			
Average H–C–H angle 105 (6)°			
(c) Pertinent intramolecular non-bonded distances < 3.45 Å			
O(6)···C(7)	2.99		
C(3)···O(10)	2.84		
C(7)···O(10)	3.04		
N(5)···O(9)	3.41		
(d) Some intermolecular distances < 3.40 Å			
N(5)···O(9 <sup>i</sup> )	3.38 Å		
N(9)···O(1 <sup>ii</sup> )	3.40		
N(5)···O(9 <sup>ii</sup> )	3.28		
N(5)···O(10 <sup>ii</sup> )	3.36		
N(2)···O(10 <sup>iii</sup> )	3.17		
C(3)···O(10 <sup>iii</sup> )	3.11		
C(7)···O(10 <sup>iii</sup> )	3.34		
C(4)···N(5 <sup>iii</sup> )	3.22		
N(8)···N(5 <sup>iii</sup> )	3.02		
O(6)···O(1 <sup>iv</sup> )	3.37		
N(2)···O(6 <sup>v</sup> )	3.27		
N(5)···O(6 <sup>v</sup> )	3.37		
C(4)···O(6 <sup>v</sup> )	3.20		
C(3)···O(6 <sup>v</sup> )	3.17		
C(3)···O(6 <sup>v</sup> )	3.37		

Superscripts refer to the following transformations which should be applied to the coordinates of the second atom.

i	$x$	$-1+y$	$z$
ii	$-\frac{1}{2}+x$	$\frac{3}{2}-y$	$-z$
iii	$\frac{1}{2}+x$	$\frac{3}{2}-y$	$-z$
iv	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
v	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$

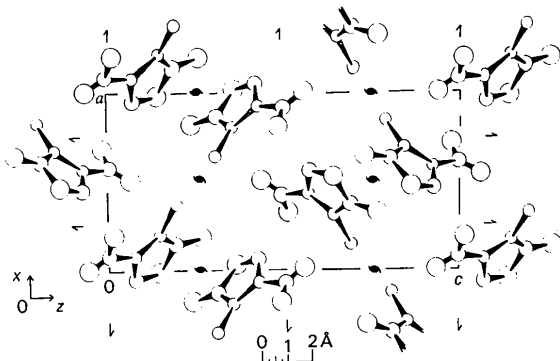
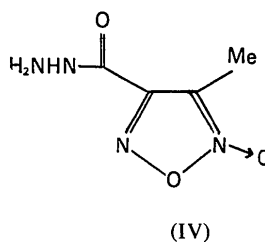
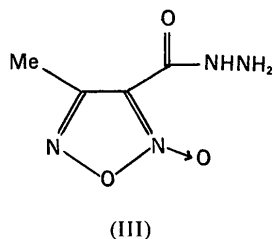


Fig. 2. The molecular packing viewed down *b*,

The atomic numbering is given in Fig. 1, and the molecular packing viewed down *b* is illustrated in Fig. 2.

### Discussion

The dimensions of the furoxan ring in (I) may be compared with those of the similar derivatives (III) (Calleri, Chiari & Viterbo, 1972) and (IV) (Germain & Viterbo, 1972).



A common feature of all three molecules is that the O(1)–N(2) bonds are longer than the O(1)–N(5) bonds. However, the O(1)–N(2) bond in (I) [1.479 (5) Å] appears to be slightly longer than the corresponding bonds in both (III) [1.427 (3) Å] and (IV) [1.450 (5) Å], although the N(2)–O(6) bonds [1.220 (5) Å in (I); 1.231 (3) Å in (III); 1.229 (4) Å in (IV)] and N(2)–C(3) bonds [respectively 1.332 (6), 1.326 (4) and 1.317 (4) Å] are very similar in all three molecules. Moreover, although the O(1)–N(5) bond in (III) [1.388 (4) Å] is significantly longer than in (IV) [1.358 (3) Å], the value observed in (I) is not significantly different from either. It may be concluded, therefore, that with the exception of the detailed differences mentioned above, the bonds within the furoxan rings of (I), (III) and (IV) do not differ markedly, and that in each case the dimensions are consistent with a degree of electron-delocalization throughout the ring systems. The exocyclic C(4)–N(8) bond [1.458 (6) Å] of (I), which links the nitro group to the ring system, is not unduly short, and suggests only limited delocalizing interaction between the  $\pi$ -bond systems of the ring and nitro moieties. This observation is consistent with the lengths of the exocyclic C–C bonds in (III) [1.480 (4) Å] and (IV) [1.492 (4) Å] which link the rings and the carboxy-hydrazide functions. It may be noted that although the furoxan ring of (I) is approximately planar and also coplanar with its immediate substituents (Table 4), the nitro group is inclined at an angle of 16.7° to the ring system.

Table 4. *Least-squares planes for (I) in the form  $lX' + mY' + nZ' = d$ , where  $X'$ ,  $Y'$  and  $Z'$  are coordinates in Å with respect to the unit-cell axial system*

(a) Plane equations.

$$\begin{array}{l} \text{Plane 1:} \quad 0.6362X' - 0.5798Y' - 0.5091Z' = -3.0938 \\ \text{Plane 2:} \quad -0.8300X' + 0.4351Y' + 0.3491Z' = 2.1279 \end{array}$$

(b) Distances (Å) of atoms from planes. Starred atoms not used to define planes.

Plane 1:	O(1)	-0.0078	N(2)	+0.0088	C(3)	-0.0066
	C(4)	+0.0015	N(5)	+0.0041		
	O(6)*	+0.0182	C(7)	*+0.0108	N(8)	*-0.0024
Plane 2:	N(8)	0.0000	O(9)	0.0000	O(10)	0.0000
	C(4)*	-0.0199				

(c) Dihedral angle (°) between planes.

$$\angle 12 \quad 16.7^\circ$$

All three molecules show considerable valence-angle distortions, and although there are minor differences between the individual values of corresponding angles within each molecule, which probably arise from the different steric requirements of nitro, methyl and carboxyhydrazide substituents in rearranged positions, the general trends observed in (I) are repeated in (III) and (IV). The endocyclic valence angles of the furazan ring of (I) lie within the range  $103.7$  ( $4^\circ$ ) [at C(3)] to  $116.6$  ( $4^\circ$ ) [at C(4)], the mean value being  $108.0^\circ$ . Slightly narrower ranges are observed for (III) [ $106.7$ – $110.9^\circ$ ] and (IV) [ $105.9$ – $111.9^\circ$ ], although the minimum and maximum values also occur at C(3) and C(4) respectively. The exocyclic valence angles are also of some interest. Thus in (I) varying degrees of expansion [C(3)N(2)O(6)  $135.3$  ( $4^\circ$ ), C(4)C(3)C(7)  $135.3$  ( $5^\circ$ ), C(3)C(4)N(8)  $125.7$  ( $4^\circ$ )] and contraction [O(1)N(2)O(6)  $117.4$  ( $4^\circ$ ), N(5)C(4)N(8)  $117.7$  ( $4^\circ$ )] are observed, while the angle C(2)C(3)C(7) has a value of  $120.9$  ( $4^\circ$ ). All such distortions are in accord both with the requirements of a planar five-membered ring, and also with the relief of steric strain between adjacent substituents. Thus the nitro and methyl groups are effectively moved apart [C(7)···N(8)  $3.30$  Å, C(7)···O(10)  $3.04$  Å], as are the methyl group and the exocyclic oxygen atom [C(7)···O(6)  $2.99$  Å]. The twisting of the nitro group from the plane of the ring also helps to reduce severe interaction.

The shortest intermolecular distance [ $3.02$  Å] separates N(8) and N(5) of adjacent molecules, while the exocyclic oxygen atom O(6) of one molecule is in close proximity [ $3.17$ – $3.37$  Å] to the ring atoms of another neighbouring molecule. The calculated density of (I) is  $1.66$  g cm $^{-3}$  which compares with values of  $1.59$  g cm $^{-3}$  and  $1.58$  g cm $^{-3}$  for (III) and (IV) respectively.

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