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## Structures of Four Related 4,5,6,7-Tetrahydro-1,2,5-oxadiazolo[3,4-*b*]pyrazines

BY CHARLOTTE K. LOWE-MA,\* JOHN W. FISCHER AND RODNEY L. WILLER†

*Chemistry Division, Research Department, Naval Weapons Center, China Lake, California 93555, USA*

(Received 13 September 1988; accepted 8 December 1989)

**Abstract.** 4,5,6,7-Tetrahydro-1,2,5-oxadiazolo[3,4-*b*]pyrazine, (I),  $C_4H_6N_4O$ ,  $M_r = 126.12$ , monoclinic,  $P2_1/n$ ,  $a = 6.584$  (1),  $b = 7.105$  (1),  $c = 11.784$  (2) Å,  $\beta = 100.86$  (1)°,  $V = 541.4$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.55$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 1.11$  cm<sup>-1</sup>,  $F(000) = 264$ ,  $T = 291$  K,  $R = 0.040$  for 1415 reflections with  $|F_o| > 4\sigma(F)$ . 4,7-Dinitroso-4,5,6,7-tetrahydro-1,2,5-oxadiazolo[3,4-*b*]pyrazine, (II),  $C_4H_4N_6O_3$ ,  $M_r = 184.12$ , orthorhombic,  $P2_12_12_1$ ,  $a = 6.151$  (1),  $b = 9.526$  (2),  $c = 12.573$  (2) Å,  $V = 736.6$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.66$  g cm<sup>-3</sup>,  $\lambda(Cu K\alpha) = 1.54178$  Å,  $\mu = 12.03$  cm<sup>-1</sup>,  $F(000) = 376$ ,  $T = 291$  K,  $R = 0.044$  for 901 reflections with  $|F_o| > 4\sigma(F)$ . 4-Nitroso-4,5,6,7-tetrahydro-1,2,5-oxadiazolo[3,4-*b*]pyrazine, (III),  $C_4H_5N_5O_2$ ,  $M_r = 155.12$ , monoclinic,  $P2_1/c$ ,  $a = 6.278$  (1),  $b = 9.902$  (2),  $c = 10.650$  (2) Å,  $\beta = 106.02$  (2)°,  $V = 636.4$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.62$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 1.25$  cm<sup>-1</sup>,  $F(000) = 320$ ,  $T = 291$  K,  $R = 0.046$  for 1126 reflections with  $|F_o| > 4\sigma(F)$ . 4,7-Dinitroso-4,5,6,7-tetrahydro-1,2,5-oxadiazolo[3,4-*b*]pyrazine, (IV),  $C_4H_4N_6O_5$ ,  $M_r = 216.11$ , monoclinic,  $P2_1/c$ ,  $a = 9.743$  (4),  $b = 6.636$  (2),  $c = 12.165$  (4) Å,  $\beta = 94.22$  (3)°,  $V = 784.4$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.83$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 1.57$  cm<sup>-1</sup>,  $F(000) = 440$ ,  $T = 291$  K,  $R = 0.055$  for 1412 reflections with  $|F_o| > 4\sigma(F)$ . The molecular geometries of all four compounds are very similar. The furazan moiety is planar and shortening of the C—N bonds to the piperazine nitrogen caused by ring fusion is

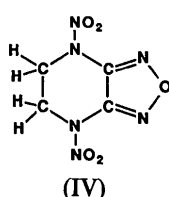
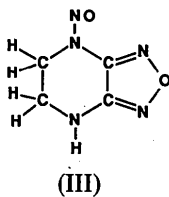
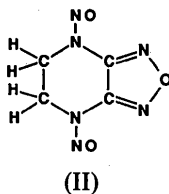
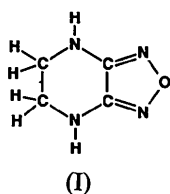
observed. All four molecules exhibit twisting about the bond between the two methylene carbons to achieve a distorted conformation in the six-membered ring. In (I) and (IV) coordination about the piperazine nitrogen is pyramidal whereas in (II) the coordination about the piperazine nitrogen becomes planar owing to the nitrosamine groups. The mononitrosamine (III) exhibits disorder in the rings that may be due to synchronous ring twists as well as exhibiting rotational disorder of the nitrosamine group. (II) exhibits no disorder of the nitrosamine groups. Molecules of (I) link together with hydrogen bonding to form chains. (III) crystallizes as hydrogen-bonded dimers. Only one form of the nitramine (IV) could be obtained as crystals suitable for a structure determination.

**Introduction.** Although the furazan (1,2,5-oxadiazolo) moiety is well-known in the literature (Boyer, 1986), few studies of compounds with furazan rings fused to saturated heterocyclic rings have been reported. As little is known about molecular geometry and conformation of these types of compounds, four related furazanopiperazines (4,5,6,7-tetrahydro-1,2,5-oxadiazolo[3,4-*b*]pyrazines) (I)–(IV), are reported here. However, the dinitro derivative, (IV), is of particular interest. Empirical density calculations (Cichra, Holden & Dickinson, 1980) and empirical detonation velocity calculations (Rothstein & Petersen, 1979) predict that nitrated derivatives of heterocyclic rings fused to furazan moieties might be of interest as potential explosive or propellant ingredients. A very early structure determination of (IV), crystallized from acetone/water,

\* Author to whom requests for information should be sent.

† Present address: Morton Thiokol, Inc., Elkton Division, Elkton, Maryland 21921, USA.

was unsatisfactory; refinement never adequately converged. While the crystallographic work reported here was in progress, Oyumi, Rheingold & Brill (1986) initiated their thermal decomposition studies of (IV). They found spectroscopically that (IV) appeared to form polymorphs dependent on crystallization conditions. We have also confirmed spectroscopically and morphologically that (IV) appears to form solvent-dependent polymorphs. Although a crystal structure of (IV) has been reported by Oyumi, Rheingold & Brill (1986), because of the potential for polymorph formation and problems with our earlier structure determination of (IV), the crystal structure of (IV) is also reported here and compared with the structures of (I)–(III).



**Experimental.** The syntheses of (I) and (IV) have been described previously by Willer & Moore (1985). Colorless, elongated platelets of (I) were crystallized from acetone. Platelet faces are {001}; axis of elongation is [100]. The synthesis of (II) was accomplished by the dropwise addition of concentrated HCl to a stirred aqueous solution of 2.25:1 molar ratio sodium nitrate to (I) at 333 K. After stirring at 333 K for 50 min and cooling to 273 K for 45 min, the yellow solid was collected by suction filtration. Crystals of (II) were grown by slow evaporation from benzene. (III) is a decomposition product of (II). All attempts to crystallize (II) by slow growth from aqueous solutions resulted in partial hydrolysis with (III) crystallizing instead. From a solution of (II) in water, kept in the dark, pale-yellow crystals of (III) were obtained by slow evaporation. Major faces of (III) were {100} and {001}. Owing to solvent-dependent variation of crystal morphology and polymorphism (see also Oyumi, Rheingold & Brill, 1986), various crystal growths of (IV) were attempted. A much earlier structure determination on a tabular crystal of (IV) grown by slow evaporation from acetone/water was unsuccessful as least-squares refinement never adequately converged. The data reported here are for

a thin, elongated, colorless platelet of (IV) grown by rapid crystallization (~15 min) from spectral-quality nitromethane. Crystals of other, especially needle-like, forms were too small and unsuitable for data collection.

All data were obtained with a Nicolet R3 diffractometer. Intensity data for (I), (III) and (IV) were obtained with graphite-monochromated Mo  $K\alpha$ . Data for (II) were obtained with nickel-filtered Cu  $K\alpha$ . Unit-cell parameters were obtained from a symmetry-constrained least-squares fit of 25 computer-centered reflections with  $2\theta$  values ranging from 13 to 34° for (I), 12 to 37° for (IV), 8 to 40° for (III), and 18 to 96° (Cu  $K\alpha$ ) for (II). Data collected with  $2\theta/\theta$  scans;  $1^\circ < 2\theta(K\alpha_1)$  to  $1^\circ > 2\theta(K\alpha_2)$ ; ratio of total background time to scan time of 1.0. Additional experimental conditions are given in Table 1.

Absences observed on precession photographs of (I) agreed with absences observed in the diffractometer data,  $h0l$ ,  $h+l=2n+1$  and  $0k0$ ,  $k=2n+1$  absent, indicating  $P2_1/n$ . The space group for (II) was determined from systematic absences in the diffractometer data. Extensive photographic and diffractometer work were performed on (III) and (IV) to confirm their space groups while looking for other polymorphs of (IV) and the presence of compound (II) in batches of (III). Intensity data for all four compounds were corrected for Lorentz and polarization effects, but not for absorption. Equivalent reflections were merged and reflections with  $|F_o| > 4\sigma(F)$  were considered observed. Initial atomic coordinates for all four structures were taken from solutions obtained with the multi-solution methods of *SHELXTL* (Sheldrick, 1983).

Refinement was with the blocked-cascade algorithm of *SHELXTL* and minimization of  $[\sum w(|F_o| - k|F_c|)^2]$ ,  $w = 1/[\sigma^2(F) + GF^2]$  for  $G = 0.0008$ . Scattering factors internal to *SHELXTL* were used. After a few cycles of least-squares refinement, at  $R$  factors of 0.09–0.20, all H atoms were observed on difference Fourier maps. All C, N and O atoms in (I), (III) and (IV) were refined anisotropically. H atoms in (I), (III) and (IV) were refined isotropically without constraints. A parameter for extinction was included in the refinements of (I) and (IV). For (II), owing to a limited number of data, only N and O atoms were refined anisotropically; C atoms were refined isotropically. H atoms were constrained to 'ride' on the C atoms but without constraints on thermal parameters.

Although only one set of data is being reported here, three structure solutions (and refinements) for three crystals of (III) all indicated the presence of the same disorder. The disorder, implied in the electron density difference maps of (III), suggested displacement of O(1) in the furazan ring, displacement of N(2) in the piperazine ring, and rotation of the

Table 1. *Experimental conditions*

	(I)	(II)	(III)	(IV)
Crystal size (mm)	0.23 × 0.40 × 0.86	~0.04 × 0.08 × 0.56	0.38 × 0.24 × 0.54	0.08 × 0.28 × 0.52
2θ range for data collection (°)	4–60	4–111	4–55	4–60
Scan speed (2θ° min <sup>-1</sup> )	Variable, 3–6	Variable, 2–6	Variable, 3–6	Fixed, 3
Octants	$\bar{h}k\bar{l}, \bar{h}kl, h\bar{k}l, hkl$	$\bar{h}kl, hkl$	$\bar{h}k\bar{l}, \bar{h}kl, \bar{h}kl, hkl$	$h\bar{k}\bar{l}, hkl$
Range of indices min., max.	10,0,17; 10,10,17	7,0,0; 7,11,14	8,0,13; 8,12,13	0,0,18; 13,9,18
Check reflections	024, 109, 520	3,2,10, 086, 403	500, 114	311, 239
R(merge)	0.0201	0.0112	0.0286	0.0083
Unique reflections	1585	935	1463	2308
Number observed (with $ F_o  > 4\sigma_F$ )	1415	901	1126	1412
Number of parameters	107	102	169	153
R	0.040	0.044	0.046	0.055
wR*	0.062	0.068	0.057	0.065
GOF	1.77	2.16	1.48	1.46

$$*wR = \{[\sum w(F_o - F_c)^2] / \sum w(F_o)^2\}^{1/2}.$$

nitrosamine group about the N(1)—N(5) bond. Each disordered 'atom' was modelled as a pair of spatially separated atoms with the sum of the population for each pair constrained to 1.0; the thermal parameters were refined anisotropically without constraints. For the rotated nitrosamine group the relative populations of the two orientations for both N(5) and O(2) were tied together, *i.e.* the site occupancy factor for N(5a) equalled that of O(2a). Additional geometric (DFIX) constraints were also applied to all of the disordered atoms in (III); equivalent bonds were constrained to have equal numerical values. The two N(3)—O(1a,1b) distances were constrained to be equivalent and refined to a value of 1.409 (6) Å. The two N(4)—O(1a,1b) distances were constrained to be equivalent and refined to a value of 1.390 (6) Å. The C(2)—N(2a,2b) and C(4)—N(2a,2b) distances were similarly constrained and refined to values of 1.339 (4) and 1.458 (5) Å, respectively. The N(5a)—O(2a) and N(5b)—O(2b) distances were fixed at 1.18 Å. Additional three-atom distance constraints as required by DFIX were also applied.

For (I) the final difference Fourier map had peaks and troughs ranging from +0.38 to -0.19 e Å<sup>-3</sup> with the two largest difference peaks of +0.38 and +0.29 e Å<sup>-3</sup> associated with the midpoints of the C(1)—C(2) and C(3)—C(4) bonds, respectively. For (II), (III) and (IV), the final difference Fourier map had peaks and troughs of 0.37 to -0.28 e Å<sup>-3</sup> for (II), 0.16 to -0.22 e Å<sup>-3</sup> for (III), and 0.26 to -0.23 e Å<sup>-3</sup> for (IV). Final atomic coordinates and thermal parameters are listed in Tables 2–5.\*

**Discussion.** Plots of the four molecules with atom numbering are shown in Figs. 1–4. Bond lengths and

\* Lists of H-atom coordinates, anisotropic thermal parameters, best-planes data and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52860 (79 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atom coordinates (× 10<sup>4</sup>) and thermal parameters (Å<sup>2</sup> × 10<sup>3</sup>) for (I)*

	x	y	z	U <sub>eq</sub> *
C(1)	2637 (1)	8329 (1)	8443 (1)	28 (1)
C(2)	4632 (1)	7925 (2)	9142 (1)	30 (1)
C(3)	4232 (2)	8483 (2)	6788 (1)	35 (1)
C(4)	6197 (2)	9024 (2)	7607 (1)	38 (1)
N(1)	2433 (1)	8876 (2)	7321 (1)	35 (1)
N(2)	6374 (1)	7970 (2)	8686 (1)	40 (1)
N(3)	4403 (2)	7479 (2)	10183 (1)	41 (1)
N(4)	1213 (1)	8147 (2)	9062 (1)	40 (1)
O(1)	2269 (1)	7605 (1)	10163 (1)	45 (1)

\* Equivalent isotropic U defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor.

Table 3. *Atom coordinates (× 10<sup>4</sup>) and thermal parameters (Å<sup>2</sup> × 10<sup>3</sup>) for (II)*

	x	y	z	U <sub>eq</sub> * or U <sub>iso</sub>
C(1)	568 (5)	5044 (3)	9202 (3)	51 (1)
C(2)	-974 (5)	4190 (4)	9735 (3)	52 (1)
C(3)	2764 (6)	5051 (4)	10801 (3)	64 (1)
C(4)	716 (6)	4770 (4)	11413 (3)	65 (1)
N(1)	2370 (4)	5555 (3)	9733 (2)	51 (1)*
N(2)	-808 (4)	3910 (3)	10794 (2)	53 (1)*
N(3)	-2452 (5)	3797 (4)	9060 (3)	78 (1)*
N(4)	74 (6)	5155 (4)	8203 (3)	75 (1)*
N(5)	3672 (7)	6432 (4)	9194 (3)	82 (1)*
N(6)	-2014 (5)	2823 (3)	11181 (3)	64 (1)*
O(1)	-1818 (5)	4381 (4)	8100 (2)	92 (1)*
O(2)	5298 (6)	6767 (4)	9692 (3)	103 (1)*
O(3)	-1764 (5)	2619 (3)	12118 (3)	80 (1)*

\* Equivalent isotropic U defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor.

angles are given in Tables 6–9. These molecules contain the elements of a piperazine ring fused to a furazan ring. The bond lengths and angles of the furazan rings of (I), (II) and (IV) are approximately the same as the furazan ring reported for 4-hydroxy-5,7-dinitrobenzofurazan (Mathew & Palenik, 1971), 7-aminofurazano[3,4-d]pyrimidine (Shefter, Evans & Taylor, 1971) and 6,7-dihydro-6,6-dimethylbenzofurazan-4(5H)-one oxime (Calleri, Chiari & Viterbo,

Table 4. Atom coordinates ( $\times 10^4$ ) and thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for (III)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}^*$	s.o.f.†
C(1)	9066 (3)	707 (2)	2940 (2)	45 (1)	
C(2)	7152 (3)	526 (2)	1858 (2)	45 (1)	
C(3)	6717 (4)	1861 (3)	4068 (2)	68 (1)	
C(4)	5251 (3)	2187 (2)	2735 (2)	63 (1)	
N(1)	8937 (2)	1460 (2)	4012 (1)	52 (1)	
N(2a)	5183 (4)	1023 (6)	1887 (6)	54 (1)	0.52 (3)
N(2b)	5212 (6)	1134 (7)	1773 (7)	54 (1)	0.48 (3)
N(3)	7679 (3)	-240 (2)	998 (2)	62 (1)	
N(4)	10745 (3)	67 (2)	2764 (2)	66 (1)	
N(5a)	10871 (9)	1728 (10)	4946 (7)	67 (2)	0.694 (4)
N(5b)	10564 (15)	1904 (23)	4959 (16)	74 (4)	0.306 (4)
O(1a)	9883 (18)	-624 (29)	1598 (16)	74 (3)	0.49 (3)
O(1b)	9978 (16)	-456 (27)	1508 (15)	74 (4)	0.51 (3)
O(2a)	10617 (4)	2399 (2)	5806 (2)	82 (1)	0.694 (4)
O(2b)	12354 (6)	1507 (5)	5011 (4)	77 (2)	0.306 (4)

\* Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

† Site occupation factor.

Table 5. Atom coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for (IV)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}^*$
C(1)	2152 (2)	280 (4)	6684 (2)	35 (1)
C(2)	2828 (2)	-1495 (3)	7104 (2)	35 (1)
C(3)	2155 (3)	1517 (4)	8566 (2)	39 (1)
C(4)	3433 (3)	305 (4)	8825 (2)	38 (1)
N(1)	1988 (2)	1921 (3)	7368 (2)	39 (1)
N(2)	3341 (2)	-1605 (3)	8197 (2)	38 (1)
N(3)	2871 (3)	-2821 (4)	6326 (2)	52 (1)
N(4)	1795 (2)	60 (3)	5644 (2)	49 (1)
N(5)	1112 (2)	3463 (3)	7012 (2)	48 (1)
N(6)	4272 (2)	-3118 (3)	8517 (2)	45 (1)
O(1)	2230 (2)	-1875 (3)	5410 (1)	58 (1)
O(2)	808 (2)	3590 (3)	6030 (2)	67 (1)
O(3)	762 (2)	4606 (3)	7726 (2)	65 (1)
O(4)	5035 (2)	-2776 (3)	9332 (2)	64 (1)
O(5)	4228 (2)	-4649 (3)	7968 (2)	59 (1)

\* Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

1978), even though some additional conjugation would be expected in these latter three compounds because of the aromatic rings fused to the furazan rings. Without constraints of fused rings, the furazan ring of 3-amino-4-methylfurazan (Viterbo & Serafino, 1978) still has the same bond lengths and angles. A recent compilation of bond lengths (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987) lists the C—N bond length for furazan rings at 1.298 (6) Å and the N—O bond length at 1.385 (13) Å which are the same as observed for (I), (II) and (IV) (Fig. 5). The fusion of the furazan ring to the piperazine ring puts a constraint on the bond lengths of the piperazine ring. The C—N bonds from C of the furazan ring to piperazine N are shortened to ~1.37–1.38 Å as compared to C—N bonds of ~1.45–1.47 Å in other unconstrained piperazines (Sekido, Okamoto & Hirokawa, 1985, and references therein), and as observed in the unconstrained half of the piperazine rings of (I), (II) and (IV).

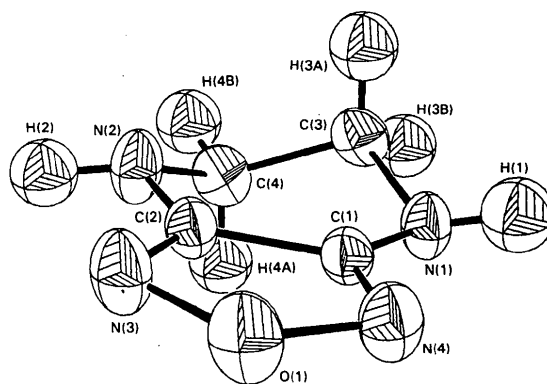


Fig. 1. Plot of (I) with 50% thermal ellipsoids.

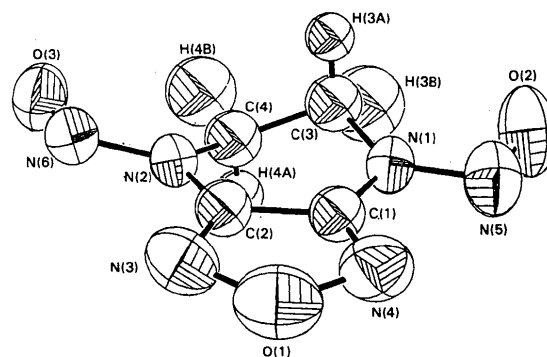


Fig. 2. Plot of (II) with 50% thermal ellipsoids.

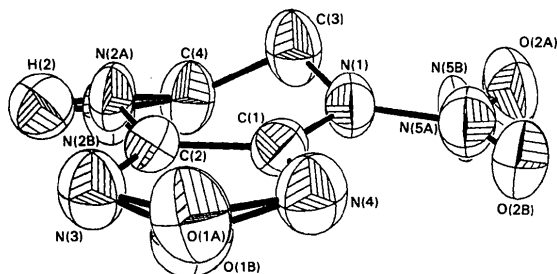


Fig. 3. Plot of (III) with 50% thermal ellipsoids.

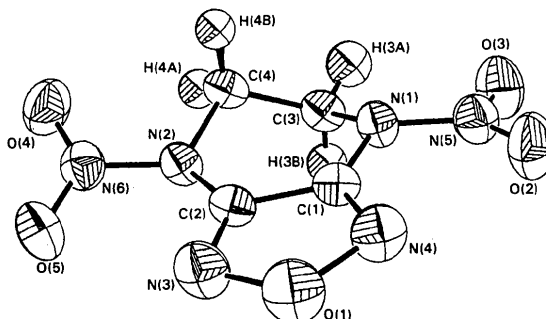


Fig. 4. Plot of (IV) with 50% thermal ellipsoids.

Table 6. Bond lengths (Å) and angles (°) for (I), with e.s.d.'s in parentheses

C(1)—C(2)	1.442 (1)	C(1)—N(1)	1.360 (1)
C(1)—N(4)	1.298 (1)	C(2)—N(2)	1.355 (1)
C(2)—N(3)	1.303 (1)	C(3)—C(4)	1.511 (1)
C(3)—N(1)	1.469 (2)	C(4)—N(2)	1.461 (2)
N(3)—O(1)	1.404 (1)	N(4)—O(1)	1.405 (1)
C(2)—C(1)—N(1)	121.6 (1)	C(2)—C(1)—N(4)	109.6 (1)
N(1)—C(1)—N(4)	128.7 (1)	C(1)—C(2)—N(2)	121.2 (1)
C(1)—C(2)—N(3)	109.3 (1)	N(2)—C(2)—N(3)	129.4 (1)
C(4)—C(3)—N(1)	109.9 (1)	C(3)—C(4)—N(2)	110.1 (1)
C(1)—N(1)—C(3)	115.0 (1)	C(2)—N(2)—C(4)	114.9 (1)
C(2)—N(3)—O(1)	105.2 (1)	C(1)—N(4)—O(1)	105.2 (1)
N(3)—O(1)—N(4)	110.6 (1)		

Table 7. Bond lengths (Å) and angles (°) for (II), with e.s.d.'s in parentheses

C(1)—C(2)	1.418 (4)	C(1)—N(1)	1.382 (4)
C(1)—N(4)	1.298 (4)	C(2)—N(2)	1.362 (4)
C(2)—N(3)	1.299 (5)	C(3)—C(4)	1.500 (5)
C(3)—N(1)	1.446 (4)	C(4)—N(2)	1.468 (5)
N(1)—N(5)	1.342 (4)	N(5)—O(2)	1.222 (5)
N(2)—N(6)	1.364 (4)	N(6)—O(3)	1.204 (5)
N(3)—O(1)	1.386 (5)	N(4)—O(1)	1.384 (5)
C(2)—C(1)—N(1)	120.7 (3)	C(2)—C(1)—N(4)	110.3 (3)
N(1)—C(1)—N(4)	128.8 (3)	C(1)—C(2)—N(2)	121.6 (3)
C(1)—C(2)—N(3)	109.0 (3)	N(2)—C(2)—N(3)	129.4 (3)
C(4)—C(3)—N(1)	113.2 (3)	C(3)—C(4)—N(2)	111.4 (3)
C(1)—N(1)—C(3)	117.8 (3)	C(1)—N(1)—N(5)	117.0 (3)
C(3)—N(1)—N(5)	125.2 (3)	N(1)—N(5)—O(2)	113.1 (3)
C(2)—N(2)—C(4)	117.2 (3)	C(2)—N(2)—N(6)	117.2 (3)
C(4)—N(2)—N(6)	125.6 (3)	N(2)—N(6)—O(3)	113.7 (3)
C(2)—N(3)—O(1)	104.8 (3)	C(1)—N(4)—O(1)	104.1 (3)
N(3)—O(1)—N(4)	117.7 (3)		

Compounds (I), (II) and (IV) all contain a non-crystallographic pseudo-twofold rotation axis through the furazano oxygen, O(1), and the mid-points of the C(1)—C(2) and C(3)—C(4) bonds (Figs. 1, 2 and 4). All four compounds exhibit twisting about the C(3)—C(4) bond as shown in Figs. 1–4. Torsional ( $\omega$ ) angles around the piperazine ring in (I), (II) and (IV) are given in Table 10.\*

Average values for equivalent bond lengths and angles for (I), (II) and (IV) are shown in Fig. 5. Comparison between the three compounds shows that the furazano N(3,4)—O(1) bond lengths are just slightly longer and the piperazine C(1,2)—N(1,2) bond lengths are just slightly shorter in (I) than in (II) and (IV), although the differences may be statistically insignificant. The angles, however, about the piperazine nitrogen do exhibit variations related to substitution at that nitrogen; the largest differences occur with nitrosamine, —NO, substitution. The piperazine N atoms in (II) are planar with angles A1, A2 and A3 about each nitrogen summing to 360.0°. (II) has the largest interior C—N—C angles, as would be expected for a planar  $sp^2$  nitrogen with

Table 8. Unconstrained bond lengths (Å) and angles (°) for (III)

C(1)—C(2)	1.428 (2)	C(1)—N(4)	1.287 (3)
C(1)—N(1)	1.384 (3)	C(3)—N(1)	1.467 (3)
C(3)—C(4)	1.498 (3)	C(2)—N(3)	1.300 (3)
C(2)—C(1)—N(1)	120.4 (2)	C(2)—C(1)—N(4)	111.2 (2)
N(1)—C(1)—N(4)	128.4 (2)	C(4)—C(3)—N(1)	111.2 (2)
C(1)—C(2)—N(3)	108.7 (2)	C(1)—N(1)—C(3)	116.9 (1)

Table 9. Bond lengths (Å) and angles (°) for (IV), with e.s.d.'s in parentheses

C(1)—C(2)	1.426 (3)	C(1)—N(1)	1.387 (3)
C(1)—N(4)	1.295 (3)	C(2)—N(2)	1.387 (3)
C(2)—N(3)	1.295 (3)	C(3)—C(4)	1.496 (4)
C(3)—N(1)	1.478 (3)	C(4)—N(2)	1.479 (3)
N(1)—N(5)	1.382 (3)	N(2)—N(6)	1.389 (3)
N(3)—O(1)	1.387 (3)	N(4)—O(1)	1.388 (3)
N(5)—O(2)	1.213 (3)	N(5)—O(3)	1.220 (3)
N(6)—O(4)	1.216 (3)	N(6)—O(5)	1.215 (3)
C(2)—C(1)—N(1)	120.2 (2)	C(2)—C(1)—N(4)	109.9 (2)
N(1)—C(1)—N(4)	129.8 (2)	C(1)—C(2)—N(2)	120.8 (2)
C(1)—C(2)—N(3)	109.8 (2)	N(2)—C(2)—N(3)	129.4 (2)
C(4)—C(3)—N(1)	109.5 (2)	C(3)—C(4)—N(2)	109.5 (2)
C(1)—N(1)—C(3)	116.1 (2)	C(1)—N(1)—N(5)	119.3 (2)
C(3)—N(1)—N(5)	117.6 (2)	C(2)—N(2)—C(4)	117.0 (2)
C(2)—N(2)—N(6)	119.3 (2)	C(4)—N(2)—N(6)	117.5 (2)
C(2)—N(3)—O(1)	104.0 (2)	C(1)—N(4)—O(1)	103.9 (2)
N(1)—N(5)—O(2)	117.4 (2)	N(1)—N(5)—O(3)	115.8 (2)
O(2)—N(5)—O(3)	126.7 (2)	N(2)—N(6)—O(4)	116.2 (2)
N(2)—N(6)—O(5)	117.0 (2)	O(4)—N(6)—O(5)	126.8 (2)
N(3)—O(1)—N(4)	112.3 (2)		

Table 10. Selected torsional angles (°) for (I), (II) and (IV)

	(I)	(II)	(IV)
N(2)—C(2)—C(1)—N(1)	-3.9	3.8	-0.5
C(2)—C(1)—N(1)—C(3)	17.5	7.5	-17.7
C(4)—C(3)—N(1)—C(1)	-44.5	-34.2	47.3
N(1)—C(3)—C(4)—N(2)	59.1	49.3	-58.6
C(3)—C(4)—N(2)—C(2)	-46.6	-39.4	42.7
C(1)—C(2)—N(2)—C(4)	19.4	13.6	-13.1

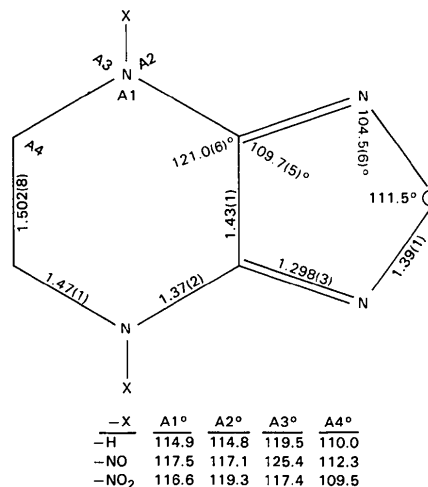


Fig. 5. Mean bond lengths (Å) and angles (°) for (I), (II) and (IV). E.s.d.'s of the means are in parentheses, for averages of four or more values.

\* See deposition footnote.

some N—N double-bond character. The planar nitrosamine groups appear to be slightly sterically crowded. Both groups of (II) are ordered with the O atoms rotated away from the furazan ring towards the methylene hydrogens (Fig. 2). The O(2)—H(3*b*) and O(3)—H(4*b*) distances are both 2.36 Å, somewhat less than the expected van der Waals distance of 2.5–2.6 Å. Hence, as compared to (I) and (IV), a larger *A*3 angle (Fig. 5) is observed in (II). Rotating the nitrosamine groups so that the nitroso oxygen points towards the furazan ring would not relieve the crowding and would be expected to be energetically even less favorable owing to the close approach of the nitroso oxygen to the furazan nitrogens. In disordered (III) the distance from the nitroso oxygen O(2*b*) to the furazan nitrogen N(4) is only 2.73 Å, significantly less than an expected van der Waals distance of 2.9 Å.

The geometry observed for the two nitrosamine groups of (II) is similar to that of other reported nitrosamines. The N—N bond lengths of 1.342 and 1.364 Å compare well to those of 1.344 Å in dimethylnitrosamine (CH<sub>3</sub>)<sub>2</sub>NNO (Rademacher & Stølevik, 1969), 1.336 Å in (cyclic) 1,4-dinitrosopiperazine (Sekido, Okamoto & Hirokawa, 1985), ~1.34–1.36 Å in (cyclic) 1,3,5-trinitroso-1,3,5-triazacyclohexane (Gilardi & George, 1984; C. K. Lowe-Ma, unpublished), and to the mean N—N bond length of 1.342 Å (with a sample standard deviation of 0.013 Å) for fifteen acyclic nitrosamine groups in thirteen compounds from the Cambridge Structural Database (CSD) (Allen, Kennard & Taylor, 1983). However, N—N bond lengths of 1.322 (6) and 1.306 (5) Å have been observed in the cyclic 1,8-dinitroso-1,8-diazadecalin (Willer, Lowe-Ma, Moore & Johnson, 1984). For the fifteen nitrosamine groups from the CSD, in addition to 1,8-dinitroso-1,8-diazadecalin, 1,4-dinitrosopiperazine, 1,3,5-trinitroso-1,3,5-triazacyclohexane and dimethylnitrosamine, the mean N=O bond length is 1.224 (18) Å for values ranging from 1.179 to 1.260 Å. The nitrosamine N=O bond lengths of (II) at 1.222 (5) and 1.204 (5) Å are as would be expected. The N—N=O angles of 113.1 (3) and 113.7 (3)° in (II) are the same as observed in dimethylnitrosamine (113.6°) and dinitrosopiperazine (113.4°).

(III) is similar to the others but exhibits disorder in the ring systems and in the orientation of the nitroso group. The disorder in the ring systems, most apparent for the amine nitrogen N(2) and the furazan oxygen O(1), was modelled with two partially occupied atoms, N(2*a*,2*b*) and O(1*a*,1*b*), spatially separated by about 0.2 Å. Each 'atom' was refined with independent, anisotropic thermal parameters, but the total population for each pair of atoms was constrained to be 1.0. Although no constraints were

applied to the relative site occupancy in each pair, the occupancy factors refined to nearly identical values, 0.52 (3) for (N2*a*) and 0.51 (3) for O(1*b*). This would suggest that the disorder in O(1) and N(2) is related and may involve synchronous twists in the rings. The disorder in (III) occurs even in the presence of intermolecular hydrogen bonding between H(2) and N(3) (Fig. 6). However, from the refined population parameters, the rotational disorder of the nitrosamine group does not seem to be obviously related to the disorder involving synchronous twists in the rings. Each 'atom' used to model the nitrosamine disorder was refined with independent, anisotropic thermal parameters, but the total population for each pair of atoms, N(5*a*,5*b*) and O(2*a*,2*b*), was constrained to 1.0. Additionally, the bonded —NO of each pair were constrained to have the same relative occupancy. The nitrosamine oriented towards the methylene hydrogens, N(5*a*)—O(2*a*), refined to a larger relative occupancy of 0.694 (4). The nitrosamine group of (III), although disordered, is still planar with angles about N(1) summing to 360.0°. As mentioned above, the planar nitrosamine results in some steric crowding near the adjacent equatorial methylene hydrogen; the O(2*a*)—H(3*b*) distance is approximately 2.4 Å. However, this orientation is preferable (~69% occupancy) to that of the opposite orientation towards the furazan ring (~31% occupancy) which has O(2*b*) approximately 2.7 Å away from N(4).

Of the four compounds reported here, only (III) exhibited any disorder, even though Oyumi, Rheingold & Brill (1986) (hereafter ORB) have speculated that low-energy conformational interconversions may explain the polymorphism observed spectroscopically in (IV). Gandolfi powder diffraction patterns of large tabular and rod-like crystals of (IV) grown slowly from acetone/water match the powder pattern calculated from the single-crystal structure reported here for a thin platelet of (IV) crystallized from nitromethane. Unit cells obtained for single crystals are also the same. However,

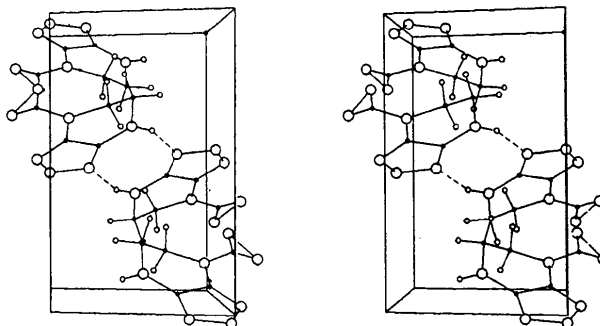


Fig. 6. Stereopacking plot for (III).

powder diffractometer scans of bulk, finely crystalline (IV), that has been rapidly crystallized from acetone, exhibit additional weak lines not predicted in the calculated powder pattern. Although one might attribute the additional weak powder diffraction lines to impurities in the bulk samples, differential scanning calorimetry (DSC) suggests otherwise. DSC of the large tabular and rod crystals shows an endotherm at about 358 K whereas *no* endotherm is observed in the DSC data of the bulk, rapidly crystallized (IV). This suggests some structural difference between forms crystallized under different conditions. From their spectroscopic data ORB postulate the existence of three other polymorphs of (IV), one of which, form *B*, is very similar but not identical to the commonly crystallized form *A*. The other two polymorphs form at higher temperatures and have different lattice symmetries. ORB suggest that form *B*, obtained by rapid crystallization from acetone, is thermally isolated from form *A*. All of our attempts to obtain crystals of another form of (IV) for single-crystal structure determination have failed; crystals obtained by rapid crystallization from acetone were unsuitable for a structure determination and all other crystals examined appear to have the same unit cell and symmetry as found for (IV). The crystal structure of (IV) reported here is the same as that of form *A* reported by ORB; the unit-cell size and space-group symmetry are the same. The bond lengths and angles for the two structures are the same within three e.s.d.'s except for the interior C—N—C angles about the piperazine nitrogens, which differ by 3.5 and five e.s.d.'s. The molecular conformation illustrated by ORB is a 'conformational enantiomorph' of that shown for (IV) in Fig. 4; pairs of the 'enantiomorphs' must be present because the space

group is centrosymmetric. In solution at room temperature conformational averaging occurs. Compared to compounds (I), (II) and (III), no unusual molecular features are observed for (IV).

All four of the furazanopiperazines reported here have observed densities that are slightly higher than the predicted (Cichra, Holden & Dickinson, 1980) values of 1.51, 1.63, 1.58 and 1.79 g cm<sup>-3</sup> for (I), (II), (III) and (IV), respectively. Both (I) and (III), with the largest percentage differences, were 3% more dense than predicted. Their higher densities are probably due to intermolecular hydrogen bonding. Two molecules of (III) are aligned side-by-side such that H(2) is 2.32 Å from N(3) of the other and vice versa, forming dimers (Fig. 6). In contrast, in (I) H(1) is 2.30 Å from N(3) in a symmetry-related molecule and H(2) is 2.44 Å from N(4) of a different symmetry-related molecule forming chains of hydrogen-bonded molecules (Fig. 7).

This work was supported by NWC Independent Research Funds. We thank Ms Debbie Hickey for assistance in obtaining the X-ray powder diffraction data, Mr David Decker for assisting with the crystallization experiments, Mr Alan Woodman for the DSC data and Dr Melvin Nadler for FTIR characterization.

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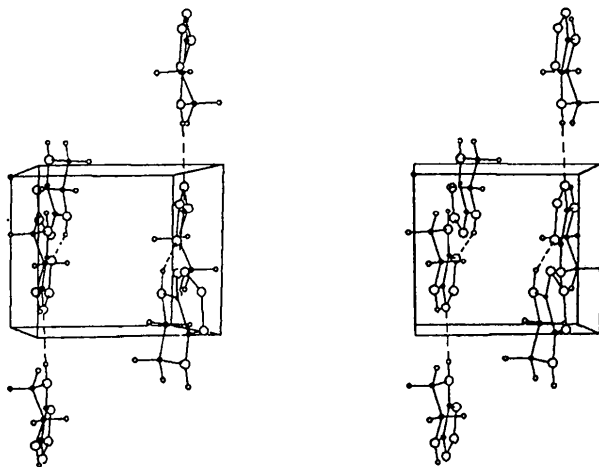


Fig. 7. Stereopacking plot for (I).