Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\rm min} = 0.83$, $T_{\rm max} = 1.18$
3372 measured reflections
3049 independent reflections
1317 observed reflections [$I > 3\sigma(I)$]

$h = 0 \rightarrow 6$
$k = 0 \rightarrow 20$
$l = -40 \rightarrow 40$
3 standard reflections monitored every 150 reflections intensity variation: 1.09%

Refinement

Refinement on F
$R = 0.068$
$wR = 0.066$
$S = 4.25$
1317 reflections
283 parameters
All H-atom parameters refined except H on methyl C18, fixed

Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\rm max} = 0.081$
$\Delta\rho_{\rm max} = 0.30$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.33$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 7. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (4)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
F1	0.9691 (6)	0.0290 (5)	0.5589 (1)	0.050 (2)
F2	0.8437 (6)	0.0300 (6)	0.6321 (1)	0.052 (2)
F4	0.1739 (6)	0.3322 (6)	0.5990 (1)	0.046 (2)
N10	0.2821 (9)	0.3259 (8)	0.5232 (2)	0.034 (3)
N11	0.439 (1)	0.1846 (10)	0.6548 (2)	0.049 (4)
C1	0.772 (1)	0.1084 (10)	0.5679 (2)	0.037 (4)
C2	0.712 (1)	0.1089 (10)	0.6054 (2)	0.039 (4)
C3	0.507 (1)	0.191 (1)	0.6173 (2)	0.037 (4)
C4	0.372 (1)	0.2570 (9)	0.5884 (2)	0.029 (3)
C4a	0.426 (1)	0.2579 (9)	0.5487 (2)	0.033 (4)
C5	0.194 (1)	0.393 (1)	0.4576 (2)	0.037 (4)
C6	0.247 (1)	0.388 (1)	0.4193 (2)	0.044 (4)
C7	0.453 (1)	0.315 (1)	0.4060 (2)	0.041 (4)
C8	0.603 (1)	0.2495 (10)	0.4334 (2)	0.037 (4)
C8a	0.553 (1)	0.2499 (9)	0.4724 (2)	0.032 (4)
C9	0.696 (1)	0.1795 (10)	0.5006 (2)	0.034 (4)
C9a	0.637 (1)	0.1806 (9)	0.5387 (2)	0.032 (4)
C10a	0.341 (1)	0.3228 (10)	0.4855 (2)	0.033 (4)
C12	0.580 (1)	0.2243 (10)	0.6867 (2)	0.039 (4)
C13	0.785 (1)	0.309 (1)	0.6846 (3)	0.046 (5)
C14	0.918 (1)	0.345 (1)	0.7160 (3)	0.046 (4)
C15	0.853 (1)	0.295 (1)	0.7528 (2)	0.042 (4)
C16	0.646 (1)	0.211 (1)	0.7553 (2)	0.050 (5)
C17	0.512 (1)	0.175 (1)	0.7235 (2)	0.043 (4)
C18	1.002 (1)	0.330 (1)	0.7882 (3)	0.069 (5)
C19	0.507 (2)	0.317 (2)	0.3649 (3)	0.066 (6)

Table 8. *Selected geometric parameters* (Å, °) *for* (4)

N10—C4a	1.326 (7)	C5—C6	1.37 (1)
N10—C10a	1.366 (8)	C5—C10a	1.403 (9)
N11—C3	1.375 (9)	C6—C7	1.43 (1)
N11—C12	1.408 (9)	C7—C8	1.39 (1)
C1—C2	1.36 (1)	C7—C19	1.48 (1)
C1—C9a	1.401 (9)	C8—C8a	1.40 (1)
C2—C3	1.43 (1)	C8a—C9	1.394 (9)
C3—C4	1.372 (9)	C8a—C10a	1.449 (9)
C4—C4a	1.421 (8)	C9—C9a	1.379 (9)
C4a—C9a	1.432 (9)		
C4a—N10—C10a	117.8 (6)	C8a—C9—C9a	120.9 (7)
N10—C4a—C9a	123.3 (7)	C4a—C9a—C9	118.4 (6)
C9—C8a—C10a	116.4 (7)	N10—C10a—C8a	123.1 (6)

The crystals of (2) were extremely thin and a rotating-anode source had to be used. Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *TEXSAN*, *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *TEXSAN*, *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *TEXSAN FINISH*. Literature survey: *CSSR* (1984).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1078). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Adamson, A. J., Banks, R. E. & Tipping A. E. (1993). *J. Fluorine Chem.* **64**, 5-10.

Alty, A. C., Banks, R. E., Fishwick, B. R., Pritchard, R. G. & Thompson, A. R. (1984). *J. Chem. Soc. Chem. Commun.* pp. 832-833.

Alty, A. C., Banks, R. E., Fishwick, B. R. & Thompson, A. R. (1985). *Tetrahedron Lett.* pp. 1345-1348.

CSSR (1984). *Crystal Structure Search and Retrieval Instruction Manual.* SERC Daresbury Laboratory, Warrington, England.

Flowers, W. T. & DeFigueredo, P. (1990). Personal communication.

Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42-46.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158-166.

Acta Cryst. (1994). C**50**, 971-974

3-Selenocyanatopyridine

S. J. Dunne, L. A. Summers and
E. I. von Nagy-Felsobuki

Department of Chemistry, The University of Newcastle, Callaghan, NSW 2308, Australia

M. F. Mackay

Department of Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia

(*Received* 11 *October* 1993; *accepted* 13 *December* 1993)

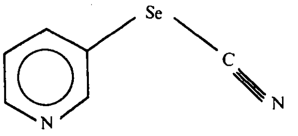
Abstract

The crystal structure of the title compound (3-pyridyl selenocyanate, $C_6H_4N_2Se$) has been determined by X-ray analysis. As expected, the Se—C_{sp} bond of length

1.863 (8) Å has greater double-bond character than the Se—C_{sp^2} bond of length 1.929 (6) Å. The C3—Se—C7 bond angle is 94.8 (3)° and the torsion angle C2—C3—Se—C7 is 46.1 (6)°. There are two short intermolecular contacts involving the Se and an N atom of two adjacent molecules [Se···N1 2.843 (7) and Se···N2 3.387 (6) Å], which, with the two atoms covalently bonded to Se, form an approximate square-planar geometry about the metal atom.

Comment

As an extension of our previous conformational studies on the methylselenylpyridines (Dunne, Summers & von Nagy-Felsobuki, 1992*a*), selenobispyridines (Dunne, Summers & von Nagy-Felsobuki, 1992*b*) and dipyridyl diselenides (Dunne, Summers & von Nagy-Felsobuki, 1993), we report the crystal structure of 3-selenocyanatopyridine, (I).



(I)

The Se—C3 bond length (see Fig. 1) of 1.929 (6) Å agrees well with those found in diphenyl diselenide [1.93 (5) Å (Marsh, 1952)], di-*p*-tolyl selenide [1.92 Å (Blackmore & Abrahams, 1955)] and selenoanisole [1.912 (13) Å (Zaripov, Golubinskii, Chmutova & Vilkov, 1978)]. The Se—C7 distance of 1.863 (8) Å is significantly shorter, as expected, due to the greater contribution of *s* character by the cyano C atom. Comparison of this bond length in the title compound with those in 1,4-diselenocyanatobenzene [1.837 (23) Å (McDonald & Petit, 1970)] and methylselenocyanate [1.851 Å (Sakaizumi, Kohri, Ohashi & Yamaguchi, 1978)], suggests that the former has less double-bond character.

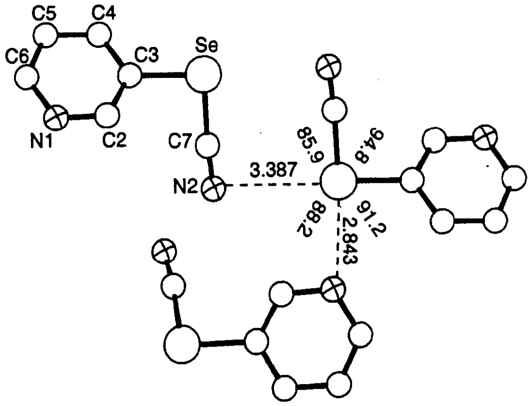


Fig. 1. The environment around the Se atom in the crystal with atomic numbering.

While the cyano C7—N2 distance of 1.139 (10) Å and the C3—Se—C7 bond angle of 94.8 (3)° are consistent with values reported for comparable structures, the selenocyanate group deviates slightly from linearity [Se—C7—N2 175.3 (6)°] as also noted for selenium diselenocyanate and 1,4-diselenocyanatobenzene (McDonald & Petit, 1970). The pyridine ring geometry deviates little from previously reported values (Sorensen, Mahler & Rastrup-Andersen, 1974). The r.m.s. deviation of the Se and ring atoms from planarity is only 0.014 Å, while the selenocyanate group is twisted from the plane, as reflected in the C2—C3—Se—C7 torsion angle of 46.1 (6)°. This is consistent with electron diffraction studies which report similar torsion angles [40 (13)° in selenoanisole (Zaripov, Golubinski, Chmutova & Vilkov, 1978), 45 (10)° in thioanisole (Zaripov, 1976), 68 (2)° in benzeneselenenyl bromide (Zaripov, Popik, Vilkov & Mannafov, 1980) and 72 (3)° in benzenesulphenyl chloride (Zaripov, Popik & Vilkov, 1980).]

Gas-phase and solution-state conformational studies of substituted aryl selenocyanates have shown that the *para*-substituted phenyl selenocyanates, 4-RC_6H_4SeCN (R = H, NO_2, NH_2), are planar when R is an electron-donating group (Yarkova, Saliufullina, Chmutova & Bautina, 1979), although the coplanarity of the C_6H_4SeCN moiety has been disputed when R is electron withdrawing (Chmutova, Bautima & Vereshchagin, 1976). *ortho*-Substituted phenyl selenocyanates, 2-RC_6H_4SeCN (R = Me, Cl, Br, NO_2), were similarly found to exist as planar or nearly planar *anti* conformers. *meta*-Substituted phenyl selenocyanates, 3-RC_6H_4SeCN (R = Me, Cl, Br, NO_2), were found to exist as a mixture of *syn* and *anti* forms: the proportion of the latter and the torsional angle (C—Se—C—N) increasing with increasing electron-withdrawing ability of the substituent R (Chmutova, Bautina & Vereshchagin, 1981). Therefore, it would be anticipated that 3-selenocyanatopyridine exists in a nonplanar form.

The electronegative N atom in pyridine withdraws electron density from the *ortho* and *para* positions of the ring, leaving the *meta* C atoms somewhat electron deficient. The increased electron density in the *meta* position favours the planar conformation of 3-selenocyanatopyridine by enhancing the C_{2p}—Se_{3p} overlap. However, steric interactions between the selenocyanate arm and adjacent ring H atoms tend to displace the system from coplanarity. The measured torsion angle (46°) must therefore result from the steric strain between C7 and H2 and the intermolecular forces exerted on the substituent arm. Chmutova & Bock (1976), and Dunne, Summers & von Nagy-Felsobuki (1992*a*) concluded from photoelectron spectra of Ph*X*Me and Py*X*Me systems, respectively, that the conjugation between the valence *np* electrons of the *X*Me group and the ring π system and, accordingly, the probability of planar conformation, decreases in the order O > S > Se > Te, as a result of both electronic and steric concerns.

Two close contacts between the Se and N atoms less than the sum of their van der Waals radii, Se···N1 (x, $\frac{1}{2} - y$, $\frac{1}{2} + z$) of 2.843 (7) Å and Se···N2 ($1 - x$, $-y$, $1 - z$) of 3.387 (6) Å, together with the two atoms covalently bonded to Se, form an approximate square-planar geometry around the Se atom (Fig. 1); the five atoms are coplanar to within 0.13 Å and the angles subtended at Se range from 85.9 (4) to 94.8 (3)°. A similar arrangement was also reported for the structure of 1,4-diselenocyanatobenzene (McDonald & Petit, 1970). In that structure, the Se atom makes intermolecular contacts with neighbouring N atoms of 3.06 and 3.32 Å, and the angles at the Se atom range from 78 to 101°. In the structure of the title compound, the contact between Se and H2 (2.92 Å), while greater than the van der Waals sum, has a significant influence upon the substituent geometry, precluding the planar conformation.

Experimental

Crystals were obtained by the procedure described by Dunne, Summers & von Nagy-Felsobuki (1992*c*).

Crystal data

$C_6H_4N_2Se$
$M_r = 183.1$
Monoclinic
$P2_1/c$
$a = 7.710$ (1) Å
$b = 8.132$ (1) Å
$c = 11.024$ (2) Å
$\beta = 108.16$ (1)°
$V = 656.8$ (3) Å^3
$Z = 4$
$D_x = 1.851$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 23$-$39°$
$\mu = 7.13$ mm^{-1}
$T = 291$ (1) K
Prismatic
0.220 × 0.135 × 0.090 mm
Colourless

Data collection

Rigaku AFC diffractometer
$\omega/2\theta$ scans
Absorption correction: *SHELX*76 Gaussian (Sheldrick, 1976)
$T_{\min} = 0.208$, $T_{\max} = 0.370$
1246 measured reflections
1032 independent reflections
752 observed reflections [$F > 10.0\sigma(F)$]

$R_{\rm int} = 0.028$
$\theta_{\max} = 65.0°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 13$
3 standard reflections monitored every 50 reflections

Refinement

Refinement on F
$R = 0.038$
$wR = 0.058$
$S = 2.82$
752 reflections
85 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F) + 0.00035F^2]$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.58$ e Å^{-3}
$\Delta\rho_{\min} = -0.68$ e Å^{-3}
Extinction correction: *SHELX*76 (Sheldrick, 1976)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Se	0.21493 (8)	0.12455 (9)	0.39283 (6)	3.17 (2)
N1	−0.0268 (7)	0.2196 (7)	0.0059 (6)	3.5 (2)
C2	0.0893 (8)	0.2029 (8)	0.1237 (6)	3.0 (2)
C3	0.0398 (8)	0.1463 (7)	0.2250 (6)	2.6 (2)
C4	−0.1410 (9)	0.1031 (8)	0.2072 (8)	3.4 (2)
C5	−0.2654 (9)	0.1266 (9)	0.0855 (8)	4.2 (2)
C6	−0.2023 (9)	0.1828 (9)	−0.0102 (8)	3.9 (2)
C7	0.3914 (8)	0.0225 (9)	0.3357 (7)	3.6 (2)
N2	0.5072 (7)	−0.0394 (9)	0.3092 (6)	4.7 (2)

Table 2. *Selected geometric parameters* (Å, °)

Se—C3	1.929 (6)	C3—C4	1.391 (9)
Se—C7	1.863 (8)	C4—C5	1.398 (10)
N1—C2	1.335 (8)	C5—C6	1.371 (13)
N1—C6	1.342 (9)	C7—N2	1.139 (10)
C2—C3	1.368 (10)		
C3—Se—C7	94.8 (3)	C2—C3—C4	119.5 (5)
C2—N1—C6	116.7 (5)	C3—C4—C5	117.3 (5)
N1—C2—C3	123.7 (5)	C4—C5—C6	118.8 (6)
Se—C3—C2	121.6 (4)	N1—C6—C5	123.9 (6)
Se—C3—C4	118.9 (5)	Se—C7—N2	175.3 (6)

During data collection, the intensities of the standard reflections gradually decreased to 7.8% of their original values. The data were scaled accordingly. The structure was solved by the heavy-atom method and refined by full-matrix least squares with *SHELX*76 (Sheldrick, 1976). The H-atom coordinates were calculated and the atoms given a common isotropic temperature factor [5.8 (10) Å^2]. Calculations were performed on a VAX8800 computer. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *Xtal*3.0 (Hall & Stewart, 1990).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates, as well as a molecular structure diagram and a stereoview of the unit cell have been deposited with the IUCr (Reference: AS1090). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Blackmore, W. R. & Abrahams, S. C. (1955). *Acta Cryst.* **8**, 323-328.
Chmutova, G. A., Bautina, I. V. & Vereshchagin, A. N. (1976). *Irz. Akad. Nauk SSSR Ser. Khim.* pp. 2469-2472; *Chem. Abstr.* (1977). **86**, 120659u.
Chmutova, G. A., Bautina, I. V. & Vereshchagin, A. N. (1981). *Irz. Akad. Nauk SSSR Ser. Khim.* pp. 1554-1559; *Chem. Abstr.* (1981). **95**, 149826t.
Chmutova, G. & Bock, H. (1976). *Z. Naturforsch. Teil B*, **31**, 1611-1615.
Dunne, S. J., Summers, L. A. & von Nagy-Felsobuki, E. I. (1992*a*). *Phosphorus Sulfur Relat. Elem.* **72**, 103-119.
Dunne, S. J., Summers, L. A. & von Nagy-Felsobuki, E. I. (1992*b*). *J. Mol. Struct.* **273**, 139-159.
Dunne, S. J., Summers, L. A. & von Nagy-Felsobuki, E. I. (1992*c*). *J. Heterocycl. Chem.* **29**, 117-119.
Dunne, S. J., Summers, L. A. & von Nagy-Felsobuki, E. I. (1993). *Phosphorus Sulfur Relat. Elem.* **78**, 173-187.
Hall, R. S. & Stewart, J. M. (1990). Editors. *Xtal*3.0 *Reference Manual.* Univs. of Western Australia, Australia, and Maryland, USA.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Marsh, R. E. (1952). *Acta Cryst.* **5**, 458-462.
McDonald, W. S. & Petit, L. D. (1970). *J. Chem. Soc.* pp. 2044-2046.
Sakaizumi, T., Kohri, Y., Ohashi, O. & Yamaguchi, I. (1978). *Bull. Chem. Soc. Jpn*, **51**, 3411-3417.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
Sorensen, G. O., Mahler, L. & Rastrup-Andersen, N. (1974). *J. Mol. Struct.* **20**, 119-126.
Yarkova, E. G., Saliufullina, N. R., Chmutova, G. A. & Bautina, I. V. (1979). *Zh. Obshch. Khim.* **49**, 2025-2030; *Chem. Abstr.* (1980). **92**, 75714.
Zaripov, N. M. (1976). *Zh. Strukt. Khim.* **17**, 741-743.
Zaripov, N. M., Golubinski, A. V., Chmutova, G. A. & Vilkov, L. V. (1978). *Zh. Strukt. Khim.* **19**, 894-899.
Zaripov, N. M., Popik, M. V. & Vilkov, L. V. (1980). *Zh. Strukt. Khim.* **21**, 38-42.
Zaripov, N. M., Popik, M. V., Vilkov, L. V. & Mannafov, T. G. (1980). *Zh. Strukt. Khim.* **21**, 37-40.

Acta Cryst. (1994). C**50**, 974–976

A High-Density Thermally Stable Explosive: Octahydro-2,5-bis(nitroimino)-imidazo[4,5-*d*]imidazole

Judith L. Flippen-Anderson

Laboratory for the Structure of Matter,
Naval Research Laboratory, Washington,
DC 20375, USA

Michael Kony and Ian J. Dagley

Materials Research Laboratory (MRL)-DSTO,
PO Box 50, Melbourne, Victoria 3032, Australia

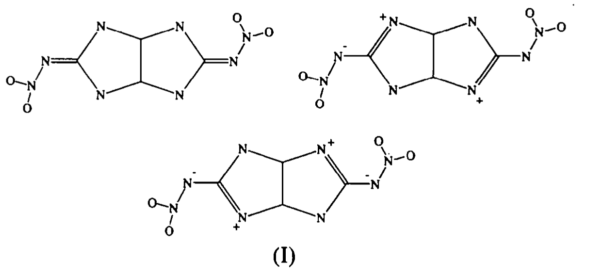
(*Received* 27 *October* 1993; *accepted* 14 *January* 1994)

Abstract

The title compound, $C_4H_6N_8O_4$, has a calculated crystal density of 1.84 Mg m^{-3}. It lies on a crystallographic twofold axis passing through the midpoint of the C4—C4^{i} bond [symmetry code: (i) $-x$, $-y$, z]. The five-membered ring has a flattened envelope conformation with C4 lying 0.17 Å out of the plane of the other four atoms. The geometry at one of the ring N atoms (N1) is planar and that at the other (N3) is slightly pyramidal. There is a *cis* junction between the fused five-membered rings (H—C—C—H = −13.1°) with a dihedral angle of 62.7° between the ring planes. The hydrogen-bonding system contains one intra-intermolecular bifurcated bond and one linear intermolecular bond.

Comment

The title compound, (I), is a nitramine explosive with unusually high thermal stability since it decomposes without melting at 599 K (Kony & Dagley, 1994). The predicted density for this compound (assuming all the N—H protons are hydrogen bonded) is 1.84 Mg m^{-3} (Cichra, Holden & Dickinson, 1980), which is in agreement with the calculated crystal density.



(I)

This X-ray structure analysis (Fig. 1) was performed to compare the structural features of (I) with those found for other energetic molecules containing N—H bonds and nitro groups. The bond lengths around C2 indicate that the double bond is delocalized, giving rise to three possible resonance forms (shown above). The X-ray results show that for (I) there are three unique N—H···O hydrogen bonds. H1 is the donor in a bifurcated bond, comprising an intramolecular bond to O2*B* and an intermolecular bond to O2*A*′ (N1—H1 = 0.940, N1···O2*B* = 2.621, H1···O2*B* = 2.075, N1···O2*A*′ = 2.863, H1···O2*A*′ = 2.015 Å, N1—H1···O2*B* = 115.4, N1—H1···O2*A*′ = 149.1 and O2*B*···H1···O2*A*′ = 88.4°), while H3 is the donor atom in a single linear intermolecular hydrogen bond to a second symmetry-related O2*A* (N3—H3 = 0.927, N3···O2*A*″ = 2.899, H3···O2*A*″ = 1.975 Å and N3—H3···O2*A*″ = 174.6°). In all, each molecule participates in ten hydrogen bonds which link it to eight neighboring molecules (Fig. 2).

2-Nitroiminoimidazolidine, the monocyclic analogue of (I) (Nordenson, 1981) shows a similar pattern of intra- and intermolecular hydrogen bonding. However, it differs from this structure in that the linear bond is an N—H···N interaction rather than an N—H···O interaction and, as a result, one of the two nitro O atoms does not participate in any hydrogen bonds. Similar hydrogen bonding was also found in the high-melting compounds nitroguanidine (Bryden, Burkardt, Hughes

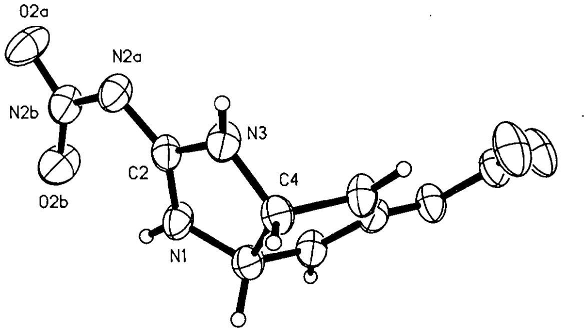


Fig. 1. Structure of (I) showing 20% probability displacement ellipsoids.