

2-Nitrimino-1-nitroimidazolidine

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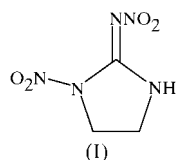
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The molecule of the title compound, C₃H₅N₅O₄, has a planar geometry. Due to the presence of a second nitro group, the lengths of the two conjugated C–N bonds are different. Nevertheless, the conjugation of the nitrimine group spreads to the nitramine group. Intermolecular N–H···O bonds connect molecules into dimers in the crystal structure.

Comment

Nitrimines, of which the title compound, (I), is an example, are of interest as highly energetic compounds (McKay, 1952). According to McKay & Wright (1948), (I) has high explosive characteristics. The efficiency of (I) is 1.3 times greater than that of TNT (trinitrotoluene) in a ballistic mortar test and 1.5 times greater according to the Trauzl-block test. In spite of the moderate value of the oxygen balance (–41.1%), the brisance of (I) is comparable with that of the more balanced (–21.6%) well known explosive compound RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine). At the same time, compound (I) is 2.8 times more sensitive to impact and 1.6 times more sensitive to friction than RDX. As a first approximation, one can suppose that in relation to the same class of high energetic compounds, the sensitivity to mechanical influence increases with increasing oxygen balance (Kamlet, 1976). RDX and (I) are both *N*-nitro compounds. In connection with this, the question arises as to why compound (I) with the poorer oxygen balance shows comparative brisance and essentially higher impact sensitivity than RDX.



At present, the most widespread theory is the hot-spot theory of explosion initiation by impact (Kamlet, 1976;

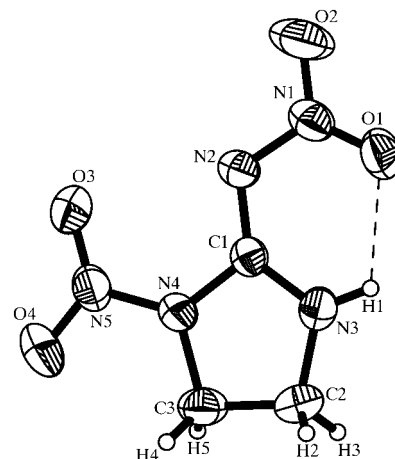


Figure 1

The molecule of (I), showing the atomic numbering scheme and displacement ellipsoids at the 50% probability level.

Dubovik, 1986). In agreement with this theory, an impact produces so-called 'hot spots', where the thermal decomposition of an explosive occurs. Many different physical and chemical factors influence the impact sensitivity: the heat yielded on decomposition, heat capacity, heat conduction, crystal size and shape, crystal lattice energy, and so on. Nevertheless, the thermal stability of an explosive (that is, the mechanism and kinetics of initial thermal decomposition) plays a main determining role. The thermal decomposition of *N*-nitro compounds starts with homolytic breaking of the least stable N–NO₂ bond (Manelis *et al.*, 1996). Investigation of the thermal decomposition of compound (I) showed that its thermal stability is essentially less than that of RDX; this agrees with the relative impact sensitivity of both explosives

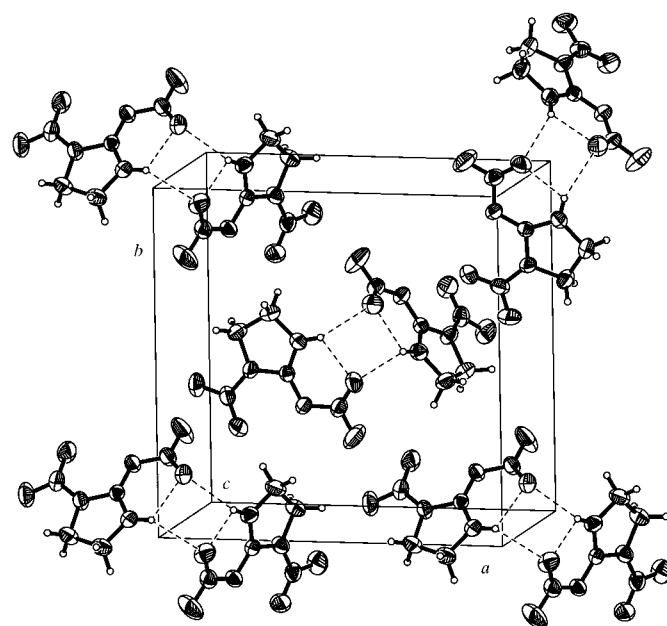


Figure 2

The molecular arrangement of (I) in the crystal structure. Dashed lines indicate hydrogen bonds.

(Astachov *et al.*, 2002). It is unlikely that the N—NO₂ bond of the nitrimine group is responsible for the low thermal stability and the high sensitivity of (I). For instance, one of the best known energetic nitrimines, nitroguanidine, has comparatively high thermal stability (McKay, 1952; Volk, 1985; Oyumi *et al.*, 1987; Liu *et al.*, 1989) and is one of the less impact-sensitive explosives of the IHE (insensitive high explosives) class (Doherty & Simpson, 1997). Therefore, one may suppose that the N—NO₂ bond of the nitramine group triggers thermal decomposition in (I). One might expect that the bond will be longer and, consequently, its strength less than the analogous bonds in RDX. It is therefore important to study the structure of (I).

The structure of (I) is similar to the structures of other nitrimines (Bryden *et al.*, 1956; Choi, 1981; Nordenson, 1981*a,b*; Nordenson & Hvoslef, 1981; Rice *et al.*, 1984; Oyumi *et al.*, 1987; Gao *et al.*, 1991; Astachov *et al.*, 2001; Vasiliev *et al.*, 2001; Allen, 2002). The molecular conformation of (I) is nearly planar (Fig. 1). Deviations from the least-squares plane through the non-H atoms are 0.078 (2) (r.m.s.) and 0.202 (2) Å (maximum). There is an intramolecular N3—H1...O1 hydrogen bond involving the nitrimine fragment of the molecule. Because of the delocalization of the π -electron density over the nitrimine fragment, the C—N, N—N and N—O bond lengths are intermediate between the values characteristic for corresponding single and double bonds (Table 1). The C1—N2 bond [1.322 (3) Å], which is technically 'double', is, in fact, slightly longer than the C1—N3 bond [1.308 (3) Å], which is technically 'single'. A strong electron-acceptor substituent, *viz.* the nitro group on atom N4, decreases the electron density on this atom. The possibility of its participation in conjugation with the nitrimine group is diminished and, as a consequence, the C1—N4 bond length is increased [1.379 (3) Å]. A similar situation is found in other nitrimines which have electron-acceptor substituents, *e.g.* 1-methyl-2-nitro-1-nitrosoguanidine (Nordenson & Hvoslef, 1981; Rice *et al.*, 1984) and nitroguanidyl azide (Vasiliev *et al.*, 2001). In these compounds, the analogous C—N bond lengths are in the range 1.389–1.408 Å. These increased values agree with the ease of nucleophilic replacement observed in experiments with these compounds (McKay & Wright, 1947; McKay, 1952; Meen & Wright, 1952; Scott *et al.*, 1956). Judging by the planar geometry of the molecule of (I) and the value of the N4—N5 bond length [1.373 (3) Å], atom N4 participates in conjugation not only with the nitroguanidyl group but also with the nitro group. Therefore, the nitrimine conjugation spreads to the nitro group in (I). Methylene groups are not involved in any conjugation. The N3—C2 [1.455 (3) Å] and N4—C3 [1.460 (3) Å] bond lengths are close to values observed in compounds with single C—N bonds (Allen, 2002), in particular, 2-nitriminoimidazolidine (Nordenson, 1981*b*). The C2—C3 bond length [1.498 (4) Å] is slightly shortened in comparison with an ordinary C—C single bond. This is probably due to some strain in the imidazolidine ring in (I). Two weak hydrogen bonds, N3—H1...O1, connect the molecules into dimers in the crystal structure (Fig. 2).

The values of the N—NO₂ bond lengths in (I) do not exceed the values of the analogous bonds in RDX [1.351 (3), 1.392 (3)

and 1.398 (3) Å; Choi & Prince, 1972]. Also, because of the conjugation in a dinitroguanidyl fragment, the N4—N5 bond length [1.373 (3) Å] in (I) is shorter than in RDX. The supposition about the increased value of the N4—N5 bond length has not been confirmed. Therefore, one cannot explain the essential difference in thermal stability and impact sensitivity of (I) and RDX based on the chemical-bond strengths in the molecules. Knowledge of the molecular structure does not help either. Nevertheless, the investigation allows one of the most probable factors to be excluded from consideration and the search for other possible reasons for the high impact sensitivity of (I).

The presence of firm intermolecular hydrogen bonds, which absorb the supplied energy, is a necessary condition of low sensitivity in explosives. One can suppose that as a result of a network of intermolecular hydrogen bonds, nitroguanidine is a low sensitive explosive (Oyumi *et al.*, 1987). At the same time, compound (I) contains no such network (Fig. 2). Moreover, it is possible that the primary reaction of thermal decomposition is not the breaking of the N4—N5 bond but the breaking of the C1—N4 bond with the imidazolidine ring opening in (I). An analysis of the above-mentioned factors and other factors will be reported elsewhere.

Experimental

Caution: the title compound should be treated as a dangerous explosive! Compound (I) was synthesized according to the method of McKay & Wright (1948). Single crystals were obtained by crystallization from a solution in ethanol.

Crystal data

C ₃ H ₅ N ₅ O ₄	Cu K α radiation
$M_r = 175.12$	Cell parameters from 24 reflections
Tetragonal, $P4_2bc$	$\theta = 23\text{--}28^\circ$
$a = 12.897$ (1) Å	$\mu = 1.41$ mm ⁻¹
$c = 8.0078$ (8) Å	$T = 293$ (2) K
$V = 1332.0$ (2) Å ³	Ellipsoidal, colourless
$Z = 8$	$0.36 \times 0.33 \times 0.30$ mm
$D_x = 1.747$ Mg m ⁻³	

Data collection

Kuma KM-4 diffractometer	$R_{\text{int}} = 0.030$
$\theta/2\theta$ scans	$\theta_{\text{max}} = 79.8^\circ$
Absorption correction: ψ scan	$h = 0 \rightarrow 15$
(<i>XPREP</i> ; Bruker, 1997)	$k = -15 \rightarrow 16$
$T_{\text{min}} = 0.605$, $T_{\text{max}} = 0.661$	$l = 0 \rightarrow 10$
847 measured reflections	2 standard reflections
769 independent reflections	every 50 reflections
651 reflections with $I > 2\sigma(I)$	intensity variation: 0.8%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.009$
$R[F^2 > 2\sigma(F^2)] = 0.029$	$\Delta\rho_{\text{max}} = 0.17$ e Å ⁻³
$wR(F^2) = 0.079$	$\Delta\rho_{\text{min}} = -0.13$ e Å ⁻³
$S = 1.01$	Extinction correction:
769 reflections	<i>SHELXL97</i>
110 parameters	Extinction coefficient:
H-atom parameters constrained	0.0151 (10)
$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2 + 0.1821P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1

Selected interatomic distances (Å).

N1—O2	1.221 (3)	N4—N5	1.373 (3)
N1—O1	1.244 (3)	N4—C1	1.379 (3)
N1—N2	1.361 (3)	N4—C3	1.460 (3)
N2—C1	1.322 (3)	N5—O3	1.208 (3)
N3—C1	1.308 (3)	N5—O4	1.216 (3)
N3—C2	1.455 (3)	C2—C3	1.498 (4)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N3—H1 \cdots O1	0.86	2.06	2.568 (2)	117
N3—H1 \cdots O1 ⁱ	0.86	2.29	3.035 (2)	144

Symmetry code: (i) $-x, 2-y, z$.

H atoms were found in a difference Fourier map and were refined as riding atoms (C—H distances were set at 0.97 Å and the N—H distance was set at 0.86 Å), with displacement parameters equal to 1.2 times those of the parent atom. The determination of the absolute structure was not carried out because of the absence of strong anomalous scatterers.

Data collection: *KM-4 Software* (Kuma, 1991); cell refinement: *KM-4 Software*; data reduction: *DATARED* in *KM-4 Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1660). Services for accessing these data are described at the back of the journal.

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