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(*Z*)-2-Nitroethenamine

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.044
wR factor = 0.119
Data-to-parameter ratio = 9.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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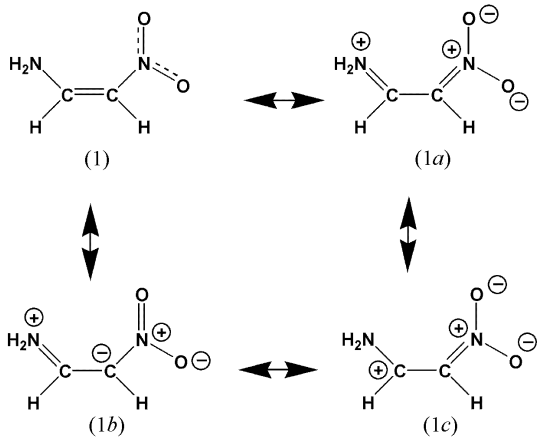
The title compound (*Z*)-2-nitroethenamine, $C_2H_4N_2O_2$, is a small energetic compound composed of only C, H, N and O, with a density of 1.513 g cm^{-3}. The molecules of this crystal structure have bond lengths and angles that are characteristic of a type of push–pull ethylenes. The overall molecular organization in stacks of almost planar parallel layers is a result of intermolecular amine-to-nitro hydrogen bonding.

Comment

Several olefins with nitro and amino substituents have been studied by X-ray crystal structure analysis (Gate *et al.*, 1985; Hazell & Mukhopadhyay, 1980; Bemm & Östmark, 1998), spectroscopy and theoretical chemistry (Karafiloglou & Marcos, 1992) because of their importance in synthetic chemistry and their biological activity (Gate *et al.*, 1985). The X-ray crystal structure of the simplest member of the nitroethenamine family, (*Z*)-2-nitroethenamine, (1), has not been reported yet and is the subject of this article.



This type of ethylene is commonly referred to as a push–pull ethylene because of the effects of the nitro and amino substituents on the π-electron distribution, as illustrated by the resonance structures of (1*a*), (1*b*), and (1*c*). In common with other members of this group, the combined effects of the electron-withdrawing nitro group and the electron-donating amino group serve to lengthen the central olefin bond of the title compound from a 'normal' value of 1.317 Å (Allen *et al.*, 1987) to the observed value of 1.363 Å. In a similar molecule (1,1-diaminodinitroethylene), the central bond is lengthened to 1.456 Å (Bemm & Östmark, 1998). This is substantially longer than the distance in the title compound, due to the stronger push–pull effect and increased steric crowding. In addition to the lengthening of the central bond, the terminal

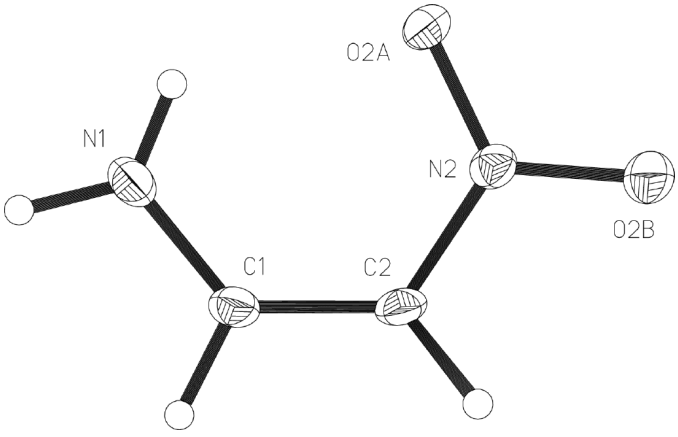


Figure 1
View of (*Z*)-2-nitroethenamine.

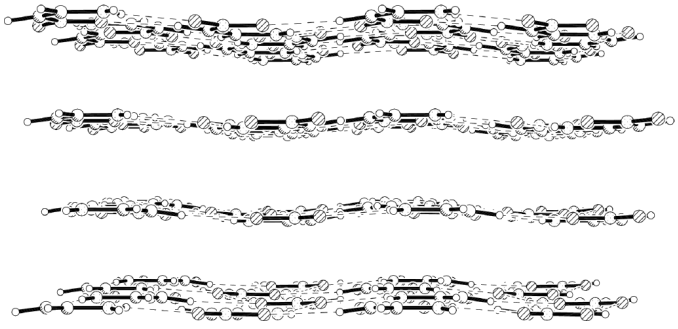


Figure 2
A view of the packing down the *b* axis showing sheets of molecules, which occupy the $(10\bar{2})$ crystallographic planes. The hydrogen-bonded sheets are not quite planar, but are slightly wavy; the mean deviation of the atoms from the best plane through each sheet is 0.133 Å.

bonds to the amino and the nitro substituents in these compounds are shortened. In the title compound, the amino C—N distance is 1.311 Å and the nitro C—N distance is 1.372 Å. These values are similar to those observed in the Cambridge Structural Database (CSD; Allen *et al.*, 1987) for three RNH–C═C-NO_2 molecules; the reported CSD amino C—N distances range from 1.303 to 1.335 Å (Gate *et al.*, 1985; Hazell & Mukhopadhyay, 1980; Diánez *et al.*, 1985; Schlueter & Cook, 1989) and the nitro C—N distances range from 1.378 to 1.395 Å. Thus, the observed terminal distances are always shorter than the expected (Allen *et al.*, 1987) Csp^2-amino and Csp^2-nitro distances of 1.336 and 1.468 Å, respectively. The push–pull effect also plays a role in reducing the barrier to rotation of the olefin bond. This barrier, which is normally very high, is lowered, permitting large distortions from 'olefinic' planarity when bulky groups are substituted on the amine (*e.g.*, see Baum *et al.*, 1992). The title molecule, (*Z*)-2-nitroethenamine, is almost entirely planar; the mean deviation from the plane through the molecule is 0.01 Å with a range of 0.00–0.02 Å. The *cis* arrangement of amino and nitro groups in this molecule also enables an intramolecular hydrogen bond. In addition, there are two unique intermolecular NH—NO_2 hydrogen bonds which tie the molecules into sheets that are almost flat; the mean deviation of the atoms in each sheet from a plane is 0.133 Å. These slightly wavy sheets (see Fig. 2) extend throughout the crystal in two dimensions and form a parallel stack. This packing is similar to that seen in the crystals of 1,1-diaminodinitroethylene (Bemm & Östmark, 1998).

Experimental

Dr Mao-Xi Zhang of the University of Chicago Chemistry Department supplied crystals of the title compound.

Crystal data

$C_2H_4N_2O_2$
M_r = 88.07
Monoclinic, $P2_1/c$
a = 5.5459 (2) Å
b = 10.3058 (3) Å
c = 6.8702 (3) Å
β = 100.131 (2)°
V = 386.54 (2) Å^3
Z = 4
D_x = 1.513 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 1596 reflections
θ = 7.8–66.8°
μ = 1.18 mm^{-1}
T = 293 (2) K
Plate, pale yellow
0.39 × 0.27 × 0.03 mm

Data collection

CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.75, T_{max} = 0.97
1860 measured reflections
650 independent reflections
593 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 66.7°
$h = -6 \rightarrow 6$
$k = -11 \rightarrow 11$
$l = -8 \rightarrow 7$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.119
S = 1.09
650 reflections
68 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0824P)^2 + 0.0213P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.144 (15)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···O2B	0.88 (2)	2.161 (19)	2.6959 (16)	118.8 (16)
N1—H1A···O2A^{i}	0.90 (2)	2.04 (2)	2.9299 (16)	169.0 (14)
N1—H1B···O2A^{ii}	0.88 (2)	2.24 (2)	2.8997 (19)	131.9 (16)

Symmetry codes: (i) $1+x, \frac{3}{2}-y, \frac{1}{2}+z$; (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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