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1,1-Diamino-2,2-dinitroethylene:† a Novel Energetic Material with Infinite Layers in Two Dimensions

Ulf Bemm and Henric Östmark

Defence Research Establishment (FOA), Weapons and Protection Division, Energetic Materials Department, S-147 25 Tumba, Sweden. E-mail: ulfb@sto.foa.se

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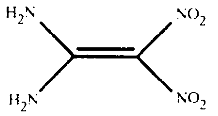
Abstract

The title compound ($C_2H_4N_4O_4$) is a novel and interesting high explosive with high performance and low sensitivity. Single-crystal X-ray diffraction studies of the compound show that the molecules in the crystal structure have bond lengths and bond angles as expected for this type of push–pull ethylene. There are two intramolecular hydrogen bonds present between the nitro-O atoms and the amino-H atoms. The geometry of the molecule indicates that there is extensive π conjugation present. The molecular packing is built up by infinite two-dimensional wave-shaped layers, with extensive intermolecular hydrogen bonding within the layers and ordinary van der Waals interactions between the layers. The crystal packing explains some of the physico-chemical properties of the compound, such as the absence of a melting point, its low solubility, and its low sensitivity to friction and impact compared with the common high explosive RDX (1,3,5-triaza-1,3,5-trinitrocyclohexane).

Comment

1,1-Diamino-2,2-dinitroethylene (FOX-7) is a novel and interesting high explosive with high performance and low sensitivity (Östmark *et al.*, 1998). The compound is a typical so-called push–pull ethylene, a group of compounds which has attracted interest for a long time because of their structural properties and stereochemistry, and since the 1970s a lot of work has been published in this area (*e.g.* Sandström, 1983; Baum, Bigelow *et al.*, 1992; Baum, Nguyen *et al.*, 1992).



FOX-7

The ethylene bond distance of 1.456 (2) Å is intermediate between a single C—C bond (1.54 Å) and a double C═C bond (1.34 Å). The molecular configuration of the C and amino-N atoms is essentially planar, while the nitro-N atoms, especially N12, are out of plane (Fig. 1). This is also verified by *ab initio* calculations (*Gaussian*94; Frisch *et al.*, 1995). The configuration of the molecule was calculated using the *B3LYP*/6–31*G*(*d*,*p*) basis set which showed exactly the same deviation out of the plane of the two nitro-N atoms, especially N12, although no intermolecular interactions were included in the *ab initio* calculations (Bemm & Östmark, 1998). This indicates that the planarity of the molecule and the nitro groups is most probably affected by strong electrostatic repulsion forces between the two O atoms O11 and O22, and the intra- and intermolecular hydrogen bonds present are not believed to have any influence. The distance between O22 and O11 is only 2.575 (2) Å giving rise to strong repulsion forces between the two nitro groups, thus introducing the twist of the two nitro groups. The N11 nitro group exhibits normal geometry, while the N12 nitro group deviates slightly from normal nitro-group geometry (Sadova & Vilkov, 1982). Two intramolecular hydrogen bonds are present between the amino groups and the nitro groups (Table 3). The above features indicate that the structure exhibits extensive π conjugation as expected. The FOX-7 molecule also possesses local symmetry in the form of an approximate twofold rotation axis through the two C atoms.

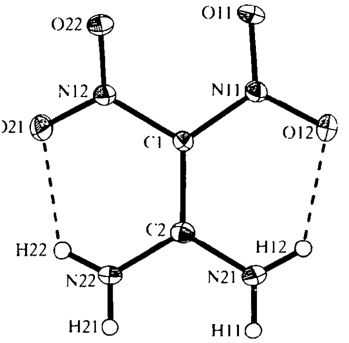


Fig. 1. Displacement ellipsoid (50% probability) drawing of FOX-7. Intramolecular hydrogen bonds are drawn as dashed lines.

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† IUPAC name: 2,2-dinitroethylene-1,1-diamine.

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The special molecular packing is most probably essential for several of the physical properties of FOX-7, *e.g.* low sensitivity to friction and impact, low solubility and absence of melting point. The molecular packing consists of wave-shaped layers with extensive intermolecular hydrogen bonding within the layers and ordinary van der Waals interactions between the layers (Fig. 2). The structures of two other energetic materials have been published, TATB (1,3,5-triamino-2,4,6-trinitrobenzene; Cady & Larson, 1965) and β-NTO (5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one; Lee & Gilardi, 1993), with the same type of molecular packing and physical properties as FOX-7. Six independent intermolecular hydrogen bonds are present (Table 3). The intermolecular hydrogen bonding is extensive and, including the two intramolecular hydrogen bonds, all the amino-H atoms are bifurcated and each nitro-O atom takes part in two hydrogen bonds. Each amino-H atom forms one short, normal hydrogen bond and one long, weak hydrogen bond. As can be seen from Table 3, the hydrogen-bond distances are rather long, but nevertheless normal for systems involving C—nitro-O···H—N (Allen *et al.*, 1997).

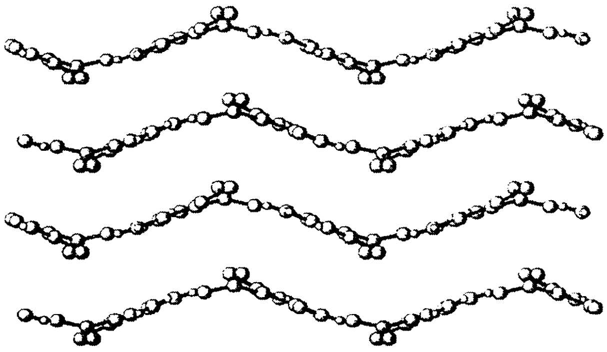

Fig. 2. The wave-shaped layered packing viewed in the (100) direction. The *c* axis is horizontal and the *b* axis is vertical.

The parameters describing the anisotropic displacement of the atoms were analyzed by the techniques described by Hirshfeld (1976) and Rosenfield *et al.* (1978) for the presence of rigid groups within the molecule. The calculations performed with the program *THMA*11 (Trueblood, 1978) show that the average mean-square displacement amplitude along the interatomic distances is 0.0015 Å^2, and the weighted R value between the reproduced and observed displacement parameters was calculated to be 0.134, using s.u.'s as atomic weights. These results indicate that it is difficult to draw any conclusions about any pronounced rigid-body motion within the molecule. This is probably due to the extensive intra- and intermolecular hydrogen bonding which greatly affects the possibility of free thermal motion of the individual atoms.

Experimental

Raw material was provided by FOA Energetic Materials Department (Östmark *et al.*, 1998; Latypov *et al.*, 1998). Crystals of FOX-7 crystallized from cold *N,N*-dimethylformamide, after two or three days.

Crystal data

$C_2H_4N_4O_4$
$M_r = 148.09$
Monoclinic
$P2_1/n$
$a = 6.941\,(1)$ Å
$b = 6.569\,(1)$ Å
$c = 11.315\,(2)$ Å
$\beta = 90.55\,(2)°$
$V = 515.9\,(1)$ Å^3
$Z = 4$
$D_x = 1.907$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 3831 reflections
$\theta = 3.4$–$25.9°$
$\mu = 0.181$ mm^{-1}
$T = 173\,(2)$ K
Prismatic
0.35 × 0.30 × 0.20 mm
Yellow

Data collection

Stoe Image Plate Diffraction System
100 frames 0–200° with increment 2°
Absorption correction: none
3831 measured reflections
977 independent reflections

883 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\rm max} = 25.97°$
$h = -8 \rightarrow 8$
$k = -7 \rightarrow 8$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.081$
$S = 1.655$
977 reflections
104 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0131P)^2 + 0.2416P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.262$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.230$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	−0.2323 (2)	0.1689 (3)	0.63691 (14)	0.0129 (4)
C2	−0.3136 (2)	0.2407 (2)	0.52539 (14)	0.0130 (4)
N11	−0.0349 (2)	0.1441 (2)	0.65814 (12)	0.0139 (3)
N12	−0.3564 (2)	0.1271 (2)	0.73375 (12)	0.0137 (3)
O11	0.02294 (18)	0.0578 (2)	0.75058 (10)	0.0190 (3)
O12	0.08126 (18)	0.2009 (2)	0.58124 (11)	0.0231 (3)
O21	−0.51939 (18)	0.0574 (2)	0.71261 (10)	0.0199 (3)
O22	−0.30366 (18)	0.1658 (2)	0.83655 (10)	0.0210 (3)
N21	−0.2009 (2)	0.3004 (3)	0.43881 (13)	0.0193 (4)
N22	−0.5027 (2)	0.2544 (2)	0.51002 (14)	0.0165 (4)

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

C1—N11	1.399 (2)	N11—O12	1.2489 (19)
C1—N12	1.426 (2)	N11—O11	1.2520 (18)
C1—C2	1.456 (2)	N12—O21	1.2420 (19)
C2—N21	1.319 (2)	N12—O22	1.2422 (19)
C2—N22	1.325 (2)		

N11—C1—N12	116.31 (14)	O11—N11—C1	120.12 (14)
N11—C1—C2	123.88 (14)	O21—N12—O22	121.02 (14)
N12—C1—C2	119.76 (14)	O21—N12—C1	118.58 (13)
N21—C2—N22	118.40 (16)	O22—N12—C1	120.37 (14)
N21—C2—C1	120.83 (16)	C2—N21—H11	121.0 (15)
N22—C2—C1	120.72 (15)	C2—N21—H12	121.1 (15)
O12—N11—O11	120.89 (14)	C2—N22—H21	119.8 (16)
O12—N11—C1	118.91 (14)	C2—N22—H22	121.9 (16)
N11—C1—C2—N21	−4.6 (3)	N12—C1—N11—O11	11.4 (2)
N12—C1—C2—N21	172.89 (15)	C2—C1—N11—O11	−171.03 (15)
N11—C1—C2—N22	177.82 (16)	N11—C1—N12—O21	−148.00 (15)
N12—C1—C2—N22	−4.7 (2)	C2—C1—N12—O21	34.3 (2)
N12—C1—N11—O12	−171.78 (15)	N11—C1—N12—O22	34.1 (2)
C2—C1—N11—O12	5.8 (2)	C2—C1—N12—O22	−143.57 (16)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N21—H11···O11^{i}	0.88 (2)	2.18 (2)	3.000 (2)	156 (2)
N21—H11···O21^{ii}	0.88 (2)	2.50 (2)	3.012 (2)	117.7 (18)
N21—H12···O12	0.87 (3)	1.97 (2)	2.608 (2)	128.8 (19)
N21—H12···O22^{ii}	0.87 (3)	2.29 (2)	3.009 (2)	140.3 (19)
N22—H21···O22^{i}	0.84 (3)	2.17 (3)	2.901 (2)	146 (2)
N22—H21···O11^{i}	0.84 (3)	2.46 (2)	3.191 (2)	147 (2)
N22—H22···O21	0.84 (2)	2.03 (2)	2.636 (2)	128 (2)
N22—H22···O12^{iii}	0.84 (2)	2.36 (2)	3.026 (2)	136 (2)

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

Graphite monochromatized Mo $K\alpha$ radiation was used. Intensity statistics indicated a centrosymmetric space-group symmetry. The selected space group $P2_1/n$ deduced from the systematic extinctions in the diffraction data is further supported by the outcome of the investigation. Preliminary O, N and C positions were obtained by the application of direct methods using the program package *SHELXS*86 (Sheldrick, 1990). The remaining atomic positions were found from subsequent calculations of difference electron-density ($\Delta\rho$) maps. In the final least-squares refinement the H atoms were refined without any positional restraints, but with a common isotropic displacement parameter.

Data collection: *IPDS Software* (Stoe & Cie, 1997). Cell refinement: *IPDS Software*. Data reduction: *IPDS Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1020). Services for accessing these data are described at the back of the journal.

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(3*RS*,4*RS*)-2-Methyl-3,4-diphenyl-5-hexen-3-ol

Rainer Sjöholm[a] and Reijo Sillanpää[b]

[a]*Department of Organic Chemistry, Åbo Akademi University, FIN-20500, Turku, Finland, and* [b]*Department of Chemistry, University of Turku, FIN-20014 Turku, Finland. E-mail: sillanpa@utu.fi*

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Abstract

The minor diastereomer (γ adduct) of the tertiary homoallylic alcohols, formed in the Zn-mediated reaction between 2-methyl-1-phenyl-1-propanone (isobutyrophenone) and 3-chloro-1-phenylpropene (cinnamyl chloride) in tetrahydrofuran/NH_4Cl(aq), was isolated and crystallized. The structure of the title compound, $C_{19}H_{22}O$, confirms that the major and minor diastereomers of the γ adduct formed in the reaction have *syn* and *anti* configurations, respectively.

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