2-Methyl-4,5-dinitroimidazole

**Richard Gilardi* and
Robin N. Evans**

Laboratory for the Structure of Matter, Naval
Research Laboratory, Washington, DC
20375-5341, USA

Correspondence e-mail: gilardi@nrl.navy.mil

Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.040
wR factor = 0.080
Data-to-parameter ratio = 11.9

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

The title compound, $C_4H_4N_4O_4$, is a stable energetic compound suitable for use as a propellant ingredient. There are two molecules in the asymmetric unit, which differ in their nitro group out-of-plane torsion values.

Comment

Nitroimidazoles have been extensively studied because of their biological activity (Boyer, 1986); their syntheses are also of interest because they are stable energetic compounds, suitable for use as propellant and explosive ingredients (Bracuti, 1999). The title molecule, (I), contains an imidazole ring with a methyl and two nitro group substituents. The conformations of mono- and dinitroimidazoles have been studied theoretically by Cho *et al.* (1998). When the nitro groups are on adjacent C atoms, as in (I), the conformational potential energy surface is difficult to predict accurately. This is because the actual conformation is a compromise between a planar structure, which would maximize π-orbital conjugation, and a structure with one or both nitro groups twisted out of plane, so as to minimize the electrostatic repulsion between neighboring nitro-group O atoms.

(I)
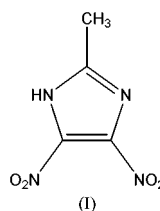
There are two molecules in the asymmetric unit of (I), one of which contains a disordered nitro group (Fig. 1). The first molecule, without disorder, adopts a pseudo-twofold conformation (with the local twofold axis down the C2—C2A methyl bond), wherein each nitro group twists approximately 19° out of the plane of the adjacent ring atoms. In the second molecule, the N15-nitro group is almost coplanar (+3.8° twist), while the N14-nitro group is disordered, and is either approximately −19° out of the plane in the major form [82.9 (5)% occupancy] or approximately 30° out-of-plane in the minor form [17.1 (5)% occupancy].

There are two short intermolecular N—H⋯N hydrogen bonds (Table 1). The crystal structure also contains several intermolecular contacts, not involving H atoms, which are less than the sum of van der Waals radii. Two of the shortest of these are near-perpendicular approaches between polar N—O bonds and C atoms in neighboring imidazole rings, suggesting a dipole–π-bond interaction. They are contacts O13⋯C4(1 − x, 1 − y, 1 − z) of 2.867 (3) Å and O12′⋯C5(1 − x, 1 − y, 1 − z) of 2.948 (5) Å; both distances are significantly

less than the van der Waals contact distance of 3.22 Å (Rowland & Taylor, 1996). These short interactions are likely to have an attractive electrostatic component; the nitro group is considered to be one of the strongest electron-withdrawing substituents known when substituted on a π-bonded system. A third, short intermolecular O···C distance is listed as the third entry in Table 1. Since it is between a methyl C atom and a nitro O atom, one might expect it to be due to C—H···O hydrogen bonding, but it has an extremely bent (106°) C—H···O angle. The contact is better described as a near-perpendicular approach of the N—O dipole to the C—C methyl bond; the N14—O11'···C2A angle is 151.0 (4)° and the C2—C2A···O11' angle is 90.6 (3)°.

Experimental

The title compound, (I), was synthesized by P. Kasu and R. Damavarapu of the ARDEC (Dover, NJ, USA) by nitration of 2-methyl-imidazole. Crystals suitable for diffraction were grown by slow evaporation of a solution in a mixture of 2-butanone and octane. The solid displayed a ^{1}H NMR peak at 2.5 p.p.m. and a melting point of 480 K.

Crystal data

$C_4H_4N_4O_4$	$Z = 4$
$M_r = 172.11$	$D_x = 1.660$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.9962$ (9) Å	Cell parameters from 1898
$b = 8.2860$ (9) Å	reflections
$c = 11.8913$ (13) Å	$\theta = 2.7–26.3°$
$\alpha = 70.702$ (2)°	$\mu = 0.15$ mm^{-1}
$\beta = 71.205$ (2)°	$T = 153$ (2) K
$\gamma = 72.983$ (2)°	Plate, pale yellow
$V = 688.50$ (13) Å^3	$0.45 \times 0.10 \times 0.03$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	2785 independent reflections
	1679 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.041$
Absorption correction: by integration (Wuensch & Prewitt, 1965)	$\theta_{max} = 26.4°$
	$h = -9 \rightarrow 10$
$T_{min} = 0.938$, $T_{max} = 0.994$	$k = -10 \rightarrow 10$
4569 measured reflections	$l = -14 \rightarrow 14$

Refinement

|	
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0255P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.080$	$(\Delta/\sigma)_{max} = 0.001$
$S = 0.86$	$\Delta\rho_{max} = 0.25$ e Å^{-3}
2785 reflections	$\Delta\rho_{min} = -0.24$ e Å^{-3}
235 parameters	Extinction correction: SHELXTL
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.0050 (13)

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

| D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N13^i	0.87 (2)	1.97 (2)	2.837 (2)	168.1 (19)
N11—H11···N3	0.92 (2)	1.92 (2)	2.837 (2)	176.9 (19)
C2A—H2B···O11^{i}	0.98	2.58	2.996 (4)	106

Symmetry code: (i) $1 + x, y - 1, z$.

All H atoms were found in difference Fourier maps, but during the refinement the methyl H atoms were placed geometrically and allowed to ride on their parent C atoms, with C—H = 0.98 Å and
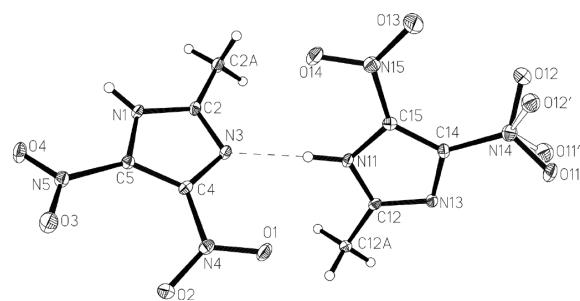
Figure 1
A view of (I), with 25% probability displacement ellipsoids. There are two molecules in the asymmetric unit. The occupation factors of the disordered nitro O atoms O11/O12 and O11'/O12' are 82.9 (5) and 17.1 (5)%, respectively.
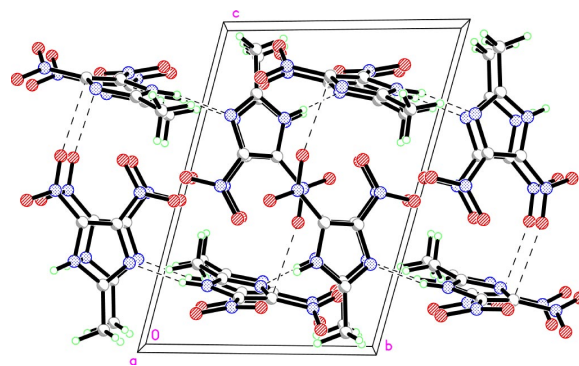
Figure 2
A packing diagram of (I). The dashed lines that illustrate the N—H···N hydrogen bonds (Table 1) are more or less horizontal in this view. The dashed lines extending in the vertical direction are short non-bonded distances between nitro N···O dipoles and C atoms in adjacent aromatic imidazole rings.

$U_{iso} = 1.5U_{eq}(C)$. Positional parameters of the amino H atoms were refined with $U_{iso} = 1.2U_{eq}(N)$. Their N—H bond distances are 0.87 (2) and 0.92 (2) Å.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXTL (Sheldrick, 1997); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

References

Boyer, J. (1986). *Nitroazoles: The C-Nitro Derivatives of Five-Membered N- and N,O-Heterocycles.* Deerfield Beach, FL, USA: VCH Publishers.
Bracuti, A. J. (1999). *J. Chem. Crystallogr.* **28**, 367–371.
Bruker (2001). *SMART* (Version 5.624) and *SAINT* (Version 6.04). Bruker AXS Inc., Madison, Wisconsin, USA.
Cho, S. G., Cheun, Y. G. & Park, B. S. (1998). *J. Mol. Struct.* (*Theochem*), **432**, 41–53.
Rowland, R. S. & Taylor, R. (1996). *J. Phys. Chem.* **100**, 7384–7391.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXTL.* Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Wuensch, B. & Prewitt, C. (1965). *Z. Kristallogr.* **122**, 24–59.