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1-Methyl-4,5-dinitro-1*H*-imidazole

Yong-Xiang Li, Xiao-Jun Wang and Jian-Long Wang*

School of Chemical Engineering and Environment, North University of China, Taiyuan, People's Republic of China
Correspondence e-mail: wangjianlong@nuc.edu.cn

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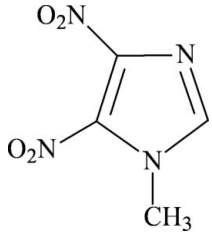
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.046; wR factor = 0.112; data-to-parameter ratio = 7.8.

In the title compound, $C_4H_4N_4O_4$, the two nitro groups are twisted with respect to the imidazole plane, making dihedral angles of 24.2 (3) and 33.4 (4)°. In the crystal structure, the molecules are linked through non-classical intermolecular C—H···O hydrogen bonds.

Related literature

For the synthesis, see: Damavarapu *et al.* (2007). For the biological activity of polynitroimidazole systems, see: Hofmann (1953); Breccia *et al.* (1982); Boyer (1986). For their detonation performance, see: Storm *et al.* (1990); Katritzky *et al.* (1993); Bulusu *et al.* (1995).



Experimental

Crystal data

$C_4H_4N_4O_4$
M_r = 172.11
Orthorhombic, $Pna2_1$
a = 8.412 (2) Å
b = 12.646 (3) Å
c = 6.563 (1) Å
V = 698.2 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.15 mm^{-1}
T = 293 K
0.40 × 0.30 × 0.20 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.944, T_{max} = 0.971
3573 measured reflections
871 independent reflections
648 reflections with $I > 2\sigma(I)$
R_{int} = 0.097

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.112
S = 0.95
871 reflections
111 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···O1^{i}	0.93	2.49	3.150 (4)	128
C4—H4A···O4^{ii}	0.96	2.48	3.428 (5)	170

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

Data collection: *RAPID-AUTO* (Rigaku, 2000); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LX2116).

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supporting information

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1-Methyl-4,5-dinitro-1*H*-imidazole

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S1. Comment

Polynitroimidazole systems have been investigated extensively owing to their biological activity (Hofmann, 1953; Breccia *et al.*, 1982; Boyer, 1986). Recently, these so called "high energy density materials" have attracted renewed attention in conjunction with their favorable detonation performance (Storm *et al.*, 1990; Katritzky *et al.*, 1993; Bulusu *et al.*, 1995). As a promising candidate, 1-methyl-4,5- dinitroimidazole was synthesized by the nitration of *N*-methyl-imidazole (Damavarapu *et al.*, 2007). Here we reprot the crystal structure of the title compound (Fig. 1).

In the crystal structure, the two nitro groups are twisted with respect to the imidazole plane, making dihedral angles of 24.2 (3)° (N3/O1, O2) and 33.4 (4)° (N4/O3, O4). The molecular packing (Fig. 2) is stabilized by non-classical intermolecular C–H···O hydrogen bonds; the first between the imidazole H atom and an oxygen of the nitro group, with C1–H1···O^{i}, the second between the methyl H atom and an oxygen of the nitro group, with C4–H4A···O4^{ii}, respectively (Table 1).

S2. Experimental

The title compound was prepared according to literature method (Damavarapu *et al.*, 2007). Single crystals suitable for X-ray diffraction were obtained by evaporation of a solution of the title compound in methanol at room temperature.

S3. Refinement

All the Friedel pairs were merged. All H atoms were positioned geometrically and treated as riding, with C–H bond lengths constrained to 0.93 ° for imidazole ring H and 0.96 ° for methyl H atoms, and with U_{iso}(H) = 1.2U_{eq}(C) for imidazole ring H atom and 1.5U_{eq}(C) for methyl H atoms.

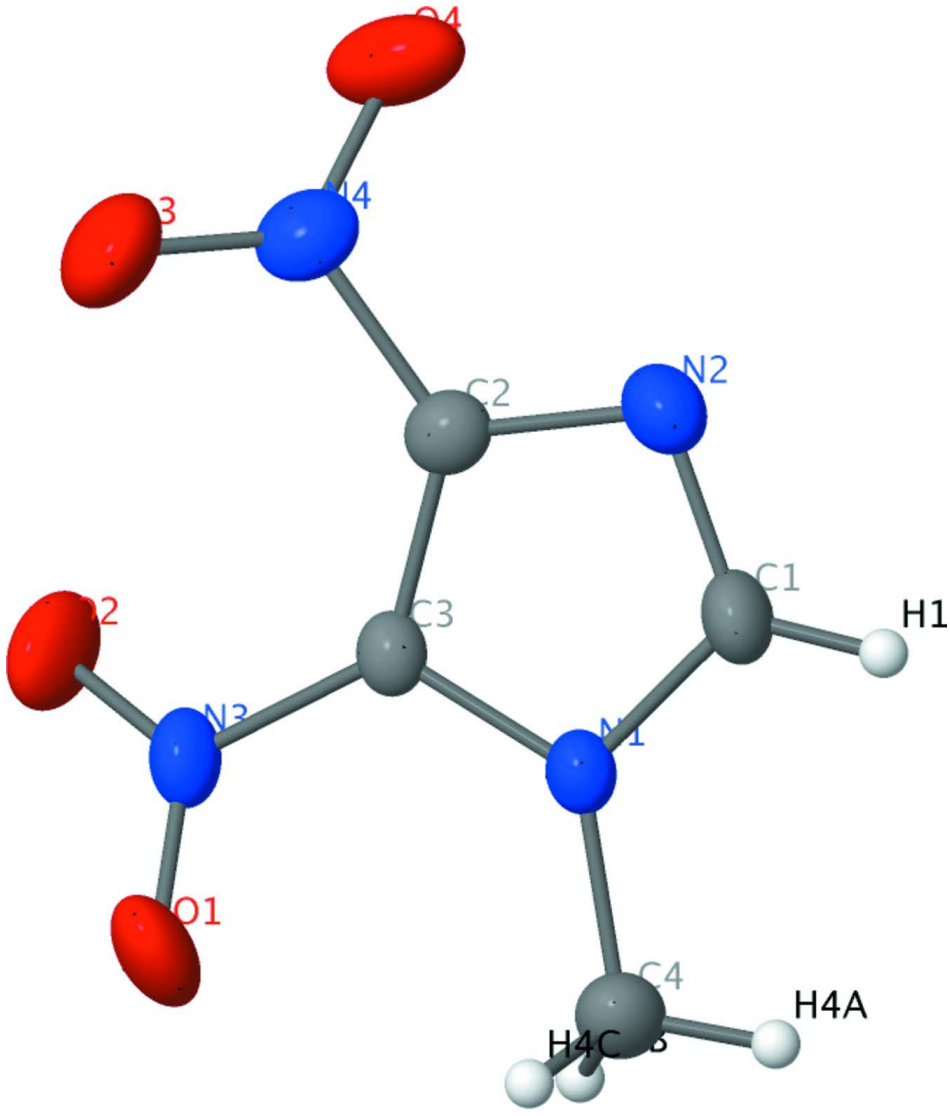

Figure 1

The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are presented as a small spheres of arbitrary radius.

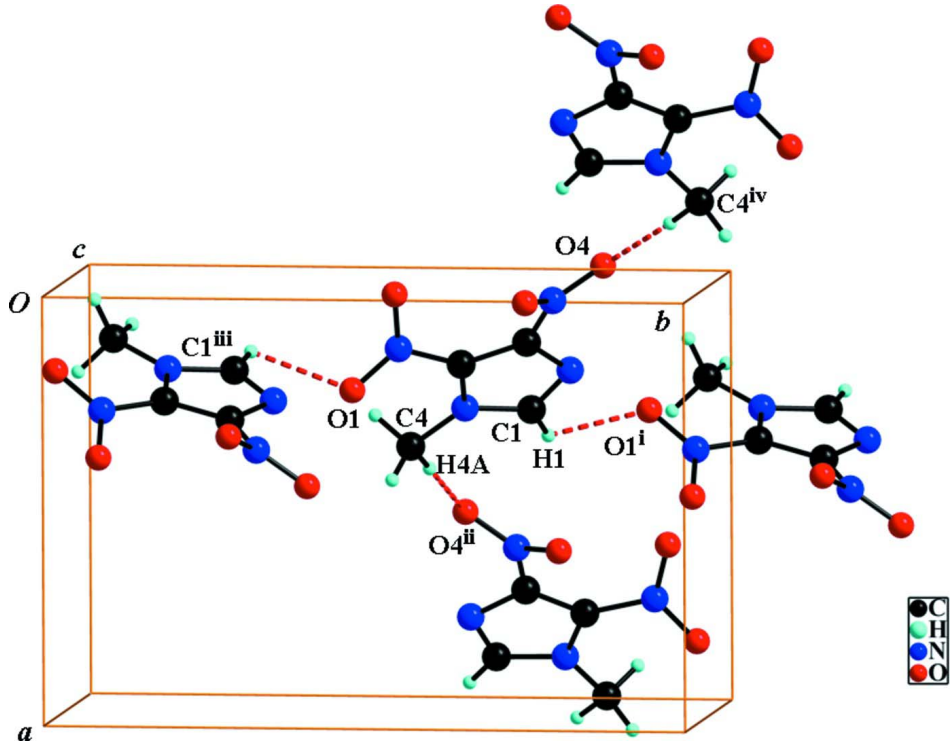

Figure 2

C–H···O interactions (dotted lines) in the crystal structure of the title compound. [Symmetry codes: (i) - x + 1/2, y + 1/2, z - 1/2; (ii) x + 1/2, - y + 3/2, z - 1; (iii) - x + 1/2, y - 1/2, z + 1/2; (iv) x - 1/2, - y + 3/2, z + 1.]

1-Methyl-4,5-dinitro-1*H*-imidazole

Crystal data

$C_4H_4N_4O_4$
M_r = 172.11
Orthorhombic, $Pna2_1$
Hall symbol: P 2c -2n
a = 8.412 (2) Å
b = 12.646 (3) Å
c = 6.563 (1) Å
V = 698.2 (3) Å^3
Z = 4
$F(000)$ = 352
D_x = 1.637 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3573 reflections
θ = 2.9–27.6°
μ = 0.15 mm^{-1}
T = 293 K
Block, colorless
0.40 × 0.30 × 0.20 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 10.00 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.944, T_{max} = 0.971
3573 measured reflections
871 independent reflections
648 reflections with $I > 2\sigma(I)$
R_{int} = 0.097
θ_{max} = 27.6°, θ_{min} = 2.9°
h = −10→10
k = −16→16
l = −8→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.112$
$S = 0.95$
871 reflections
111 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.147 (18)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.2730 (4)	0.7411 (2)	0.2853 (6)	0.0530 (8)
H1	0.3251	0.7751	0.1789	0.064*
C2	0.1370 (3)	0.7145 (2)	0.5486 (5)	0.0449 (7)
C3	0.1843 (3)	0.61741 (19)	0.4808 (5)	0.0378 (6)
C4	0.3530 (4)	0.5610 (3)	0.1731 (6)	0.0607 (9)
H4A	0.3955	0.5988	0.0585	0.091*
H4B	0.2780	0.5092	0.1262	0.091*
H4C	0.4377	0.5264	0.2447	0.091*
N1	0.2728 (2)	0.63562 (17)	0.3106 (4)	0.0410 (6)
N2	0.1915 (4)	0.79129 (19)	0.4271 (5)	0.0561 (7)
N3	0.1551 (3)	0.51403 (18)	0.5576 (4)	0.0490 (7)
N4	0.0529 (3)	0.7419 (2)	0.7316 (5)	0.0569 (7)
O1	0.2496 (3)	0.44510 (19)	0.5115 (6)	0.0806 (9)
O2	0.0370 (3)	0.5008 (2)	0.6601 (5)	0.0773 (9)
O3	0.0716 (4)	0.6874 (3)	0.8832 (5)	0.0878 (10)
O4	−0.0300 (3)	0.8211 (2)	0.7273 (6)	0.0839 (10)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0718 (17)	0.0401 (15)	0.0470 (18)	−0.0025 (13)	0.0072 (16)	0.0127 (15)
C2	0.0424 (13)	0.0501 (16)	0.0421 (16)	0.0026 (10)	−0.0036 (12)	−0.0010 (13)
C3	0.0393 (12)	0.0394 (13)	0.0346 (13)	−0.0021 (9)	−0.0019 (11)	0.0059 (11)

C4	0.0676 (18)	0.0527 (19)	0.062 (2)	0.0108 (14)	0.0197 (17)	0.0053 (17)
N1	0.0471 (10)	0.0376 (12)	0.0384 (12)	0.0002 (9)	0.0032 (11)	0.0074 (11)
N2	0.0737 (16)	0.0423 (14)	0.0524 (18)	0.0039 (11)	0.0002 (15)	0.0042 (12)
N3	0.0560 (13)	0.0463 (14)	0.0446 (15)	−0.0099 (11)	−0.0002 (13)	0.0116 (12)
N4	0.0537 (13)	0.0690 (17)	0.0479 (16)	−0.0004 (14)	−0.0017 (13)	−0.0132 (15)
O1	0.0872 (16)	0.0502 (13)	0.104 (3)	0.0139 (11)	0.0169 (18)	0.0335 (15)
O2	0.0832 (18)	0.0780 (17)	0.071 (2)	−0.0301 (13)	0.0296 (16)	0.0049 (14)
O3	0.116 (2)	0.098 (2)	0.0499 (17)	0.0005 (17)	0.0167 (17)	0.0044 (15)
O4	0.0717 (14)	0.106 (2)	0.074 (2)	0.0307 (13)	−0.0068 (15)	−0.0273 (19)

Geometric parameters (Å, º)

C1—N2	1.318 (5)	C4—N1	1.470 (4)
C1—N1	1.344 (4)	C4—H4A	0.9600
C1—H1	0.9300	C4—H4B	0.9600
C2—N2	1.337 (4)	C4—H4C	0.9600
C2—C3	1.365 (4)	N3—O2	1.212 (3)
C2—N4	1.436 (4)	N3—O1	1.218 (4)
C3—N1	1.361 (4)	N4—O3	1.220 (5)
C3—N3	1.423 (3)	N4—O4	1.222 (4)
N2—C1—N1	112.9 (3)	H4A—C4—H4C	109.5
N2—C1—H1	123.5	H4B—C4—H4C	109.5
N1—C1—H1	123.5	C1—N1—C3	105.7 (2)
N2—C2—C3	111.0 (3)	C1—N1—C4	124.1 (3)
N2—C2—N4	119.5 (3)	C3—N1—C4	130.2 (2)
C3—C2—N4	129.2 (3)	C1—N2—C2	104.5 (2)
N1—C3—C2	105.9 (2)	O2—N3—O1	125.1 (3)
N1—C3—N3	122.7 (2)	O2—N3—C3	117.8 (3)
C2—C3—N3	131.3 (3)	O1—N3—C3	117.2 (3)
N1—C4—H4A	109.5	O3—N4—O4	123.8 (4)
N1—C4—H4B	109.5	O3—N4—C2	118.8 (3)
H4A—C4—H4B	109.5	O4—N4—C2	117.3 (3)
N1—C4—H4C	109.5		
N2—C2—C3—N1	0.4 (3)	C3—C2—N2—C1	−0.3 (4)
N4—C2—C3—N1	−174.1 (3)	N4—C2—N2—C1	174.8 (3)
N2—C2—C3—N3	−179.5 (3)	N1—C3—N3—O2	−155.1 (3)
N4—C2—C3—N3	6.0 (5)	C2—C3—N3—O2	24.8 (5)
N2—C1—N1—C3	0.2 (4)	N1—C3—N3—O1	23.5 (4)
N2—C1—N1—C4	179.3 (3)	C2—C3—N3—O1	−156.6 (3)
C2—C3—N1—C1	−0.3 (3)	N2—C2—N4—O3	−143.7 (4)
N3—C3—N1—C1	179.6 (3)	C3—C2—N4—O3	30.5 (5)
C2—C3—N1—C4	−179.4 (3)	N2—C2—N4—O4	34.1 (4)
N3—C3—N1—C4	0.5 (5)	C3—C2—N4—O4	−151.8 (3)
N1—C1—N2—C2	0.1 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O1^{i}	0.93	2.49	3.150 (4)	128
C4—H4*A*···O4^{ii}	0.96	2.48	3.428 (5)	170

Symmetry codes: (i) −*x*+1/2, *y*+1/2, *z*−1/2; (ii) *x*+1/2, −*y*+3/2, *z*−1.