



Crystal structure of 3,3'-biisoxazole-5,5'-bis-(methylene) dinitrate (BIDN)

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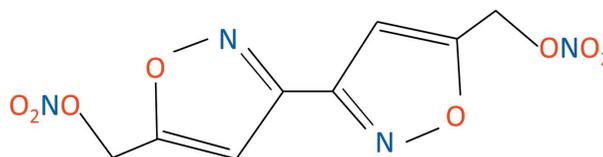
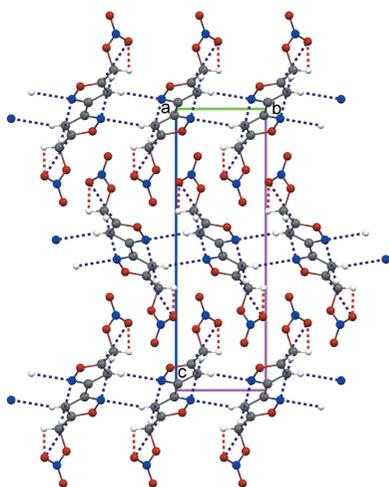
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Keywords: crystal structure; 3,3'-bis-isoxazole-5,5'-bis-methylene dinitrate; energetic material; density; FTIR; Raman; and ultraviolet absorption peaks.**CCDC reference:** 1540757**Supporting information:** this article has supporting information at journals.iucr.org/e

The molecular structure of the title energetic compound, C₈H₆N₄O₈, is composed of two planar isoxazole rings and two near planar alkyl-nitrate groups (r.m.s deviation = 0.006 Å). In the crystal, the molecule sits on an inversion center, thus $Z' = 0.5$. The dihedral angle between the isoxazole ring and the nitrate group is 69.58 (8)°. van der Waals contacts dominate the intermolecular interactions. Inversion-related rings are in close slip-stacked proximity, with an interplanar separation of 3.101 (3) Å [centroid–centroid distance = 3.701 (3) Å]. The measured and calculated densities are in good agreement (1.585 versus 1.610 Mg m⁻³).

1. Chemical context

Isoxazole compounds have attracted much interest in recent years because of their potential usefulness in medicine, agriculture, and in the field of energetic materials (Galenko *et al.*, 2015; Wingard *et al.*, 2017). The title compound is an isoxazole-based energetic material that has been synthesized recently in our laboratory. It has potential use as a trinitrotoluene replacement in melt-castable and Composition B formulations, and as an energetic plasticizing ingredient in nitrocellulose-based propellant formulations. The compound is composed of two heterocyclic isoxazole rings, each bonded to an alkyl nitric ester group. The heterocyclic base has non-bonded electron lone pairs which can exhibit Lewis-base behavior towards electrophilic materials such as nitrocellulose, whereas the alkyl nitric esters provide miscibility and compatibility with commonly used energetic plasticizers.



2. Structural commentary

The molecule (see Fig. 1) consists of two isoxazole rings bonded to two alkyl nitric ester groups. There are no unusual bond lengths or angles. The rings are planar (r.m.s. deviation = 0.0003 Å), and adopt a co-planar *trans* geometry, perhaps to minimize lone-pair interactions of the nitrogen atoms, similar to 3,3'-bisoxazole and 5,5'-diphenyl-3,3'-bisoxazole (Cannas & Marongiu, 1968; van der Peet *et al.*, 2013). Atom C4 is co-

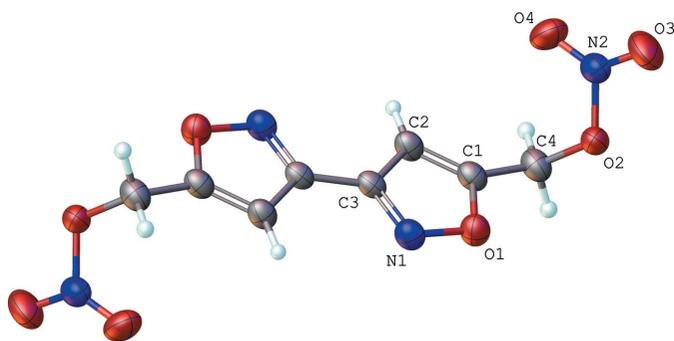


Figure 1
Molecular conformation and atom-numbering scheme. Non-labeled atoms are generated by inversion ($-x, 1-x, 1-z$). Non-hydrogen atoms are shown as 50% probability displacement ellipsoids.

planar with the ring [deviation = 0.062 (3) Å]. Similarly, atoms C4/O2/N2/O3/O4 adopt a near planar conformation (r.m.s deviation = 0.006 Å). The dihedral angle between the isoxazole ring and the nitrate group is 69.58 (9)°.

3. Supramolecular features

Figs. 2 and 3 show the packing of the title compound along the *a* and *b* axes, respectively. Bifurcated contacts between the N1

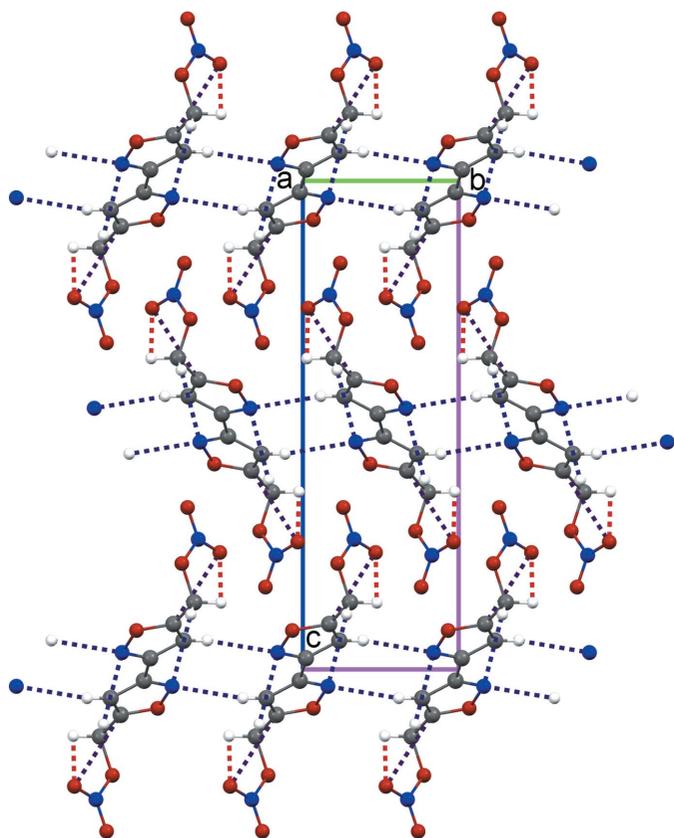


Figure 2
Crystal packing viewed along the *a* axis. Dashed lines represent contacts between atoms N1...H2, N11...H4A, and C11...O4 (blue) and O41...H4B (red).

and H atoms of adjacent molecules [$N1 \cdots H4A^i = 2.704$ (4) Å and $N1 \cdots H2^{ii} = 2.656$ (4) Å]; symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x, y-1, z$] dominate the intermolecular interactions. Inversion-related ($1-x, 1-y, 1-z$) isoxazole rings are in close slip-stacked proximity, with an interplanar separation of 3.101 (3) Å [ring centroid–centroid distance = 3.701 (3) Å].

4. Database survey

An open literature search, as well as a search of the Cambridge Structural Database (Groom *et al.*, 2016) and the Crystallography Open Database (Gražulis *et al.*, 2009) yielded many hits for bis-isoxazole-containing compounds and several on 3,3' and 5,5' bis-isoxazole-based compounds, the most pertinent studies relating to the title compound being the crystal structures of 3,3'-bisoxazole (Cannas & Marongiu, 1968; CCDC 1111317, BIOXZL) and 5,5'-diphenyl-3,3'-bisoxazole (van der Peet *et al.*, 2013; CCDC 935274). In these compounds, the rings also adopt planar *trans* conformations, similar to that observed in the title compound.

5. Synthesis and crystallization

The synthesis of the title compound has been reported recently (Wingard *et al.*, 2017). Briefly, a solution of sodium bicarbonate was added to a mixture of dichloroglyoxime (0.191 mol), propargyl alcohol (0.956 mol), and 1.9 L of

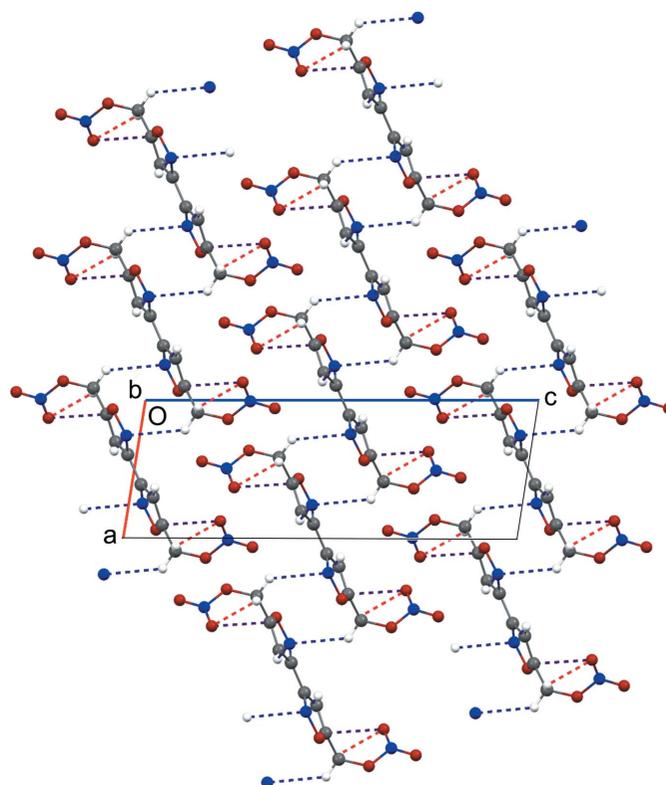


Figure 3
Crystal packing viewed along the *b* axis. Dashed lines represent contacts between atoms N1...H4A and C11...O4 (blue), and O4...H4B (red).

Table 1
Experimental details.

Crystal data	
Chemical formula	C ₈ H ₆ N ₄ O ₈
<i>M_r</i>	286.17
Crystal system, space group	Monoclinic, <i>P2₁/n</i>
Temperature (K)	297
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.1917 (5), 5.5299 (5), 17.4769 (12)
β (°)	99.233 (7)
<i>V</i> (Å ³)	590.65 (8)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.15
Crystal size (mm)	0.4 × 0.2 × 0.1
Data collection	
Diffractometer	Agilent SuperNova, Dualflex, EosS2
Absorption correction	Multi-scan (SCALE3 ABSPACK in <i>CrysAlis PRO</i> ; Rigaku OD, 2015; Bourhis <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.678, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	4487, 1079, 903
<i>R_{int}</i>	0.027
(sin θ/λ) _{max} (Å ⁻¹)	0.602
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.041, 0.105, 1.06
No. of reflections	1079
No. of parameters	92
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.19, -0.18

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008).

methanol to produce the intermediate compound 5,5'-dihydroxymethyl-3,3'-bis-isoxazole (75% yield). Then, this compound (0.120 mol) was added portionwise over ten minutes to 90% nitric acid (150 ml) placed in a 250 ml round-bottom flask equipped with a stir bar, and cooled in an ice-water bath. No exotherm was observed during the addition. The reaction mixture was stirred for four hours while the water-ice bath was warmed to room temperature. The reaction mixture was poured onto ice, resulting in the formation of a white precipitate, which was collected by Büchner filtration and dried, giving the title compound (92% yield). Slow solvent evaporation of a solution in acetonitrile yielded suitable single crystals for the X-ray diffraction experiments at room temperature. Based on the cell dimensions and molecular weight, the calculated crystal density of 1.609 Mg m⁻³ at 297 K is in excellent agreement with the value of 1.585 Mg m⁻³ measured using a pycnometer at room temperature.

Spectroscopic data: FTIR (Nicolet iS50, attenuated total reflectance, cm⁻¹): 3144 (*w*), 3032 (*w*), 2923 (*w*), 1643 (*m*), 1605 (*m*), 1421 (*m*), 1359 (*m*), 1351(*m*), 1278 (*s*), 1259 (*m*), 1209 (*m*), 1075 (*m*), 1021 (*w*), 955 (*m*), 926 (*s*), 912 (*s*), 845 (*s*), 824 (*s*), 753 (*s*), 649 (*m*), 582 (*m*). Raman (Nicolet iS50, 1064 nm; cm⁻¹): 3143 (*m*), 3027 (*w*), 2977 (*m*), 2855.59 (*w*), 1621 (*w*), 1552 (*s*), 1476 (*m*), 1422 (*w*), 1354 (*w*), 1299 (*w*) 1279 (*w*), 1146 (*w*), 1020 (*w*) 960 (*m*), 922 (*w*), 847 (*m*), 728 (*w*), 667 (*w*), 645 (*w*), 585 (*m*), 489 (*m*), 449 (*w*), 381 (*w*), 373 (*w*), 249 (*w*), 218 (*w*), 161.70 (*w*). UV (acetonitrile solvent, nm): 220 nm (max).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The hydrogen atoms were refined using a riding model with C—H = 0.93 or 0.97 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C).

Acknowledgements

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supporting information

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: ShelXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

3,3'-Biisoxazole-5,5'-bis(methylene) dinitrate

Crystal data

$C_8H_6N_4O_8$

$M_r = 286.17$

Monoclinic, $P2_1/n$

$a = 6.1917$ (5) Å

$b = 5.5299$ (5) Å

$c = 17.4769$ (12) Å

$\beta = 99.233$ (7)°

$V = 590.65$ (8) Å³

$Z = 2$

$F(000) = 292$

$D_x = 1.609$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1878 reflections

$\theta = 2.4$ – 25.2 °

$\mu = 0.15$ mm⁻¹

$T = 297$ K

Irregular, colourless

$0.4 \times 0.2 \times 0.1$ mm

Data collection

SuperNova, Dualflex, EosS2
diffractometer

Radiation source: fine-focus sealed X-ray tube,
Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 8.0945 pixels mm⁻¹

ω scans

Absorption correction: multi-scan
(SCALE3 ABSPACK in CrysAlisPro; Rigaku
OD, 2015; Bourhis *et al.*, 2015)

$T_{\min} = 0.678$, $T_{\max} = 1.000$

4487 measured reflections

1079 independent reflections

903 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 25.3$ °, $\theta_{\min} = 2.4$ °

$h = -7 \rightarrow 7$

$k = -6 \rightarrow 5$

$l = -21 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.105$

$S = 1.06$

1079 reflections

92 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.168P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.19$ e Å⁻³

$\Delta\rho_{\min} = -0.18$ e Å⁻³

Extinction correction: SHELXL-2016/4
 (Sheldrick 2015b),
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.077 (8)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C4	0.5869 (4)	0.8027 (4)	0.63740 (11)	0.0621 (6)
H4A	0.714559	0.780169	0.612468	0.075*
H4B	0.553186	0.974123	0.636451	0.075*
C3	0.1082 (3)	0.5201 (3)	0.52299 (9)	0.0446 (5)
C1	0.3989 (3)	0.6693 (3)	0.59298 (10)	0.0513 (5)
C2	0.1987 (3)	0.7337 (3)	0.55899 (10)	0.0512 (5)
H2	0.133409	0.885170	0.559012	0.061*
N1	0.2447 (3)	0.3392 (3)	0.53455 (9)	0.0558 (5)
N2	0.5082 (3)	0.8284 (4)	0.76635 (11)	0.0660 (5)
O2	0.6372 (2)	0.7230 (3)	0.71689 (8)	0.0610 (5)
O1	0.4340 (2)	0.4322 (2)	0.57971 (8)	0.0603 (4)
O4	0.3714 (3)	0.9669 (4)	0.73937 (12)	0.0920 (6)
O3	0.5589 (3)	0.7599 (4)	0.83151 (10)	0.1017 (7)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C4	0.0688 (13)	0.0653 (15)	0.0515 (11)	−0.0108 (11)	0.0070 (10)	−0.0053 (9)
C3	0.0621 (11)	0.0348 (9)	0.0377 (9)	−0.0046 (8)	0.0103 (7)	0.0013 (7)
C1	0.0674 (13)	0.0421 (11)	0.0444 (10)	−0.0060 (9)	0.0088 (9)	−0.0012 (8)
C2	0.0678 (13)	0.0361 (10)	0.0478 (10)	−0.0027 (9)	0.0037 (9)	−0.0010 (8)
N1	0.0665 (11)	0.0421 (10)	0.0571 (9)	−0.0043 (8)	0.0046 (8)	−0.0043 (7)
N2	0.0596 (11)	0.0725 (13)	0.0640 (12)	−0.0003 (10)	0.0042 (9)	−0.0189 (9)
O2	0.0597 (8)	0.0670 (10)	0.0536 (8)	0.0124 (7)	0.0009 (6)	−0.0115 (7)
O1	0.0649 (9)	0.0490 (9)	0.0637 (8)	0.0005 (7)	0.0002 (7)	−0.0044 (6)
O4	0.0747 (11)	0.0866 (13)	0.1133 (14)	0.0257 (10)	0.0113 (10)	−0.0237 (11)
O3	0.1055 (14)	0.144 (2)	0.0538 (10)	−0.0022 (13)	0.0082 (9)	−0.0135 (11)

Geometric parameters (\AA , $^\circ$)

C4—H4A	0.9700	C1—C2	1.334 (3)
C4—H4B	0.9700	C1—O1	1.355 (2)
C4—C1	1.487 (3)	C2—H2	0.9300
C4—O2	1.443 (2)	N1—O1	1.402 (2)
C3—C3 ⁱ	1.465 (4)	N2—O2	1.395 (2)

C3—C2	1.411 (2)	N2—O4	1.182 (2)
C3—N1	1.304 (2)	N2—O3	1.193 (2)
H4A—C4—H4B	107.9	O1—C1—C4	115.83 (18)
C1—C4—H4A	109.1	C3—C2—H2	127.8
C1—C4—H4B	109.1	C1—C2—C3	104.42 (17)
O2—C4—H4A	109.1	C1—C2—H2	127.8
O2—C4—H4B	109.1	C3—N1—O1	105.57 (15)
O2—C4—C1	112.39 (17)	O4—N2—O2	117.91 (19)
C2—C3—C3 ⁱ	129.4 (2)	O4—N2—O3	130.4 (2)
N1—C3—C3 ⁱ	118.8 (2)	O3—N2—O2	111.70 (19)
N1—C3—C2	111.83 (16)	N2—O2—C4	114.35 (16)
C2—C1—C4	133.91 (19)	C1—O1—N1	107.99 (14)
C2—C1—O1	110.19 (16)		
C4—C1—C2—C3	176.7 (2)	C2—C1—O1—N1	-0.1 (2)
C4—C1—O1—N1	-177.37 (15)	N1—C3—C2—C1	0.0 (2)
C3 ⁱ —C3—C2—C1	179.9 (2)	O2—C4—C1—C2	115.6 (2)
C3 ⁱ —C3—N1—O1	-179.97 (18)	O2—C4—C1—O1	-67.9 (2)
C3—N1—O1—C1	0.08 (19)	O1—C1—C2—C3	0.0 (2)
C1—C4—O2—N2	-82.9 (2)	O4—N2—O2—C4	1.0 (3)
C2—C3—N1—O1	-0.1 (2)	O3—N2—O2—C4	-178.72 (19)

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