

Synthesis of bis-Isoxazole-bis-Ethylene Dinitrate and bis-Isoxazole-tetra-Ethylene Tetranitrate: Potential Energetic Plasticizers

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Abstract: The syntheses and characterizations of two new energetic compounds based on a bis-isoxazole scaffold are presented. The syntheses employ a metal-free [3 + 2] cycloaddition of an alkyne and a nitrile oxide. In addition, we report the molecular structure of these compounds as de-

termined by single crystal x-ray diffractometry. Both materials have favourable sensitivity properties and low melting points. Their energetic properties indicate potential use as propellant plasticizers.

Keywords: energetic materials • nitrates • explosives • propellants • plasticizer • isoxazole

1 Introduction

Design and synthesis of new energetic materials with tailored properties is an area of significant interest. Power, sensitivity, and stability are considered, along with environmental impact and cost. Further concerns include formulation compatibility and longevity. In the realm of propellants, plasticizers are commonly used in formulations to improve the physical properties of the combined material. An energetic plasticizer can improve the energy content of the formulation in addition to providing the needed mechanical properties. The most well-known and widely used energetic plasticizer is nitroglycerin (NG), an oily liquid first invented in 1847 [1] and used extensively in energetics [2–4]. While the energy associated with NG is desirable, its volatility and high sensitivity to heat and impact are not advantageous. NG begins to thermally decompose at 50 °C [5] and requires chemical stabilization to prevent premature volatilization/decomposition into reactive gaseous products during long-term aging [6]. New energetic plasticizers with improved stability are needed.

There is interest in materials that can exhibit Lewis basic behavior towards electrophilic energetic materials like nitrocellulose or nitramines. The isoxazole ring supplies that Lewis basic quality through the nonbonded electron lone pairs. The ethyl nitrate pendant chains are intended both to soften and to give the materials high miscibility with other commonly used energetic plasticizers through better wetting and plasticization properties.

The compounds described herein are the ethyl derivatives of the previously reported 3,3'-bis-isoxazole-5,5'-bis-methylene dinitrate [7] and 3,3'-bis-isoxazole-4,4',5,5'-tetramethylene dinitrate [8]. Extending an alkyl chain is known to soften a material, so the materials reported herein are ex-

pected to show greater miscibility and plasticizing properties. While the additional carbon content will reduce the energy output and oxygen balance, the extended alkyl chains may serve to increase the fluidity and plasticity of the material.

2 Experimental Section


Note: we did not experience any issues in synthesizing and handling the materials described in this article. Nonetheless, they should be handled with extreme care, implementing standard safety procedures for handling energetic materials.

Chemicals and solvents were used as received from Sigma-Aldrich. NMR spectra were recorded using a 400 MHz Bruker instrument. The chemical shifts quoted in ppm refer to typical standard tetramethylsilane in DMSO- d_6 as the solvent. Melting points and decomposition temperatures were measured at a heating rate of 5 °C min⁻¹ using a TA instru-

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ments DSC Q2000 instrument. Infrared spectra were measured with a ThermoFisher Nicolet iS50 FTIR instrument.

Impact sensitivity testing was performed using a modified Picatinny Arsenal drop hammer, and friction sensitivity was performed using a BAM friction apparatus in accordance with NATO STANAG guidelines. ESD sensitivity was performed using a Firing Test System Model 931.

Single crystals of compounds **2** and **4** were characterized with a SuperNova, Dualflex, EosS2 diffractometer using a Mo K α ($\lambda=0.71073$ Å) radiation source and an EosS2 charged coupled device (CCD) detector at room temperature. CrysAlis PRO and Mercury were used in data collection, cell refinement, and data reduction. [9,10] The molecular structure was determined with SHELXT using intrinsic phasing and refined with SHELXL using least squares minimization [11]. The hydrogen atoms were refined using a riding model with C–H=0.93 or 0.97 Å and $U_{iso}(H)=1.2 U_{eq}(C)$. Table 1 in the supplementary lists the data collection, and structure refinement details. The crystallographic information files for **2** and **4** can be obtained free of charge from the Cambridge Crystallographic Centre by means of <http://www.ccdc.cam.ac.uk/structures/>.

2,2'-([3,3'-biisoxazole]-5,5'-diyl)bis(Ethane-1-ol) (**1**)

Dichloroglyoxime [12] (5.0 g, 31.9 mmol, 1.00 eq) and 3-butyne-1-ol (12.1 mL, 159.3 mmol, 5 eq) were combined with 150 mL of ethanol in a flask with a stir bar. Sodium bicarbonate (6.7 g, 79.7 mmol, 2.5 eq.) was dissolved in 320 mL water, and added dropwise to the reaction mixture over 5 hours. The resulting yellow solution was concentrated *in vacuo*. Cold water (300 mL) was added to the residual solid material. The product was isolated by Büchner filtration and washed with additional cold water. The shiny off-white solid was dried overnight to yield 4.4 g (62 %) product. ^1H NMR (400 MHz, DMSO- d_6); 6.75 (s, C–H, 2H), 4.95 (t, –OH, 2H), 3.76 (q, –CH₂–CH₂–OH, 4H), 2.98 (t, CH₂–CH₂–OH, 4H). ^{13}C NMR (100 MHz, DMSO- d_6); 173.77 (N–C–C), 154.4 (O–C–C), 100.64 (–CH), 58.9 (–CH₂–CH₂–OH), 30.4 (–CH₂–CH₂–OH); IR; $\nu_{\text{OH}}=3282\text{ cm}^{-1}$. $T_m=188.9^\circ\text{C}$.

Table 1. Sensitivities of bis-isoxazole nitrate esters.

Compound	IS ^[a] [J]	FS ^[b] [N]	ESD ^[c] [J]
2	> 36	> 350	3.125
4	> 36	> 350	3.125
RDX	6.2	> 350	0.125

[a] IS=impact sensitivity, drop weight. [b] FS=friction sensitivity. [c] ESD=electrostatic discharge.

[3,3'-biisoxazole]-5,5'-Diylbis(Ethane-2,1-diyl) Dinitrate (**2**)

Acetic anhydride (7 mL, 74 mmol, 17 eq) and glacial acetic acid (7 mL, 122 mmol, 27 eq) were combined in a round bottom flask with a stir bar. The flask was cooled in an ice bath. Once cold, nitric acid (0.5 mL, 12 mmol, 2.7 eq) was added and the mixture was stirred in the ice bath for 1 hour. The bis-isoxazole (**1**) (1.0 g, 4.5 mmol, 1 eq) was added, and went into solution after several minutes. The reaction was stirred overnight, allowing the ice bath to slowly warm to RT. Pipetted the reaction mixture in 200 mL water to precipitate white solid product. Filtered, and washed the solid with additional water. Dried overnight to obtain 1.36 g (97 %) of BIDNE (**2**) as a white powder. ^1H (400 MHz, DMSO- d_6); 6.95 (s, C–H, 2H), 4.88 (t, –CH₂–CH₂–ONO₂, 4H), 3.36 (t, CH₂–CH₂–ONO₂, 4H). ^{13}C (100 MHz, DMSO- d_6); 171.3 (N–C–C), 154.4 (O–C–C), 101.4 (–CH), 70.6 (–CH₂–CH₂–ONO₂), 24.7 (–CH₂–CH₂–ONO₂); IR; $\nu_{\text{NO}}=1629$, 1590 cm^{-1} . $T_m=76.3^\circ\text{C}$; $T_{\text{dec}}=200.5^\circ\text{C}$.

2,2',2'',2'''-([3,3'-biisoxazole]-4,4',5,5'-tetrayl)Tetrakis(Ethane-1-ol) (**3**)

3-Hexyn-1,6-ol (3.64 g, 31.9 mmol, 5.0 eq) and NaHCO₃ (1.34 g, 15.9 mmol, 2.5 eq) were combined with 100 mL n-butanol, and heated to 120 °C in an oil bath with stirring. Dissolved dichloroglyoxime [12] (1.0 g, 6.37 mmol, 1.0 eq) in 30 mL n-butanol, and added dropwise to the reaction mixture over 1 hour. Once the addition is complete and while the reaction is still heated to 120 °C, 10 mL of water was added dropwise. Reaction was allowed to stir for 10 minutes at temperature. The reaction was cooled and concentrated *in vacuo*. Cold water (200 mL) was added to the residual solid material. The product was isolated by Büchner filtration and washed with additional water. The off-white solid was dried overnight to yield 0.52 g product. An additional 0.4 g product crystallized from the filtrate and was collected by Büchner filtration and dried. Overall, 0.92 g (46 %) product was obtained. ^1H (400 MHz, DMSO- d_6); 4.91, 4.66 (each a t, –OH, each 2H), 3.73, 3.50 (each a q, –CH₂–CH₂–OH, each 4H), 2.98, 2.73 (each a t, CH₂–CH₂–OH, each 4H); ^{13}C (100 MHz, DMSO- d_6); 169.2 (N–C–C), 153.8 (O–C–C), 112.1 (O–C–C), 60.4, 58.7 (–CH₂–CH₂–OH), 29.0, 25.8 (–CH₂–CH₂–OH); IR; $\nu_{\text{OH}}=3277\text{ cm}^{-1}$. $T_m=153.7^\circ\text{C}$.

[3,3'-biisoxazole]-4,4',5,5'-tetrayltetrakis(Ethane-2,1-diyl) Tetranitrate (**4**)

Acetic anhydride (6.6 mL, 70.4 mmol, 44 eq) and glacial acetic acid (6.6 mL, 115.3 mmol, 72 eq) were combined in a flask with a stir bar. The flask was cooled in an ice bath. Once cold, nitric acid (0.54 mL, 12.8 mmol, 8 eq) was added and the mixture was stirred in the ice bath for 1 hour. The bis-isoxazole (**3**) (0.5 g, 1.6 mmol, 1 eq) was added, and

went into solution after several minutes. The reaction was stirred overnight, allowing the ice bath to slowly warm to RT. Pipetted the reaction mixture in 200 mL water to precipitate white solid product. Filtered, and washed the solid with additional water. Dried overnight to obtain 0.7 g (89%) of BITNE (**4**) as a white solid. ^1H (400 MHz, $\text{DMSO}-d_6$); 4.86, 4.68 (each a t, $-\text{CH}_2-\text{CH}_2-\text{ONO}_2$, each 4H), 3.39, 3.11 (each a t, $\text{CH}_2-\text{CH}_2-\text{ONO}_2$, each 4H). ^{13}C (100 MHz, $\text{DMSO}-d_6$); 168.2 (N—C—C), 154.2 (O—C—C), 111.5 (O—C—C), 72.6, 70.7 ($-\text{CH}_2-\text{CH}_2-\text{ONO}_2$), 23.3, 20.3 ($-\text{CH}_2-\text{CH}_2-\text{ONO}_2$); ν_{NO} = 1645, 1626, 1613 cm^{-1} . T_m = 69.5 °C; T_{dec} = 188.3 °C.

3 Results and Discussion

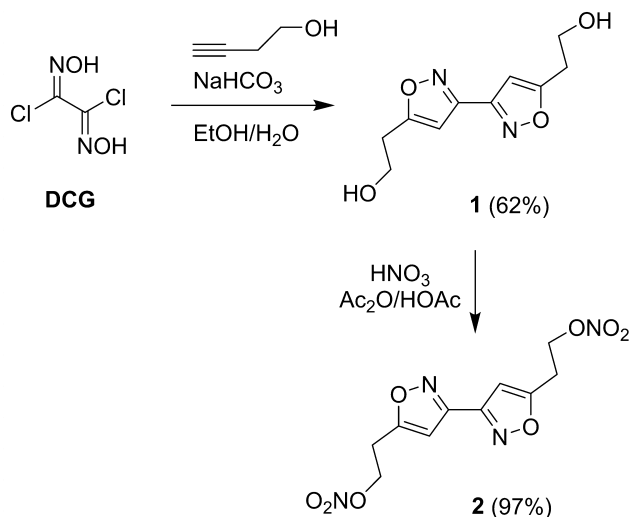
Isoxazoles are commonly synthesized via the cycloaddition of hydroximoyl chloride with nitrile oxides in the presence of base [13,14]. Dichloroglyoxime is often used as the source of hydroximoyl chloride in energetics research [15–17]. The 3,3'-bis-isoxazole ring system is formed through the cyclization of an alkyne with dichloroglyoxime. The extended alkyl chains result in somewhat lower cyclization yields than the previously reported methyl derivatives [7,8].

To produce **1**, dichloroglyoxime [12] and an excess of 3-butyn-1-ol were combined in ethanol, to which an aqueous solution of sodium bicarbonate was added dropwise over several hours (Scheme 1). The long addition time minimizes dimerization/oligomerization of the nitrile oxide intermediate [18–20]. Nitration of **1** under Bachmann conditions produces [3,3'-bis(isoxazole)-5,5'-diylbis(ethane-2,1-diyl) dinitrate (**2**) in excellent yield. Product isolation was difficult from nitration of **1** via treatment with 100% nitric acid, possibly because the product can sequester excess hydronium ions. Dinitrate **2** is hydrolytically stable.

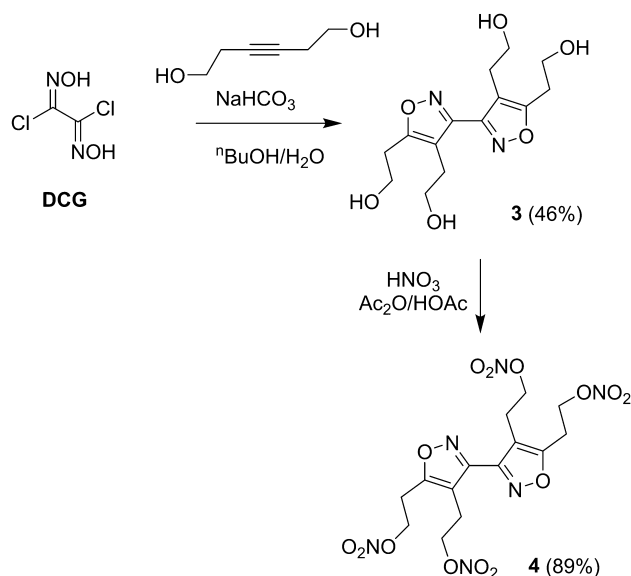
The cycloaddition to make **3** requires refluxing the reaction in n butanol (Scheme 2). To prevent decomposition of

the dichloroglyoxime, the 3-hexyn-1,6-diol and sodium bicarbonate are combined and the DCG is added slowly as a solution in n butanol. A small amount of water is required to solvate the base, and can be present in the reaction mixture or can be added dropwise after the addition of the DCG. Compound **3** can be nitrated to tetranitrate **4** under Bachmann conditions in good yield. Product isolation from nitration of **3** via treatment with 100% nitric acid was problematic, as the product can hold excess hydronium ions hostage and will not readily precipitate.

Dinitrate **2** and tetranitrate **4** were tested for sensitivity to impact, friction, and ESD (Table 1). Compared to a class 1 sample of RDX, both **2** and **4** were significantly less sensitive with respect to impact and electrostatic discharge. The insensitivity of these materials can largely be attributed to the poor oxygen balance. The performance properties of **2** and **4** are summarized in Table 2. Compound **2** has performance slightly under that of TNT, while compound **4** has predicted performance characteristics similar to TNT. Furthermore, the melting temperatures of both compounds are well below 100 °C, with a sizeable gap between the melting and decomposition temperatures. In particular, compound **2** has an especially high decomposition temperature at 200.5 °C. A common decomposition pathway of nitroxymethyl groups under heat is the scission of the side chain via the loss of formaldehyde [21]. In a compound with a nitroxymethyl moiety, the nitrate ester functionality can be lost under thermal stress through a radical pathway, resulting in formation of an aldehyde or carboxylic acid group [22]. There is additional driving force for this transformation if the nitroxymethyl is attached to an aromatic ring, as the carbonyl functionality will be in conjugation. However, a nitroxyethyl group has a lower driving force to form the alde-



Scheme 1. Synthesis of bis-isoxazole diol **1** and dinitrate **2**.



Scheme 2. Synthesis of bis-isoxazole tetraol **3** and tetranitrate **4**.

Table 2. Properties of bis-isoxazole nitrate esters.

	2	4	TNT	NG
T_m [°C] ^[a]	76.3	69.5	80.4	14
T_{dec} [°C] ^[b]	200.5	188.3	295.0	50.0
Ω_{CO_2} [%] ^[c]	−86.6	−71.5	−74	3.5
Ω_{CO} [%] ^[d]	−35.6	−26.0	−24.7	24.7
ρ [g cm ^{−3}] ^[e]	1.565	1.568	1.654	1.6
P_{cj} [GPa] ^[f]	17.0	19.6	20.5	25.3
V_{det} [km s ^{−1}] ^[g]	6910	7245	6950	7700
I_{sp} [s] ^[h]	200.8	205.7	–	243.8
ΔH_f° [kJ mol ^{−1}] ^[i]	−56.2	−135.2	−59.3	−370

[a] T_m = onset melting temperature. [b] T_{dec} = onset decomposition temperature. [c] Ω_{CO_2} = CO₂ oxygen balance. [d] Ω_{CO} = CO oxygen balance. [e] ρ = experimental density determined by x-ray diffraction. [f] P_{cj} = calculated detonation pressure. [g] V_{det} = calculated detonation velocity. [h] I_{sp} = calculated specific impulse. [i] ΔH_f° = molar enthalpy of formation.

hyde or carboxylic acid, and consequently, an increase in the observed thermal onset of decomposition.

Single crystal x-ray diffraction and structure analysis of the title compounds confirmed unequivocally their identity and revealed their molecular configuration. Figures 1a and b reveal the molecular structures of molecules **2** and **4**, respectively. Both molecules are centrosymmetric with each asymmetric unit containing one-half the molecule and the other half generated by the symmetry codes 2−*x*, 1−*y*, 1−*z* (**2**) or 1−*x*, *y*, 1/2−*z* (**4**). Their bond lengths and angles are in the usual ranges of typical isoxazole and alkyl nitric ester

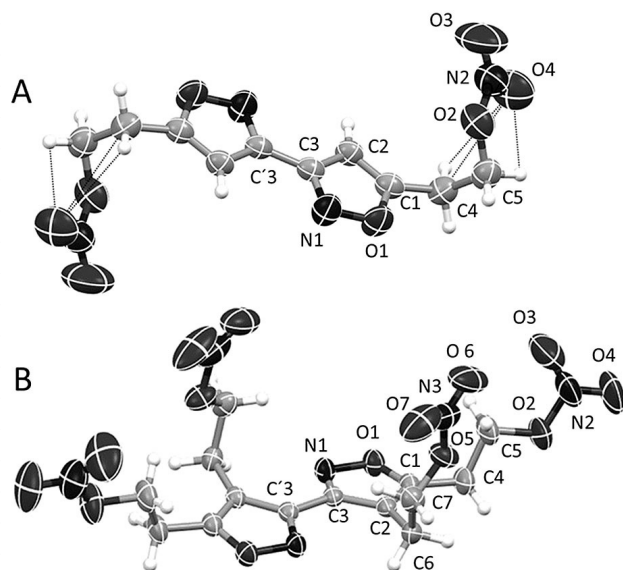


Figure 1. Molecular conformation and atom-numbering schemes of molecules **2** (A) and **4** (B). Non-labeled atoms of **2** and **4** are generated by inversion; symmetry codes: (2−*x*, 1−*y*, 1−*z*) and (1−*x*, *y*, 1/2−*z*) for **2** and **4**, respectively. Non-hydrogen atoms are shown as 50% probability displacement ellipsoids.

compounds [8, 23–26]. The isoxazole rings adopt a *trans* planar configuration [r.m.s deviation of 0.0019 (**3**) and 0.0015 (**4**) Å for molecule **2** and **4**, respectively], suggesting a delocalized aromatic π system with reduced nitrogen atoms' lone pair interaction. Similarly, the nitrate groups of both molecules adopt a planar configuration (r.m.s deviations = 0.0011 (**2**) Å for molecule **2** and 0.0024 (**2**) Å for molecule **4**). In molecule **2**, the atoms C1/C4/C5 form a plane that subtends respective dihedral angles of 71.4 (3)° and 80.3 (2)° with respect to the isoxazole and nitrate planes, whereas in molecule **4** the corresponding plane forms dihedral angles of 8.1 (2)° and 6.8 (3)° relative to the ring and nitrate planes. In contrast, its C2–C6–C7 plane subtends dihedral angles of 74.2 (2)° and 62.5 (2)° relative to the ring and nitrate planes, respectively.

Intra- and intermolecular interactions impact the packing and stability of the crystal. Figure 1a shows the intramolecular interactions of molecule **2**. Trifurcated contacts between O4 and C4, H4A, and H5A atoms govern these interactions. The intermolecular distances range between 2.297 and 3.110 Å, with the O4–H5B = 2.297 (3) Å being the shortest. Similarly, the O and H atoms play a key role in the intramolecular interactions of molecule **4** (not shown). Specifically, the O3 atoms form bifurcated contacts with the H5A and H5B atoms, the O5 atoms form contacts with H5B atoms, and the O7 atoms form bifurcated contacts with H5A and H7B atoms. These contact distances range between 2.44 and 2.625 Å. In addition, molecule **4** presents bifurcated contacts between the N1 atoms and its inversion related H6B and C6 atoms (1−*x*, *y*, 1/2−*z*), and it exhibits a pair of H···H contacts (H4B···H6A = H'4B'···H'6A' = 2.395 (1) Å; symmetry code: (i) 1−*x*, *y*, 1/2−*z*).

Figures 2a and 2b show the respective packing of molecules **2** and **4**. The H and O atoms of molecule **2** govern its intermolecular interactions. The ring H2 atoms interact with the O atoms of adjacent molecules [H2···O3ⁱ = 2.608 (4) Å; symmetry code: (i) 2−*x*, 1−*y*, −*z*], whereas the H5A atoms interact with the N1 atoms the adjacent molecules [H5A···N1ⁱ = 2.738 (3) Å]. In addition, the O4 atoms interact with the O3 atom of nearest neighboring molecules [O4···O3ⁱⁱ = 2.848 (6) Å; symmetry code: (ii) −1 + *x*, *y*, *z*]. This interaction is relatively strong, as the O4···O3 distance is shorter than the sum of the O-atom van der Waals radii (3.7 Å). Similarly, in molecule **4** the H···O dominate the intermolecular interactions. Specifically, the O6 atoms form contacts with the H5A and H7B atoms of adjacent molecules [H5A···O6ⁱ = 2.474 (1) Å and O6···H7Bⁱⁱ = 2.714 (3) Å; symmetry codes: (i) *x*, 1−*y*, 1/2 + *z* and (ii) *x*, 1−*y*, −1/2 + *z*]. In addition, the O4 atoms interact with the H4B atoms of adjacent molecules [O4···H4Bⁱⁱ = 2.715 (3) Å; symmetry code: (i) 3/2−*x*, 1/2−*y*, −1/2 + *z*].

Molecule **2** crystallizes in the triclinic *P*-1 space group with one molecule in the unit cell, whereas molecule **4** crystallizes in the orthorhombic *Pbcn* space group with four molecules in the unit cell. The structure of **2** reveals the isoxazole rings stack along the *a* axis [centroid-to-centroid dis-

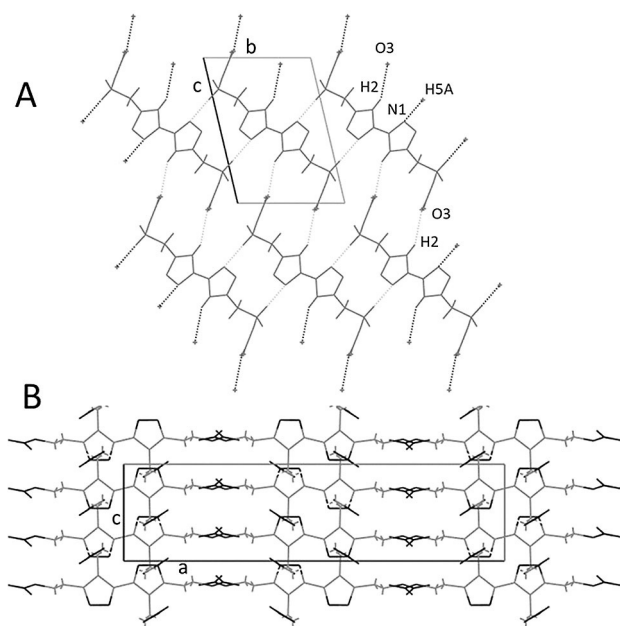


Figure 2. Crystal packing of **2** viewed along the *a* axis (A) and **4** viewed along the *b* axis (B).

tance = 4.959 (1) Å; plane-to-plane shift of 3.418 (6) Å], with the inversion-related rings in close slip-stacked proximity [centroid–centroid distance = 3.732 (3) Å; plane-to-plane shift = 1.058 (6) Å]. In contrast, some of the rings of molecules **4** stack along the *b* axis [centroid–centroid distance = 10.965 (1) Å; plane-to-plane shift of 0.960 (1) Å], forming periodic columns along the *c* axis with the ethyl nitric oxide pendants directed along the *a* axis. Based on the molecular mass and lattice constants of compounds **2**, we obtain a density of 1.565 g cm^{−3} at room temperature and list it in Table 2. The density of compound **4** is nearly identical that of compound **2** at room temperature. With the previously reported nitroxymethyl compounds, the tetranitrate [8] has a density of 1.786 g cm^{−3} compared to the dinitrate [7] at 1.585 g cm^{−3}. There appears to be a leveling off of density with respect to the number of nitro groups and the length of alkyl chains added to the molecule.

4 Conclusions

In summary, the syntheses, properties, and crystal structures of two new bis-isoxazole-based energetic materials have been presented. Compounds **2** and **4** are insensitive, with low melting points. These are favorable characteristics for potential melt-castable secondary explosives and propellant plasticizers.

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