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High-density insensitive energetic materials: 2,4,6-tris(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine†

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An efficient and reliable synthesis of 2,4,6-tris(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine (**1**) has been developed. The ether **1** was fully characterized by IR and multinuclear NMR spectroscopy, and X-ray crystal structure determinations. The compound exhibits good density, excellent thermal stability, and high performance, while impact sensitivities are comparable to TNT.

Introduction

Fluoronitro compounds have found interesting applications in energetic materials science, as incorporation of fluorine into nitrated molecules significantly improves their thermal and chemical stability, compatibility with others ingredients of propellants or explosives, and safety profile of a compound.^{1–6} Energetic molecules that contain a C(NO₂)₂F moiety typically show lower impact sensitivity than similar compounds that contain a C(NO₂)₃ moiety.^{7,8}

These fluorine and oxygen rich energetic compounds are promising ingredients of metallized formulations for composite propellants, explosives and pyrotechnics.^{9–14} Given the importance of C(NO₂)₂F moiety in energetic compounds and the fact that a large majority of promising explosives and propellant ingredients contain a high nitrogen heterocyclic backbone, it is not surprising that combination of these structural motifs in a molecule is a topic of current interest to the energetic material community.

Fluorodinitroethanol has long been recognized as a useful precursor for the design and synthesis of high density thermostable energetic compounds, and a spectacular range of its derivatives, namely esters, formals and nitramines, have been reported.^{15–17} In contrast, fluorodinitroethanol ethers are more limited in nature. Frankel *et al.*¹⁸ reported an inefficient synthesis of 2,4,6-tris(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine

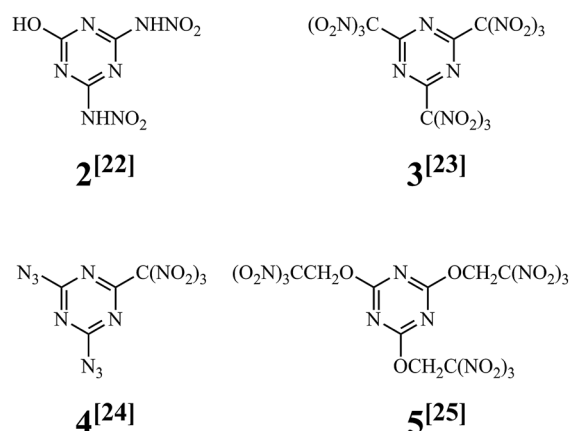


Fig. 1 Energetic 1,3,5-triazine derivatives.

(**1**), a rare example of a heteroaryl fluorodinitroethyl ether, but neither physical characterization (only melting point 76–77 °C was given), crystal structure, thermal stability, sensitivity, nor explosive performance were specified.

1,3,5-Triazine scaffold are privileged structures present within an extensive array of energetic materials, and a few reviews describe the recent publications relating to these compounds.^{19–21} The basis for the design of energetic triazines is commercially available and inexpensive cyanuric chloride. Previous works by our group and others have shown the construction of 1,3,5-triazines bearing –C(NO₂)₃, –OCH₂–C(NO₂)₃, –N₃ and other explosophoric moieties (for example, compound **2–5**, Fig. 1) to be an efficient way of generating energetic materials with superior performance. Herein we wish to describe an efficient synthesis and full characterization of ether **1** and present the first X-ray crystal structure of this compound along with detailed explanation of the higher packing density of **1** in comparison with its trinitroethoxy analog **5**.

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Results and discussion

The original procedure for preparation of compound **1** involved prolonged refluxing a mixture of cyanuric chloride (**6**) and fluorodinitroethanol (**7**) in methylene chloride in the presence of pyridine, giving target crude product as viscous yellow oil in 38% yield. Tedious purification had reproducibility problems and the yield of pure colorless solid compound **1** was low (in our hands, no more than 15% of the pure product).

The nucleophilicity of alcohol **7** was not sufficient to yield ether **1** for a short period of time. A significant problem with this reaction is the proclivity of the alcohol to undergo a rapid retro-Mannich fragmentation under basic conditions, which is driven to the formation of fluorodinitromethanide salts. It is obvious that the type of the base used to generate of an alkoxide from the alcohol is very important for the success of this reaction.

Our investigation was focused on the reaction of cyanuric chloride with alcohol **7** under a variety of conditions. Such reaction parameters, as the solvent effect, temperature, reaction time were varied (Table 1), but the key advance was the use of an optimal base. Among several solvents we screened, the cheapest and most common solvent such as acetone gave the best results. Gratifyingly, an efficient procedure for the formation of ether **1** was rapidly identified. While a number of inorganic bases such as K_2CO_3 and Na_2CO_3 were viable promoters, Na_3PO_4 gave rise to the best results. Accordingly, simple stirring of the reactants in the presence of Na_3PO_4 in acetone at room temperature during 4 h provided after recrystallization pure ether **1** in 83%

Table 1 Conditions screening for synthesis of compound **1**^a

| Entry | Solvent | Base | <i>T</i> , °C | <i>t</i> , ^b h | Yield, ^c % |
|-------|---------------------------------|---------------------------------|---------------|---------------------------|-----------------------|
| 1 | CH ₂ Cl ₂ | NEt ₃ | 40 | 10 | 23 ^d |
| 2 | MeCN | NEt ₃ | 20 | 3 | 27 ^d |
| 3 | Acetone | NEt ₃ | 20 | 3 | 30 ^d |
| 4 | Acetone | Pyridine | 20 | 2 | 28 ^d |
| 5 | Acetone | Pyridine | 0 | 12 | 38 ^d |
| 6 | Acetone | KOH ^e | −10 | 0.5 | 52 ^d |
| 7 | Acetone | NaOH ^e | −10 | 0.5 | 69 ^d |
| 8 | Acetone | Na ₂ CO ₃ | 20 | 7 | 56 |
| 9 | Acetone | K ₂ CO ₃ | 20 | 4 | 43 |
| 10 | Acetone | Na ₃ PO ₄ | 20 | 4 | 85 |
| 11 | MeCN | Na ₃ PO ₄ | 20 | 5 | 81 |
| 12 | DMF | Na ₃ PO ₄ | 0 | 3 | 62 ^d |
| 13 | DMSO | Na ₃ PO ₄ | 0 | 2 | 53 ^d |
| 14 | CH ₂ Cl ₂ | Na ₃ PO ₄ | 20 | 48 | 58 |

^a The cyanuric chloride (0.01 mol), fluorodinitroethanol (0.033 mol) and base (0.033 mol) were mixed together and the reaction was stirred for the selected time at selected temperature. ^b Time at which TLC (CCl₄/MeCN, 3 : 1) indicated complete disappearance of the starting reagents. ^c Yield of crude product. ^d Viscous oil. ^e Used a 40% aqueous solution.

yield, which is more than five times greater than that obtained at Frankel's conditions.¹⁸ The ether **1** could be synthesized in multigram quantities with only filtration over a pad of silica gel and crystallization from CCl₄/CHCl₃ necessary to obtain the desired product in pure form.

The compound **1** was characterized by NMR, IR spectroscopy, and elemental analysis. In the ¹H NMR, a resonance of the methylene moiety was observed at δ = 5.96 ppm as a doublet with a ³J_(H,F) coupling constant of 15.7 Hz. The ¹³C NMR spectrum of compound **1** has three signals. Both carbon resonances of the CH₂CF(NO₂)₂ moieties were observed as doublets; for CF(NO₂)₂ appeared at 120.0 ppm (¹J_(C,F) = 292.1 Hz) and, for CH₂, at 65.0 ppm (²J_(C,F) = 19.3 Hz). A signal for the triazine ring was observed at δ = 172.7 ppm. The ¹⁹F NMR spectrum showed a broadened triplet at δ = −111.8 ppm.

The structure of ether **1** was unequivocally confirmed by single crystal X-ray diffraction study. An asymmetric unit cell of compound **1** contains one molecule occupying general position (Fig. 2). One of fluorodinitroethoxy group is disordered over two positions in the ratio of ca. 7 : 3, and in general one can consider an asymmetric unit cell as containing two independent molecules. Selected geometrical characteristics are listed in Table 2. While all three exocyclic N–C–O–C torsion angles are close to 180° as expected, the C–O–C–C angles that define the shape of molecule are found to be also close to 180° (except for the major part of disordered substituent).

In our recent study on trinitroethoxy-triazine **5**, orientation of the trinitroethoxy moieties was found to be somewhat different (Table 1S in ESI†). Two out of three trinitroethoxy groups deviated from the plane of the triazine ring (the C–O–C–C torsion angles were found to be far from 180°). Such a difference in molecular conformation can be responsible for sizable

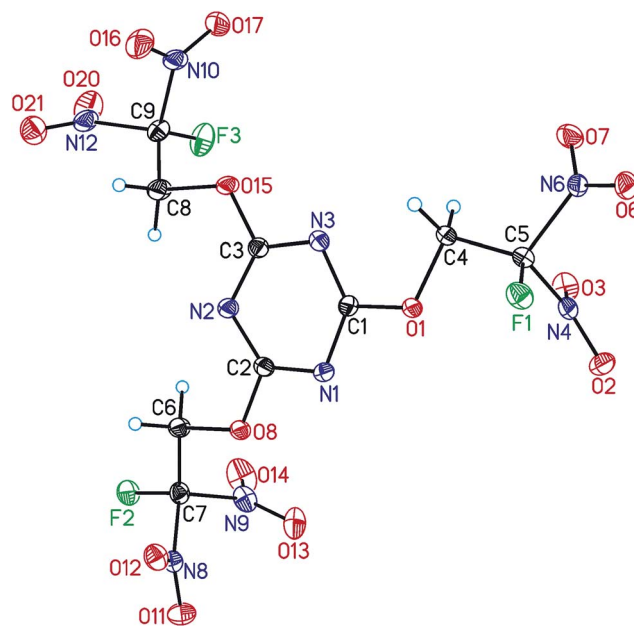


Fig. 2 General view of ether **1** with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Minor part of the disorder is not shown for clarity.



Table 2 Selected torsion angles ($^{\circ}$) defining molecular conformation of ether 1^a

| Torsion angle | <i>b</i> | |
|-------------------|-------------|-----------|
| N1–C1–O1–C4 | 175.78(14) | |
| C1–O1–C4–C5 | –174.02(14) | |
| O1–C4–C5–N4 | 57.24(17) | |
| O1–C4–C5–F1 | –64.36(17) | |
| O1–C4–C5–N6 | 172.95(13) | |
| N2–C2–O8–C6 | –0.4(2) | |
| C2–O8–C6–C7 | 161.21(14) | |
| O8–C6–C7–N7(F2) | –178.02(13) | |
| O8–C6–C7–N8 | 61.6(2) | |
| O8–C6–C7–N9 | –58.34(18) | |
| N3–C3–O15–C8 | –170.52(15) | |
| C3–O15–C8–C9 | –148.01(19) | –171.0(4) |
| O15–C8–C9–N10 | –53.2(3) | 52.4(7) |
| O15–C8–C9–N11(F3) | 67.8(3) | –72.6(7) |
| O15–C8–C9–N12 | –168.5(2) | 166.5(4) |

^a More detailed list of torsion angles in comparison with those for compound 5 is given in Table 1S in ESI. ^b In the right column, geometry of the minor part of the disordered fluorodinitroethoxy moiety is shown.

increase of packing density observed upon a replacement of a nitro group in the trinitroethoxy moiety by fluorine atom (1.879 g cm^{–3} for the ether 5 and 1.933 g cm^{–3} for 1).

At the first glance, it seems expected that the replacement with heavy and small fluorine atom should lead to condense the crystal packing. At the same time, analysis of the literature data show that replace one nitro group of the trinitromethyl moiety with fluorine atom may increase or decrease (or nearly insignificant changes) in packing density.^{4,6,25–27} We have suggested⁶ that changes in density are related to the degree of participation of the trinitromethyl or fluorodinitromethyl moieties in intermolecular bonding. To check this suggestion we described the crystal packing of molecules 1 in terms of combination of ordinary geometrical approach and analysis of the pair intermolecular interactions of the central molecule with its closest environment²⁸ and compared results with those obtained recently for compound 5.²⁵ In the latter, the strongest intermolecular connection was found to be due to stacking interaction between the 1,3,5-triazine rings. Significant contribution to the crystal packing stability was also provided by O \cdots π , C–H \cdots O and NO₂ \cdots NO₂ interactions. Evidently, in the crystal structure of compound 5, except for stacking interaction, the nitro groups are involved in all the other interactions. It means that a replacement of a nitro group with fluorine atom should be reflected in the crystal packing pattern and, as a consequence, in the packing density.

Analysis of the crystal packing of compound 1 (Fig. 2, Table 2S in ESI[†]) demonstrates that intermolecular connection is provided by O \cdots π , F \cdots π , C–H \cdots O and NO₂ \cdots NO₂ interactions. The CF(NO₂)₂ group is involved in all intermolecular contacts (Fig. 3).

The fluorine atoms participate in 6 (out of 14) interactions with the closest neighbors. The strongest intermolecular

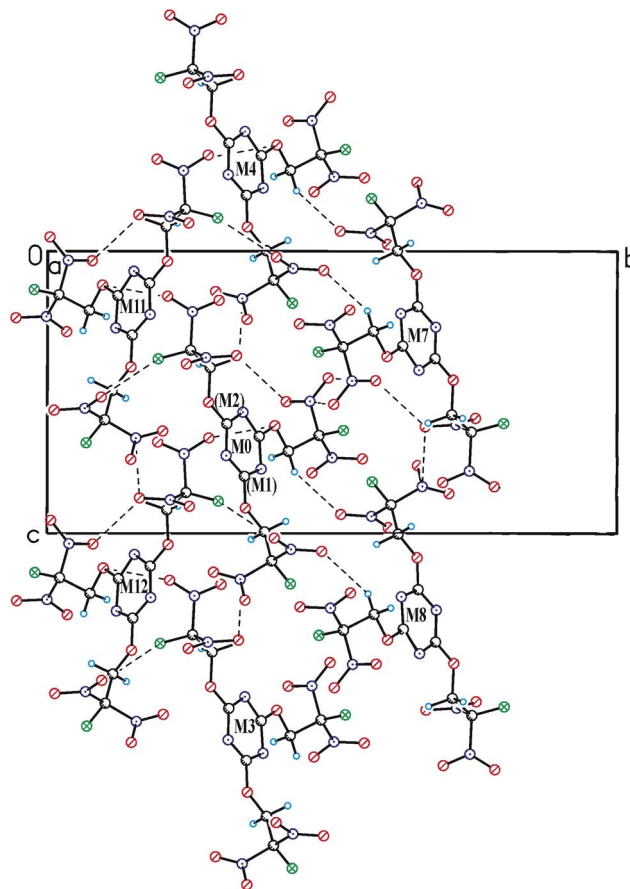


Fig. 3 Projection of the crystal packing of fluorodinitro compound 1 onto the *bc* plane. Molecules of the closest surroundings of the central molecule M0 are denoted by numbers which correspond to entries from Table 2. Letters in parentheses correspond to molecules located above or below the plane of the figure (obtained by a translation along the axis *a*). Only neighbours with the energy higher than 3 kcal mol^{–1} are shown.

connection is provided by C–H \cdots O, O \cdots π and F \cdots π interactions. Probably, the latter type (F \cdots π) replaces stacking interaction found in the crystal of trinitroethoxy analog 5. As stated above, molecular conformation of molecule 1 is different from that of molecule 5. Steric reasons lead to impossibility for the triazine rings to interact to each other. However sterically available region in vicinity of the triazine ring is suitable for small fluorine atom to form close contacts with triazine that increases the role played by the fluorine group. We believe that this is the reason of significant increase of crystal packing density of fluorodinitroethoxy-triazine 1 relative to its trinitroethoxy analog 5.

The thermal stability of the ether 1 was determined by differential scanning calorimetric (DSC). When heated using a 5 °C min^{–1} ramp rate, compound 1 melted at 76 °C and began to decompose at 230 °C. With heating rates of 10 °C min^{–1}, decomposition occurred at 242 °C.

The experimental impact and friction sensitivity values were determined for the ether 1 with standard BAM drop hammer and friction tester techniques. The impact and friction



sensitivities of **1** are measured to be 15 J and 295 N, respectively, which are very similar than those of TNT (15 J, 350 N), and lower than those of RDX (7.4 J, 120 N).

The heat of formation was experimentally measured by combustion calorimetry to be $-1110 \text{ kJ mol}^{-1}$ (-2.066 kJ g^{-1}).²⁹ The compound **1** has a positive oxygen balance with respect to the formation of CO ($\Omega_{\text{CO}} = +13.4\%$), and a negative oxygen balance with respect to CO₂ ($\Omega_{\text{CO}_2} = -13.4\%$).

These data, taken together with the density at ambient temperature, allow for the prediction of the detonation performance for compound **1** using the computational methods developed by Smirnov *et al.*³⁰ The detonation pressure (P) was predicted to be 25.5 GPa and the detonation velocity (D) of 7850 m s^{-1} compared with NG ($D = 7800 \text{ m s}^{-1}$, $P = 23.2 \text{ GPa}$) and better compared with TNT ($D = 7015 \text{ m s}^{-1}$, $P = 19.4 \text{ GPa}$). Thus, the results of our calculations show that compound **1** exhibits a somewhat better detonation performance than NG with respect to detonation velocity and detonation pressure while its impact sensitivity are similar to TNT.

Conclusions

A straightforward and scalable pathway has been successfully developed to synthesize 2,4,6-tris(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine (**1**). A few key advantages and highlights associated with this pathway include: (i) 83% yield, which is more than five times greater than that previously achieved, (ii) the duration of the reaction is much shorter (4 vs. 12 h) (iii) using inexpensive commercially available starting materials, and (iv) column chromatography was not needed.

The ether **1** was fully characterized by spectral methods. The structure was confirmed with single-crystal X-ray diffraction analyses. The melt-castable energetic compound **1** displays excellent thermal stability, good oxygen balance and high density due to extensive involvement of the fluorine groups in intermolecular interaction. It is similar to TNT with respect to its sensitivity properties and is predicted to be a more high performance material.

The development of new fluorodinitroethanol derivatives which exploit the insensitivity and thermal stability of the fluorinated building block is currently under investigation.

Experimental

Caution! Fluorodinitroethanol and compound **1** should be handled as potentially explosive material!

General

All the reagents were of analytical grade, purchased from commercial sources, and used as received. Infrared spectra were determined in KBr pellets on a Perkin-Elmer Model 577 spectrometer. The ¹H, ¹³C, and ¹⁴N NMR spectra were recorded on a Bruker AM-300 instrument at 300.13, 75.47, and 21.68 MHz, respectively. The chemical shift values (δ) are expressed relative to the chemical shift of the [D]solvent or to external standard without correction nitromethane (¹⁴N) and CClF₃ (¹⁹F).

Analytical TLC was performed using commercially pre-coated silica gel plates (Silufol UV₂₅₄), and visualization was effected with short-wavelength UV-light. Melting points were determined on Gallenkamp melting point apparatus and they are uncorrected. The decomposition points were recorded on a thermogravimetric analyzer (TGA) at a scan rate of $5 \text{ }^\circ\text{C min}^{-1}$ or $10 \text{ }^\circ\text{C min}^{-1}$. Elemental analyses were obtained by using a CHNS/O Analyzer 2400 (Perkin-Elmer instruments Series II).

X-ray crystallography

X-ray experiments were carried out using SMART APEX2 CCD ($\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$, graphite monochromator, ω -scans) at 100 K and room temperature (298 K). The results described in article correspond to low temperature study as more accurate. All structures were solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in anisotropic approximation. The details of data collection and crystal structures refinement are summarized in Table 3S in ESI.†

2,4,6-Tris(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine (**1**)

To a solution of fluorodinitroethanol (5.08 g, 33 mmol) and trichlorotriazine (1.84 g, 10 mmol) in absolute acetone (22 mL) were added and Na₃PO₄ (5.41 g, 33 mmol) in small portions. The resulting slurry was stirred at room temperature for 5 h (TLC monitoring). The mixture was filtered off and the filtrate was evaporated under *vacuo* gave a colorless solid which was washed with cold water ($5 \times 20 \text{ mL}$) and dried. Recrystallization from CCl₄/CHCl₃ (1/1) gave a colorless solid ether **1** (4.46 g, 83%), mp 76–77 °C. ¹H NMR (acetone-*d*₆): $\delta = 5.96 \text{ ppm}$ (d, $^3J_{\text{(H,F)}} = 15.7 \text{ Hz}$, 6H, OCH₂). ¹³C{¹H} NMR (acetone-*d*₆): $\delta = 65.0 \text{ ppm}$ (d, $^3J_{\text{(C,F)}} = 19.3 \text{ Hz}$, OCH₂), 120.0 (d, $^1J_{\text{(C,F)}} = 292.1 \text{ Hz}$, C(NO₂)₂F), 172.7 ppm (N=C–O). ¹⁴N NMR (acetone-*d*₆): $\delta = -24.1 \text{ ppm}$. ¹⁹F NMR (acetone-*d*₆): $\delta = -111.8 \text{ ppm}$ ($^3J_{\text{(F,H)}} = 15.7 \text{ Hz}$). IR: $\nu = 3211, 3139, 2987, 2834, 1606, 1587, 1567, 1403, 1338, 1315, 1251, 1238, 1160, 1133, 1108, 1087, 850, 815, 804, 759 \text{ cm}^{-1}$. Elemental analysis calcd (%) for C₉H₆F₃N₃O₁₅ (537.19): C 20.12, H 1.13, N 23.47; found: C 20.09, H 1.17, N 23.41.

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