1,2-Bis(5-(trinitromethyl)-1,2,4-oxadiazol-3-yl)diazene: A Water Stable, High-Performing Green Oxidizer

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ARTICLE

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Trinitromethane moieties are very important for the design and development of high performing dense green oxidizers. The novel oxidizer 1,2-bis(5-(trinitromethyl)-1,2,4-oxadiazol-3-yl)diazene, **14** is stable in water in contrast to 1,2,4-oxadiazoles with other electron withdrawing substituents at the C5-position. Compound **14** is a CNO-based oxidizer with positive oxygen balance (+6.9%), moderate thermostability, and mechanical insensitivity that may find useful applications in the field of green rocket propallant.

Nitro has been found to be a versatile functional group for high performing materials in the field of high energy density materials (HEDMs).[1] Nitrogen rich parent molecules with functional groups such as nitro, nitro ester, and nitroamine exhibit excellent detonation performance.[2] These substituents are mainly useful to the overall performance of an energetic compound by enhancing the density and oxygen balance. The trinitromethyl group has the highest oxygen content and it is one of the most promising moieties for constructing high energy density oxidizers.[3] Earlier, neutral trinitromethane was used as a classical reagent for the synthesis of polynitro compounds. However, it is highly acidic and unstable at room temperature.[4] In recent years, several methods have been developed for the synthesis of trinitromethyl-based heterocyclic compounds by nitration of different functional groups such as ethyl acetate or acetonyl or nitrile.[5] Introducing the trinitromethyl moiety into a small heterocyclic ring results in a high performing oxidizer for green rocket propulsion applications. Therefore, significant research toward the development of eco-friendly oxidizers has been carried out to replace ammonium perchlorate (AP) oxidizer (Figure 1A, 1B).[6]

Heterocyclic compounds with polynitro groups are less thermally stable and are highly sensitive to mechanical stimuli due to having extensive close O···O and N···O contacts on the molecular surfaces.[7] Some heterocyclic compounds are found to be unstable with respect to moisture. Notably polynitro groups at the C5-position of 1,2,4-oxadiazoles are sensitive to water and 1,2,4-oxadiazol-5-ones often are formed. In previous studies, the electron withdrawing groups such as nitroamine or dinitromethane groups at the C5-position of the 1,2,4-oxadiazole derivatives form carbonyl derivatives during the workup process or upon reaction with water as a solvent (Figure 1C).[8] Now 1,2-bis(5-(trinitromethyl)-1,2,4-oxadiazol-3-yl)diazene, **14** was obtained from the nitration of the previously reported diammonium 5,5'-dinitromethyl-3,3'-azo-1,2,4-oxadiazolate **13**[9] using a mixture of concentrated sulfuric acid and nitric acid at 0 °C for 3 hours. The yellow solid **14**, was formed and isolated by pouring the reaction mixture into ice water followed by filtration (Scheme 1).

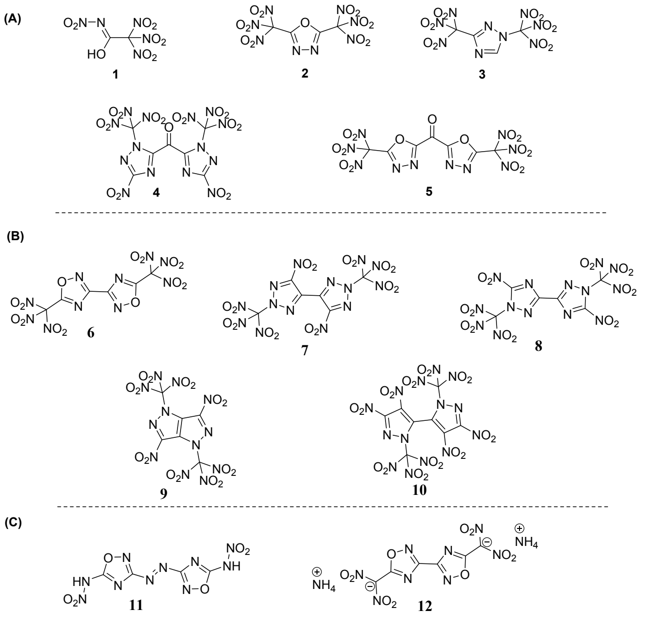
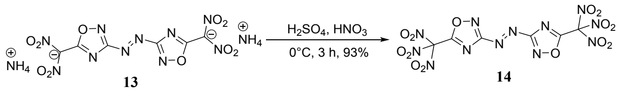


Figure 1. (A) Our research efforts on the development of highly dense oxidizers (1-5). (B) Selected examples from the literature (6-10). (C) Water sensitive 1,2,4-oxadiazoles (11 and 12).



Scheme 1. Synthesis of 1,2-bis(5-(trinitromethyl)-1,2,4-oxadiazol-3-yl)diazene **14**.

Given the conditions under which **14** is synthesized suggests that it has high stability in water without reaction to form the associated carbonyl derivative (Figure S7-9, SI).[8] Compound **14** was fully characterized by infrared (IR), and multinuclear magnetic resonance (NMR) spectroscopy, differential scanning calorimetry (DSC), and elemental analysis. In the ^{15}N NMR spectrum, there are four signals, nitrogen atoms of trinitromethyl and azo bridge are found at $\delta = +143.6$ ppm (N1) and $\delta = -40.4$ ppm (N4), while the nitrogen atoms in the 1,2,4-oxidazole ring are found at $\delta = +4.0$ ppm (N2) and $\delta = -130.6$ ppm (N3), respectively (Figure S5, SI).

Suitable crystals of **14** were obtained in chloroform by allowing hexane to diffuse into the solution. It crystallized in the triclinic space group *P*-1 with a crystal density of 1.897 g cm^{-3} at 100 K (Figure 2a). The details of crystallography and structure, including bond lengths and bond angles, are available in the SI. As expected, the two 1,2,4-oxadiazole rings and the azo-bridge are coplanar. The torsion angles of C(1)-N(1)-N(1)-C(1), O(1)-N(3)-C(1)-N(1) and O(1)-N(3)-C(1)-N(2) are 180.0°, 178.5° (2) and -1.0° (3), respectively. The trinitromethyl groups on the 1,2,4-oxidazole ring are arranged in tetrahedral geometry, which is comparable with similar compounds reported in the literature.[6]

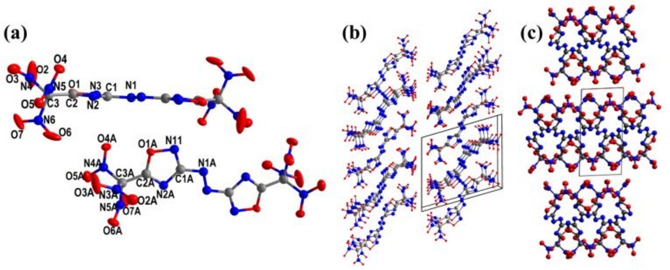


Figure 2. (a) Molecular structure of **14**. (b) Ball-and-stick packing diagram of **14** viewed down the a axis. (c) Ball-and-stick packing diagram of **14** viewed down the b axis.

Polynitro derivative **14** contains a high amount of oxygen (48.26%). To understand the additional insight into the relationship between structure and physical properties, two-dimensional fingerprint spectra and Hirshfeld electrostatic surface plots were analyzed systematically using Crystalexplorer 17.5 software (Figure 3).[10] The red and blue dots on the Hirshfeld surface analysis represent high and low close-contact populations, respectively. In Figure 4a, the red dots indicate strong intermolecular (N···O and O···N) interactions, and the relative contribution of the contacts are reflected in regular 2D fingerprint plots in Figure 4b. The major interactions are O···O (54.4%), N···O (32.2%) and N···N (6.4%) for **14**, suggests that it is high sensitive.

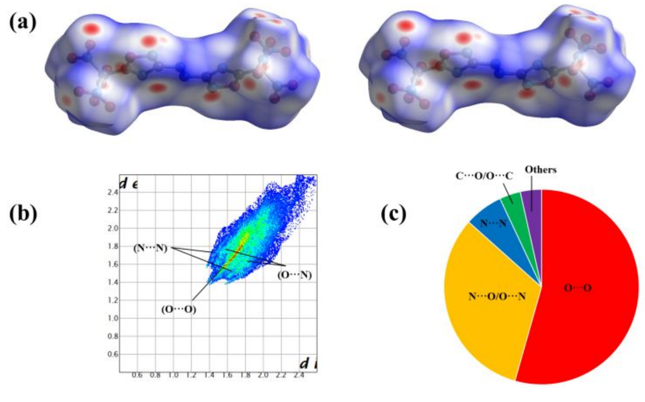


Figure 3. Hirshfeld surface calculations and 2D fingerprint plots in the crystal structures of **14** (a,b), Pie graph for **14** showing the percentage contributions of the individual (c).

The physicochemical properties for **14**, and standard energetic oxadiazoles for comparison are reported in Table 1. The thermal stabilities (onset temperature) of the crystals, **14**, were measured by differential scanning calorimetry (DSC) with a heating rate of 5 °C min^{-1}. Due to the presence of two trinitromethyl moieties, **14** exhibits low thermostability of 125 °C (T_{onset}), which is higher compared with polynitro azoles **2** and **5**. Densities of the polynitro compound, **14** was measured using a gas pycnometer at 25 °C and found to have a high density of 1.85 g·cm^{-3}. The heats of formation for **14** was calculated using the Gaussian 03 suite of programs (SI).[11] Compound **14** has excellent high positive heats of formation of 461.4 kJ mol^{-1} / 0.99 kJ g^{-1} compared with other oxidizers due to the presence of azo-bridge between two polynitro 1,2,4-oxadiazole rings. Detonation properties were calculated using Explo5 (version 6.01) code program[12] and **14** has good detonation properties (*vD* = 8722 m s^{-1}; P = 33.15 GPa). Because of polynitro groups, **14** exhibit a positive oxygen balance (+6.9%) with respect to the formation of CO_2 during combustion. Further, the combined N+O content and specific impulse (I_{sp}) of **14** (N+O = 84%; I_{sp} = 256.2 s) is better than the polynitro derivatives **1, 2, 5, 6** and exceeds the toxic AP (N+O = 65%, I_{sp} = 157 s) oxidizer, suggesting **14** as a green, high performing oxidizer. Impact and friction sensitivity values were measured using BAM drop hammer and friction tester techniques. Based on high percentage O···O and N···O interactions in the molecular structure of **14**, which suggests an increase in sensitivity that were comparable with experimental impact sensitivity of 5 J and friction sensitivity of 80 N.[13]

In summary, we report the synthesis of 1,2-bis(5-(trinitromethyl)-1,2,4-oxadiazol-3-yl) diazene, **14** in excellent yields (93%) and fully characterized by advanced spectroscopic techniques. It is one of the examples of stable, insoluble, and unreacted polynitro 1,2,4-oxadiazol derivative with water. The physicochemical properties of all compounds were determined. Notably, **14** exhibit excellent detonation properties, and having a positive oxygen balance which results in high specific impulse as an applicable green, and high performing oxidizer for use as a replacement for toxic AP in solid rocket propellant formulations in various civil and military applications.

Table 1. Energetic properties and detonation parameters of **14** compared with other energetic materials

	T_d^a (℃)	P^b [g·cm^{-3}]	ΔH_f^c[kJ mol^{-1}] / kJ g^{-1}	I_{sp}^d (s)	D^e [m s^{-1}]	P^f [GPa]	IS^g [J]	FS^h [N]	N+O^i (%)	OB^j (%)
14	125	1.85	461.4/0.99	256.2	8722	33.15	5	80	84	+6.9
1^k	137	1.84	-134.6/-0.56	209	7503	23.00	19	20	89	+30.1
2^l	102	1.92	29.4/0.08	225	8229	29.20	4	240	87	+21.7
5^m	108	1.89	60.3/0.13	247	8665	32.70	4	60	82	+3.4
6^n	124	1.94	61.9/0.14	243	8814	34.50	10	80	83	+7.3
AP^o	>200	1.95	-295.8/-2.52	157	6368	15.80	15	>360	65	+27.2
ADN^o	159	1.81	-149.8/-1.13	202	7860	23.60	3-5	64-72	97	+25.8

[a] Decomposition temperature (onset); [b] Density measured by a gas pycnometer at 25 °C; [c] Calculated molar enthalpy of formation in solid state; [d] Calculated specific impulse; [e] Calculated detonation velocity; [f] Calculated detonation pressure; [g] Impact sensitivity; [h] Friction sensitivity; [i] Combined nitrogen and oxygen content; [j] Oxygen balance based on CO_2. For a compound with the molecular formula of $C_aH_bO_cN_d$, Ω_{CO2} (%) = 1600 [(c - a - b)/Mw], Mw = molecular weight of compound; [k] ref. 6a; [l] ref. 6d; [m] ref. 6e; [n] ref. 6b; [o] ref. 6g.

Data Availability

Details of experimental procedures, characterizations, theoretical calculations, X-ray crystal diffraction data and crystal structures for compounds **14** (CCDC 2106963), and copies of NMR spectra are provided in the ESI.†

Author Contributions

A. K. C. performed all the experiments and analysis of the data. R. J. S. performed X-ray analysis and solved the crystal structures. A. K. C. and J. M. S. discussed the results and wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

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