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# 5,5′-Bis-(trinitromethyl)-3,3′-bi-(1,2,4-oxadiazole): a stable ternary CNO-compound with high density†

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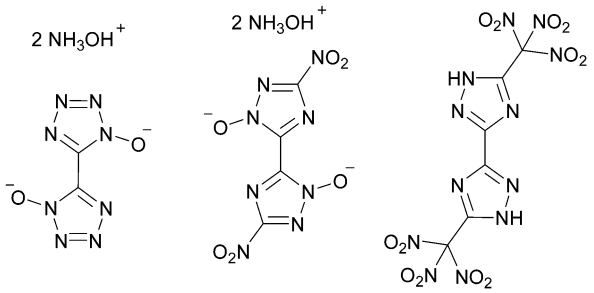
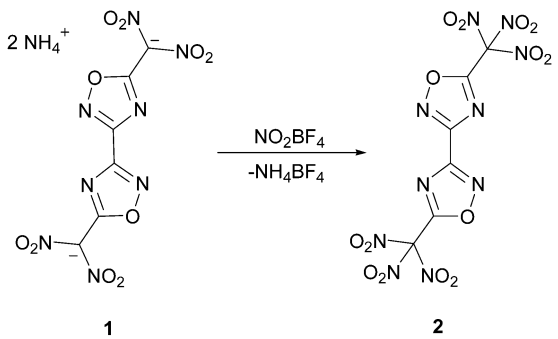
**5,5′-Bis-(trinitromethyl)-3,3′-bi-(1,2,4-oxadiazole) is a new ternary CNO-compound. It has been synthesized by nitration of diammonium 5,5′-bis-(dinitromethanide)-3,3′-bi-(1,2,4-oxadiazole) with nitronium tetrafluoroborate. Single crystal X-ray diffraction studies show a remarkable high density. Thermal stability and sensitivities of the new compound were determined by differential scanning calorimetry (DSC) and standardized drop hammer and friction tests.**

The challenges in the development of the field of energetic materials include – besides better environmental acceptance – the search for materials with preferably high densities, which result in higher performance values.[1] This and other requirements have been fulfilled for secondary explosives by various high nitrogen containing materials such as bi-tetrazole[2] and bi-triazole[3] derivatives (Scheme 1). However, the field of energetic oxidizers for propellants requires in particular a high oxygen content for providing oxygen to the actual fuel for a complete combustion.[1] Furthermore, oxidizers are the main ingredient in composite propellants (up to 70 wt%),[4] hence a high density results in space-saving effects. It is also desired that the compounds do not explode, but burn fast in an open flame test. It has been shown that novel oxidizers including one or more trinitromethyl moieties do not explode.[5] In this communication a hydrogen atom free bi-(1,2,4-oxadiazole) with two trinitromethyl moieties attached at its 5-position is presented. 5,5′-Bis-(trinitromethyl)-3,3′-bi-(1,2,4-oxadiazole) **2** ($TNM_2$-BOD) is analogous to 5,5′-bis-(trinitromethyl)-3,3′-bi-(1,2,4-triazole) synthesized by Petrie *et al.* in 2012 (Scheme 1),[6] just by replacing the NH-group by an oxygen atom (Scheme 1).

The nitration of previously reported diammonium 5,5′-bis-(dinitromethanide)-3,3′-bi-(1,2,4-oxadiazole) **1**[7] with nitronium tetrafluoroborate was performed in anhydrous acetonitrile at 0 °C for one hour (Scheme 2). The solvent was evaporated and the resulting crude product was extracted with anhydrous diethylether. $TNM_2$-BOD **2** was obtained as colourless crystals suitable for X-ray diffraction. The optimization of the synthesis (yield 27%) is under investigation. It was characterized using $^{13}C$ and $^{14}N$ NMR, IR and Raman spectroscopy, mass spectrometry and elemental analysis. Additionally X-ray diffraction measurements were performed.




Scheme 1 From left to right: structures of TKX-50,[2] MAD-X1[3] and 5,5′-bis(trinitromethyl)-3,3′-bi-(1,2,4-triazole).[5]




Scheme 2 Synthesis of bi-(1,2,4-oxadiazole) derivative **2** from **1**.

The vibrational analysis shows the characteristic asymmetric $NO_2$ stretching vibrations $\nu_{as}$ at 1608 $cm^{-1}$ in the IR, and at 1621 $cm^{-1}$ in the Raman spectrum. The symmetric $NO_2$ stretching vibrations $\nu_s$ are observed at 1271 $cm^{-1}$ in the IR, and at 1275 $cm^{-1}$ in the Raman spectrum.[8,9] The $^{13}C$ NMR spectrum shows the chemical

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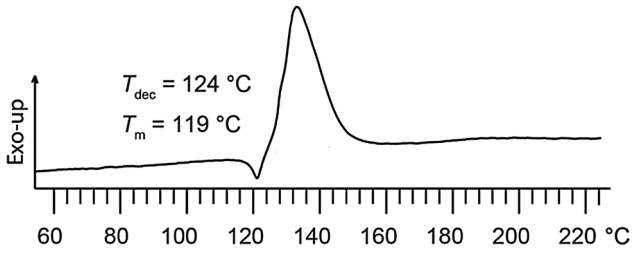


Fig. 1 DSC plot of $TNM_2$-BOD (**2**), recorded with a heating rate of 5 °C $min^{-1}$.

shifts of the carbon atoms in the ring and the trinitromethyl moiety in the expected range: $\delta$ = 163.8 (C5), 160.2 (C3) and 117.8 ($C(NO_2)_3$) ppm.[10] The nitro groups in the $^{14}N$ NMR spectrum are shifted to $\delta$ = −35 ppm.[11] Compound **2** has a high oxygen balance with respect to the formation of CO during combustion with 29.3%, and a moderate oxygen balance with respect to $CO_2$ with 7.3%.[12] According to DSC measurements compound **2** melts at $T_m$ = 119 °C with subsequent decomposition at $T_{dec}$ = 124 °C ($T_{onset}$, Fig. 1). This has been checked using a melting apparatus (Büchi). Furthermore **2** burns without residues in the open flame as required for energetic oxidizers. The sensitivities towards shock and friction were determined using a drop hammer tester and a friction tester according to BAM standard methods.[13] According to the UN recommendations on the transport of dangerous goods[14] $TNM_2$-BOD **2** shall be classified as sensitive against both impact (10 J) and friction (80 N) at a grain size of <100 μm. For a practical use as an energetic oxidizer the benchmark sensitivities are defined not to be higher than that of pentaerythrityl tetranitrate (PETN: impact sensitivity = 4 J, friction sensitivity = 80 N). Thus, the sensitivities of compound **2** are in an acceptable range.

$TNM_2$-BOD crystallizes from diethyl ether or dichloromethane as very thin colourless plates in the monoclinic space group $P2_1/c$ with four molecules per unit cell and a remarkable high density of 2.02 g $cm^{-3}$ at 100 K. A measurement at ambient temperature showed a density of 1.94 g $cm^{-3}$. Fig. 2 presents the molecular structure of $TNM_2$-BOD with perpendicular and lateral views of the rings demonstrating the planarity of the bi-(1,2,4-oxadiazole) unit.

Compared to other solid trinitromethyl containing materials, which tend to have X-ray densities between 1.47 (2,4,6-trimethyl-1-(2,2,2-trinitroethyl)benzene)[15] and 2.05 g $cm^{-3}$ (hexanitroethane),[9] $TNM_2$-BOD **2** belongs to the compounds showing the highest densities.[16] Among the hydrogen free and neutral CNO-compounds $TNM_2$-BOD **2** displays a remarkably high density, which lies in the range of that observed for various furazane derivatives,[17] although not reaching the values of the pernitroalkanes hexanitroethane (2.05)[9] and octanitrocubane (1.98),[18] or per-nitroarenes as hexanitrobenzene (1.99).[19] In contrast to the volatile hexanitroethane,[9] $TNM_2$-BOD shows practically no tendency to sublime at ambient temperature, however.

The high density might be explained by the presence of weak attractive electrostatic interactions (short contacts) between the nitro groups within the trinitromethyl moieties. In the crystal, intramolecular as well as intermolecular short N···O contacts are observed. Such interactions have been widely observed for the solid state in polynitro compounds.[21] Within the molecules of **2** a series of N···O distances are found, which are clearly

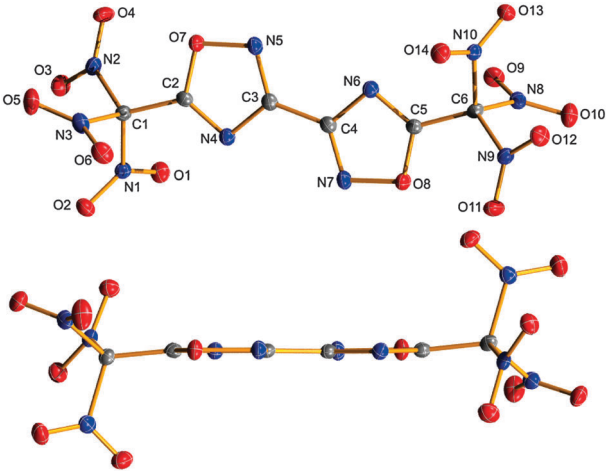


Fig. 2 Molecular structure of $TNM_2$-BOD; selected bond lengths [Å], angles [°] and torsion angles [°]: N1–O2 1.208(2), C1–C2 1.492(3), N1–O1 1.218(2), N1–C1 1.525(3), N2–O3 1.209(2), N2–O4 1.214(3), N2–C1 1.529(3), O5–N3 1.209(2), O7–C2 1.347(3), O7–N5 1.407(2), N3–O6 1.211(2), N3–C1 1.549(3), N5–C3 1.307(3), N4–C2 1.290(3), C3–C4 1.466(3), N4–C3 1.374(3); O2–N1–O1 128.4(2), O2–N1–C1 117.1(2), C2–O7–N5 105.2(2), C3–N5–O7 102.9(2), C2–N4–C3 100.8(2), N5–C3–N4 116.0(2), N5–C3–C4 121.2(2), C2–C1–N1 111.1(2), C2–C1–N2 116.2(2), C2–C1–N3 110.3(2), N1–C1–N3 106.8(2) and C2–O7–N5–C3 −0.4(2), O7–N5–C3–N4 0.4(2), C5–N6–C4–C3 −178.0(2), N5–C3–C4–N7 −178.6(2), N4–C3–C4–N7 1.5(3), N5–C3–C4–N6 −0.1(3), N4–C3–C4–N6 180.0(2), C4–N6–C5–C6 173.5(2).

shorter than the sum of van der Waals radii (N,O = 3.07 Å),[20] as shown in Fig. 3. The distances N1···O3, N2···O5 and N3···O2 are about 2.55 Å (Fig. 2, black dashed), while for N2···O1 and N1···O6, a distance around 2.94 Å (Fig. 3, gray dashed) is observed. Overall the TNM group arranges to the typical propeller-like orientation of the nitro groups with torsion angles C2–C1–N–O between −36.6(3)° and −50.9(2)° (Fig. 3).[22] There are also weak attractions of N2 and O1 from the TNM group to O7 and N4, respectively, of the oxadiazole ring (Fig. 3, light blue dashed). Very similar interactions are observed in the second trinitromethyl group at the opposite side of the molecule.

There is also a series of short intermolecular N···O contacts observed in the crystal, indicating the presence of weak interactions between the single molecules in the solid state. The respective atom distances are listed in Table 1. The interactions occur mostly between the oxygen atoms of the nitro groups and all nitrogen atoms of the rings (N4, N5, N6 and N7). No intermolecular contacts between the bi-(1,2,4-oxadiazole) rings shorter than the sum of van der Waals radii are observed (Fig. 4).

The hitherto unknown CNO-compound $TNM_2$-BOD has been synthesized by nitration of diammonium 5,5′-bis(dinitromethanide)-3,3′-bi-(1,2,4-oxadiazole) using nitronium tetrafluoroborate. The density, as measured from single crystal X-ray studies at 100 K (2.02 g $cm^{-3}$) and at ambient temperature (1.94 g $cm^{-3}$), is remarkably high. This can be rationalized by various intra- and intermolecular electrostatic N···O interactions involving the nitro groups. The new compound $TNM_2$-BOD represents a rare example of a ternary CNO-species. As compared to the volatile hexanitroethane, it combines its properties with those of the bi-(1,2,4-oxadiazole) ring system and represents an interesting non volatile high-energetic alternative.

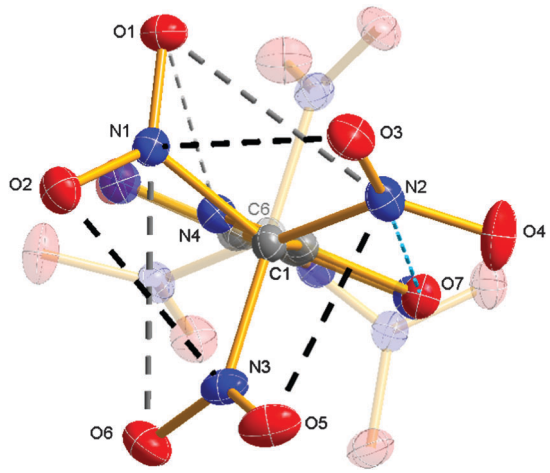


Fig. 3 View along C1–C6 displaying the intramolecular interactions within the trinitromethyl moiety; atom distances [Å] and torsion angles [°]: N1–O3 2.543(2), N1–O6 2.967(2), N2–O1 2.924(3), N2–O5 2.568(3), N2–O7 2.981(2), N3–O2 2.566(2), N4–O1 2.896(2); C2–C1–N1–O1 −50.9(2), C2–C1–N2–O4 −36.6(3), C2–C1–N3–O6 −42.9(2) and ∑vdW radii (N,O) = 3.07 Å.[20]

Table 1 Intermolecular distances shorter than ∑vdW radii [Å]

| | |
|---|---|
| N1···O12 | 2.927(3) |
| N3···O1 | 2.945(3) |
| N6···O3 | 2.946(2) |
| N10···O3 | 3.010(3) |
| N4···O12 | 3.011(2) |
| N5···O11 | 3.040(3) |
| N7···O4 | 3.055(3) |

∑vdW radii (N,O) = 3.07 Å.[8]

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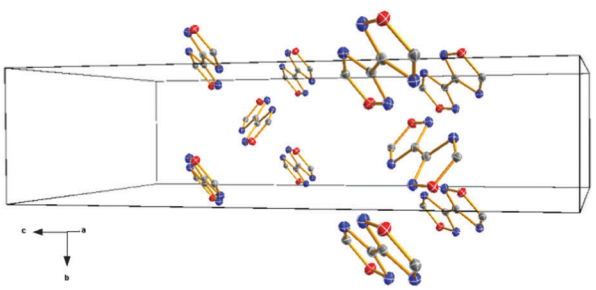

Fig. 4 Unit cell content with omitted trinitromethyl groups for demonstrating the orientation of the bi-(1,2,4-oxadiazole) units in one direction and their wave-like arrangement.

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