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RESEARCH ARTICLE

# 1,3,4-Oxadiazole Bridges: A Strategy to Improve Energetics at the Molecular Level

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**Abstract:** Many energetic materials synthesized to date have limited applications because of low thermal and/or mechanical stability. This limitation can be overcome by introducing structural modifications such as a bridging group. In this study, a series of 1,3,4-oxadiazole-bridged furazans was prepared. Their structures were confirmed by $^{1}$H and $^{13}$C NMR, infrared, elemental, and X-ray crystallographic analyses. The thermal stability, friction sensitivity, impact sensitivity, detonation velocity, and detonation pressure were evaluated. The hydroxylammonium salt **8** has an excellent detonation performance ($D$ = 9101 m s$^{-1}$, $P$ = 37.9 GPa) and insensitive properties (IS = 17.4 J, FS = 330 N), which show its great potential as a high-performance insensitive explosive. Using quantum computation and crystal structure analysis, the effect of the introduction of the 1,3,4-oxadiazole moiety on molecular reactivity and the difference between the sensitivities and thermal stabilities of mono- and bis-1,3,4-oxadiazole bridges are considered. The synthetic method for introducing 1,3,4-oxadiazole and the systematic study of 1,3,4-oxadiazole-bridged compounds provide a theoretical basis for future energetics design.

## Introduction

Research and development of energetic materials have attracted significant attention over the past few decades. Although cyclotetramethylenetetranitramine (HMX) and hexanitrohexaazaisowurtzitane (CL-20) have been recommended as high-performance compounds for a long time, their use has diminished owing to their instability.[1-4] As a result, current research is focused on improving the stability, especially mechanical and thermal stabilities of these energetic materials. Modifications at the interface (cladding and mixing) and crystal levels (co-crystal and host-guest assembly) of HMX and CL-20 have been reported several times.[5-9] Along with the refinement of classical high-energy explosives, studies on new high energy density materials are under way focusing on the synthesis of five- or six-ring heterocyclic systems (including furazan, tetrazine, tetrazole and triazole) because of their high-energy content and green explosion products.[10-13] With a combination of various energetic rings and groups, these compounds are expected to exhibit excellent performance and moderate sensitivity.

Common ways to modify heterocycles at the molecular scale, including the introduction of various explosophores, such as nitro, dinitromethyl, and trinitromethyl, and amino groups.[14-17] In addition, the introduction of a bridge between two energetic units has been shown to have a dramatic effect on performance. As seen in Figure 1, the bridge is mainly a functional group such as carbonyl, ethylene, azo, and azoxy. Bis(5-(trinitromethyl)-1,3,4-

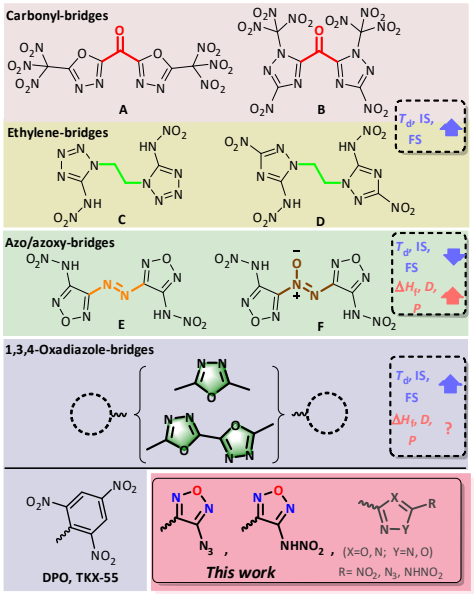


**Figure 1.** Energetic derivatives with different bridges.

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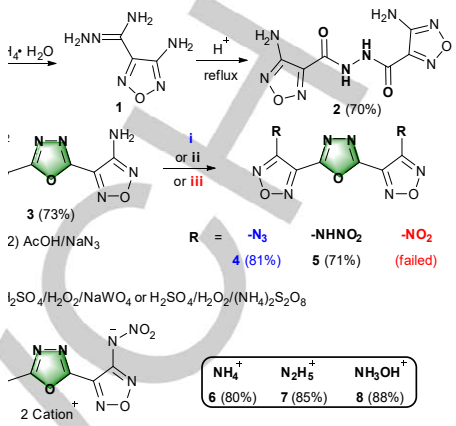
oxadiazol-2-yl)methanone (**A**)[18] and bis(3-nitro-1-(trinitromethyl)-1*H*-1,2,4-triazol-5-yl)methanone (**B**),[19] which have a carbonyl group introduced into the conjugated system, show better stability ($T_d$ ≥ 108 °C, IS ≥ 4 J, FS ≥ 60 N) than most trinitromethyl compounds. 1,2-Bis(4,5-dihydro-5-nitroimino-1*H*-tetrazol-1-yl)ethane (**C**)[20] and *N*,*N*'-(1,1'-(ethane-1,2-diyl)bis(3-nitro-1*H*-1,2,4-triazole-5,1-diyl))dinitramide (**D**)[21] are representatives of azoles linked by ethylene, which decreases the acidity of the ring NH and broadens the options for the design of desirable energetic compounds. Generally, azo or azoxy bridges enhance the heat of formation as well as detonation performance of energetic compounds, as demonstrated for 3,3'-dinitramino-3,3'-azobifurazan (**E**)[22] and 3,3'-dinitramino-3,3'-azoxybifurazan (**F**).[23] In contrast, the thermal and mechanical stabilities of nitraminofurazans with azo or azoxy bridges are reduced, especially for compound **F** ($T_d$ = 70 °C, IS = 1 J, FS = 16 N). Surprisingly, research on 1,3,4-oxadiazole-linked energetic compounds is limited despite the fact that 2,5-bis-(2,4,6-trinitrophenyl)-1,3,4-oxadiazole (**DPO**) and 5,5'-bis(2,4,6-trinitrophenyl)-2,2'-bi(1,3,4-oxadiazole) (TKX-55) exhibit high thermal stabilities (**DPO**, 331 °C; TKX-55, 335 °C) and are reported as heat-resistant explosives.[24-25]

1,3,4-Oxadiazole, the only oxadiazole isomer that does not contain an oxygen-nitrogen bond, exhibits a wide variety of biological activities.[26-28] To determine the influence of the stable 1,3,4-oxadiazole on the properties of energetic compounds, we performed a systematic study of a set of 1,3,4-oxadiazole-bridged energetic derivatives (compounds **3**–**8** and **11**–**16**). All compounds are characterized by multinuclear NMR and IR spectroscopy, elemental analyses, and differential scanning calorimetry (DSC). Theoretical and crystalline investigations of these compounds were performed in order to understand their reaction activity, detonation properties and structural features. These compounds have the characteristic high detonation performance and reasonable stability, which highlight the introduction of 1,3,4-oxadiazole bridges as a promising strategy to improve energetic compounds.

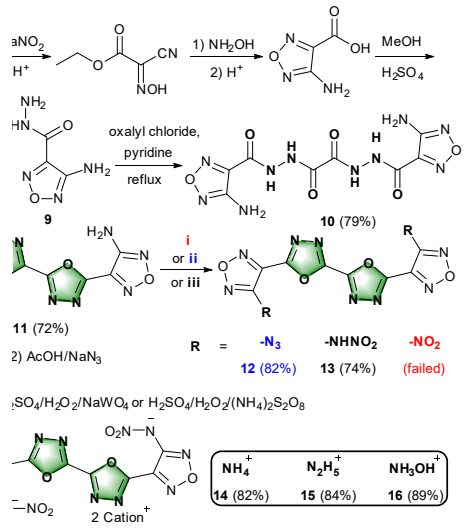
## Results and Discussion

**Synthesis and Crystallographic Analysis.** The syntheses of **1–8** (Scheme 1) start from commercially available malononitrile. Using this starting compound, 4-amino-1,2,5-oxadiazole-3-carbohydrazonamide (**1**) is synthesized sequentially through a series of four steps.[29-30] Compound **2** (yield: 70%) is synthesized from **1** in hot hydrochloric acid solution (crystal structure and proposed mechanism shown in Figure 2 and Scheme 3, respectively), from which **3** (yield: 73%) is synthesized through intramolecular cyclization in 20% fuming sulfuric acid. Unfortunately, treatment of amine **3** with various oxidizing materials, such as $H_2O_2/H_2SO_4$, $H_2O_2/CF_3COOH$, or $H_2O_2/H_2SO_4/(NH_4)_2S_2O_8$ does not produce the nitro derivative. However, when compound **3** is added to a solution of $NaNO_2$ in concentrated $H_2SO_4$, followed by AcOH and a solution of $NaN_3$, azide **4** (yield: 81%) is obtained. The nitration of **3** is carried out using 100% $HNO_3$ to yield nitroamine **5** (yield: 77%), whose energetic salts (**6–8**, yields: 80–88%) are synthesized by reaction with different bases.

In Scheme 2, 4-amino-1,2,5-oxadiazole-3-carbohydrazide (**9**) is prepared by a four-step reaction from commercially available ethyl cyanoacetate according to a reported procedure.[31-32] Compound **9** is then treated with oxalyl chloride in pyridine to form N'[1],N'[2]-bis(4-amino-1,2,5-oxadiazole-3-carbonyl)oxalohydrazide (**10**, yield: 79%). The dehydration of **10** in 20% oleum results in the formation of intermediate **11** (yield: 72%). Interestingly, as with compound **3**, attempts to oxidize the amino group in compound **11** by various reagents were unsuccessful. The low reactivity of the amino group in compounds **3** and **11** may be due to the strong electron-withdrawing effect of the 1,3,4-oxadiazole ring (as see below). The nitramino- and azide-functionalized compounds, **12** and **13**, (yields: 82% and 74%, respectively) are then synthesized from compound **11** through nitrification and diazotization-substitution, respectively. Subsequently, three energetic derivatives (**14–16**, yields: 82–89%) are prepared by treating **13** with different bases.




**Scheme 1.** Synthesis of compounds **1**–**8**.




**Scheme 2.** Synthesis of compounds **9**–**16**.

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**X-ray Crystal Structure Determinations.** Compound **2**·$H_2O$ crystallizes in the orthorhombic space group $P2_12_12$ with two formula moieties in the unit cell. The molecular structure of **2**·$H_2O$ is shown in Figure 2a. The N−N distance in 2 (1.3969 Å) is slightly shorter than the typical N−N single bond distance of about 1.45 Å. The C−N distance in the hydrazine segment is 1.3349 Å, which is significantly shorter than the typical C−N single bond distance of about 1.48 Å and even shorter than the C−N double bond distance of 1.35 Å.[33] The carbonyl groups are coplanar with the backbones, and the N−N bond in the hydrazine segment is rotated to form a cross-shaped molecular structure with a dihedral angle of 85.07°. As seen in Figure 2b, the **2**·$H_2O$ molecules are arranged in wavelike layers along the *b*-axes. Two "V" shaped layers of molecules open in opposite directions and assume a staggered arrangement to form wavelike layers. Owing to the high degree of molecular distortion, the spacing between two adjacent wave layers is 4.3252 Å.

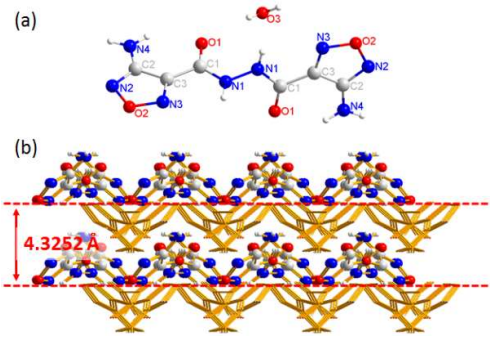


**Figure 2.** (a) Molecular structure. (b) Packing diagram of **2**·$H_2O$.

Compound **6**·$H_2O$ crystallizes in the monoclinic space group *C*2/*c* (Figure 3a). Because of the combined effects of steric hindrance and intermolecular interactions, the dihedral angle defined by the furazan and 1,3,4-oxadiazole rings in **6** is 10.51°. The **6**·$H_2O$ crystal exhibits an ordered planar layer stacking. Two adjacent layers (spacing of 3.1898 Å) are connected by N(6)-H(6A)…O(4) and N(6)-H(6C)…O(4) hydrogen bonds, which propagate throughout the crystal layers to form infinite chains (Figure 3b). In the same layer, the **6**·$H_2O$ molecules are regularly arranged line by line (Figure 3c). The O(5)-H(5)…N(2) and O(5)-H(5)…O(3) hydrogen bonds connect two adjacent anions in the same line, and two adjacent lines are connected by hydrogen bonds with ammonium ions [N(6)-H(6A)…O(1), N(6)-H(6B)…O(3), N(6)-H(6B)…O(4), N(6)-H(6D)…O(3), N(6)-H(6D)…O(4), and N(6)-H(6D)…N(5)].

Azide **12** (Figure 4a) crystallizes in the monoclinic space group $P2_1/c$ ($Z$ = 4) with a calculated density of 1.792 g cm$^{-3}$ (173 K). The C–$N_3$ bond lengths are 1.3913 [C(1)-N(3)] and 1.4002 Å [C(8)- N(12)], which are nearly identical to the same bond in 2,5,8-triazido-*s*-heptazine (1.401 Å).[34] Contrary to expectation, the two 1,3,4-oxadiazole rings and the two 1,2,5-oxadiazole rings are not coplanar [N(5)-C(2)-C(3)-N(6) = 171.98°, N(7)-C(4)-C(5)-N(8) = -173.21°, N(9)-C(6)-C(7)-N(10) = -178.59°]. Moreover, the azide group slightly twists out of plane owing to steric effects [N(2)-N(3)-C(1)-C(2) = -177.93°, C(7)-C(8)-N(12)-N(14) = -177.06°]. Zigzag-motif rows are formed by molecules of 12 positioned exactly opposite one another (84.20°) (Figure 4b).[35] The vertical distance

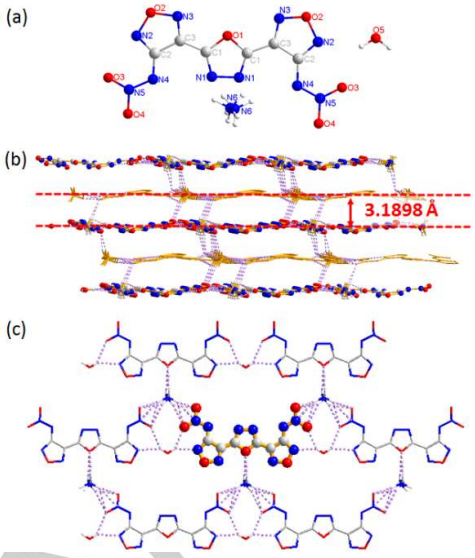


**Figure 3.** (a) Molecular structure. (b) 2D layer-by-layer stacking of **6**·$H_2O$. (c) Hydrogen bonds between molecules in the same layer

between two adjacent molecules in the same row is 3.0781 Å. Because the molecules do not have hydrogen atoms, there is no hydrogen bond interaction between them in the structure (Figure 4c).

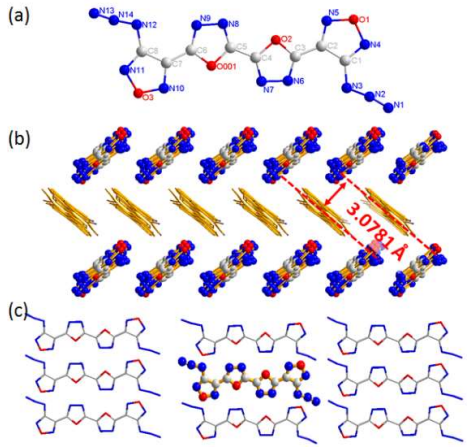


**Figure 4.** (a) Molecular structure. (b) 3D cube layer-by-layer stacking of **12**. (c) Arrangement of molecules in the same 3D cube layer.

Compound **14**·2$H_2O$ crystallizes in the monoclinic space group $P2_1/n$ with a calculated density of 1.737 g cm$^{-3}$ at 220 K, which is slightly lower than that of the four-ring azide **12** (1.792 g cm$^{-3}$).The symmetrical unit of the structure consists of one molecule each of the oxadiazole-furan nitramine and ammonium cations, as well as one crystal water (Figure 5a). The entire four-ring system is nearly coplanar with twist angles of N(2)-N(1)-C(1)-C(2) = -179.17° and C(1)-C(2)-C(3)-N(5) = -171.06°. Similar to 1,1-diamino-2,2-dinitroethene (FOX-7),[36-37] **14**·2$H_2O$ forms wavelike stacks with a layer spacing of 2.9216 Å. As in the **6**·$H_2O$ crystal, the N(7)-H(7D)…O(5), N(7)-H(7B)…O(5), N(7)-H(7B)…N(5), and N(7)-

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H(7B)…N(3) hydrogen bonds are connected between the layers (Figure 5b). In the same layer, a hydrogen bond network consisting of N(7)-H(7B)…N(3), N(7)-H(7A)…N(6), N(7)-H(7C)…O(4), N(7)-H(7C)…N(1), O(5)-H(5B)…O(4), and O(5)-H(5A)…N(5) is formed and connects an anion with 6 other surrounding anions. (Figure 5c).

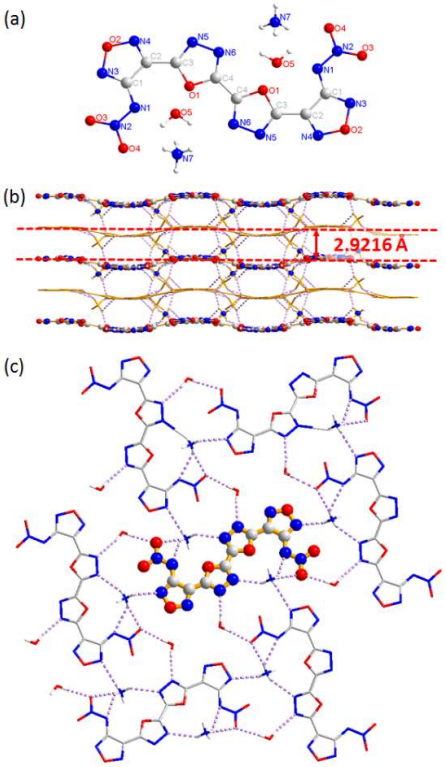
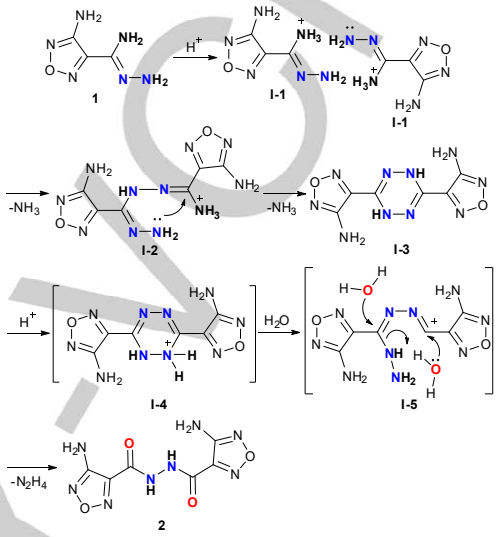



**Figure 5.** (a) Molecular structure. (b) 2D layer-by layer stacking of **14**·2$H_2O$. (c) Hydrogen bonds between molecules in the same layer..

**Analysis of Synthesis Mechanism and Reaction Activity.** The 1,2-diacylhydrazine unit (as in compound **2**) is generally constructed through the substitution of hydrazide with ester or acid chloride.[38-39] There are few reports about building 1,2-dihydrazine structures from the amidine group. Therefore, it is necessary and meaningful to predict the mechanism of formation for compound **2** from **1**. First, two protonated products (**I-1**) undergo an intermolecular reaction, in which the hydrazine group of one molecule attacks the amine oxime carbon in the other molecule (Scheme 3). This leads to the loss of one ammonia molecule to yield intermediate **I-2**. Adduct **I-2** undergoes cyclization accompanied by the elimination of a second ammonia molecule to form 1,4-dihydro-1,2,4,5-tetrazine structure **I-3**. Apparently, the formation of compound **2** occurs during the opening of the protonated dihydrotetrazine ring in **I-4**, which is converted from **I-3** by acid attack. **I-4** is then converted to **2** by the attack of two water molecules and loss of one hydrazine molecule. Surprisingly, both compounds **3** and **11**, exhibit a strong inactivity toward oxidizing reagents during synthesis. However, 3,3'-diamino-4,4'-bifurazan (DABF), which lacks the 1,3,4-oxadiazole bridge, can be oxidized directly to the nitro derivative by a mixture of $H_2O_2$ and $CF_3COOH$.[40] To study the effect of the 1,3,4-oxadiazole bridge on the reactivity of aminofurazans, the natural charges and frontier orbital distributions of compounds **3** and **11** and **DABF** were calculated by quantum chemistry (DFT) and compared.[41] As shown in Figure S2 and Table S2-S4, the introduction of the 1,3,4-oxadiazole ring reduces both the nitrogen charges and contribution of the amino groups to the highest occupied molecular orbital (HOMO), which results in the decrease of amino reactivity.




**Scheme 3.** Proposed mechanism for the synthesis of 2 from 1

**Physical and Detonation Properties.** The physicochemical properties of compounds **4**–**8**, **12-16** are compared with 1,1-diamino-2,2-dinitroethene (FOX-7), 1,3,5-trinitro-1,3,5-triazine (RDX) and HMX in Table 1. The decomposition temperatures (onset) of all compounds are between 67 and 214 °C. Among these compounds, nitroamines **5** and **13** have the lowest thermal stability commencing decomposition at 67 and 90 °C, respectively. The most thermally stable compound is the ammonium salt **14** (214 °C), which is comparable to RDX (204 °C) and FOX-7 (220 °C). The order of thermal stability for the mono-1,3,4-oxadiazole-bridged compounds is **5** (67 °C) < hydroxylamine salt **8** (169 °C) = azide **4** (169 °C) < hydrazine salt **7** (190 °C) < ammonium salt **6** (210 °C). Interestingly, the bis-1,3,4-oxadiazole-bridged compounds show the same trend. Comparison of the decomposition temperatures of the two series of 1,3,4-oxadiazole-bridged compounds leads to a surprising conclusion. Tetracyclic compounds, **12**–**16,** in general, decompose at higher temperatures than the analogous tricyclic compounds with the same groups. This can be rationalized by the superior molecular stability of the former structures, which is derived from a large conjugated system. The greater thermal stability of bis-1,3,4-oxadiazole-bridged compounds compared with that of mono-1,3,4-oxadiazole-bridged compounds is not accidental and has been shown by several studies. Recent research by our group further showed that the bis-1,3,4-oxadiazole-bridged compounds, [5,5'-bis(4-nitro-1*H*-pyrazol-3-yl)-2,2'-bi(1,3,4-oxadiazole), **BNPBO** and 5,5'-bis(1,4-dinitro-1*H*-pyrazol-3-yl)-2,2'-bi(1,3,4-oxadiazole), **BDPBO**] have better thermal stabilities than the mono-1,3,4-oxadiazole bridged [2,5-bis(4-nitro-1*H*-pyrazol-3-yl)-

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**Table 1.** Physical and Detonation Properties of Compounds **4–8**, **12-16** compared with **DNBF**, FOX-7, RDX and HMX

| Compd | $T_{dec}$[a] [°C] | $\rho$[b][g cm$^{-3}$] | $\Delta H_f$[c][kJ mol$^{-1}$/ kJ g$^{-1}$] | $D$[d][m s$^{-1}$] | $P$[e][GPa] | IS[f][J] | FS[g][N] |
|---|---|---|---|---|---|---|---|
| **4** | 169 | 1.76 | 1359.8/4.72 | 8728 | 31.2 | 21.9 | 280 |
| **5** | 67 | 1.91 | 711.8/2.18 | 9211 | 38.0 | - | - |
| **6** | 210 | 1.82 | 420.2/1.17 | 8700 | 32.2 | 24.5 | 360 |
| **7** | 190 | 1.79 | 783.5/2.01 | 8914 | 33.3 | 11.0 | 280 |
| **8** | 169 | 1.88 | 553.9/1.41 | 9101 | 37.9 | 17.4 | 330 |
| **12** | 191 | 1.79 | 1370.2/3.85 | 8545 | 29.8 | 4.9 | 120 |
| **13** | 90 | 1.92 | 793.3/2.01 | 9058 | 36.2 | 6.9 | 120 |
| **14** | 214 | 1.87 | 539.6/1.26 | 8745 | 33.1 | 9.8 | 240 |
| **15** | 200 | 1.86 | 890.2/1.94 | 8993 | 34.9 | 7.7 | 240 |
| **16** | 186 | 1.87 | 680.8/1.48 | 8926 | 35.8 | 6.9 | 240 |
| **DNBF**[h] | 80 | 1.94 | 526.0/2.04 | 9086 | 40.3 | 1.5 | 48 |
| FOX-7[i] | 220 | 1.88 | -130.0/-0.88 | 8870 | 34.0 | 25 | 340 |
| RDX[j] | 204 | 1.80 | 70.3/0.32 | 8795 | 34.9 | 7.4 | 120 |
| HMX[j] | 280 | 1.91 | 74.8/0.25 | 9144 | 39.2 | 7.4 | 120 |

[a] Thermal decomposition temperature (onset) under nitrogen gas (DSC, 5 °C/min). [b] Density measured with a gas pycnometer (25 °C). [c] Calculated heat of formation. [d] Calculated detonation velocity. [e] Calculated detonation pressure. [f] Impact sensitivity. [g] Friction sensitivity. [h] Ref. [22]. [i] Ref. [42]. [j] Ref. [43].

1,3,4-oxadiazole, **BNPO** and 2,5-bis(1,4- dinitro-1*H*-pyrazol-3-yl)-1,3,4-oxadiazole), **BDPO**].[44] Therefore, we analyzed the molecular thermal stabilities of 1,3,4-oxadiazole-bridged compounds by calculating the trigger bond dissociation enthalpies (TBDE).[45-47] The result is consistent with the trend of the measured decomposition temperatures (Figure 6a), that is, the greater the dissociation energy, the higher the decomposition temperature. Additionally, the TBDE of the unreported 1,3,4-oxadiazole-bridged compounds with some common energetic units were calculated and analyzed (Figure 6b). Overall, the thermal stability of bis-1,3,4-oxadiazole-bridged compounds is higher than that of mono-1,3,4- compounds both in theory and in practice.

For the azide compounds, the introduction of one more 1,3,4-oxadiazole ring increases the density from 1.76 (**4**) to 1.79 g cm$^{-3}$ (**12**). Nitroamine derivatives **5**–**8** and **13**–**16** exhibit good to excellent densities between 1.79 and 1.92 g cm$^{-3}$. Among these derivatives, compounds **5** (1.91 g cm$^{-3}$) and **13** (1.92 g cm$^{-3}$) have the highest density, which is comparable to that of HMX (1.91 g cm$^{-3}$). The heats of formation were calculated using the Gaussian 09 suite of programs. As expected, the introduction of an additional 1,3,4-oxadiazole ring results in higher heats of formation for **12**–**16** (539.6–1370.2 kJ mol$^{-1}$) compared with those for mono-1,3,4-oxadiazole-bridged compounds **4**–**8** (420.2–1359.8 kJ mol$^{-1}$). Using the measured densities and calculated heats of formation, the detonation performances were calculated using the EXPLO5_V6.01 program.[48] The detonation velocity and detonation pressure of compounds **4**–**8** and **12**–**16** are in the range of 8545–9211 m s$^{-1}$ and 29.8–38.0 GPa, respectively (Figure 8a). Except for azides **4** (8728 m s$^{-1}$), **6** (8700 m s$^{-1}$), **12** (8545 m s$^{-1}$), and **14** (8745 m s$^{-1}$), these energetic compounds outperform FOX-7 (8870 m s$^{-1}$) and RDX (8795 m s$^{-1}$) in terms of detonation velocity. Among these compounds, the detonation velocities of nitroamine **5** (9211 m s$^{-1}$), hydroxylammonium salt **8**

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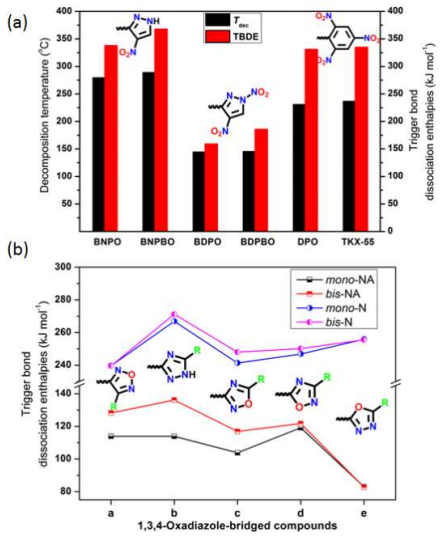


**Figure 6.** (a) Decomposition temperatures and trigger bond dissociation enthalpies (TBDE) of **BNPO**, **BNPBO**, **BDPO**, **BDPBO**, **DPO**, and TKX-55. (b) TBDE of series a–e of 1,3,4-oxadiazole-bridged compounds

(9101 m s$^{-1}$), and nitroamine **13** (9058 m s$^{-1}$) are close to those of 3,3'-dinitramino-4,4'-bifurazan (DNBF, 9086 m s$^{-1}$) and HMX (9144 m s$^{-1}$).

To study the safety of these energetic compounds as energetic materials, their impact sensitivities (IS) and friction sensitivities (FS) were measured.[49] With the exception of 5, the IS values of all compounds are in the range of 4.0 to 24.5 J, while the FS value is in the range of 120 to 360 N. Tricyclic energetic compounds, **4** and **6**–**8**, have better mechanical stability (IS = 11.0–24.5 J, FS = 280–360 N) than the high-energy explosives RDX (IS = 7.5 J, FS = 120 N) and HMX (IS = 7.0 J, FS = 112 N) (Figure 7b). Tetracyclic energetic compounds, **12**–**16**, are more sensitive (IS = 4.9–9.8 J, FS = 120–240 N) than the tricyclic series. Among these compounds, **12** (IS = 4.9 J) is the most unstable compound in terms of impact sensitivity. However, its stability is better than those of nitraminofurazans with azo, azoxy, and other bridges. In terms of friction sensitivity, **12**–**16** are less sensitive than HMX (FS = 112 N), and **14**–**16** (FS = 240 N) are even more stable than RDX (FS = 120 N).

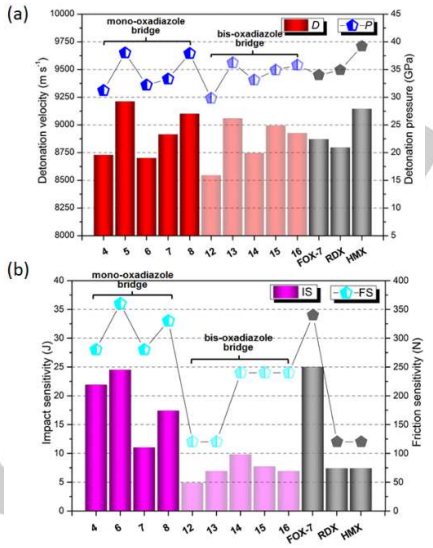


**Figure 7**. Comparison of (a) detonation performances. (b) Sensitivities of 4–8, 12–16, FOX-7, RDX, and HMX.

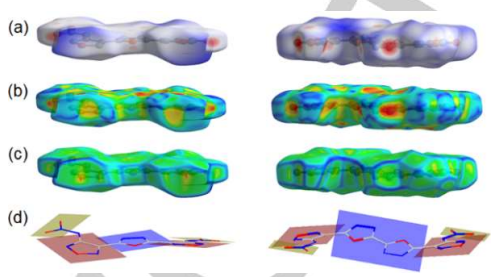


**Figure 8.** Hirshfeld surfaces of anions in **6**·$H_2O$ and **14**·2$H_2O$: (a) 3D $d_{norm}$ surface, (b) shape index, (c) curvedness, and (d) distortion of anions in **6**·$H_2O$ and **14**·2$H_2O$.

The Hirshfeld surfaces and associated fingerprint plots of the crystals were obtained to demonstrate the intermolecular interactions.[50] The 3D $d_{norm}$ surfaces in Figure 8a and Figure S9 show that the oxygen atoms of nitro groups in the anions of **6**·$H_2O$ and **14**·2$H_2O$ act as acceptor sites for hydrogen bonds. The shape index (Figure 8b) shows that the adjacent anions in **14**·2$H_2O$ are more in contact than those in **6**·$H_2O$. The crystal of **12**, which has a complex color distribution, is the bumpiest one in all crystals (Figure S9). The curvedness analysis in Figure 8c show that the **14**·2$H_2O$ anion is divided into several planes. The dihedral angle between the furan and 1,3,4-oxadiazole rings in the **6**·$H_2O$ anion crystal is 10.51° (Figure 8d), which is lower than that in **14**·2$H_2O$ (10.90°). The dihedral angle between the nitrosamino group and furan ring is 1.27°, which is also lower than that in **14**·2$H_2O$ (2.22°). Combined crystal analyses of **6**·$H_2O$ and **14**·2$H_2O$ shows that the bis-1,3,4-oxadiazole bridge is more distorted than the mono-1,3,4-oxadiazole bridge, which may explain the lower mechanical stability of bis-1,3,4-oxadiazole-bridged compounds compared with that of mono-1,3,4-oxadiazole-bridged-compounds. In the **6**·$H_2O$ anion, N···O, O···O, and O···H interactions lead the way, accounting for 23.7%, 20.6%, and 19.5% of the interactions, respectively (Figure 9). On the other hand, in the **14**·2$H_2O$ anion, O···H and N···H interactions account for more than half of the interactions (27.1% and 27.6%,

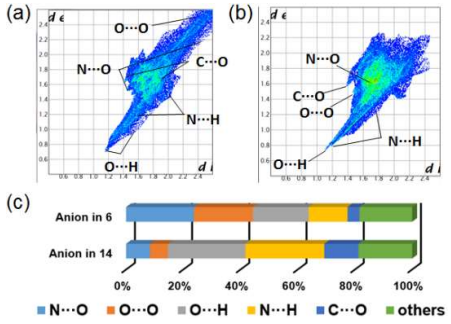


**Figure 9.** 2D fingerprint plots of the anions in (a) **6**·$H_2O$ and (b) **14**·2$H_2O$. (c) Population of close contacts of anions in **6**·$H_2O$ and **14**·2$H_2O$ in the crystal stacking.

respectively). This means that hydrogen bonds are the main intermolecular interactions in **14**·2$H_2O$.

## Conclusion

In summary, a family of new mono- and bis-1,3,4-oxadiazole-bridged furazans was synthesized and fully characterized. The mono-1,3,4-oxadiazole-bridged compounds were prepared on the basis of a rarely reported reaction starting from amidine. In addition, the reaction mechanism for the synthesis of **2** was proposed and the chemical inactivity of **3** and **11** toward oxidation were studied computationally. Experiments and quantum chemistry calculations proved that the 1,3,4-oxadiazole ring improves the stability of energetic compounds. Additionally, the thermal stability of the bis-1,3,4-oxadiazole-bridges was higher than that of the mono-1,3,4-oxadiazole bridges. The detonation performances of nitroamine **5** (9211 m $s^{-1}$, 38.0 GPa), hydroxylammonium salt **8** (9101 m $s^{-1}$, 37.9 GPa), and nitroamine **13** (9058 m $s^{-1}$, 36.2 GPa) were better than that of RDX (8795 m $s^{-1}$, 34.7 GPa) and even close to that of the highly explosive HMX (9144 m $s^{-1}$, 39.2 GPa). This systematic study of 1,3,4-oxadiazole-bridged energetic compounds, analysis of the effect of the 1,3,4-oxadiazole bridge on the reactivity and performance of the compounds, and design and synthesis of 1,3,4-oxadiazoxle-bridged compounds provides a theoretical basis for future energetics design.

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