Energetic Materials

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Bis(4-nitraminofurazanyl-3-azoxy)azofurazan and Derivatives: 1,2,5-Oxadiazole Structures and High-Performance Energetic Materials

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Abstract: *Bis(4-nitraminofurazanyl-3-azoxy)azofurazan (**1**) and ten of its energetic salts were prepared and fully characterized. Computational analysis based on isochemical shielding surface and trigger bond dissociation enthalpy provide a better understanding of the thermal stabilities for nitramine-furazans. These energetic compounds exhibit good densities, high heats of formation, and excellent detonation velocity and pressure. Some representative compounds, for example, **1** (v_D: 9541 m s^{-1}; P: 40.5 GPa), and **4** (v_D: 9256 m s^{-1}; P: 38.0 GPa) exhibit excellent detonation performances, which are comparable with current high explosives such as RDX (v_D: 8724 m s^{-1}; P: 35.2 GPa) and HMX (v_D: 9059 m s^{-1}; P: 39.2 GPa).*

In recent decades, research on energetic materials has grown to a high level.[1] When considering the newly designed energetic compounds in practical applications, positive heats of formation, high detonation performance, high density, and lower sensitivity are the main concerns.[2] To design new high-performance energetic materials, introducing energy-rich functional groups such as -NO_2, -$NHNO_2$, -N=N-, and -N=N(O)- as substituents on azole frameworks is a recently emerging methodology.[3] In particular, the energetic compounds based on azole frameworks are highly desirable, especially those frameworks with high nitrogen content and high positive enthalpy, for example, tetrazoles, tetrazines, 1,2,5-oxadiazoles (furazans), and 1,2,5-oxadiazole 2-oxides (furoxans).[4] Among the combinations between functional moiety and azole backbone, the family of nitramino-furazans has gained particular attention because of its high detonation properties.[5] The assembly of diverse N−O building blocks as both a nitramino substituent and within a furazan ring has proven to be a promising strategy for the design of high-energy-density materials (HEDM).[5b]

As is seen for these nitramino-furazans, the more ring structures present in a molecule, the higher the heat of formation (in kJ mol^{-1}).[5] It can be easily attributed to the presence of a larger number of nitrogen atoms and -C=N-bonds in the two ring systems. In addition, by comparing the heats of formation of the directly coupled furazans (4,4′-dinitramino-3,3′-bifurazan), 4,4′-bis(nitramino)azofurazans (DNAF), and 4,4′-bis(nitramino)azoxyfurazans (DNAXF), it is found that azo and azoxy linkages also play an important role in increasing the heat of formation.[5] Among all of the derivatives of DNAF and DNAXF, bis(4-nitraminofurazanyl-3-azoxy)azofurazan (**1**), which has four furazan rings and three azo(xy) linkages in one molecule, draws particular attention because of its large calculated heat of formation and good theoretical detonation properties.[6] Given this background, we herein report that **1,** as well as ten of its nitrogen-rich ionic derivatives (**2**–**11**), were efficiently synthesized and fully characterized (Scheme 1). Additionally, theoretical calculations, such as, isochemical shielding surfaces and trigger bond dissociation enthalpies, have been performed, and provide a deeper understanding of the structure–property relationships for the compounds **1**, DNAF, and DNAXF.

The starting materials, diaminofurazan (DAF) and 3,3′-diamino-4,4′-azoxyfurazan (DAAF) were synthesized based on literature precedent (Scheme 1).[5b] The introduction of an azo linkage based on DAAF is described in another reference in which potassium bromate was selected as the oxidizing agent to yield bis(4-aminofurazanyl-3-azoxy)azofurazan (ADAAF).[7] The nitration of ADAAF was carried out by using 100 % HNO_3 to yield **1**. Energetic salts (**2**–**11**) were obtained by reacting **1** with various nitrogen-rich bases. The structures of bis(4-nitraminofurazanyl-3-azoxy)azofurazan and its energetic salts (**1**–**11**) are supported by IR, ^{1}H, ^{13}C NMR spectroscopy, and elemental analysis. The structures of **1**, **2**, **7**, and **8** were additionally confirmed by single-crystal X-ray diffraction analysis.

The thermal stabilities of **1**–**11** were measured by using differential scanning calorimetry (DSC; Table 1). The decomposition temperatures of **1**–**11** ranged from 120 (**1**) to 209 °C (**8** and **11**). It is interesting that **1** has a higher decomposition temperature in comparison with those of DNAF and DNAXF. For nitramine-furazans, having two and four furazan building blocks, these differences in thermal stability awakened our interest, and two computational methods were applied to provide a better understanding. First, the spatial magnetic

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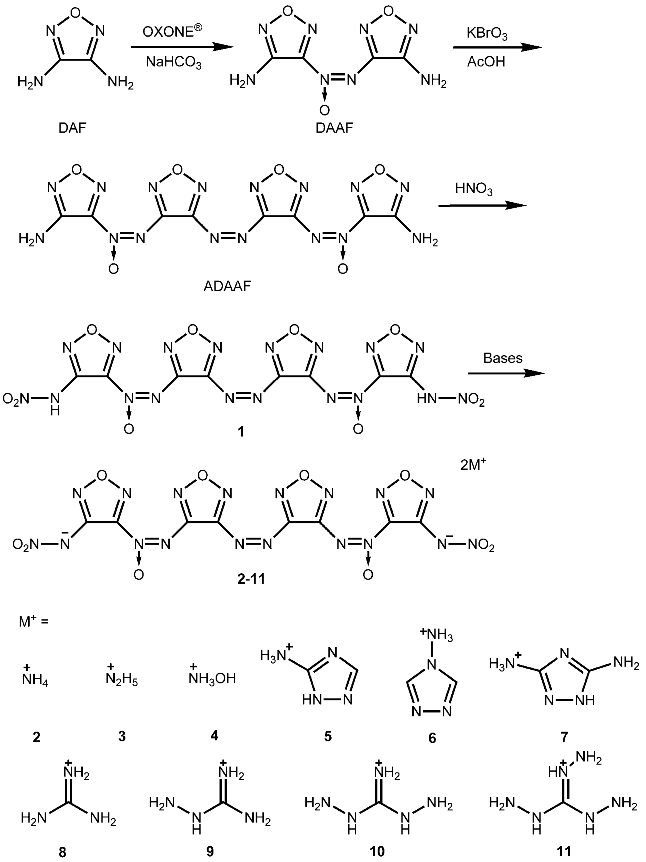

Scheme 1. Synthesis of bis(4-nitraminofurazanyl-3-azoxy)azofurazan (**1**) and its energetic salts (**2**–**11**).

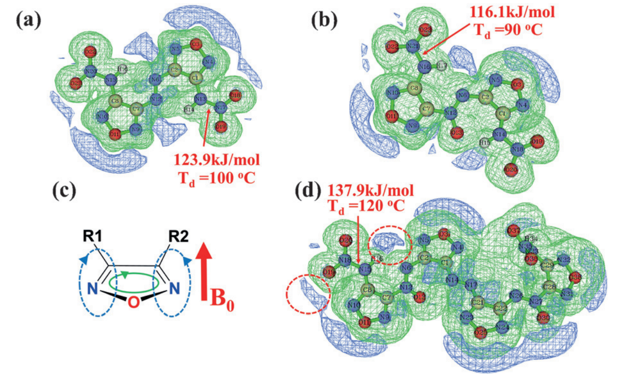

Figure 1. Visualization of the spatial magnetic properties of DNAF, DNAXF, and **1** as ICSS maps (0.70 ppm shielding, other values' shielding can be viewed in the Supporting Information). a) The ICSS map of DNAF. b) The ICSS map of DNAXF. c) The diagrammatic illustration of the relationship between external magnetic field (red arrow), induced current (green ring), and induced magnetic field (blue ring) in substituted furazan system d) The ICSS map of compound **1**.

properties of **1**, DNAF, and DNAXF were calculated and visualized with Multiwfn program[8] as isochemical shielding surfaces (ICSS), which has been demonstrated to be related to molecular thermal stability.[9] As shown in Figure 1, the aromaticity indexes as well as electron delocalization of the functional groups and the ring moieties in **1**, DANF, and DNAXF can be demonstrated. In general, the π delocalization in the furazan ring is the strongest and shows the biggest shielding space. In contrast, the shielding space around the N−NO_2 groups is much weaker, especially for the N−NO_2 group close to the N-oxide in DNAXF (Figure 1b). Compared to those of DNAF and DNAXF, the N−NO_2 groups in **1** were found to take part in the delocalized π-electron system based on two shielding clouds at both ends (Figure 1d). The electron delocalization of N−NO_2 groups of DNAF can also be visualized in Figure 1a, but judging by the size, the effect is lower than that of **1**. Second, the trigger bond dissociation enthalpies (TBDE), which are strongly related to the thermal decomposition in **1**, were also calculated for DNAF and DNAXF as shown in Figure 1. As can be seen, the values of TBDE have the order of **1** (137.9 kJ mol^{-1}) > DNAF (123.9 kJ mol^{-1}) > DNAXF (116.1 kJ mol^{-1}), and is in agreement with the order of the thermal stabilities of these three

Table 1: Physical and detonation properties of **1**–**11** compared with those of RDX and HMX.

Compd.	T_d[a] [°C]	OB[b] [%]	N[c] [%]	d[d] [g cm^{-3}]	$\Delta_f H$ [e] [kJ mol^{-1}/kJ g^{-1}]	ν_D[f] [m s^{-1}]	P[g] [GPa]	IS[h] [J]	FS[i] [N]	I_{sp}[j] [s]
1	120	−22.0	49.4	1.88	1623.4/3.18	9541	40.5	2	10	283
2	154	−27.6	48.3	1.75	1507.7/2.60	8893	33.5	15	120	275
3	175	−32.2	53.7	1.78	1791.2/3.27	9065	35.0	14	120	280
4	124	−22.2	48.6	1.83	1600.2/2.78	9256	38.0	15	120	285
5	151	−44.8	53.7	1.78	1949.1/2.87	8768	31.8	21	160	255
6	181	−44.8	53.7	1.72	2242.5/3.31	8649	30.5	17	120	265
7	189	−45.2	55.4	1.80	1913.7/2.70	8890	32.4	25	240	250
8	209	−40.8	53.5	1.75	1464.5/2.33	8716	31.0	26	240	249
9	195	−41.3	55.3	1.71	1688.3/2.57	8584	29.1	22	240	254
10	203	−41.9	57.0	1.73	1904.3/2.77	8803	30.7	19	160	258
11	209	−42.3	58.5	1.75	2217.8/3.09	9015	32.2	15	120	264
RDX	204	−21.6	37.8	1.82	80.0/0.36	8724	35.2	7.4	120	258
HMX	280	−21.6	37.8	1.91	104.8/0.36	9059	39.2	7.4	120	266

[a] Thermal decomposition temperature. [b] Oxygen balance for $C_aH_bO_cN_d$: $1600(c-2a-b/2)/Mw$; Mw = molecular weight. [c] Nitrogen content. [d] Density at 25 °C. [e] Calculated heat of formation. [f] Detonation velocity. [g] Detonation pressure. [h] Impact sensitivity. [i] Friction sensitivity. [j] Special impulse.

compounds. Our theoretical results suggested that the assembly of more furazan building blocks in one molecule could efficiently improve the total electron delocalization effect and enhance the bond order at both ends.

Density is an important physical parameter for energetic materials. The experimental densities of **1**–**11** are in the range of 1.71 to 1.88 $g\,cm^{-3}$. It is noteworthy that the densities of **1**, **4**, and **7** fall within the range designated for new HEDMs (1.8–2.0 $g\,cm^{-3}$), and are comparable with the commonly used high explosives RDX and HMX. To evaluate energetic properties of these newly prepared compounds, computation of heats of formation were performed by using Gaussian 09 program package.[10] The gas-phase heats of formation of **1** and its anion were obtained by using the isodesmic reaction approach.[11] The enthalpy of sublimation for neutral **1** was predicted by using Trouton's rule based on the melting point.[12] The solid-phase heats of formation of energetic the salts **2**–**11** were calculated on the basis of the Born–Haber energy cycle[13] (more details about the calculation of heats of formation can be found in the Supporting Information). With three azo(xy) groups and a large number of N−O, N−N bonds in these structures, the calculated heats of formation of **1**–**11** are in the range of 1464.5 to 2242.5 $kJ\,mol^{-1}$ and 2.33 to 3.31 $kJ\,g^{-1}$. The heat of formation of **6** (2242.5 $kJ\,mol^{-1}$) ranks at the top of the density series with CHNO explosives such as 4,4′,6,6′-tetraazido-2,2′-azo-1,3,5-triazine (2171 $kJ\,mol^{-1}$).[14] Remarkably, the highest value in terms of kilojoules per gram is that of **4** (3.31 $kJ\,g^{-1}$), and it is nine times greater than that of RDX (0.36 $kJ\,g^{-1}$) and HMX (0.36 $kJ\,g^{-1}$).

Oxygen balance is an expression which indicates the excess or deficiency in an energetic compound required to convert all carbon into CO_2 and all hydrogen into H_2O. It can be used to classify an energetic compound as an explosive or oxidant. Of all these compounds, only **1** (−22.0%) and **4** (−22.2%) have an oxygen balance close to that of RDX (−21.6%) and HMX (−21.6%). The oxygen balance values of the other energetic salts vary from −27.6% (**2**) to −45.2% (**7**). For energetic propellant fuels, high nitrogen content is advantageous for smokeless combustion.[15] Nitrogen content values of these new compounds are in the range of 48.3% (**2**) to 58.5% (**11**), all of which are higher than those of RDX (37.8%) and HMX (37.8%).

The detonation performance of energetic materials is characterized by their detonation velocity (v_D) and detonation pressure (P). With the experimental densities and calculated heats of formation in hand, the detonation performances of **1**–**11** were evaluated by using EXPLO5 (v6.02) program.[16] From Table 1, the detonation velocities of these energetic compounds range from 8573 $m\,s^{-1}$ (**6**) to 9541 $m\,s^{-1}$ (**1**), and **1** displays the highest v_D value. The calculated detonation pressures fall in the range of 29.8 (**6**) to 40.5 GPa (**1**). The energetic performances of **1** (v_D: 9541 $m\,s^{-1}$; P: 40.5 GPa) and **4** (v_D: 9256 $m\,s^{-1}$; P: 38.0 GPa) are superior to those of high explosive benchmarks RDX (v_D: 8724 $m\,s^{-1}$; P: 35.2 GPa) and HMX (v_D: 9059 $m\,s^{-1}$; P: 39.2 GPa). The values of impact and friction sensitivity of **1**–**11** were determined by using a standard BAM Fallhammer and a BAM friction tester. Not surprisingly, **1** shows the highest impact and friction sensitivity of 2 J and 10 N, respectively. By pairing with different cations, the ADNAF-based salts are well stabilized and exhibit better impact and friction sensitivities (14–16 J for IS and 120–240 N for FS) than their parent compound. Among them, the hydrazinium, hydroxylammonium, and triaminoguanidinium salts, which have high detonation properties and acceptable sensitivities, may serve as promising replacements of RDX.

Suitable crystals of **1**, **2**·2 H_2O, **7**, and **8** for single-crystal X-ray diffraction were obtained through slow evaporation from solvents. Their crystal structures are shown in Figure 2. The energetic compound **1** crystallizes in the monoclinic space group $P2_1/c$, whose asymmetric unit contains a half independent energetic molecule. Crystals of **2**·2 H_2O, **7**, and **8** all crystallize in the triclinic space group P-1.The asymmetric units of the first two compounds contain one independent molecule of **2**·2 H_2O and **7**, respectively. In the case of **8**, the asymmetric unit contained two halves of the bis(4-nitraminofurazanyl-3-azoxy)azofurazanate anions and two guanidinium cations. In the case of **1**, only one kind of hydrogen-bonding interaction is found to be intermolecular N3-H3⋯N7A with a distance of 2.479 Å (D⋯A). The hydrogen-bonding interactions in energetic salts **2**·2 H_2O, **7**, **8** are more extensive, and most of them are observed between cations and anions. The decreasing mechanical sensitivity of energetic salts can be rationalized in terms of considerable hydrogen-bonding interactions.

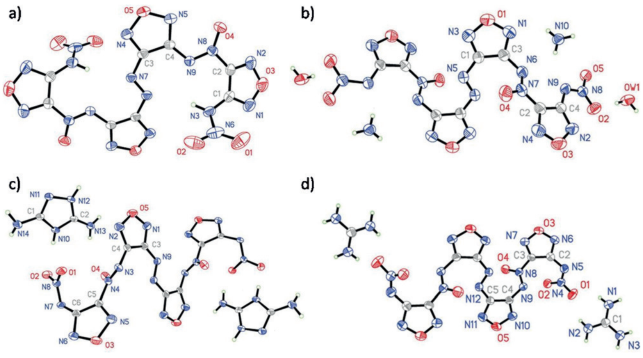

Figure 2. The molecular structure of a) **1**, b) **2**·2 H_2O, c) **7**, and d) **8** with thermal ellipsoids shown at 50% probability.[17]

Inspired by the recently reported azo/azoxy-based furazan energetic materials, a new compound, bis(4-nitraminofurazanyl-3-azoxy)azofurazan (**1**), which has four furazan rings and three azo(xy) linkages in one molecule was designed and synthesized. Subsequently, a series of nitrogen-rich energetic salts (**2**–**11**) were synthesized and fully characterized. These energetic compounds exhibit high densities of 1.71–1.88 $g\,cm^{-3}$ and good decomposition temperatures in the range of 120–209 °C. In addition, the calculated isochemical shielding surface maps and trigger bond dissociation enthalpies of **1**, DNAF, and DNAXF has provided a better understanding of structure–property relationship in terms of thermal stability. With a large number of N−O and N−N bonds in these new structures, the calculated heats of formation of **1**–**11** are relatively high and fall in the range of 1464.5 to 2242.5 $kJ\,mol^{-1}$ (2.33 to 3.31 $kJ\,g^{-1}$). On the basis of experimental physicochemical parameters and calculated detonation performances, some representative compounds, **1** (v_{D}: 9541 m s^{-1}; P: 40.5 GPa) and **3** (v_{D}: 9256 m s^{-1}; P: 38.0 GPa) are comparable to RDX (v_{D}: 8724 m s^{-1}; P: 35.2 GPa) and HMX (v_{D}: 9059 m s^{-1}; P: 39.2 GPa). More importantly, most of the energetic salts possess acceptable impact and friction sensitivities, which are up to 14 J and 120 N, respectively. This work also highlights the assembly of nitroamino-based furazan with azo(xy) linkages as a favorable strategy for the design and syntheses of new HEDMs.

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[17] CCDC 1469644 (**1**), 1469685 (**2**·2 H_2O), 1477926 (**7**), and 1477928 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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