

Supporting Information

Taming of 3,4-Di(nitramino)furazan

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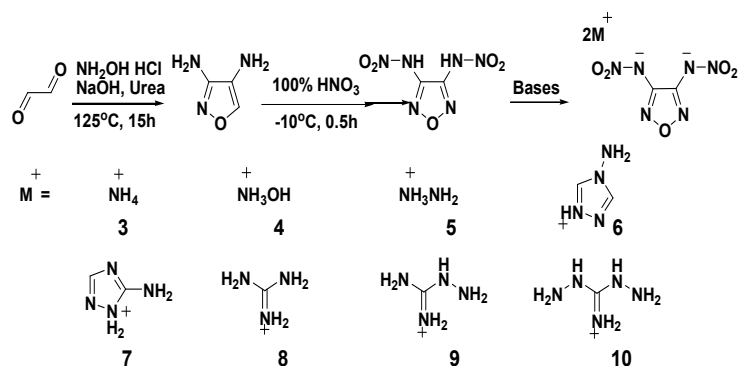
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Experimental section

CAUTION!!! We strongly recommend that 3,4-dinitraminofurazan not be isolated because of its high sensitivity. 3,4-Dinitraminofurazan and its derivatives are high-performance energetic materials, therefore, these materials should be handled with care using the best safety practices.

General Methods. Reagents were purchased from Acros Organics and Aldrich as analytical grade and were used as received. ¹H and ¹³C spectra were collected on a Bruker AVANCE 300 nuclear magnetic resonance spectrometer operating at 300.13, and 75.48 MHz, respectively. A Bruker AVANCE 500 nuclear magnetic resonance spectrometer operating at 50.69 MHz was used to collect ¹⁵N spectra data. CD₃CN and DMSO-*d*₆ were employed as solvent and locking solvent. Chemical shifts are given relative to Me₄Si for ¹H and ¹³C spectra and MeNO₂ for ¹⁵N NMR. Melting and decomposition (onset) points were measured by differential scanning calorimeter (TA Instruments Co., model Q20) at a scan rate of 5 °C min⁻¹. Infrared (IR) spectra were recorded using KBr pellets on a BIORAD model 3000 FTS spectrometer. Densities were measured using a Micromeritics AccuPyc 1330 gas pycnometer at room temperature. Elemental analyses (C, H, N) were performed with an Exeter CE-440 elemental analyzer. Impact and friction-sensitivity measurements were tested by employing a standard BAM Fallhammer and a BAM friction tester.



Scheme S1. Synthesis of 3,4-di(nitramino)furazan (**1**) and its energetic salts (**3-10**).

3,4-Dinitraminofurazan (1): 3,4-Diaminofurazan [1.0 g (10 mmol)] was added slowly to 100% nitric acid (2 mL) at -10 °C. The reaction mixture was stirred at the same temperature for 0.5 h. In this process, some precipitate formed. The precipitate was filtered, washed with trifluoroacetic acid and dried in air. Compound **1** (1.25 g, 66%) was obtained.

White solid. T_m : 93 °C. T_d : 99 °C. ^1H NMR: δ 12.04 ppm (s). ^{13}C NMR: δ 147.5 ppm. Elemental analysis for $\text{C}_2\text{H}_2\text{N}_6\text{O}_5$ (190.07): calcd C 12.64, H 1.06, N 44.21 %. Found: C 12.87, H 0.67, N 47.23 %. *IS*: < 1 J. *FS*: < 5 N.

General procedure for preparation of salts **3-10**

A solution of $\text{NH}_3 \cdot \text{H}_2\text{O}$, 50% hydroxylamine solution, hydrazine monohydrate, 4-amino-1,2,4-triazole, 3-amino-1,2,4-triazole, guanidine carbonate, aminoguanidine bicarbonate, or diaminoguanidine hydrochloride in 10 mL of CH_3CN was added to a solution of **1** in 10 mL of CH_3CN . Immediately, a white precipitate formed. The precipitate was filtered off, washed with CH_3CN , and dried in air.

Diammonium 3,4-dinitraminofurazanate (**3**)

White solid. T_d : 191 °C. ^1H NMR: δ 7.19 ppm (s). ^{13}C NMR: δ 154.2 ppm. IR (KBr): ν = 2838, 1790, 1755, 1678, 1547, 1488, 1071, 1015, 908, 883, 845, 797, 770, 557 cm^{-1} . Elemental analysis for $\text{C}_2\text{H}_8\text{N}_8\text{O}_5$ (224.14): calcd C 10.72, H 3.60, N 49.99 %. Found: C 10.85, H 3.57, N 49.58 %. *IS*: 8 J. *FS*: 240 N.

Dihydroxylammonium 3,4-dinitraminofurazanate (**4**)

White solid. T_d : 181 °C. ^1H NMR: δ 9.82 ppm (br). ^{13}C NMR: δ 152.2 ppm. IR (KBr): ν = 3451, 3216, 3105, 2915, 1609, 1526, 1491, 1427, 1379, 1321, 1292, 1009, 895, 868, 818, 772, 689, 560 cm^{-1} . Elemental analysis for $\text{C}_2\text{H}_8\text{N}_8\text{O}_7$ (256.13): calcd C 9.38, H 3.15, N 43.75 %. Found: C 9.25, H 3.22, N 43.88 %. *IS*: 5 J. *FS*: 120 N.

Dihydrazium 3,4-dinitraminofurazanate (**5**)

White solid. T_m : 206 °C. T_d : 225 °C. ^1H NMR: δ 7.22 ppm (br). ^{13}C NMR: δ 153.3 ppm. IR (KBr): ν = 3568, 3438, 3339, 2745, 2626, 1800, 1742, 1600, 1549, 1490, 144, 1354, 1097, 1013, 967, 914, 885, 851, 802, 770, 559 cm^{-1} . Elemental analysis for

C₂H₁₀N₁₀O₅ (254.16): calcd C 9.45, H 3.97, N 55.11 %. Found: C 9.46, H 3.87, N 56.13 %. *IS*: 12 J. *FS*: 160 N.

Di(4-amino-1,2,4-triazolium) 3,4-dinitraminofurazanate (6)

White solid. *T*_m: 147 °C. *T*_d: 172 °C. ¹H NMR: δ 8.97 ppm (s, 2H), 7.59 ppm (br). ¹³C NMR: δ 150.0, 144.0 ppm. IR (KBr): ν = 3287, 3211, 3122, 3062, 2994, 1637, 1558, 1525, 1497, 1424, 1387, 1337, 1301, 1271, 1219, 1071, 978, 927, 885, 854, 804, 770, 724, 661, 614 cm⁻¹. Elemental analysis for C₆H₁₀N₁₄O₅ (358.23): calcd C 20.12, H 2.81, N 54.74 %. Found: C 20.03, H 2.69, N 55.14 %. *IS*: 22 J. *FS*: 240 N.

Di(3-amino-1,2,4-triazolium) 3,4-dinitraminofurazanate (7)

White solid. *T*_d: 122 °C. ¹H NMR: δ 9.20 (br), 8.17 ppm (s, 1H). ¹³C NMR: δ 152.2, 151.2, 141.1 ppm. IR (KBr): ν = 3389, 3150, 3088, 2755, 1690, 1626, 1489, 1423, 1358, 1295, 1123, 1051, 1019, 951, 848, 809, 744, 621, 552 cm⁻¹. Elemental analysis for C₆H₁₀N₁₄O₅ (358.23): calcd C 20.12, H 2.81, N 54.74 %. Found: C 20.20, H 2.74, N 55.19 %. *IS*: 28 J. *FS*: 360 N.

Diguanidinium 3,4-dinitraminofurazanate (8)

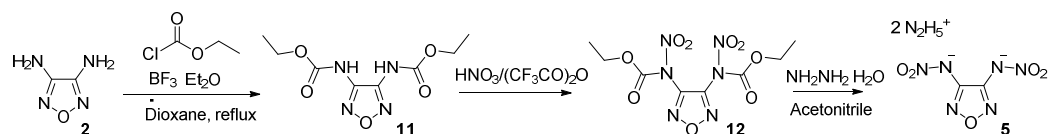
White solid. *T*_d: 282 °C. ¹H NMR: δ 7.10 ppm (s). ¹³C NMR: δ 158.0, 153.6 ppm. IR (KBr): ν = 3454, 3353, 3188, 2806, 1690, 1653, 1581, 1542, 1482, 1404, 1354, 1315, 1149, 1069, 1018, 914, 886, 847, 802, 768, 721, 588 cm⁻¹. Elemental analysis for C₄H₁₂N₁₂O₅ (308.22): calcd C 15.59, H 3.92, N 54.53 %. Found: C 15.77, H 3.84, N 54.26 %. *IS*: 30 J. *FS*: 360 N.

Di(aminoguanidinium) 3,4-dinitraminofurazanate (9)

White solid. *T*_m: 174 °C. *T*_d: 217 °C. ¹H NMR: δ 8.94 ppm (s, 1H), 7.14 ppm (s, 4H), 4.77 ppm (s, 2H). ¹³C NMR: δ 158.9, 153.3 ppm. IR (KBr): ν = 3420, 3331, 3251, 3185, 1673, 1543, 1483, 1331, 1295, 1211, 1106, 1015, 886, 847, 804, 767, 723, 618 cm⁻¹. Elemental analysis for C₄H₁₄N₁₄O₅ (338.24): calcd C 14.20, H 4.17, N 57.97 %. Found: C 14.57, H 4.28, N 55.06 %. *IS*: 28 J. *FS*: 360 N.

Di(diaminoguanidinium) 3,4-dinitraminofurazanate (10)

White solid. *T*_m: 187 °C. *T*_d: 213 °C. ¹H NMR: δ 8.84 ppm (s, 2H), 7.27 ppm (s, 2H), 4.64 ppm (s, 4H). ¹³C NMR: δ 160.0, 153.5 ppm. IR (KBr): ν = 3364, 3434, 3312, 3215, 3000, 1682, 1487, 1545, 1487, 1387, 1335, 1055, 1016, 957, 869, 820, 768, 728, 564 cm⁻¹. Elemental analysis for C₄H₁₆N₁₆O₅ (368.27): calcd C 13.05, H 4.38, N 60.85 %. Found: C 12.95, H 4.30, N 60.19 %. *IS*: 25 J. *FS*: 160 N.



Scheme S2. An alternative synthetic route to **5** from N-ethoxycarbonyl protected 3,4-diaminofurazan.

3,4-*N,N'*-bis(ethoxycarboxamido)-1,2,5-oxadiazole (11)

In a 25 mL round-bottomed flask, a mixture of ethyl chloroformate (2.2 mmol) 3,4-diaminofurazan (1 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (10 mol%) in dioxane (15 mL) was heated to reflux. The reaction mixture was monitored by TLC until the starting material was gone. After reaction completion, the crude reaction mixture was evaporated with air and then taken up with water (75 mL) and extracted with ethyl acetate (3 x 20 mL). The organic layer was dried over anhydrous MgSO_4 , filtered and evaporated to obtain the crude product, which was purified by silica column chromatography using ethyl acetate/ n-hexane (1:5) as eluent to yield the pure product 3,4-*N,N'*-bis(ethoxycarboxamido)-1,2,5-oxadiazole (**11**) in good yield 80%. ^1H NMR (CDCl_3 , 300 MHz) δ 8.64 (s, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 1.32 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 153.4, 144.6, 63.4, 14.4 ppm.

Diethyl (1,2,5-oxadiazole-3,4-diyl)bis(nitrocarbamate) (12)

A 10 mL two-necked flask with a thermometer, and 100% nitric acid (2 mL) was cooled to 0 °C. Acetic anhydride (3 mL) was added slowly at the same temperature. 3,4-*N,N'*-Bis(ethoxycarboxamido)-1,2,5-oxadiazole (1 mmol) was added to the mixed acid carefully and the reaction temperature was allowed to rise to room temperature. After stirring for 12 h, the mixture was poured into ice-water. The white precipitate (**12**) was collected, washed with cold water, and dried in vacuum. T_m : 78 °C. T_d : 124 °C. ^1H NMR (CD_3CN , 300 MHz) δ 4.38 ppm (q, $J = 7.1$ Hz, 2H), 1.27 ppm (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (CD_3CN , 75 MHz) δ 148.7, 147.8, 67.8, 14.2 ppm. IR (KBr): $\nu = 3585, 2994, 2796, 1803, 1622, 1526, 1472, 1319, 1201, 1098, 1007, 968, 858, 736, 538\text{ cm}^{-1}$. Elemental analysis for $\text{C}_8\text{H}_{10}\text{N}_6\text{O}_9$ (334.20): calcd C 28.75, H 3.02, N 25.15 %. Found: C 29.14, H 3.19, N 25.02 %. *IS*: 36 J. *FS*: 240 N.

Dihydrazium 3,4-dinitraminofurazanate

Solid 3,4-*N,N'*-(dinitro)-bis(ethoxycarboxamido)-1,2,5-oxadiazole (0.5 g, 1.50 mmol) was dissolved in CH_3CN (30 mL). A solution of hydrazine monohydrate (0.17 g, >98%) in a mixture of methanol (2 mL) and water (2 mL) was added. The mixture was stirred for 1 h. The white precipitate was collected by filtration, washed with methanol, and recrystallized in water. The pure product was obtained as a white solid (0.30 g, 80%).

In Figure S1, selected ^{15}N NMR spectra of **1**, **3**, **4**, and **5** are shown. The assignments are based on the literature values for the peaks¹ and compared with calculated spectra [B3LYP/6-311+g(2d,p) with IEF-PCM continuum solvation models of the Gaussian 03 program].^{2,3}

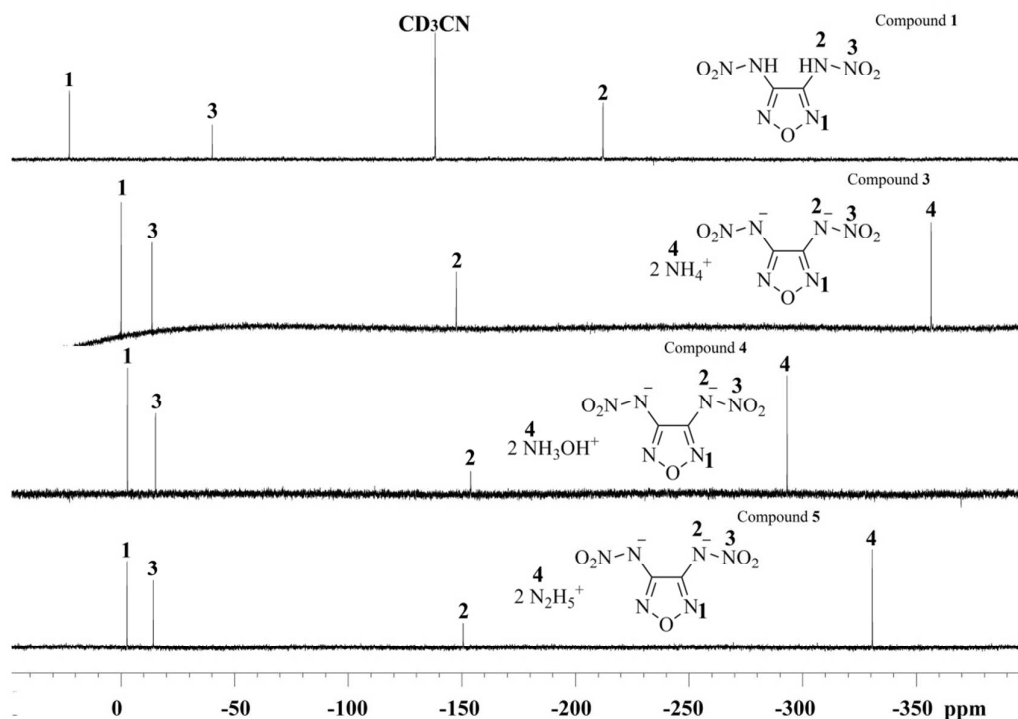


Figure S1. ^{15}N NMR spectra of compounds **1**, **3**, **4**, and **5**.

X-ray Crystallography.

Data collection was performed and the unit cell was initially refined using *APEX2* [v2014.3-0].⁴ Data reduction was performed using *SAINT* [v7.68A]⁵ and *XPREF* [v2014/2].⁶ Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2008/1].⁷ The structure was solved and refined with the aid of the programs *SHELXL-2014/7* within *WingX*.⁸ The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model (Table S1).

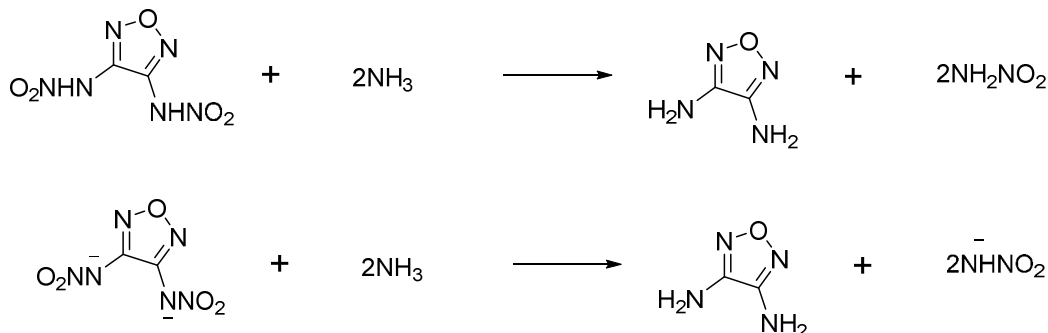
Table S1. Selected crystal parameters of **1**, **3**·2H₂O, **5**·H₂O and **12**.

Empirical formula	C ₂ H ₂ N ₆ O ₅ (1)	C ₂ H ₁₂ N ₈ O ₇ (3·2H₂O)	C ₂ H ₁₂ N ₁₀ O ₆ (5·H₂O)	C ₈ H ₁₀ N ₆ O ₉ (12)
Formula weight	190.10	260.20	272.22	334.22
Temperature/K	150	150	296	296

Crystal system	Monoclinic	Triclinic	Orthorhombic	Triclinic
Space group	P2 ₁ /c	P-1	Pna2 ₁	P-1
<i>a</i> /Å	11.0976(7)	3.7177(2)	19.3262(11)	7.9009(16)
<i>b</i> /Å	5.7127(4)	9.6263(5)	3.6054(2)	9.3741(19)
<i>c</i> /Å	10.4325(7)	14.2216(7)	15.2342(9)	11.064(2)
α /°	90	82.456(2)	90	109.257(7)
β /°	93.244(3)	89.502(2)	90	107.931(8)
γ /°	90	86.436(2)	90	95.355(8)
Volume/Å ³	660.33(8)	503.58(5)	1061.50(11)	718.5(3)
<i>Z</i>	4	2	4	2
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.912	1.716	1.703	1.545
μ/mm^{-1}	0.184	1.469	0.159	0.142
<i>F</i> (000)	384	272	568	344
CCDC number	1422578	1422579	1422580	1422581

Theoretical calculations

The heats of formation for **1** and its anion were determined using isodesmic reactions (**Scheme S3**). The calculations were carried out using Gaussian 03 (Revision D.01) suite of programs.² The geometric optimization and frequency analyses of the structures were calculated using B3LYP/6-31+G** level,⁹ and single energy points were calculated at the MP2/6-311++G** level.¹⁰ The heats of formation for 3,4-diaminofurazan, nitramide, nitramide anion, ammonium ion, hydroxylammonium ion, hydrazinium ion, 4-amino-1,2,4-triazolium ion, 3-amino-1,2,4-triazolium ion, guanidinium ion, aminoguanidinium ion, and diaminoguanidinium ion, were obtained by atomization approach using G2 ab initio method¹¹ (**Table S2**). The heats of formation of other compounds in Scheme S1 were determined from the NIST WebBook.¹²



Scheme S3. Isodesmic reactions for calculating heats of formation for **1** and 3,4-dinitraminofurazanate anion.

Table S2. Enthalpies of the gas-phase species M^+ (G2 method).¹¹

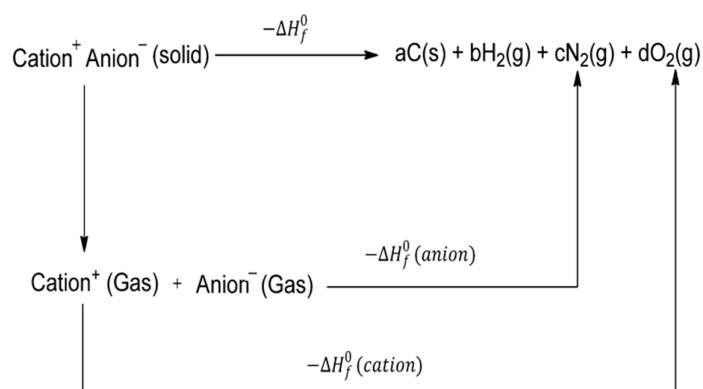
M	ΔH_f° (kJ mol ⁻¹)
3,4-diaminofurazan	196.1
nitramide	17.2
nitramide anion	-84.0
ammonium	626.4
hydroxylammonium	669.5
hydrazinium	770.0
4-amino-1,2,4-triazolium	942.9
3-amino-1,2,4-triazolium	807.2
aminoguanidine	667.4
diaminoguanidine	769.0
guanidine ion	575.9

Based on the literature, the heat of sublimation is estimated with Trouton's rule.¹³ The solid phase heat of formation of **1** was calculated with equation 1, in which T_d represents the decomposition temperature.¹³

$$\Delta H_f(s) = \Delta H_f(g) - \Delta H_{sub} = \Delta H_f(g) - 188[\text{J mol}^{-1} \text{ K}^{-1}] \times T_d \quad (1)$$

For energetic salts, the solid-phase heat of formation is calculated on the basis of a Born-Haber energy cycle (Scheme S4).¹⁴ The number is simplified by equation 2:

$$\Delta H_f^\circ(\text{salt}, 298 \text{ K}) = \Delta H_f^\circ(\text{cation}, 298\text{K}) + \Delta H_f^\circ(\text{anion}, 298\text{K}) - \Delta H_L \quad (2)$$



Scheme S4. Born–Haber Cycle for the formation of energetic salts.

in which ΔH_L can be predicted by using the formula suggested by Jenkins, et al.¹⁴ (equation 3):

$$\Delta H_L = U_{\text{pot}} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \quad (3)$$

In this equation, n_M and n_X depend on the nature of the ions Mp^+ and Xq^- , respectively. The equation for lattice potential energy U_{pot} (equation 4) has the form:¹⁴

$$U_{\text{POT}} [\text{kJ mol}^{-1}] = \gamma(\rho_m/M_m)^{1/3} + \delta \quad (4)$$

where ρ_m [g cm^{-3}] is the density of the salt, M_m is the chemical formula mass of the ionic material, and values for γ ($\text{kJ mol}^{-1} \text{cm}$) and δ (kJ mol^{-1}) are assigned literature values.¹⁴ By using the measured room temperature densities, all thermodynamic parameters of the newly prepared compounds are listed in Table S3. The heats of detonation for **1** and **3-10** were obtained by using EXPLO5 (v6.01).¹⁵ **1** possesses a very high heat of detonation value as a neutral energetic compound which indicates its highly sensitive nature according to a recently reported general trend between heats of detonation and impact sensitivities.¹⁶

Table S3. The densities, calculated lattice energy and calculated heat of formation of **1**, **3-10**, RDX and HMX.

	$\rho^{[a]}$ [g cm^{-3}]	$\Delta_f H_{\text{Lat}}^{[b]}$	$\Delta_f H^{[c]}$ [$\text{kJ mol}^{-1}/\text{kJ g}^{-1}$]	$Q^{[d]}$ [kJ g^{-1}]
1	1.899	-	287.5/1.51	6.45
3	1.716	1479.4	36.7/0.16	5.15
4	1.857	1449.7	152.6/0.60	6.48
5	1.873	1458.5	344.8/1.36	6.01
6	1.787	1259.7	889.4/2.48	4.41
7	1.700	1236.1	641.6/1.79	4.80
8	1.654	1295.0	120.1/0.39	5.11
9	1.645	1247.7	350.4/1.04	5.74
10	1.736	1233.0	568.3/1.54	5.06
RDX	1.800	-	70.3/0.32	5.73
HMX	1.905	-	74.8/0.25	5.69

[a] Density was measured by gas pycnometer at room temperature. [b] Calculated lattice energy. [c] Calculated heat of formation. [d] Calculated heat of detonation.

Electrostatic potential surfaces (ESP) analysis

Electrostatic potential surfaces (ESP) analysis for **1** was calculated using the B3LYP/6-31+G** method at the optimized structures (Figure S2). Recent studies have shown that the positive region of ESP is related to high sensitivity towards impact and friction.¹⁷ In the case of DNAF, the large positive regions are located in the oxygen atom in the ring and nitro-amino explosophore which might also theoretically confirms the high sensitivities of DNAF.

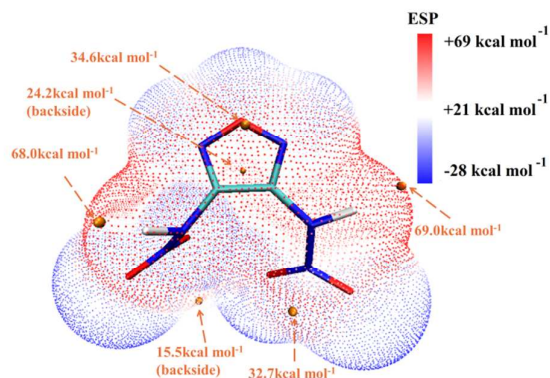


Figure S2. ESP of 3,4-di(nitramino)furan (**1**). Significant surface local maxima of ESP are marked as orange spheres.

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