

Supporting Information

1. Materials and Methods

Caution! 3-Nitramino-4-nitrofurazane, dinitraminoazoxyfurazane and their salts are energetic materials with sensitivities towards shock and friction. Therefore, proper security precautions (safety glass, face shield, earthed equipment and shoes, Kevlar gloves and ear plugs) have to be applied while synthesizing and handling the described compounds.

All chemicals and solvents were employed as received (Sigma-Aldrich, Fluka, Acros) without further purification unless otherwise stated.

1.1. NMR Spectroscopy

^1H and ^{13}C NMR spectra were recorded using a JEOL Eclipse 270 (JEOL, Akishima, Japan), JEOL EX 400 (JEOL, Akishima, Japan) or a JEOL Eclipse 400 (JEOL, Akishima, Japan) instrument. The chemical shifts quoted in ppm in the text refer to tetramethylsilane (^1H , ^{13}C).

1.2. Vibrational Spectroscopy

Infrared spectra were measured using a Perkin Elmer Spectrum One FT-IR spectrometer (Perkin Elmer, Waltham, MA, United States of America) as KBr pellets. Raman spectra were recorded on a Bruker MultiRAM Raman Sample Compartment D418 (Bruker, Billerica, MA, United States of America) equipped with a Nd-YAG-Laser (1064 nm) and a LN-Ge diode as detector.

1.3. Mass Spectrometry and Elemental Analysis

Mass spectra of the described compounds were measured at a JEOL MStation JMS 700 (JEOL, Akishima, Japan) using either DEI or FAB technique. To measure elemental analyses a Netzsch STA 429 (Netzsch, Waldkraiburg, Germany) simultaneous thermal analyzer was employed.

1.4. Differential Thermal Analysis

Differential thermal analysis (DTA) measurements to determine the decomposition temperatures of compound **2–8** were performed at a heating rate of $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ with an OZM Research DTA 552-Ex (OZM, Pardubice, Czech Republic) instrument.

1.5. Sensitivity Testing

The impact sensitivity tests were carried out according to STANAG 4489 [1] modified instruction [2] using a BAM (Bundesanstalt für Materialforschung) drophammer [3]. The friction sensitivity tests were carried out according to STANAG 4487 [4] modified instruction [5] using the BAM friction tester. The classification of the tested compounds results from the “UN Recommendations on the Transport of Dangerous Goods” [6]. Additionally all compounds were tested upon the sensitivity towards electrical discharge using the Electric Spark Tester ESD 2010 EN[7].

2. X-Ray Diffraction

2.1. Instrument and Refinement Software

Suitable single crystal of compounds **3–6**, **8** and **12** were picked from the crystallization mixtures and mounted in Kel-F oil, transferred to the N₂ stream of an Oxford Xcalibur3 diffractometer (Oxford Diffraction Ltd, Abingdon, United Kingdom) with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector. The data collection was performed using the CrysAlis CD software [8], the data reduction with the CrysAlis RED software [9]. The solution and refinement of all structures were performed using the programs SIR-92 [10], SHELXS-97 [11] and SHELXL-97 [12] implemented in the WinGX software package [13] and finally checked with the PLATON software [14]. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined. The absorptions were corrected with the SCALE3 ABSPACK multi-scan method [15].

2.2. Crystallographic Data and Refinement Parameters

Table S1. Crystallographic data and refinement parameters of compound **3–5**.

	3	4	5
Formula	C ₂ H ₂ N ₄ O ₃	C ₄ H ₁₂ N ₁₄ O ₆	C ₂ H ₄ N ₆ O ₆
FW (g·mol ⁻¹)	130.08	175.08	208.11
Crystal system	orthorhombic	orthorhombic	monoclinic
Space Group	<i>Pna</i> 2 ₁	<i>Pbca</i>	<i>Pc</i>
Color/Habit	yellow/platelet	colorless/block	colorless/plate
Size [mm]	0.04 × 0.08 × 0.22	0.05 × 0.18 × 0.39	0.04 × 0.24 × 0.33
<i>a</i> [Å]	14.9183(9)	5.0351(3)	5.6470(9)
<i>b</i> [Å]	5.3962(3)	8.9523(4)	10.8713(15)
<i>c</i> [Å]	11.6551(8)	26.1215(11)	6.0744(8)
α [°]	90.0	90.0	90.0
β [°]	90.0	90.0	103.985(15)
γ [°]	90.0	90.0	90.0
<i>V</i> [Å ³]	938.26(10)	1177.45(10)	361.86(9)
<i>Z</i>	8	8	2
ρ_{calc} [g cm ⁻³]	1.789	1.975	1.910
μ [mm ⁻¹]	0.171	0.193	0.187
F(000)	528	704	212
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173	173	173
θ min-max [°]	4.2, 26.5	4.3, 26.5	4.2, 27.0
Dataset <i>h</i> ; <i>k</i> ; <i>l</i>	−18:18; −6:6; −14:14	−6:6; −10:11; −32:32	−4:7; −13:9; −7:7
Reflect. coll.	6140	7539	1401
Independ. refl.	1019	1216	779

Table S1. *Cont.*

	3	4	5
R_{int}	0.059	0.039	0.038
Reflection obs.	822	1002	592
No. parameters	179	113	132
R_1 (obs)	0.0398	0.0400	0.0502
wR_2 (all data)	0.1020	0.0975	0.0996
S	1.08	1.12	1.05
Resd. Dens.[e Å ⁻³]	-0.22, 0.22	-0.20, 0.26	-0.26, 0.26
Device type	Oxford XCalibur3 CCD	Oxford XCalibur3 CCD	Oxford XCalibur3 CCD
Solution	SIR-92	SIR-92	SIR-92
Refinement	SHELXL-97	SHELXL-97	SHELXL-97
Absorpt. corr.	multi-scan	multi-scan	multi-scan
CCDC	1415341	1415340	1415342

Table S2. Crystallographic data and refinement parameters of compound **6**, **8** and **12**.

	6	8	12
Formula	C ₂ H ₄ N ₆ O ₅	C ₅ H ₇ N ₁₃ O ₅	C ₁₀ H ₁₄ N ₂₆ O ₇
FW [g mol ⁻¹]	192.11	329.24	610.47
Crystal system	monoclinic	monoclinic	triclinic
Space Group	$P2_1/n$	$P2_1$	$P-1$
Color / Habit	colorless, block	yellow, platelet	yellow, block
Size [mm]	0.10 × 0.14 × 0.35	0.02 × 0.30 × 0.35	0.08 × 0.19 × 0.38
a [Å]	10.3798(4)	7.4532(4)	6.6964(8)
b [Å]	5.1636(2)	6.8696(3)	7.4364(8)
c [Å]	13.8832(6)	12.3413(5)	12.9964(12)
α [°]	90	90	77.394(9)
β [°]	108.754(4)	101.495(5)	77.827(9)
γ [°]	90	90	63.649(11)
V [Å ³]	704.59(5)	619.21(5)	561.13(12)
Z	4	2	1
$\rho_{\text{calc.}}$ [g cm ⁻³]	1.811	1.766	1.807
μ [mm ⁻¹]	0.173	0.155	0.153
$F(000)$	392	336	312
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173	173	173
θ min-max [°]	4.2, 26.0	4.2, 26.5	4.2, 26.4
Dataset h ; k ; l	-12:11; -6:6; -10:17	-9:7; -8:7; -15:15	-8:8; -9:8; -16:16
Reflect. coll.	3423	5017	4006
Independ. refl.	1377	1395	2291
R_{int}	0.020	0.027	0.020
Reflection obs.	1194	1280	1803
No. parameters	134	236	227
R_1 (obs)	0.0296	0.0274	0.0518
wR_2 (all data)	0.0740	0.0692	0.1197
S	1.09	1.03	1.10
Resd. Dens.[e Å ⁻³]	-0.18, 0.22	-0.16, 0.18	-0.24, 0.32

Table S2. *Cont.*

	6	8	12
Device type	Oxford XCalibur3	Oxford XCalibur3	Oxford XCalibur3
	CCD	CCD	CCD
Solution	SIR-92	SIR-92	SIR-92
Refinement	SHELXL-97	SHELXL-97	SHELXL-97
Absorpt. corr.	multi-scan	multi-scan	multi-scan
CCDC	1415343	1057626	1057627

3. Explosive Performance

3.1. Heat of Formation Calculations

Heats of formation of compounds **3–12** were calculated using the atomization method (Equation S1) using room temperature CBS-4M enthalpies summarized in Table S3 [16–20].

$$\Delta_f H^\circ_{(g, M, 298)} = H_{(Molecule, 298)} - \sum H^\circ_{(Atoms, 298)} + \sum \Delta_f H^\circ_{(Atoms, 298)} \quad (S1)$$

Table S3. CBS-4M electronic enthalpies for atoms C, H, N and O and their literature values for atomic $\Delta_f H^\circ_{298}/\text{kJ}\cdot\text{mol}^{-1}$.

Atoms	$-H^{298}/\text{a.u.}$	NIST [21]
H	0.500991	218.2
C	37.786156	717.2
N	54.522462	473.1
O	74.991202	249.5

Quantum chemical calculations were carried out using the Gaussian G09 program package [22–24]. The enthalpies (H) and free energies (G) were calculated using the complete basis set (CBS) method of Petersson and coworkers in order to obtain very accurate energies. The CBS models use the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated CBS limit. CBS-4 begins with an HF/3-21G(d) geometry optimization; the zero point energy is computed at the same level. It then uses a large basis set SCF calculation as a base energy, and an MP2/6-31 + G calculation with a CBS extrapolation to correct the energy through second order. An MP4(SDQ)/6-31 + (d,p) calculation is used to approximate higher order contributions. In this study, we applied the modified CBS.

For neutral compounds **3** and **4** the sublimation enthalpy, which is needed to convert the gas phase enthalpy of formation to the solid state one, was calculated by the *Trouton* rule. In the case of the ionic compounds, the lattice energy (U_L) and lattice enthalpy (ΔH_L) were calculated from the corresponding X-ray molecular volumes according to the equations provided by Jenkins and Glasser [25,26]. With the calculated lattice enthalpy the gas-phase enthalpy of formation was converted into the solid state (standard conditions) enthalpy of formation. These molar standard enthalpies of formation (ΔH_m) were used to calculate the molar solid state energies of formation (ΔU_m) according to Equation S2.

$$\Delta U_m = \Delta H_m - \Delta n RT \quad (S2)$$

(Δn being the change of moles of gaseous components)

Table S4. Calculation results.

M	$-H^{298}$ ^[a] /a.u.	$\Delta_f H^\circ(\text{g}, \text{M})$ /kJ·mol ⁻¹ ^[b]	V_M/nm^3 ^[c]	$\Delta U_L, \Delta H_L$ (4); ^[d] ΔH_{sub} ^[e] (3) /kJ·mol ⁻¹	$\Delta_f H^\circ(\text{s})$ ^[f] /kJ·mol ⁻¹	Δn ^[g]	$\Delta_f U(\text{s})$ ^[f] /kJ·kg ⁻¹
ANF (3)	521.26512	235.0	—	78.2	156.7	4.5	1290.7
NNF(4)	725.520689	327.2	—	63.6	263.6	5.5	1583.7
NNF ⁻	725.027281	89.3	—	—	—	—	—
Hx ⁺	131.863249	686.4	—	—	—	—	—
5	—	775.7	0.184	516.0, 521.0	254.7	8.0	1319.3
NH ₄ ⁺	56.796608	635.3	—	—	—	—	—
6	—	724.6	0.179	519.7, 524.7	199.9	7.5	1137.4
TABTr ²⁺	704.327388	2032.9	—	—	—	—	—
7	—	2211.5	0.507	1369.9, 1377.4	834.1	20.0	1617.6
TATOT ⁺	555.474133	1080.0	—	—	—	—	—
8	—	1169.3	0.315	448.4, 453.4	715.9	12.5	2268.9
DNAAF ²⁻	1224.647003	570.3	—	—	—	—	—
11	—	2603.2	0.448	1882.9, 1887.8	715.4	18.5	1527.8
12	—	2730.4	0.572	1016.3	1023.7	23.5	2891.6

^[a] CBS-4M electronic enthalpy; ^[b] gas phase enthalpy of formation; ^[c] molecular volumes taken from X-ray structures and corrected to room temperature; ^[d] lattice energy and enthalpy (calculated using Jenkins and Glasser equations); ^[e] enthalpy of sublimation (calculated by Trouton rule); ^[f] standard solid state enthalpy of formation; ^[g] solid state energy of formation.

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