

**Boosting Energetic Performance by Trimerizing Furoxan**

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Boosting Energetic Performance by Trimerizing Furoxan

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The introduction of N-oxides is a useful approach in improving oxygen balance, density and detonation properties of energetic compounds. Here we present the design and syntheses of a new series of trifuroxan compounds **4** – **6**. The structures of **4** and **5** were determined by single crystal X-ray diffraction. Compound **5** is the first representative of furoxan fused 1,2-diazocine. The zero oxygen balance along with moderate sensitivities (IS = 19 J, FS = 80 N) and detonation properties (D = 9417 m s⁻¹, P = 39.2 GPa) of compound **5** makes it a promising replacement for RDX and HMX. The high density, positive oxygen balance and detonation properties of compound **6** which approach those of CL-20 may help it to find potential application as a high energy density oxidizer.

Considerable interest has been focused on the design and synthesis of new energetic compounds over the last few decades. A new approach in the development of energetic materials is the combination of highly endothermic heterocycles containing both nitrogen and oxygen.¹ Furazan and furoxan (furazan-N-oxide), with high positive heats of formation of 196.8 and 198.5 kJ mol⁻¹ and with nitrogen and oxygen contents of 62.8% and 69.7%, respectively, are important energetic units which have been widely investigated in the synthesis of high energy density materials (HEDMs).²

Energetic heterocyclic compounds comprised of the furazan or furoxan moieties feature high heats of formation, good thermal stabilities, high densities and a large amount of active oxygen.³ Use of simple nitrofurazans or nitrofuroxans is not practical as an explosive because of poor thermal stability and the ease of nucleophilic displacement of the nitro groups.⁴ However, when bifurazan or trifurazan rings are substituted with nitro groups, such as 4,4' – dinitro – 3,3' – bifurazan⁵ or BNFF (3,4-bis(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole-2-

oxide),⁴ far greater stability was observed which makes them more favorable for practical applications. BNFF has a low melting point of 110 °C and good thermal stability, high density (1.875 g/cm³), high heat of formation of 732.2 kJ mol⁻¹ and moderate sensitivity, making it a promising melt castable explosive and propellant.⁶ The analogues of BNFF have also been studied comprehensively by LLNL and other research groups.^{6–7} The densities were improved by oxidizing the amino groups in trifurazan into azo or nitro groups (Figure 1).

The zwitterionic nature of the N-oxide bond tends to give rise to large dipole moments, which often lead to increases in crystal densities. N-oxides also increase the oxygen balance of a molecule and provide a stabilizing effect for some heterocyclic systems. The introduction of the N-oxide functional group can also enhance reduction in sensitivity towards external stimuli.⁸ The replacement of furazan rings by furoxan groups in a molecule can possibly increase its density, oxygen balance and heat of formation, thereby improving the detonation performance. In our continuing efforts of investigating furoxan-based energetic compounds,^{2k,9} we designed and synthesized a new series of energetic trifuroxan compounds.

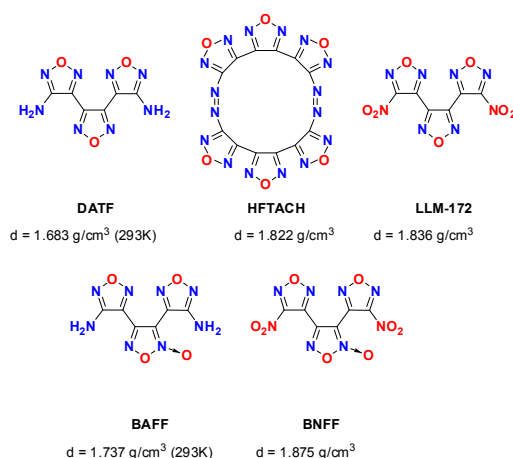


Figure 1. Densities of energetic trifurazans compared with BAFF and BNFF.

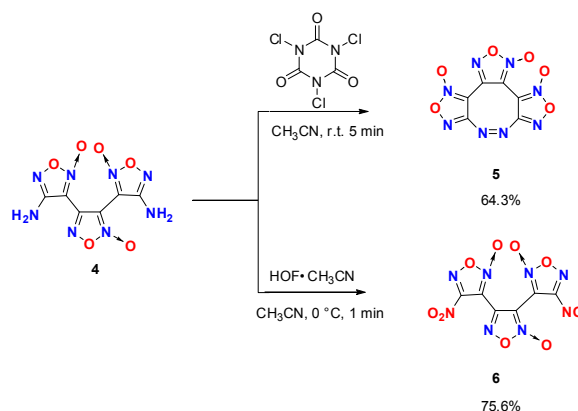
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3-Hydroximoyl-4-aminofuroxan was prepared based on the literature.¹⁰ The first attempt was to react 3-hydroximoyl-4-aminofuroxan with NaNO_2 in concentrated HCl in order to prepare 3-chlorohydroximoyl-4-aminofuroxan which could undergo dimerization to give a trifuroxan structure by treating with dilute aqueous K_2CO_3 solution.⁴ However, the intermediate, 3-chlorohydroximoyl-4-aminofuroxan, was not obtained under these reaction conditions, likely due to the amino group in the 4-position reacting under diazotization reaction conditions. Therefore, **1** was prepared by protecting the 4-amino group of 3-hydroximoyl-4-aminofuroxan.¹⁰ Hydroximoyl chloride, **2**, was synthesized by diazotization of **1** by reacting with NaNO_2 in concentrated HCl and subsequently precipitating the white solid from the reaction mixture. Treating an ether suspension of **2** with 0.5 eq of an aqueous 3% K_2CO_3 solution at 0°C with stirring overnight gave the trifuroxan, **3**, in moderate yield. The amino group in **3** can be easily deprotected by reacting **3** with 10 eq of 11% HCl at 40°C for 8 h to give the diamine compound **4** (Scheme 1).

Compound **4** was oxidized effectively in reaction with trichloroisocyanuric (TCICA) acid, forming an intramolecular azo bridge to give the furoxan fused 1,2-diazocine compound (**5**), which is different from the reaction of trifurazan diamine with TCICA which gives a macrocyclic product.¹¹ The structure of **5** was determined by single crystal X-ray diffraction. While in the process of preparing dinitro compound **6**, the reactions of **4** with numerous oxidizing materials, such as a mixture of 50% H_2O_2 and H_2SO_4 or a mixture of 50% H_2O_2 , Na_2WO_4 and H_2SO_4 , were studied under a variety of conditions and it was found that only $\text{HOF}\cdot\text{CH}_3\text{CN}$ was successful in oxidizing the diamine **4** to **6**.

All the compounds were fully characterized by infrared (IR), ^1H and ^{13}C NMR spectroscopy, and elemental analysis. The ^{15}N NMR spectra of compound **4** – **6** are shown in Figure 2. The assignments of the peaks are based on GIAO NMR calculations with Gaussian 03 program.¹² Due to the asymmetry of **4** – **6**, each compound gives eight nitrogen signals. Two amino groups (δ -292.45 ppm, δ -329.85 ppm) in **4** were observed at the highest field as expected. Two signals (δ +140.56 ppm, δ +139.34 ppm) of the azo group in **5** were observed at the lowest field. All of the other nitrogen signals lie in the range from +1.52 to -25.40 ppm. The signals for compound **6** locate in a narrow range between +3.38 to -36.24 ppm.



Scheme 2. Oxidation of compound **4**.

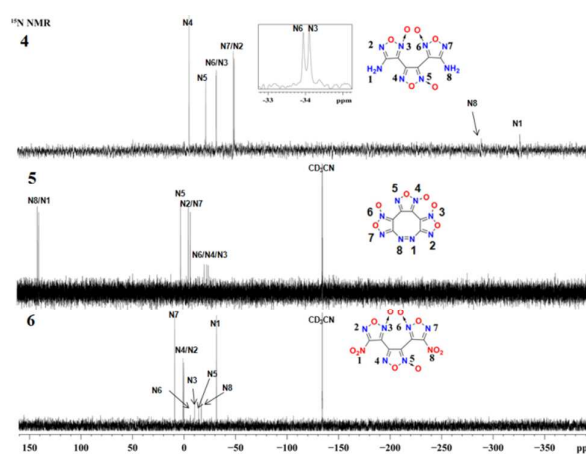
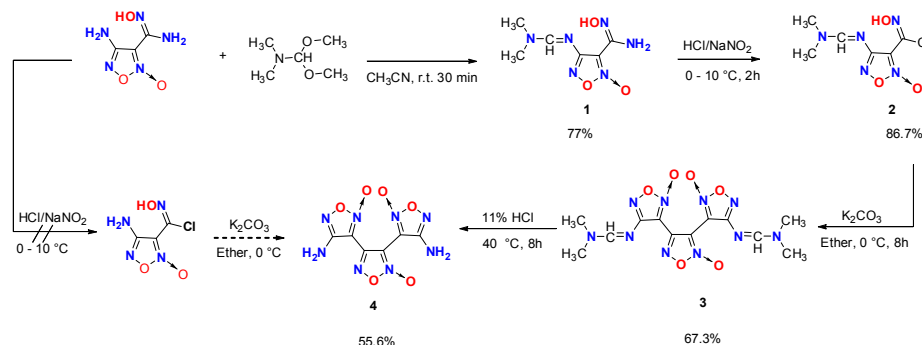


Figure 2. ^{15}N spectra of **4** – **6**.

The structures of **4** and **5** were determined by single crystal X-ray diffraction (Figure 3). Crystals of **4** and **5** suitable for X-ray diffraction were obtained by slow evaporation of acetonitrile (**4**) or dichloromethane (**5**) solutions at room temperature. Compound **4** crystallizes in the monoclinic space group $P2_1/c$ with four molecular units in the unit cell with calculated density of 1.833 g cm^{-3} at 150 K. One intramolecular hydrogen bond $[\text{N}(1)\text{--H}(1\text{B})\cdots\text{O}(10)]$ and three intermolecular hydrogen bonds $[\text{N}(20)\text{--H}(20\text{A})\cdots\text{O}(6)^a$, $\text{N}(20)\text{--H}(20\text{B})\cdots\text{N}(3)^b$ and $\text{N}(1)\text{--H}(1\text{A})\cdots\text{N}(18)^c$, symmetry code a: $-x+1, y-1/2, -z+3/2$; b:



Scheme 1. Synthetic routes for compound **4**.

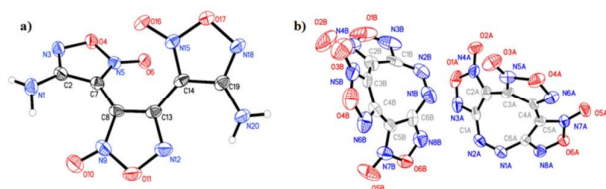


Figure 3. The molecular structure of **4** (a) and **5** (b). Displacement ellipsoids are shown at the 50% probability level.

x-1, -y+3/2, z-1/2; c: x+1, -y+3/2, z+1/2] were observed in the crystal structure of **4**. Compound **5** crystallizes in the orthorhombic space group Pca_21 with eight molecular units in the unit cell and a calculated density of 1.929 g cm^{-3} at 173 K. The N=N double bonds in **5** with lengths of N1A-N2A = $1.225(14) \text{ \AA}$ and N1B - N2B = $1.235(18) \text{ \AA}$ are shorter than the azo bond in similar compounds whose lengths are $1.252(5) \text{ \AA}$,¹³ $1.2606(18) \text{ \AA}$ ¹⁴ or $1.264(6) \text{ \AA}$.¹⁵ As a result of the shorter N=N bond in **5**, it packs more efficiently resulting in a higher density of 1.895 g cm^{-3} .

The physical properties of **4** – **6** compared with the properties of RDX, HMX and CL-20 are summarized in Table 1. These compounds exhibit good thermal stability where dinitro compound **6** is the least thermally stable compound melting at 145.0°C and then decomposing. The experimentally determined densities of **4** – **6** ($1.787 - 1.914 \text{ g cm}^{-3}$) were obtained using a gas pycnometer at 25°C . The presence of a higher number of N-oxide moieties in **4** – **6** increases their densities dramatically by $\sim 0.1 \text{ g cm}^{-3}$ as expected comparing with the corresponding trifurazan analogues (Figure 4).

The heats of formation for **4** – **6** were calculated by Gaussian 03 (Revision E.01)¹² suite of programs using the isodesmic reactions shown in the Supporting Information. As given in Table 1, the heats of formation of **4** – **6** lie in the range from 492.8 to $894.9 \text{ kJ mol}^{-1}$. Together with the measured densities, their detonation properties were evaluated by using EXPLO5 6.01 program.¹⁶ The detonation performances of **5** (D_v : 9417 m s^{-1} , P : 39.6 GPa) and **6** (D_v : 9503 m s^{-1} , P : 40.8 GPa) are superior to RDX and HMX, and comparable to CL-20. Compounds **5** and **6** have oxygen balances of 0 and +18.6%.

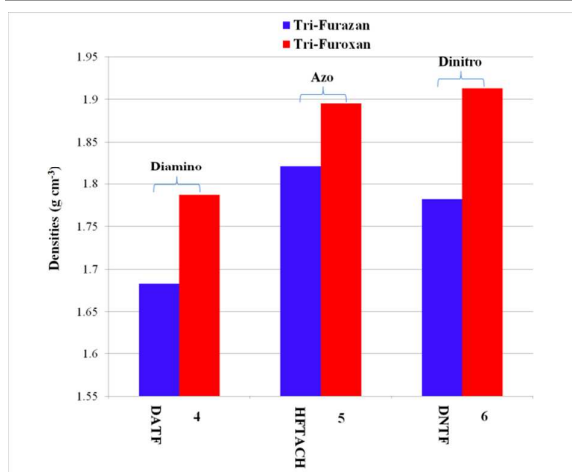


Figure 4. Comparison of the densities of **4** – **6** with corresponding trifurazans.

Table 1. Physiochemical properties of compound **4** – **6**

Entry	T_d^a [$^\circ \text{C}$]	ρ^b [g cm^{-3}]	ΔH_f^c [kJ mol^{-1}]	D_v^d [m s^{-1}]	P^e [GPa]	IS^f (J)	FS^g (N)	Ω_{CO}^h [%]
4	183.6	1.787	492.8	8480	31.0	13	240	-11.3
5	161.1	1.895	894.9	9417	39.6	19	80	0
6	145.0 ⁱ /146.5	1.914	579.2	9503	40.8	3	40	+18.6
RDX	204	1.800	70.3	8795	34.9	7.4	120	0
HMX	280	1.905	75.0	9144	39.2	7.4	120	0
CL-20	195	2.038	403.2	9706	45.2	4	48	+11.0

^a Decomposition temperature (onset temperature at heating rate of $5^\circ \text{C min}^{-1}$).

^b Density, measured with gas pycnometer (25°C). ^c Calculated heat of formation.

^d Calculated detonation velocity (EXPLO5 V6.01). ^e Calculated detonation pressure (EXPLO5 V6.01).

^f Impact sensitivity. ^g Friction sensitivity. ^h Oxygen balance for CaHbOcNd, $1600 (c-a-b/2)/MW$; MW = molecular weight; ⁱ Melting point.

Additionally, **5** exhibits lower sensitivities towards impact (19 J) and friction (80 N) thus comparing more favorably to CL-20, and showing great potential as a high energy density material.

Conclusions

In conclusion, a series of new energetic trifuroxans **4** – **6** were designed and synthesized. The strategy of selective protecting and deprotecting C-NH₂ group was developed. The structures of the new compounds were fully characterized; the molecular structures of **4** and **5** were determined by single crystal X-ray diffraction. Compound **5** possesses a high density of 1.895 g cm^{-3} and is thermally stable up to 161.1°C , representing the first example possessing furoxan fused 1,2-diazocine structure. Along with a zero oxygen balance and superior detonation performance (D_v : 9417 m s^{-1} , P : 39.6 GPa) relative to RDX and HMX as well as reasonable sensitivities ($IS = 19 \text{ J}$, $FS = 80 \text{ N}$), it exhibits a promising potential as an high energy density material. Compound **6** has a +18.6% oxygen balance with detonation properties (D_v : 9503 m s^{-1} , P : 40.8 GPa) and similar sensitivity ($IS = 3 \text{ J}$, $FS = 40 \text{ N}$) to CL-20, which suggests potential application as an oxidizer or solid rocket propellant additive.

Experimental Section

Caution: All the nitrogen-rich compounds used are energetic materials and may explode under certain conditions. Appropriate safety precautions should be taken when preparing and handling.

General Methods

Reagents were purchased from Aldrich, AK Scientific and Acros Organics and were used as received. ^1H , and ^{13}C spectra were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300.13, and 75.48 MHz, respectively, and a 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer operating at 50.69 MHz for ^{15}N spectra. Chemical shifts in ^{13}C and ^{15}N NMR spectra are reported relative to Me_4Si and MeNO_2 , respectively. The melting and decomposition points were obtained on a differential scanning calorimeter (TA Instruments Co., model Q2000) at a scan rate of $5^\circ \text{C min}^{-1}$. IR

spectra were recorded using KBr pellets for solids on a Thermo Nicolet AVATAR 370 FTIR. Densities were determined at 25 °C by employing a Micromeritics AccuPyc 1340 II gas pycnometer. Elemental analyses were carried out using an Exeter CE-440 or Elemental vario MICRO cube elemental analyzer. Impact and friction sensitivity measurements were made using a standard BAM Fallhammer and a BAM friction tester, respectively.

Gaussian calculations

The geometric optimization and frequency analyses of the structures are calculated via B3LYP functional with the 6-31+G** basis set, single-point energies were calculated at the MP2/6-311++G** level. The small molecular energies are calculated at the G2 level. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. The heat of sublimation was calculated based on Trouton's rule by using the equation $\Delta H_{\text{sub}} = 0.188 \times T$.

3-Aminohydroximoyl-4-dimethylaminomethyleneamino-furoxan (1)¹⁰: Prepared according to the literature. Yield 77%.

3-Chlorohydroximoyl-4-dimethylaminomethyleneamino-furoxan (2): To a suspension of **1** (1.07 g, 5 mmol) in water (6 mL) was added concentrated HCl (6 mL). While maintaining the reaction temperature between -5 to 0 °C, a solution of sodium nitrite (0.52 g, 7.5 mmol) in water (5 mL) was added dropwise. The solution was stirred for one hour, allowed to come to ambient temperature over another hour. The white precipitate formed was collected by filtration, and air dried to yield 1.01 g (86.7%) of **2**. T_{dec} : 144.6 °C; IR (cm^{-1}) $\tilde{\nu}$ = 3262, 2954, 2920, 2820, 1629, 1605, 1581, 1526, 1478, 1432, 1406, 1362, 1292, 1254, 1113, 1077, 1018, 981, 918, 837, 751, 719, 603, 588; ^1H NMR ($\text{DMSO}-d_6$): 13.40 (1H, s, N-OH), 8.27 (1H, s, N=CH), 3.44 (3H, s, -CH₃), 3.11 (3H, s, -CH₃); $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$): δ 160.23, 156.52, 120.75, 108.61, 40.21, 34.18. EA ($\text{C}_6\text{H}_8\text{Cl}_1\text{N}_5\text{O}_3$, 223.61): Calcd, C, 30.85; H, 3.45; N, 29.98; Found, C: 30.82; H: 3.43; N: 29.98.

3,4-Bis(4'-dimethylaminomethyleneaminofuroxano-3')furoxan (3)

furoxan (3): Compound **2** (0.94 g, 4 mmol) was suspended in diethyl ether (20 mL) and 3% potassium carbonate solution (2 mmol) was added at 0 – 5 °C. The reaction mixture was stirred for 2 hours at 0 °C and then at ambient temperature overnight. The diethyl ether was removed by blowing air, the white solid was filtered, washed with 10% aqueous ammonia (5 mL) and air dried to give **3**, yield 0.53 g (67.3%). T_{dec} : 170.2 °C; IR (cm^{-1}) $\tilde{\nu}$ = 3153, 2929, 1630, 1518, 1480, 1433, 1390, 1362, 1336, 1254, 1209, 1110, 1064, 987, 956, 931, 894, 835, 769, 754, 728, 680, 582. ^1H NMR (CD_3CN): 8.07 (2H, s, =CH); 3.05 (3H, s, -CH₃); 3.04 (3H, s, -CH₃); 2.80 (3H, d, -CH₃); 2.77 (3H, d, -CH₃); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN): δ 161.66, 161.57, 157.01, 156.97, 144.15, 105.64, 104.11, 103.58, 41.41, 41.37, 34.74, 34.67. EA ($\text{C}_{12}\text{H}_{14}\text{N}_{10}\text{O}_6$, 394.30): Calcd, C, 36.55; H, 3.58; N, 35.52; Found, C: 36.70; H: 3.60; N: 35.16.

3,4-Bis(4'-aminofuroxano-3')furoxan (4): Compound **3** (0.20 g, 0.5 mmol) was added to a mixture of concentrated HCl (1 mL) and water (3 mL) and the suspension was stirred at 40 °C for 8h. The solid was collected by filtration and washed with ice water (2 mL), recrystallized from acetonitrile to give **4** as a white solid, yield 0.08 g (55.6%). T_{dec} : 183.6 °C; IR (cm^{-1}) $\tilde{\nu}$ =

3444, 3411, 3333, 1624, 1587, 1560, 1523, 1464, 1432, 1401, 1264, 1213, 1185, 1111, 1056, 963, 935, 827, 765, 731, 697, 649. ^1H NMR (CD_3CN): 5.45 (2H, s, NH₂); 5.15 (2H, s, NH₂); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN): δ 156.63, 156.03, 144.66, 104.28, 103.58, 100.38 ppm. ^{15}N NMR (ppm): -7.58; -23.83; -33.94; -34.10; -50.68; -51.47; -292.45; -329.85 ppm. EA ($\text{C}_6\text{H}_4\text{N}_8\text{O}_6$, 284.15): Calcd, C, 25.36; H, 1.42; N, 39.44; Found, C: 25.14; H: 1.23; N: 37.37.

5: To a solution of compound **4** (0.28 g, 1 mmol) in acetonitrile (10 mL) was added dropwise trichloroisocyanuric acid (0.46 g, 2 mmol) in acetonitrile (8 mL) at room temperature. After the addition was completed, the reaction mixture was stirred for another 30 min at room temperature. The solid was filtered and washed with acetonitrile (3 mL). The filtrate was concentrated and purified by column chromatography (EtOAc/Hexane = 5/95). Compound **5** was obtained as a yellow solid, yield 0.18 g (64.3%). $M.P.$ 144.5 °C, T_{dec} : 167.4 °C; IR (cm^{-1}) $\tilde{\nu}$ = 1663, 1618, 1570, 1550, 1421, 1401, 1205, 1091, 1045, 985, 963, 830, 753, 715, 687, 460. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3Cl_3): δ 157.71, 157.24, 138.97, 98.77, 94.42, 92.47 ppm. ^{15}N NMR (ppm): 140.56, 139.34, 1.52, -6.08, -8.00, -21.43, -23.80, -25.40 ppm. EA ($\text{C}_6\text{H}_8\text{N}_8\text{O}_6$, 280.12): Calcd, C, 25.73; N, 40.00; Found, C: 26.00; H: 0.35; N: 37.99.

3,4-Bis(4'-nitrofuroxano-3')furoxan (6): Compound **4** (0.14 g, 0.5 mmol) in acetonitrile (5 mL) was stirred at 0 °C, then freshly prepared $\text{HO} \cdot \text{CH}_3\text{CN}$ acetonitrile solution (11 mL, 0.348 N) was added to the reaction mixture. After stirring for 1 min, the solvent was removed by air, and the residue was extracted by ethyl acetate (3 × 5 mL), and **6** was isolated by column chromatography (EtOAc/Hexane = 5/95). Compound **6** was obtained as a white solid, yield 0.13 g (75.6%). $M.P.$ 145.0 °C, T_{dec} : 146.5 °C; IR (cm^{-1}) $\tilde{\nu}$ = 1661, 1636, 1618, 1580, 1567, 1546, 1489, 1454, 1414, 1375, 1335, 1303, 1244, 1203, 1103, 1082, 1052, 984, 962, 951, 834, 797, 770, 753, 741, 675, 638, 538, 502, 477, 457. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN): δ 158.02, 148.99, 141.88, 103.05, 101.66, 100.01 ppm. ^{15}N NMR (ppm): 3.38, -4.43, -5.25, -11.58, -15.58, -19.42, -21.87, -36.24 ppm. EA ($\text{C}_6\text{H}_8\text{N}_8\text{O}_{10}$, 344.11): Calcd, C, 20.94; N, 32.56; Found, C: 21.44; H: 0.46; N: 32.70.

Conflicts of interest

There are no conflicts to declare.

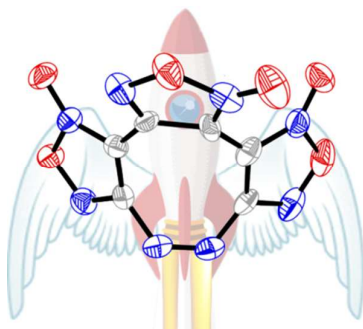
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TOC



A new series of trifuroxans were designed and synthesized. The large numbers of N-oxide bonds in the molecules contribute to boost their energetic performances.