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ARTICLE

Finding Furoxan Rings

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Abstract: A furoxan ring is derived from a dinitromethyl group. A plausible mechanism is proposed based on ^{1}H, ^{13}C and ^{15}N NMR spectral analysis where a dinitromethyl group releases one molecule of nitric acid to form an unstable nitrile oxide and its dipole isomer which cyclize to a furoxan ring [3,4-bis(4-nitro-1,2,5-oxadizaol-3-yl)-1,2,5-oxadiazole-*N*-oxide (**5**)]. This new method of constructing a furoxan (1,2,5-oxadiazole 2-oxide) ring offers a potentially efficient way to obtain excellent energetic materials. In order to stabilize the dinitromethyl-containing precursor [3-(dinitromethyl)-4-nitro-1,2,5-oxadiazole (**4**)], a series of new energetic salts was synthesized and fully characterized. These materials exhibit high densities, excellent detonation properties and acceptable sensitivities. For example, the hydrazinium salt **9** has a high density of 1.92 g cm^{-3}, a detonation velocity of 9437 m s^{-1} and a detonation pressure of 41.3 GPa, which approach those properties of CL-20 (ρ, 2.03 g cm^{-3}; $v_{D,}$ 9406 m s^{-1}; P, 44.6 GPa) and which are superior to those of HMX (ρ, 1.90 g cm^{-3}; $v_{D,}$ 9320 m s^{-1}; P, 39.2 GPa).

Introduction

Furoxan is a heterocycle of the isoxazole family and an amine oxide derivative of furazan which has been shown to exert a variety of NO-related bioactivities, including mutagenicity, immuno suppression, central muscle relaxant properties, anticonvulsive effects, and monoamino oxidase inhibition among others.[1]Since the discovery of the furoxan ring in 1896, studies of its properties have been ongoing. The furoxan ring can be synthesized using many different methodologies, for example, cyclization of nitrile oxides,[2] oxidation of *o*-nitro and amino groups,[3] denitrification of *o*-nitro and azide groups,[4] condensation of chloroxime,[5] dehydrogenation of two *o*-oxime groups,[6] oxidation of carboxylic acid,[7] dehydration of *o*-nitro and oxime groups,[8] and oxidation of the C=C moiety when bonded to the benzene ring[7a,b,9] (Fig. 1). Furoxans have attracted much interest in energetic materials chemistry since they have high nitrogen and oxygen content and often have high density.[10] In recent years, many research efforts have been focused on the properties and applications of compounds based on a furoxan ring.[11] No new routes to obtain the furoxan ring have been reported recently.

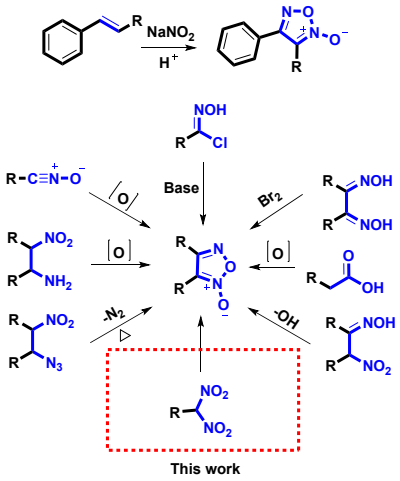

Fig. 1 Methods of constructing the furoxan ring.

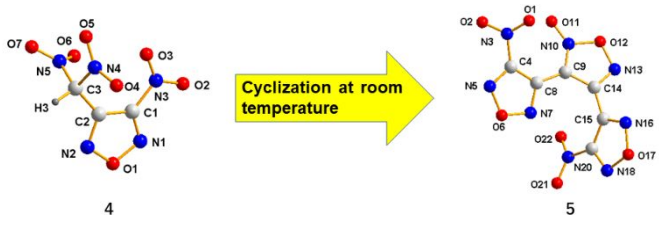

Fig. 2 Formation of a furoxan ring from a dinitromethyl-containing compound.

In our continuing efforts to develop new high energy density materials (HEDMs) which contain the furoxan ring, it was found that dinitromethyl groups attached to nitro furazan cyclized to a furoxan ring at room temperature (Fig. 2). Although compound **4** is stable when maintained at -10 °C, it cyclizes slowly to the furoxan product **5** at 25 °C. This was monitored by thin-layer chromatography [ethyl:hexane (1:2)]. The structures for **4** and **5** were confirmed by X-ray single crystal diffraction.

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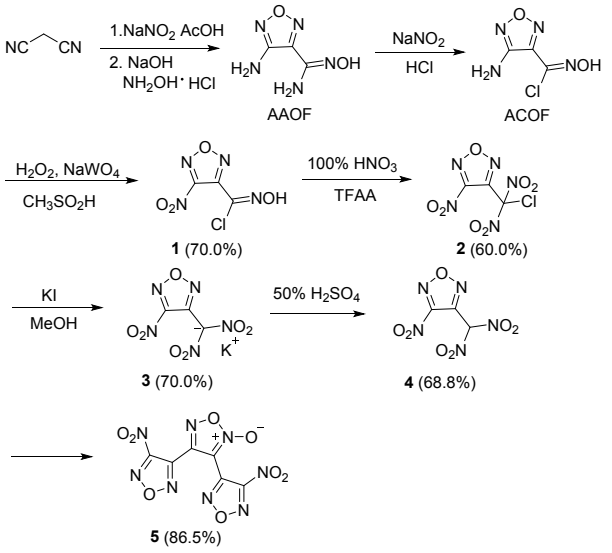
Electronic Supplementary Information (ESI) available: crystal refinements, calculation detail, X-ray crystallographic files in CIF format for **3**, **4**, **5**, and **8** [CCDC number: 1968919, 1968921, 1968922, and 1968920]. See DOI: 10.1039/x0xx00000x

Compound **5** which was reported earlier attracted the attention of the energetic materials community because it has a crystal density of 1.93 g/cm^3 with a heat of formation of 657 kJ mol^{-1}, a decomposition temperature of 292 °C, and an excellent detonation velocity of 9250 m s^{-1}.[5b,12] The dinitromethyl group is an important functional group in the design of energetic compounds and can be synthesized by many methods.[13]As a result the new method for synthesis of the furoxan ring provides a potentially efficient way to synthesize energetic compounds with that moiety. To stabilize compound **4**, a series of its energetic salt derivatives were synthesized and they were shown to exhibit good properties.

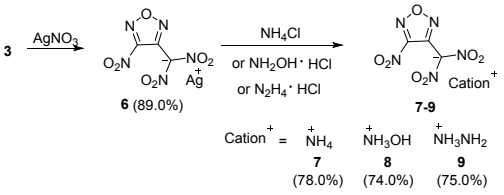
Results and discussion

Synthesis

As shown in Scheme 1, AAOF and ACOF were synthesized according to previously reported methods.[12b] A procedure for the preparation of **1** by oxidation of ACOF using70% aqueous H_2O_2 and a tungsten-based catalyst, $(Bmim)_4W_{10}O_{23}$, was found.[5b] In this work, **1** was obtained by using aq. 50% H_2O_2 in the presence of sodium tungstate and methane sulfonic acid with ACOF. Initially the reaction mixture was stirred at 25 °C, and then heated at 50 ºC for 2 h followed by an extractive work-up to obtain **1** as a pale yellow liquid. Compound **1** was nitrated with 100% nitric acid in trifluoroacetic anhydride (TFAA) at 0 ºC to give **2** as a pale yellow solid. When **2** was treated with potassium iodide in methanol, the potassium salt **3** did not precipitate but after the methanol was removed, the residue was washed with chloroform and recrystallized from acetone to yield **3**. Compound **4** was obtained by acidification of **3** with 50% sulfuric acid. Recrystallization of **4** from dichloromethane at room temperature gave the unexpected crystalline compound **5**. Solid **4** was characterized by ^{1}H and ^{13}C NMR. After 24 hours at 25 °C, **4** had been converted to a mixture of **4** and **5**. Compound **4** was stable when stored at -10 °C for extended periods.



Scheme 1 Synthesis of **1**-**5**.



Scheme 2 Synthesis of energetic salts **6**-**9**.

A series of energetic salts of **4** was designed and synthesized (Scheme 2). The silver salt **6** was easily obtained by reacting **3** with silver nitrate in water. Salts **7**-**9** were obtained alternatively by a metathesis reaction of **6** with ammonium chloride, hydroxylamine hydrochloride or hydrazine hydrochloride, respectively.

Mechanism study

In an attempt to understand the cyclization process which **4** undergoes to form **5**, ^{1}H, ^{13}C and ^{15}N NMR spectra were monitored over a 24 hour period using $CDCl_3$ as the locking solvent (Fig. 3-5). Initially only signals of **4** were observed. After 24 hours, a proton signal at 9.7 ppm (Fig. 4) and a broad nitrogen peak at -49.7 ppm (Fig. 6 – 24 hr) were observed which can be assigned to nitric acid. From the ^{13}C (Fig. 5) and ^{15}N NMR spectra, it was found that a portion of **4** cyclized to **5** after 24 hours.

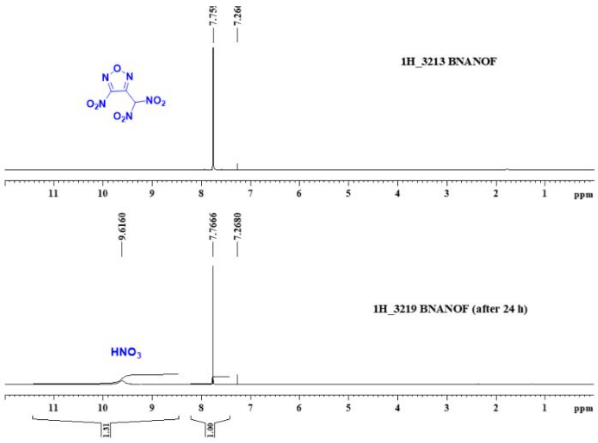


Fig. 3 ^{1}H NMR spectra of **4** in $CDCl_3$ at t = 0 and t = 24 h.

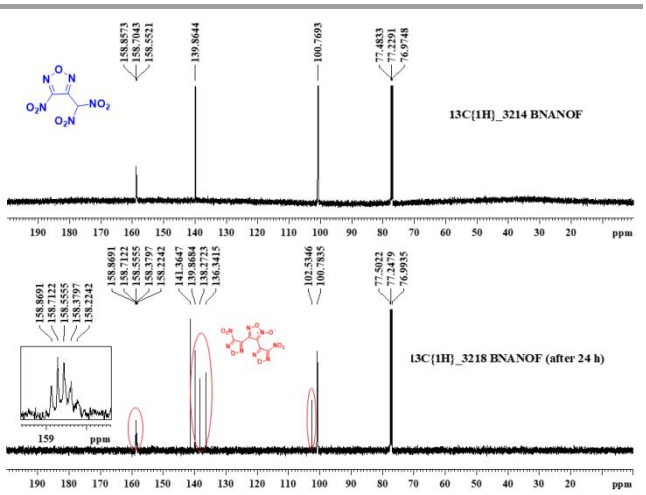


Fig. 4 ^{13}C NMR spectra of **4** in $CDCl_3$ t = 0 and t = 24h.

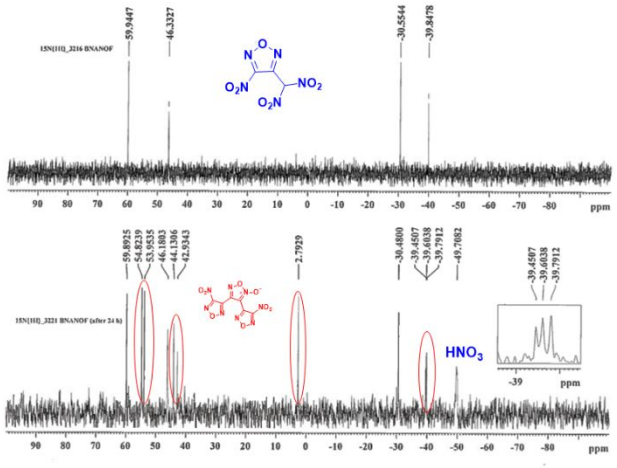
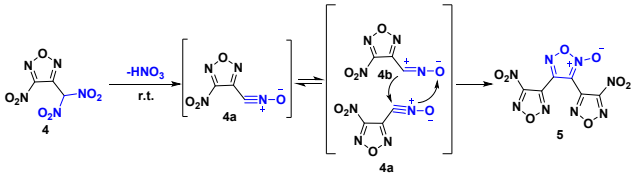


Fig. 5 ^{15}N NMR spectra of **4** in $CDCl_3$ t = 0 and t = 24h.



Scheme 3 A plausible mechanism for formation of **5**.

A plausible mechanism for the formation of **5** is given in Scheme 3. A molecule of nitric acid is readily released by **4** at ambient temperature which leads to the extremely unstable isomers of alkyne and alkene-based nitrile oxide derivatives **4a** and **4b**. Later the two isomers undergo rapid cyclization to form stable furoxan **5** at 25 °C.

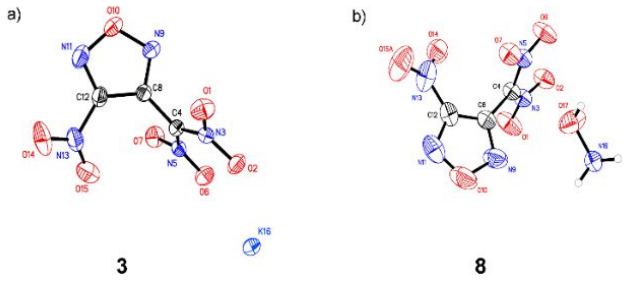


Fig. 6 Single crystal X-ray structures of (a) **3** and (b) **8**.

Structure

Compounds **3**-**5** and **7**-**9** were fully characterized by infrared (IR), ^1H and ^{13}C NMR spectroscopy, and elemental analysis. Crystals of **3, 4, 5**, and **8**, suitable for single-crystal X-ray diffraction structuring, were obtained at room temperature (except **4** at -15 °C) by slow evaporation of an acetone (**3**), dichloromethane (**4**), chloroform (**5**), or acetonitrile (**8**) solution, respectively. The crystal structures of **4** and **5**, and **3** and **8** are shown in Fig. 2 and 6, respectively.

Physicochemical and energetic properties

The physicochemical and energetic properties for **3**–**5** and **7**–**9** are summarized in Table 1. Thermal stabilities were determined using differential scanning calorimetry (DSC) at a heating rate of 5 °C min^{-1}. Compound **4** decomposed at 58 °C which increased to 231 ºC after cyclizing to **5**. The energetic salts **3**, **7**, **8**, and **9** decomposed at 196, 131, 130, and 161 ºC, respectively, without melting. The densities of compounds **3**–**5** and **7**–**9** were measured with a gas pycnometer at room temperature. As

Table 1. Properties of energetic compounds (**3**–**5** and **7**–**9**).

Comp.	T_d[a] (°C)	d[b] (g cm^{-3})	ΔH_f[c] (kJ g^{-1})	v_D[d] (m s^{-1})	P[e] (GPa)	IS[f] (J)	FS[g] (N)	OB[h] (%)	I_{sp}[i] (s)
3	196	2.04	-0.23	8081	29.5	2	120	24.9	222.5
4	58	1.88	0.62	8900	35.7	8	240	25.5	259.7
5	231[j]	1.81	1.93	9043	35.5	14	360	9.9	273.4
7	131	1.88	0.27	9158	38.2	5	160	13.6	269.5
8	130	1.83	0.47	9028	37.0	4	80	19.0	271.1
9	161	1.92	0.85	9437	41.3	5	40	9.6	277.3
ADN[k]	159	1.81	-	-	-	3-5	64-72	25.8	202[l]
RDX[m]	210	1.82	0.36	8748	34.9	7.4[n]	120	0	-
HMX[m]	280	1.90	0.36	9320	39.5	7.4	120	0	-
CL-20[o]	210	2.03	0.90	9406	44.6	4	94	11.0	-

*[a] Decomposition temperature (onset) under nitrogen gas (DSC, 5 °C/min). [b] Density measured by gas pycnometer (25 °C). [c] Heat of formation. [d] Detonation pressure (calculated with Explo5 v6.01). [e] Detonation velocity (calculated with Explo 6.01). [f] Impact sensitivity. [g] Friction sensitivity. [h] Oxygen balance (based on CO) for CaHbOcNd, 1600(c-a-b/2)/MW, MW = molecular weight. [i] Specific impulse (values obtained from Explo5 v6.01 and calculated at an isobaric pressure of 70 bar and initial temperature of 3300 K). [j] Compound **5** has a melting point of 109 °C. [k] Ref. 16. l Calculated with Explo5 v6.01.m Ref. 17. [n] Idaho expt'l value. [o] Ref. 18.*

expected, the potassium salt (**3**) has the highest density at 2.04 g cm^{-3}. Others are in the range from 1.81 to 1.92 g cm^{-3}. The heats of formation were computed by using the method of isodesmic reactions with the Gaussian 03 suite of programs (Scheme S1).[14] All the compounds have positive heats of formation except **3** (-0.23 kJ g^{-1}) ranging from 0.27 to 1.93 kJ g^{-1}. Among them, **5** has the highest heat of formation of 1.93 kJ g^{-1} which arises from the high heats of formation of the furoxan and furazan rings.

To evaluate the detonation performance of compounds **3–5** and **7–9**, the detonation velocity and pressure were calculated using the EXPLO5 (version 6.01) program package[15] by using the calculated heats of formation and measured densities. Compound **9** exhibits the highest detonation velocity (9437 m s^{-1}) and pressure (41.3 GPa) values cellent detonation velocities (8900 m s^{-1}, 9043 m s^{-1}, 9158 m s^{-1}, and 9028 m s^{-1}, respectively) which are higher than that of RDX (v_D, 8748 m s^{-1}). The specific impulse values (*I*sp), a measure of the efficiency of a propellant (in seconds), were also calculated (Explo 5 v6.01) for all compounds. These values range from 222.5 to 277.3 s, which are higher than that of ADN (202 s). All the compounds exhibit positive oxygen balances ranging from 9.6% to 25.5% (Table 1). For initial safety testing, the impact and friction sensitivities of **3**-**5** and **7**-**9**, were measured by employing BAM standard methods.[19] Neutral compounds **4** (IS, 8 J; FS, 240 N) and **5 (**IS, 14 J; FS, 360 N) were less sensitive towards impact and friction than the energetic salts **3**, **7**-**9**.

Conclusions

In summary, 3,4-bis(4-nitro-1,2,5-oxadizaol-3-yl)-1,2,5-oxadiazole-N-oxide (**5**) was obtained by an unexpected cyclization of 3-(dinitromethyl)-4-nitro-1,2,5-oxadiazole (**4**) at 25 °C in absence of a catalyst. To understand the mechanism of the cyclization of **4** to **5**, the ^1H, ^{13}C and ^{15}N NMR spectra were monitored at the beginning and after 24 hours. Nitric acid was detected by ^1H and ^{15}N NMR spectral measurements after 24 hours which shows the formation of a molecule of nitric acid by the dinitromethyl group on standing at 25 °C. Compounds **4** and **5** were fully characterized by infrared (IR), ^1H and ^{13}C NMR spectroscopy, elemental analysis and single-crystal X-ray diffraction structuring. Compound **5** has a measured density of 1.81 g cm^{-3} with a heat of formation of 1.93 kJ g^{-1}, a melting point of 109 °C, an onset decomposition temperature of 231 °C, a detonation velocity of 9043 m s^{-1}, and impact sensitivity of 14 J, which makes it a highly desirable energetic ingredient for melt-pour formulations. A series of energetic salts of **4** were also synthesized and characterized. They exhibit high densities (1.83-2.04 g cm^{-3}), acceptable decomposition temperatures (130-196 °C), good detonation properties (v_D, 8081-9437 m s^{-1}; *P*, 21.5–41.3 GPa), and moderate sensitivities (IS, 2-5 J; FS, 40-160 N), which suggest potential applications as primary explosives.

Experimental section

Caution! All of the new compounds should be treated with extreme care. Although we have encountered no difficulties in preparing these compounds in this work, manipulations must be carried out by using appropriate standard safety precautions. Eye protection must be worn. Mechanical actions of these energetic materials involving scratching or scraping must be avoided!

General Methods

Reagents were purchased from Aldrich and Acros Organics and were used as received. ^1H, and ^{13}C spectra were recorded on a 300/500 MHz (Bruker AVANCE 300/500) nuclear magnetic resonance spectrometers operating at 300.13/500.17, and 75.48/36.14 MHz, respectively. $CDCl_3$, CD_3CN, d_6-acetone,or d_6-DMSO were used as solvent and locking solvent. ^{15}N spectra were obtained on a 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer operating at 50.69 MHz. Chemical shifts in the ^1H and ^{13}C spectra are reported relative to Me_4Si and ^{15}N relative to nitromethane. The melting and decomposition (onset temperature) points were obtained on a differential scanning calorimeter (TA Instruments Co., model Q2000) at a heating rate of 5 °C min^{-1}. IR spectra were recorded using KBr pellets with a FTIR spectrometer (Thermo Nicolet AVATAR 370). Density was determined at room temperature by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Elemental analyses (C, H, N) were performed on a Vario Micro cube Elementar Analyser. Impact and friction sensitivity measurements were made using a standard BAM Fallhammer and a BAM friction tester

3-Chlorocarbohydroxymoyl-4-nitro-1,2,5-oxadiazole (1)

Sodium tungstate (1.65 g, 5.0 mmol) was added slowly to 30% hydrogen peroxide solution (12 mL) at 0 °C. 3-Amino-4-chlorocarbohydroxymoyl-1,2,5-oxadiazole (0.49 g, 3.0 mmol) in methanesulfonic acid (3 mL) was added to the solution with stirring at 0 °C. The reaction mixture was warmed to room temperature slowly and then held at 50 ºC for 2 h. It was diluted with water (30 mL) and extracted with ethylacetate (3 × 15 mL). The combined organic layer was dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated on a rotary evaporator under vacuum to dryness to obtain product 1 (0.41 g, 70.0% yield) as a pale yellow liquid. ^1H NMR (d_6-acetone): δ 12.9 (br, 1H); ^{13}C NMR (d_6-acetone): δ 158.2, 145.3, 124.0.

3-(Chlorodinitromethyl)-4-nitro-1,2,5-oxadiazole (2)

Compound **1** (0.96 g, 5 mmol) dissolved in chloroform (5 mL) was added dropwise to mixture of trifluoroacetic acid anhydride (3.5 mL) and 100% nitric acid (2 mL) with stirring at a reaction temperature below 0 °C. After the addition was complete, the ice bath was removed, and the reaction mixture was allowed to warm slowly to room temperature. It was stirred for another 3 h, and then poured into ice water (30 mL) and extracted with chloroform (3 x 10 mL). The organic phases were combined, washed with water and brine, dried over sodium sulfate, and then evaporated under vacuum to provide **2** (0.76 g, 60.0% yield) as a pale yellow solid. ^{13}C NMR: δ 157.5, 143.6, 113.9; elemental analysis (%) calcd. for $C_3ClN_5O_7$ (253.51): C, 14.21; H, 0; N, 27.23; found: C, 14.17; H, 0.19; N, 26.48.

Potassium dinitro(4-nitro-1,2,5-oxadiazol-3-yl)methanide (3)

Potassium iodide (0.17 g, 1 mmol) in methanol (5 mL) was added to **2** (0.25 g, 1 mmol), the reaction mixture was stirred overnight at room temperature. Methanol was evaporated on a rotary evaporator under vacuum, the brown residue was washed with chloroform until colorless and recrystallized from acetone to give **3** (0.18 g, 70.0% yield) as a light yellow crystal. T_d (onset): 196 °C. ^{13}C NMR (d_3-acetone): δ = 160.2, 145.4, 120.9; IR (KBr pellet): $\tilde{\upsilon}$ 3449, 157, 1555, 1509, 1470, 1401, 1378, 1353, 1303, 1265, 1241, 1159, 1053, 1003, 902, 877, 833, 810, 784, 748, 568 cm^{-1}; elemental analysis (%) calcd. for $C_3KN_5O_7$ (257.16): C, 14.01; H, 0.00; N, 27.23; found: C, 14.08; H, 0.21; N, 26.5.

3-(Dinitromethyl)-4-nitro-1,2,5-oxadiazole (4)

Concentrated sulfuric acid (1 mL) was added dropwise into a stirred mixture of **3** (0.26 g, 1 mmol) and water (0.5 mL) at 5 ºC. After the addition was complete, the mixture was stirred for another 30 minutes, and then extracted with dichloromethane (6 × 5 mL). The combined extracts were concentrated under vacuum to provide white solid **4** (0.33 g, 68.8% yield). Compound **4** should be stored in the refrigerator. T_d (onset): 58 °C. ^{1}H NMR (d_6-acetone): δ 7.7 (s, 1H); ^{13}C NMR (d_6-acetone): δ 158.7, 139.9, 100.7; IR (KBr pellet): $\tilde{\upsilon}$ 3423, 2984, 2897, 1612, 1578, 1551, 1506, 1463, 1403, 1353, 1323, 1297, 1260, 115, 1158, 1053, 1036, 1005, 957, 909, 890, 849, 834, 803, 782, 745, 631, 619, 575, 530, 403 cm^{-1}; elemental analysis (%) calcd. for $C_3HN_5O_7$ (219.07): C, 16.45; H, 0.46; N, 31.97; found: C, 16.49; H, 0.67; N, 30.45.

3,4-Bis(4-nitro-1,2,5-oxadizaol-3-yl)-1,2,5-oxadiazole-N-oxide (5)

Compound **4** (0.22 g, 1 mmol) was dissolved in chloroform at room temperature. Compound **5** (0.27 g, 86.5% yield) was recrystallized from chloroform as a colorless crystal. T_d (onset): 231 °C. ^{13}C NMR (d_3-chloroform): δ 158.7, 158.5, 141.2, 138.3, 136.4, 102.2; IR (KBr pellet): $\tilde{\upsilon}$ 3448, 1638, 1586, 1564, 1516, 1448, 1412, 1384, 1355, 1318, 1285, 1176, 1119, 1038, 1001, 961, 907, 881, 832, 806, 732, 619, 510 cm^{-1}; elemental analysis (%) calcd. for $C_6N_8O_8$ (312.11): C, 23.09; H, 0; N, 35.90; found: C, 23.45; H, 0.20; N, 36.36.

Silver dinitro(4-nitro-1,2,5-oxadiazol-3-yl)methanide (6)

Compound **3** (0.26 g, 1 mmol) was dissolved in distilled water (5 mL), silver nitrate (0.17 g, 1mmol) was added. The yellow solid was filtered, washed with water, and dried in air, giving **6** (0.29 g, 89.0% yield). T_d (onset): 103 °C. ^{13}C NMR (d_6-acetone): δ = 160.0, 144.7, 120.9 ppm. IR (KBr pellet): $\tilde{\upsilon}$ 3431, 2121, 1753, 1638, 1586, 1565, 1515, 1448, 1384, 1355, 1318, 1176, 1121, 1037, 1000, 961, 906, 880, 833, 06, 732, 61, 509 cm^{-1}; elemental analysis (%) calcd. for $C_3AgN_5O_7$ (325.93): C, 11.06; H, 0; N, 21.49; found: C, 10.98; H, 0.14; N, 20.4.

General procedure for salts 7-9

Compound **6** (0.33 g, 1 mmol) was added to an ethyl acetate solution (15 mL) of ammonium chloride (0.053 g, 1 mmol), hydroxylammonium chloride (0.069 g, 1 mmol), or hydrazinium chloride (0.069 g, 1 mmol). After stirring for 2 h at room temperature, silver chloride was removed by filtration and washed with a small amount of methanol. The filtrate was concentrated under reduced pressure and dried in vacuum to yield **7**-**9**.

Ammonium dinitro(4-nitro-1,2,5-oxadiazol-3-yl)methanide (7)

Yellow solid, 78.0% yield. T_d (onset): 131 °C. ^{1}H NMR (d_3-acetonitrile): δ 5.9 (s, 1H); ^{13}C NMR (d_3-acetonitrile): δ 160.3, 145.2, 121.6; IR (KBr pellet): $\tilde{\upsilon}$ 3286, 3109, 1585, 1561, 1511, 1467, 1407, 1347, 1368, 1262, 1145, 1054, 1004, 914, 864, 832, 809, 753, 741, 664, 612, 588 cm^{-1}; elemental analysis (%) calcd. for $C_3H_4N_6O_7$ (236.1): C, 15.26; H, 1.71; N, 35.6; found: C, 15.41; H, 1.71; N, 35.24.

Hydroxylammonium dinitro(4-nitro-1,2,5-oxadiazol-3-yl)methanide (8)

Yellow solid, 74.0% yield. T_d (onset): 130 °C. ^{1}H NMR (d_3-acetonitrile): δ 8.7 (br, 4H); ^{13}C NMR (d_3-acetonitrile): δ 160.2, 145.1, 121.7; IR (KBr pellet): $\tilde{\upsilon}$ 3445, 2962, 2721, 1578, 1555, 1509, 1471, 1401, 1385, 1354, 1303, 1265, 1159, 1053, 1003, 902, 877, 833, 810, 784, 62, 624, 568 cm^{-1}; elemental analysis (%) calcd. for $C_3H_4N_6O_8$ (252.10): C, 14.29; H, 1.60; N, 33.34; found: C, 13.82; H, 1.40; N, 31.72.

Hydrazinium dinitro(4-nitro-1,2,5-oxadiazol-3-yl)methanide (9)

Yellow solid, 75.0% yield. T_d (onset): 161 °C. ^{1}H NMR (d_6-acetone): δ = 3.7 (br, 5H); ^{13}C NMR (d_6-DMSO): δ = 159.6, 140.5, 120.5; IR (KBr pellet): $\tilde{\upsilon}$ 3448, 3051, 1580, 1508, 1464, 1401, 139, 1378, 1354, 1302, 1268, 1241, 1159, 1083, 1053, 1003, 962, 902, 877, 810, 833, 784, 747, 568 cm^{-1}; elemental analysis (%) calcd. for $C_3H_5N_7O_7$ (251.12): C, 14.35; H, 2.01; N, 39.05; found: C, 13.87; H, 1.87; N, 36.96.

Conflicts of interest

There are no conflicts to declare.

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19 (a) http://www.bam.de. (b) A 20 mg sample was subjected to a drop-hammer test with a 5 or 10 kg dropping weight. The impact sensitivity was characterized according to the UN recommendations (insensitive, >40 J; less sensitive, 35 J; sensitive, 4 J; very sensitive, 3 J).

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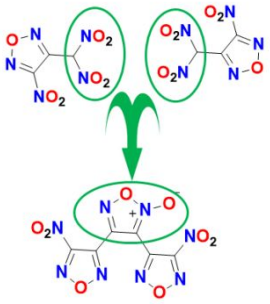

Dinitromethyl groups form an unstable nitrile oxide and its dipole isomer which cyclize to a furoxan ring.