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ARTICLE

An Azo-bridged Triazole Derived from Tetrazine

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Dedicated to Professor Dr. Dr. h.c. mult. Herbert W. Roesky on the occasion of his 85th Birthday

Abstract. A new approach to the synthesis of 5,5′-dinitro-3,3′-azo-1*H*-1,2,4-triazole (**3**) starting from 3,6-dihydrazinyl-1,2,4,5-tetrazine (DHT) was discovered. Nitrogen-rich energetic salts of **3** were synthesized in high yields. It is unusual that all the salts were less thermally stable than the neutral compound **3**. Of all the compounds, the decomposition temperature of 217 °C, as well as being insensitive towards impact and friction, which suggests potential application as an environmentally friendly nitrogen-rich energetic material.

Introduction

Nitrogen-rich heterocycles such as triazole, tetrazole, and tetrazine have been widely used to synthesize energetic compounds because they have high positive heats of formation arising from the large number of inherently energetic C–N, N–N, C=N, and N=N bonds.[1] Energetic compounds containing these nitrogen-rich heterocycles have attracted increasing interest because they exhibit excellent energy derived from their high heats of formation. In addition to energy, safety is also considered to be a key factor in designing and synthesizing energetic materials; however, the pursuit of high energy concomitantly with the search for good safety is quite often contradictory.[2] It was found that the combination of an azo group and nitrogen-rich heterocycles leads to the development of compounds with high energy and good stabilities. The azo linkage not only increases the heat of formation but also dramatically enhances the stability of the corresponding compound. Several azo-bridged triazoles,[3] tetrazole,[4] and tetrazine,[5] were reported in the literature (Figure 1). Only energetic salts of 5,5′-azotetrazolate including the ammonium salt **5** were reported since its neutral compound decomposes at room temperature.[4,6] Although 3,3’-azobis(6-amino-1,2,4,5-tetrazine) (**6**) was synthesized many years ago, only a complex mixture of various *N*-oxides of (**6**) has been reported.[7] Relative to azo bridged tetrazole and tetrazine compounds, triazoles are more attractive because the neutral compounds are stable at room temperature and they can be functionalized by nitration or by forming energetic salts.

5,5′-Dinitro-3,3′-azo-1*H*-1,2,4-triazole (**3**) was first synthesized by reacting 5-amino-3-nitro-1*H*-1,2,4-triazole (ANTA) with potassium permanganate in concentrated HCl (Scheme 1A).[3b] However, 5,5′-diamino-3,3′-azo-1*H*-1,2,4-triazole (**1**) was not accessible by using 3,5-diamino-1*H*-1,2,4-triazole as a starting material under similar conditions. In 2011, *Klapötke’s* group reported the synthesis of **1** by first forming 1-acetyl-diaminotriazole (**1a**) (Scheme 1 B)[3c] which 1was rearranged by heating in decalin to give its isomer 5-acetylaminotriazole (**1b**). A subsequent reaction with potassium permanganate in alkaline solution gave the azo-bridged triazole **1**. In our fused ring compounds research, **1** was obtained unexpectedly from 3,6-dihydrazinyl-1,2,4,5-tetrazine (DHT), which was nitrated to **3** (Scheme 1C). Since the triaminoguanidinium salt of **3** exhibited high stability and attractive explosive properties,[8] other nitrogen-rich salts such as ammonium, hydroxylammonium, hydrazinium, 5-aminotetrazinium, and 1,5-diaminotetrazinium salts of **3** were also examined in this work.

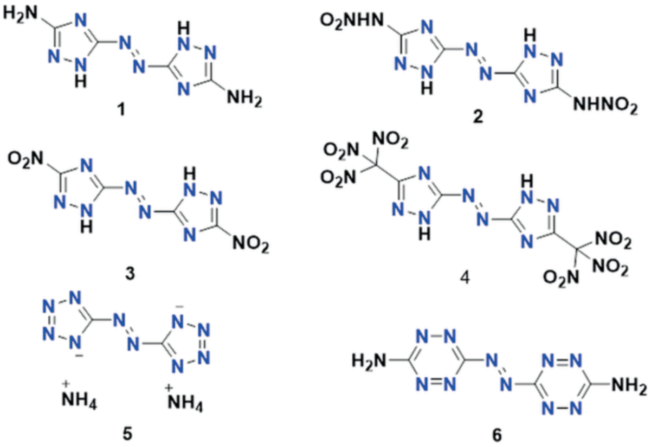

Figure 1. Structures of some azo-bridged triazoles, tetrazole and tetrazine.

Result and Discussion

Synthesis and Characterization

As shown in Scheme 2, when DHT[9] (**7**) was reacted with cyanogen bromide in 3 N HCl at reflux, compound **1** precipi-

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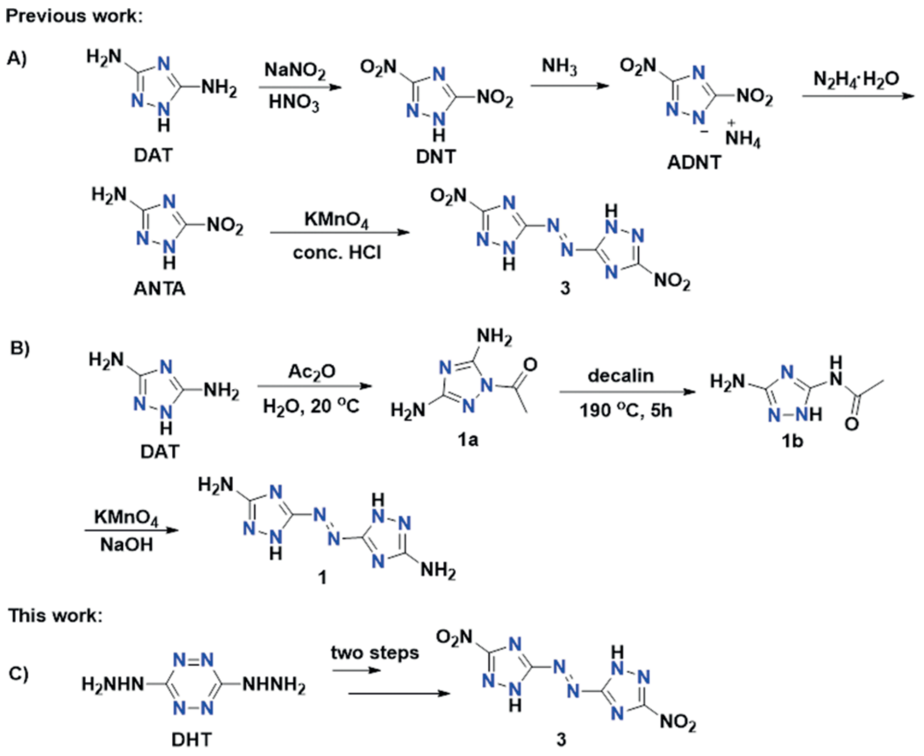


Scheme 1. Syntheses of azo-bridged triazoles.

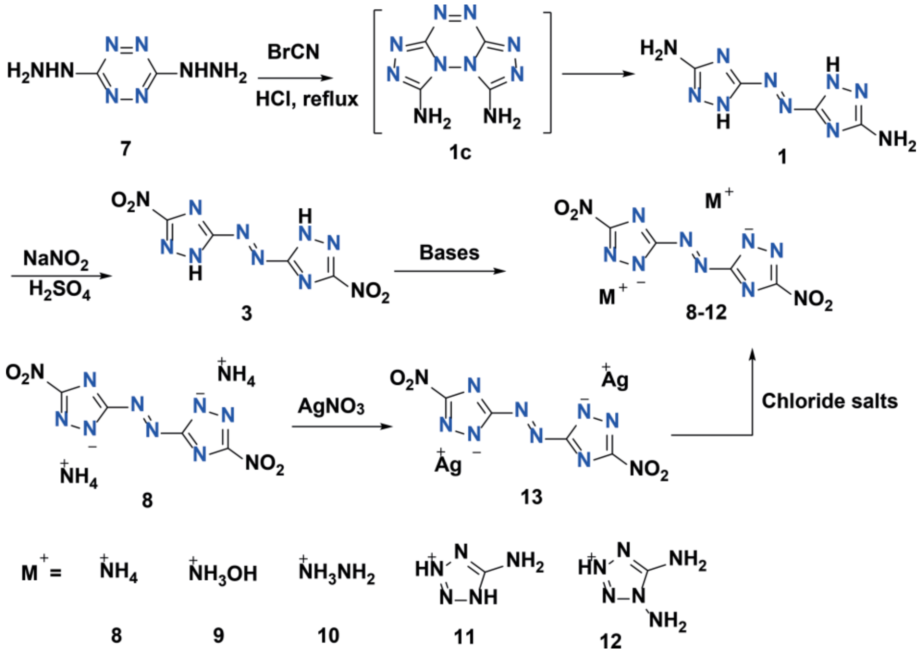
tated from the mixture. Compound **1** is insoluble in water and organic solvents. The ^{13}C NMR spectrum was obtained by adding sodium hydroxide to deuterium oxide as the solvent. Initially compound **1** was mistaken for fused ring compound **1c** since they have similar NMR spectra. The product from the reaction of DHT and BrCN was **1** rather than **1c**, which was confirmed after the product was further treated with sodium nitrite and 60 % sulfuric acid where **3** was formed rather than the nitro derivative of **1c**. The triazole proton is acidic, and can be neutralized by bases such as ammonia, hydroxylamine, and hydrazine yielding energetic salts **8–10**. Nitrogen-rich salts **11** and **12** were prepared from metathetical reactions of the silver salt **13**, obtained from the reaction of the neutral compound **3** with silver nitrate, with 5-aminotetrazolium and 1,5-diaminotetrazolium chlorides. These energetic salts of the dianion were obtained in good yields as yellow powders. All energetic compounds were fully characterized with IR and multinuclear NMR spectroscopy as well as elemental analysis, and differential scanning calorimetry except silver salt **13** which doesn't dissolve in any solvent tried. Thus, its NMR spectroscopic data are not available. The hydroxylammonium salt **9** was additionally characterized by low temperature single-crystal X-ray spectroscopy.

Single crystals of **9** suitable for X-ray diffraction measurements were obtained from distilled water. A crystal with dimensions $0.27 \times 0.11 \times 0.04$ mm^3 was selected and mounted on a nylon loop with paratone oil on a XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was kept at a steady $T = 100.00(10)$ K during data collection. The structure was solved with the ShelXT[10] solution program using dual methods and by using Olex2[11] as the graphical interface. The model was refined with ShelXL 2018/3[12] using full-matrix least-squares minimization on F^2. Compound **9**·6H_2O crystallizes in the triclinic space group $P\bar{1}$ with one molecule of **9** and six molecules of water in the unit cell and a calculated density of 1.635 g·cm^{-3} at 100 K. Selected crystal parameters of **9**·6H_2O are given in Table 1.

As shown in Figure 2a, the unit cell contains one crystallographically independent molecule of **9** and six co-crystallized solvent molecules of water. The azo bond adopts a stable *E* configuration due to its lower active energy than the *Z* configuration. The bond length of N1–N1' in the azo group [1.259(2) Å] is slightly longer than that of typical N–N double bonds (1.245 Å),[13] which results from π–π conjugation between the N1–N1' bond and the triazole rings. The cation, anion and water molecules are connected to each other through hydrogen bonds (N–H···O, O–H···O, N–H···N, O–H···N) (Figure 2a). The two triazole rings are parallel to each other as is confirmed by their dihedral angle of 0°, but they are not coplanar with a distance of 0.2398 Å. As a result, the anion moieties formed face-to-face π-π stacking in the packing diagram of **9**·6H_2O (Figure 2b). The perpendicular distance between adjacent sheets is only 3.2 Å, which is even shorter than the interplanar spacing in graphite (3.4 Å).

Physicochemical and Energetic Properties

The physicochemical and energetic properties of **3** and **8–12** are summarized in Table 2. Thermal stabilities (onset temperatures) were determined using differential scanning calo-



Scheme 2. Syntheses of compounds **1**, **3**, **8**–**13**.

Table 1. Selected crystal parameters of **9**·6H$_2$O.

	9·6H$_2$O
Empirical formula	$C_4H_{20}N_{12}O_{12}$
D_{calcd}/g·cm^{-3}	1.635
m /mm^{-1}	1.401
Formula weight	428.32
Color	yellow
Shape	needle
Size /mm^3	0.27 × 0.11 × 0.04
T /K	100.00(10)
Crystal system	triclinic
Space group	$P\bar{1}$
a /Å	6.02027(17)
b /Å	7.2024(3)
c /Å	10.3041(3)
α /°	94.814(3)
β /°	102.017(3)
γ /°	91.154(3)
V /Å^3	435.13(3)
Z	2
Z'	1
Wavelength /Å	1.54184
Radiation type	Cu K_a
Q_{min} /°	4.405
Q_{max} /°	77.238
Measured refl's.	7515
Indep't refl's	1755
Refl's I ≥ 2 s(I)	1576
R_{int}	0.0413
Parameters	167
Restraints	0
Largest peak	0.182
Deepest hole	–0.291
GooF	1.053
wR_2 (all data)	0.0899
wR$_2$	0.0859
R_1 (all data)	0.0367
R_1	0.0332

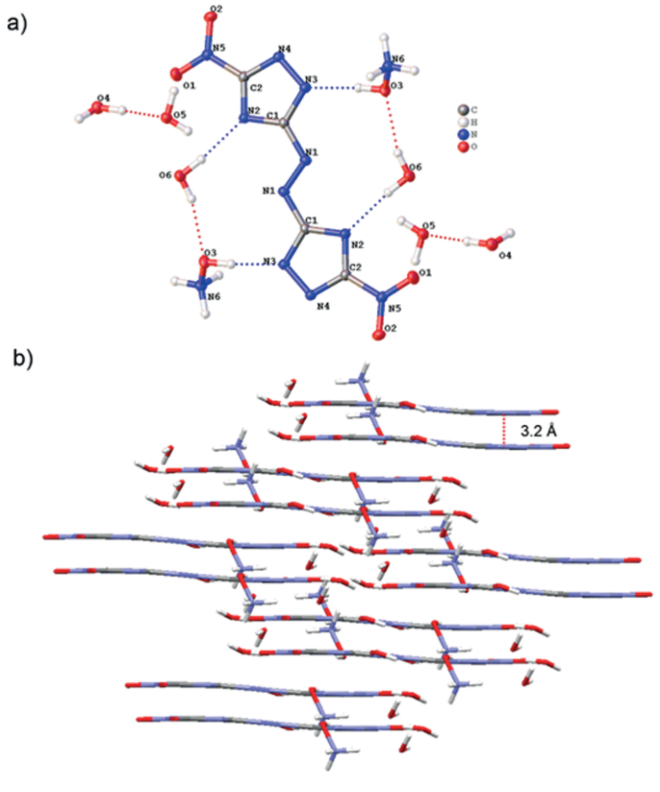


Figure 2. (a) Single-crystal X-ray structures of **9**·6H$_2$O (dashed lines indicate hydrogen bonding). (b) Crystal packing diagrams for **9**·6H$_2$O.

rimetry (DSC) at a heating rate of 5 K·min^{-1}. The neutral compound **3** was the most thermally stable decomposing at 289 °C without melting. The energetic salts decomposed between 181 and 231 °C; **11** and **12** also exhibited melting points at 102 and 168 °C, respectively. This is a unique example where ener-

Table 2. Properties of energetic compounds **3** and **8–12**.

Compound	T_m a) /°C	T_d a) /°C	db /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	–	289	1.88	2.25	8952	34.7	>40	>360	–6.3	244
8·H_2O	–	231	1.76	1.48	8665	29.5	>40	>360	–16.7	229
9·H_2O	–	182	1.82	1.10	8857	33.0	>40	>360	–10.0	243
10	–	217	1.80	2.08	9114	32.9	>40	>360	–25.1	237
11·H_2O	102	194	1.71	2.92	8226	25.8	>40	>360	–22.6	225
12	168	181	1.79	3.13	8702	29.4	>40	>360	–24.6	226
ADN j)	–	159	1.81	–	–	–	3–5	64–72	25.8	202^{k}
RDX l)	–	210	1.82	0.36	8748	34.9	7.4 m)	120	0	–
HMX l)	–	280	1.90	0.36	9320	39.5	7.4	120	0	–

a) Decomposition temperature (onset) under nitrogen (DSC, 5°K·min^{-1}). 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 $C_aH_bO_cN_d$, 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) Reference[15]. k) Calculated with Explo5 v6.01. l) Reference[16]. m) Idaho expt'l value.

getic salts are less stable than their neutral precursor. The densities of compounds **3** and **8–12** were measured with a gas pycnometer at room temperature. Compound **3** has the highest density of 1.88 g·cm^{-3}, while its salts range from 1.71 to 1.82 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, Supporting Information).[14] All the compounds exhibited positive heats of formation falling from 1.10 to 3.13 kJ·g^{-1}. Among them, **11** and **12** had higher heats of formation of 2.92 and 3.13 kJ·g^{-1}, respectively, which arises from the high heat of formation of the tetrazole ring.

To evaluate the detonation performance of compounds **3** and **8–12**, the detonation velocity and pressure were calculated using the EXPLO5 (version 6.01) program package[17] by using the calculated heats of formation and measured densities. Among all the compounds, hydrazinium salt **10** exhibited the highest detonation velocity (9114 m·s^{-1}) which is higher than that of RDX (8748 m·s^{-1}) and comparable to that of HMX (9320 m·s^{-1}). However, its detonation pressure (32.9 GPa) is lower than that of RDX (34.9 GPa). Next is compound **3** with a detonation velocity of 8952 m·s^{-1} which was higher than that of RDX. The detonation velocities of salts **8**, **9**, and **12** are between 8665 and 8702 m·s^{-1} which are comparable to that of RDX. The specific impulse values (I_{sp}), a measure of the efficiency of a propellant (in seconds), are also calculated (Explo 5 v6.01) for all compounds. These values ranged from 225 to 244 s, which are higher than that of ADN (202 s). All the compounds exhibited negative oxygen balances ranging from –6.3 % to –25.1 % (Table 2). For initial safety testing, the impact and friction sensitivities of **3** and **8–12**, were measured by employing BAM standard methods.[18] All the compounds were insensitive towards impact and friction.

Conclusions

A new strategy was developed to synthesize 5,5′-diamino-3,3′-azo-1*H*-1,2,4-triazole (**1**) by reacting 3,6-dihydrazinyl-1,2,4,5-tetrazine with cyanogen bromide at reflux in 3*N* hydrochloric acid. 5,5′-Dinitro-3,3′-azo-1*H*-1,2,4-triazole (**3**) was synthesized by treating 5,5′-diamino-3,3′-azo-1*H*-1,2,4-triazole with sodium nitrite and 60 % sulfuric acid, in which the approach is first reported. These high-nitrogen energetic materials were synthesized in high yields and fully characterized by ^{1}H, ^{13}C NMR spectroscopy, IR, elemental analysis, and differential scanning calorimetry, as well as by X-ray diffraction study (**9**). Compound **3** and salts **8–12** exhibit good performance properties such as high heats of formation, moderate thermal stabilities, and good densities, and insensitivities. The calculated detonation velocities of **3**, **8**, **9** and **12** are superior to that of RDX and compound **10** is comparable to that of HMX, which implies that they could be of interest as environmentally friendly nitrogen-rich energetic materials.

Experimental Section

Caution! All of the materials reported in this work should be treated with extreme care, though we have encountered no difficulties in preparing them. 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. ^{1}H, 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. D_2O or [D_6]DMSO was used as solvent and locking solvent. Chemical shifts in the ^{1}H and ^{13}C spectra are reported relative to Me_4Si. 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 K·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.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-2032004 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

5,5′-Diamino-3,3′-azo-1*H*-1,2,4-triazole hydrate (1·H_2O): To 3 N hydrochloric acid (3 mL) was added DHT[9] (0.14 g, 1 mmol) and cyanogen bromide (0.21 g, 2 mmol). The mixture was heated at reflux for 6 h. The reaction was cooled to room temperature in order to precipitate the product. The solid was filtered, washed with water and air dried to give **1** as yellow solid (0.17 g, 87 %). T_d (onset): 387 °C. **^{13}C NMR** (D_2O, NaOH): δ = 169.4, 164.5. **IR** (KBr): $\tilde{\nu}$ = 3454, 2682, 1628, 1491, 1466, 1412, 1351, 1144, 1101, 1054, 956, 890, 800, 760, 706, 678, 596, 464 cm^{-1}. $C_4H_8N_{10}O$ (212.18): calcd. C, 22.64; H, 3.80; N, 66.02 %; found: C, 22.92; H, 3.32; N, 65.74 %.

5,5′-Dinitro-3,3′-azo-1*H*-1,2,4-triazole (3): A solution of **1**·H_2O (0.21 g, 1 mmol) in 60 % sulfuric acid (2 mL) was added dropwise to a solution of sodium nitrite (2.07 g, 30 mmol, 30 equiv.) in water (2 mL) at 50 °C. The mixture was stirred at 60 °C for 3 h. After cooling to room temperature the mixture was acidified with sulfuric acid (20 %) until no additional evolution of nitrogen dioxide was observed. The mixture was extracted with diethyl ether. The combined organic extracts were washed with brine, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure to give **3** (0.10 g, 40 %) as a yellow solid. T_d (onset): 293 °C. **^1H NMR** ([D_6]DMSO): δ = 4.1 (br). **^{13}C NMR** ([D_6]DMSO): δ = 163.8, 163.2. **IR** (KBr): $\tilde{\nu}$ = 3586, 3442, 3309, 2737, 2545, 1891, 1618, 1545, 1485, 1433, 1397, 1351, 1323, 1185, 1052, 1030, 911, 840, 741, 652, 612, 516, 423 cm^{-1}. $C_4H_2N_{10}O_4$ (254.13): calcd. C, 18.91; H, 0.79; N, 55.12 %; found: C, 18.90; H, 0.94; N, 55.47 %.

General Procedure for Salts 8–10: Aqueous ammonia, hydrazine, and hydroxylammine (2 equiv., 2 mmol) was added to a suspension of **3** (0.25 g, 1 mmol) in water (10 mL) at room temperature. After stirring for 2 h, water was evaporated to yield the corresponding nitrogen-rich salts of 3,3’-dinitro-5,5’-azo-1,2,4-triazolate (**8**–**10**) as yellow solids.

Diammonium 3,3’-dinitro-5,5’-azo-1,2,4-triazolate (8·H_2O): Yield 92 %; T_d (onset): 231 °C. **^1H NMR** ([D_6]DMSO): δ = 7.3 (br). **^{13}C NMR** ([D_6]DMSO): δ = 170.4, 165.1. **IR** (KBr): $\tilde{\nu}$ = 3427, 3263, 3023, 2844, 2447, 1701, 1686, 1655, 1637, 1560, 1527, 1483, 1459, 1419, 1384, 1321, 1299, 1126, 1066, 1021, 845, 764, 750, 664, 608, 513 cm^{-1}. $C_4H_{10}N_{12}O_5$ (306.20): calcd. C, 15.69; H, 3.29; N, 54.89 %; found: C, 16.29; H, 3.16; N, 54.46 %.

Dihydroxylammonium 3,3’-dinitro-5,5’-azo-1,2,4-triazolate (9·H_2O): Yield 91 %; T_d (onset): 182 °C. **^1H NMR** ([D_6]DMSO): δ = 9.8 (br). **^{13}C NMR** ([D_6]DMSO): δ = 170.2, 165.1. **IR** (KBr): $\tilde{\nu}$ = 3422, 3256, 3203, 2926, 2684, 2468, 2341, 1618, 1560, 1529, 1486, 1421, 1388, 1332, 1305, 1220, 1184, 1132, 1011, 845, 753, 661, 617, 512, 452 cm^{-1}. $C_4H_{10}N_{12}O_7$ (338.20): calcd. C, 14.21; H, 2.98; N, 49.70 %; found: C, 14.53; H, 3.17; N, 51.19 %.

Dihydrazinium 3,3’-dinitro-5,5’-azo-1,2,4-triazolate (10): Yield 90 %; T_d (onset): 217 °C. **^1H NMR** ([D_6]DMSO): δ = 7.1 (br), 6.4 (s). **^{13}C NMR** ([D_6]DMSO): δ = 170.4, 165.1. **IR** (KBr): $\tilde{\nu}$ = 3425, 3345, 3281,318, 3060, 2973, 2849, 2731, 2652, 2439, 2149, 1701, 1686, 1637, 1600, 1560, 1485, 1420, 1386, 1316, 1122, 1080, 956, 843, 771, 763, 752, 660, 512, 463 cm^{-1}. $C_4H_8N_{12}O_6$ (318.22): calcd. C, 15.10; H, 3.17; N, 61.62 %; found: C, 15.21; H, 3.53; N, 61.79 %.

Disilver 3,3’-dinitro-5,5’-azo-1,2,4-triazolate (13): Compound **3** (0.25 g, 1 mmol) was dissolved in distilled water (10 mL), silver nitrate (0.34 g, 2 mmol) was added. The red solid was filtered, washed with water, and dried in air, giving **13** (0.46 g, 98 %). T_d (onset): 284 °C. **IR** (KBr): $\tilde{\nu}$ = 3587, 3422, 2921, 2844, 2443, 1655, 1637, 1532, 1486, 1384, 1315, 1121, 843, 750, 662, 625, 518 cm^{-1}. $C_4Ag_2N_{10}O_4$ (467.85): calcd. C, 10.27; H, 0; N, 29.94 %; found: C, 10.00; H, 0.48; N, 31.31 %.

General Procedure for Salts 11 and 12: Compound **13** (0.47 g, 1 mmol) was added to a methanol solution (15 mL) of 5-aminotetrazolium chloride (0.24 g, 2 mmol), or 1,5-diaminotetrazolium chloride (0.27 g, 2 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 vacuo to yield **11** and **12**.

Bis(5-aminotetrazolium) 3,3’-dinitro-5,5’-azo-1,2,4-triazolate hydrate (11·H_2O): Yield 86 %; T_m (onset): 102 °C. **^1H NMR** ([D_6]DMSO): δ = 7.6 (br). **^{13}C NMR** ([D_6]DMSO): δ = 163.1, 162.7, 156.2. **IR** (KBr): $\tilde{\nu}$ = 3419, 3336, 3219, 2345, 1701, 1653, 1561, 1499, 1458, 1385, 1313, 1265, 1143, 1068, 1049, 1000, 839, 772, 736, 678, 655, 442 cm^{-1}. $C_6H_{10}N_{20}O_5$ (442.28): calcd. C, 16.29; H, 2.28; N, 63.34 %; found: C, 16.61; H, 2.65; N, 65.08 %.

Bis(1,5-diaminotetrazolium) 3,3’-dinitro-5,5’-azo-1,2,4-triazolate (12): Yield 80 %; T_m (onset): 168 °C. **^1H NMR** ([D_6]DMSO): δ = 6.0 (br). **^{13}C NMR** ([D_6]DMSO): δ = 162.9, 162.7, 154.2. **IR** (KBr): $\tilde{\nu}$ = 3325, 3240, 3152, 2930, 2743, 2345, 1655, 1570, 1560, 1457, 1427, 1385, 1329, 1309, 1177, 1110, 1078, 1020, 1003, 931, 834, 773, 744, 687, 653, 606 cm^{-1}. $C_6H_{10}N_{22}O_4$ (454.3): calcd. C, 15.86; H, 2.22; N, 67.83 %; found: C, 15.68; H, 2.58; N, 67.10 %.

Supporting Information (see footnote on the first page of this article): Supporting information contains crystallographic data and theoretical calculations.

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Keywords: Decomposition temperature; Energetic salts; Heterocycles; Azo-bridged; Nitration

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