High-Energy-Density Materials

Deutsche Ausgabe: DOI: 10.1002/ange.201412303
Internationale Ausgabe: DOI: 10.1002/anie.201412303

Energetic Materials with Promising Properties: Synthesis and Characterization of 4,4′-Bis(5-nitro-1,2,3-2*H*-triazole) Derivatives**

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Abstract: *Using a variety of functionalization strategies, derivatives of 4, 4′-bis(5-nitro-1,2,3-2H-triazole) were designed, synthesized, and characterized. The isomers were separated, their structures were confirmed with single-crystal X-ray analysis, and their properties were determined by differential scanning calorimetry, density, impact sensitivity, heat of formation, and detonation velocity and pressure (calculated by EXPLO5 V6.01). Those materials were found to exhibit superior detonation performance when compared with the other fully carbon-nitrated bis(azoles).*

Energetic compounds with improved densities and heats of formation are of great value in achieving high detonation velocities and pressures. Fully carbon-nitrated bis(azole) compounds such as 4,4′,5,5′-tetranitro-2,2′-bis(1*H*-imidazole) (**1**),[1] 3,3′,5,5′-tetranitro-4,4′-bis(1*H*-pyrazole) (**2**),[2] 5,5′-dinitro-3,3′-bis(1,2,4-triazole) (**3**),[3] and their derivatives have been studied extensively as high-energy-density materials (HEDMs). The larger the number of catenated nitrogen atoms in a single chain, the greater the positive impact on creating compounds with higher heats of formation and densities as well as enhanced detonation properties (Figure 1).

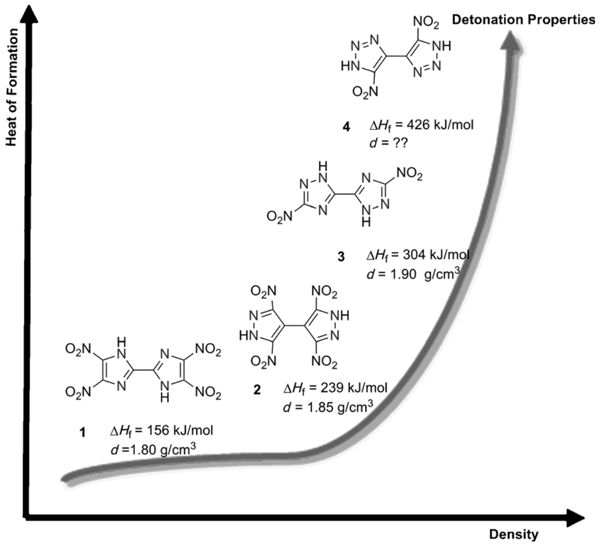

Figure 1. Fully carbon-nitrated bis(azole) compounds (heats of formation were calculated at B3LYP/6-31$^+$G**//MP2/6-311^{++}G**).

Derivatives of 5-nitro-1,2,3-2*H*-triazole were reported recently by our group;[4a] higher heats of formation, densities (3-amino-5-nitro-1,2,4-1*H*-triazole:[4b] $d = 1.82\ \mathrm{g\,cm^{-3}}$, 4-amino-5-nitro-1,2,3-2*H*-triazole:[4c] $d = 1.84\ \mathrm{g\,cm^{-3}}$) and better thermal stabilities were observed for some derivatives of 1,2,3-2*H*-triazole in comparison with the analogous derivatives of its isomer, 1,2,4-1*H*-triazole. The derivatives of **3** have been reported[3,5] as insensitive energetic materials that exhibit promising potential to replace RDX. Since 4,4′-bis(5-nitro-1,2,3-2*H*-triazole) (**4**) was calculated to possess a higher heat of formation than that of **3**, the derivatives of **4** were expected to have superior detonation properties. As far as we know, only compound **4** and its potassium salt have been previously reported, and the properties of **4** and its derivatives are still unknown.[6] It was also worthwhile to investigate the influence of the substituted position in the 4,4′-bis(5-nitro-1,2,3-2*H*-triazole) system, on detonation properties. Herein, we report the synthesis and the characterization of **4** with a variety of functionalized derivatives; methylation, amination, and N-oxidation strategies were employed to develop more powerful, less sensitive, and eco-friendly energetic materials.

4,4′-Bis(5-nitro-1,2,3-2*H*-triazole) (**4**) was synthesized based on a previous report.[6] However, unlike the reported colorless or light-brown crystals, we obtained **4** as a sticky product that is hygroscopic. Diammonium 4,4′-bis(5-nitro-1,2,3-2*H*-triazolate) (**5**), the precursor for methylation, amination, and *N*-oxidization reactions, was realized by bubbling gaseous ammonia through a diethyl ether solution of **4** for five minutes and then removing the solvent under vacuum. The remaining solid was washed with cold ethanol to obtain a brown solid (**5**; yield 92%). Since the hydroxylammonium salts usually exhibit superior detonation properties compared with most organic cations when combined with a common anion, the dihydroxylammonium 4,4′-bis(5-nitro-1,2,3-2*H*-triazolate) (**6**; yield 90%) was formed by reacting **4** with an excess of 50% hydroxylamine aqueous solution in ether (Scheme 1).

Methylation, amination, and *N*-oxidation are effective methods used to functionlize energetic compounds to achieve materials with improved thermal stability, heat of formation, density, sensitivity, and so on.[4a,7] The methylation or amination of 4,5-dinitro-1,2,3-triazole is reported to form a single product.[4a] However, when compound **5** was methy-

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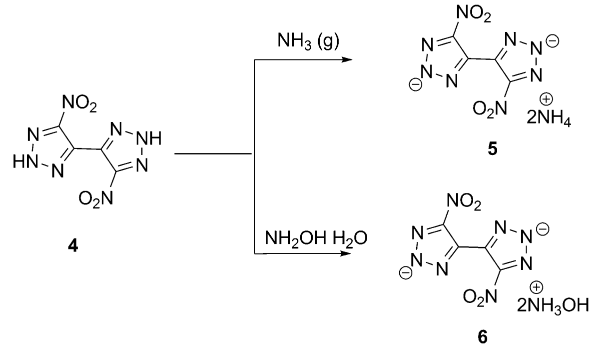
[**] This work was supported by the Office of Naval Research (N00014-12-1-0536) and the Defense Threat Reduction Agency (HDTRA 1-11-1-0034). We are indebted to Dr. Orion Berryman for crystal structures (NSF—CHE1337908).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201412303.

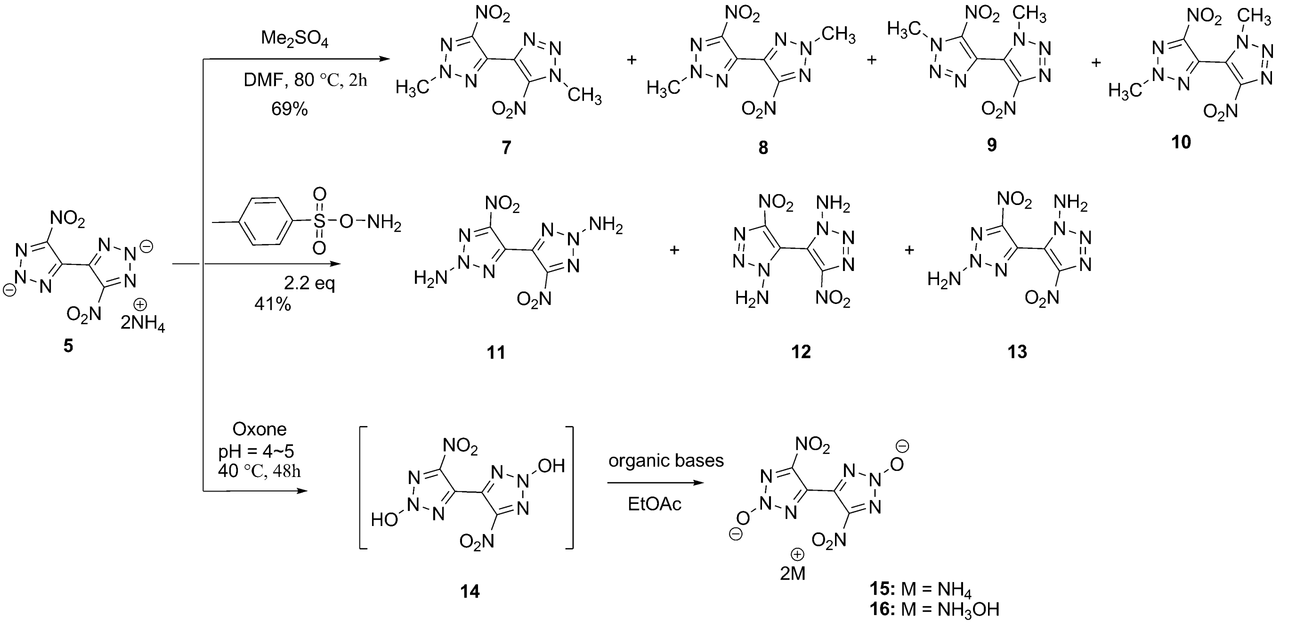


Scheme 1. Preparation of salts of **4**.

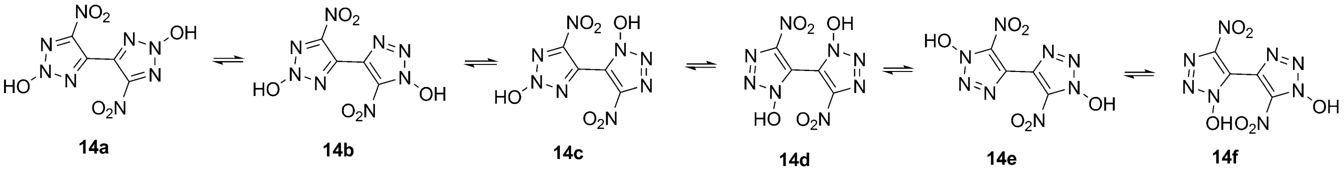
lated by reaction with dimethyl sulfate in DMF at 80 °C for 2 h, four isomers, compounds **7**–**10** (69 %), were obtained; only trace amounts of **7** were found which were detected by proton NMR spectroscopy (Scheme 2). The reaction of freshly prepared *o*-*p*-toluenesulfonyl-hydroxylamine (THA) with **5** led to the formation of three isomers, compounds **11**–**13** (41 %). The isomers could be isolated by column chromatography except that compounds **12** and **13** existed in a mixture even after column chromatographic separation. Compounds **12** and **13** can be further isolated by washing with methanol; **12** was obtained as a residual white solid and **13** was isolated as a yellow solid after evaporation of methanol. After isolation, **8**, and **12** were found to be the major products. The polarities of the products obtained from methylation and amination reactions are **7** < **8** < **9** < **10**, and **11** < **12** < **13**, respectively.

When **5** was treated with Oxone in a buffer solution (pH 4–5) at 40 °C for 48 h, a yellow oil, **14**, was isolated by extracting with ethyl acetate. The reactions of **14** in ethyl acetate with bases such as aqueous ammonia and hydroxylamine give the corresponding salts **15** and **16** (Scheme 2), Compound **16** was found to be a sticky compound even after being pumped under vacuum for several days. The anion of **16** was confirmed by ESI (Supporting information Figure S8).

The structures of 4,4′-bis(5-nitro-1,2,3-2*H*-triazole) and its derivatives were confirmed by IR, ^{1}H, and ^{13}C NMR, elemental analysis, and ^{15}N NMR spectroscopic data in some cases. However, for compound **7**, only IR and ^{1}H NMR data are provided owing to the lack of sufficient compound to fully characterize. The proton NMR spectra show that the chemical shifts (in CD_3CN) of methyl groups range from 4.12 ppm to 4.46 ppm, while amino groups for **11**–**13** have shifts between 6.33 ppm and 7.08 ppm. The ^{13}C NMR spectrum indicates that the carbon atom connecting two triazole rings lies in the range between 124.0–134.1 ppm, while the one bonded to the nitro group is located between 142.9–152.9 ppm. The introduction of the N−O group causes the chemical shifts of C5-NO_2 and C4 to move upfield. The same trends were also observed in the 3,4,5-trinitropyrazol-1-ol,[7h] and 3,3′-dinitro-5,5′-bis(1,2,4-triazol-1,1-diol) systems.[5a] However, in the ^{13}C NMR spectrum of compound **15**, three peaks ($\delta = 122.8$, 126.2, 130.2 ppm) for C4 and C4′, and two peaks ($\delta = 136.6$, 141.6 ppm) for C5 and C5′ were detected; this is probably due to the insufficient concentration of the isomers, which are very difficult to isolate. Six possible tautomeric forms of compound **14** are suggested in Scheme 3; those tautomers have been studied at level of theory of MP2/6-311++G**//B3LYP/6-31+G**. The stability order of **14a** > **14d** > **14c** > **14b** > **14f** > **14e** is predicted. The **14a** form is shown to be the most-stable while **14e** is predicted to be the most-unstable tautomer. The corresponding energy difference in the gas phase between the tautomer **14a**, and **14d**, **14c**, **14b**, **14f**, **14e** is 11.8 kJ mol^{-1}, 20.5 kJ mol^{-1}, 29.2 kJ mol^{-1}, 37.7 kJ mol^{-1}, and 60.9 kJ mol^{-1} respectively (Supporting Information, Table S6).



Scheme 2. The functionalization of compound **5**.



Scheme 3. Tautomeric forms of **14**.

The ^{15}N NMR spectra of compounds **11** and **13** were recorded in CD_3CN and that of **12** was recorded in $[D_6]$DMSO solution and are given in Figure 2. The chemical shifts are measured relative to CH_3NO_2 as external standard. The assignments of the nitrogen signals were determined by using heteronuclear multiple bond correlation (HMBC) and based on reported values of similar compounds.[4] In the case of the symmetrical structure, only five nitrogen signals were observed, while for compound **13**, owing to asymmetry, 10 nitrogen signals are found. The chemical shifts of amino groups can be assigned to the resonance peaks ranging between −279.20 to −299.03 ppm. The chemical shifts for nitro groups lay between −26.12 to −27.99 ppm.

Suitable crystals of **6**, **10**, and **12** for X-ray single diffraction were grown from water, acetonitrile, and ethyl acetate/methanol, respectively. Their crystal structures are shown in Figure 3. Salt **6**, which crystallizes as yellow prisms in the triclinic $P\bar{1}$ space group, contains one molecule of water, and consists of two molecules per unit cell. The unit cell of **10**, which crystallizes in the monoclinic space group $P2_1/c$, contains four formula moieties, while **12** crystallizes in the tetragonal $I4_1/a$ space group with 8 molecules per unit cell. Each nitro group is located in the plane of its connected triazole ring. The two triazole planes form a dihedral angle of 34°, 52°, and 57° for **6**, **10**, and **12**, respectively. A large number of intermolecular O−H···N, N−H···N, and O−H···O hydrogen bonds between the cation and anion were observed for compound **6**; while for compound **10**, the only hydrogen bond is C6−H6A···O4, and for compound **12**, the hydrogen bonds of N5−H5A···N2 and N5−H5B···N1 help to increase the density and thermal stability. More details involving the crystal structures, including CCDC numbers, are provided in the Supporting Information.

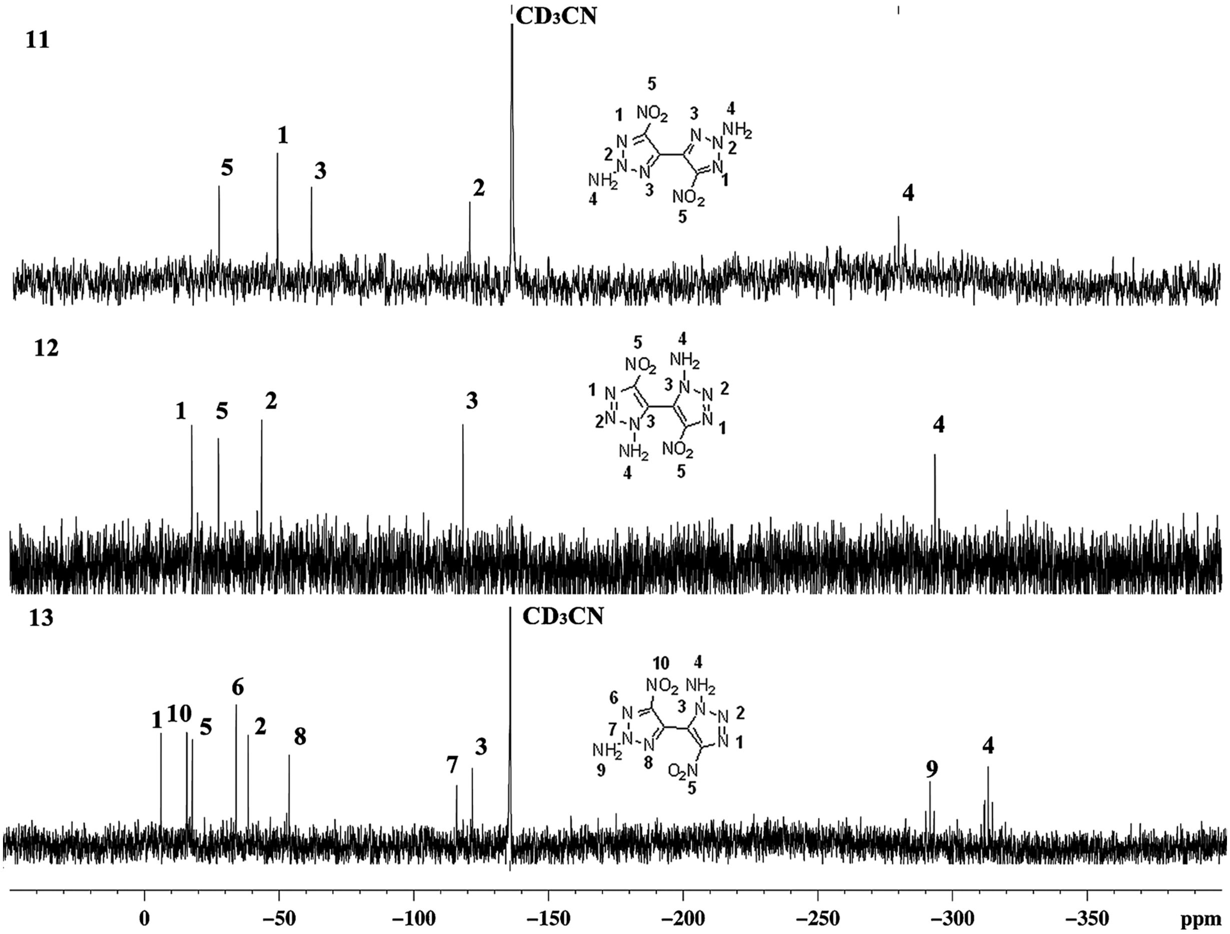


Figure 2. ^{15}N NMR spectra of compounds **11**, **12**, and **13**.

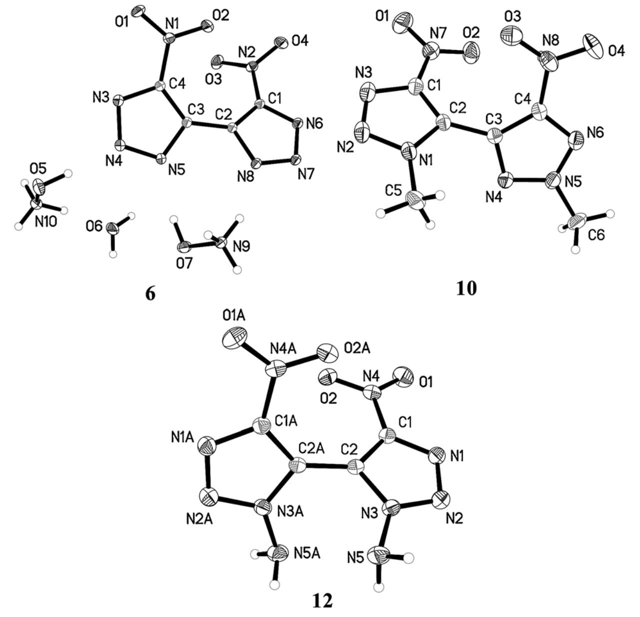


Figure 3. Crystal structures of **6**, **10**, and **12**.

The physical and detonation properties of all of the compounds are given in Table 1. Most of the compounds are thermally stable to 191 °C (**13**), which is comparable to RDX ($T_{\mathrm{dec}} = 210$ °C), except for **4**, **6**, and **16**, which decompose at 155 °C, 166 °C, and 172 °C, respectively; **7–10** have melting points over the range 139 °C to 165 °C, and **8** and **10** sublime at 227 and 275 °C, respectively. These compounds could be usable as melt-cast explosives. Densities between 1.63 and 1.88 $\mathrm{g\,cm^{-3}}$ were obtained using a gas pycnometer at room temperature; salt **16** exhibits the highest density at 1.88 $\mathrm{g\,cm^{-3}}$. Introduction of N−O and N−NH_2 increases the density of **5** by 0.08 to 0.14 $\mathrm{g\,cm^{-3}}$. All of the isomers show similar sensitivities towards impact; the ammonium salts and compounds **7**, **8**, **9**, and **10** are insensitive to impact (≥ 40 J). The impact sensitivity of **16** was not measured owing to its stickiness. Amination products **11–13** are the most impact sensitive at 9–10 J but are superior to RDX.

The heats of formation were calculated based on the Gaussian 03 (Revision D.01) suite of programs at level of theory of MP2/6-311++G**//B3LYP/6-31+G**.[8,9] The heats of formation for all the neutral compounds were obtained by using gas-phase heats of formation and subtracting the heat of sublimation (84 $\mathrm{kJ\,mol^{-1}}$). The heats of formation for the salts were calculated by employing Born–Haber energy cycles.[10] All compounds have highly endothermic enthalpies of formation in the range from 152.2 $\mathrm{kJ\,mol^{-1}}$ (**15**) to 581.1 $\mathrm{kJ\,mol^{-1}}$ (**12**). Compounds **11–13** have higher positive heats of formation than the other compounds; the introduction of the N−O group (**15** and **16**) lowers the heat of formation at about 132 $\mathrm{kJ\,mol^{-1}}$. The heats of formation of the isomers which have a substituent group at the N2 position were found to be lower than those bonded at the other nitrogen atom positions in the triazole ring.

The detonation pressure *P* and velocity *D* were calculated with EXPLO5 v6.01[11] by using the calculated values of the heats of formation and the experimentally measured densities. The calculated detonation velocities fall in the range between 7563 $\mathrm{m\,s^{-1}}$ (**8**) and 9171 $\mathrm{m\,s^{-1}}$ (**16**), and detonation pressures from 21.3 GPa (**8**) to 39.1 GPa (**16**), most of which exhibit properties competitive with those of RDX. Aminated products exhibit better detonation properties than those of the methylated ones. Interestingly, compound **12** shows slightly better detonation properties than those of compounds **11** and **13**. Furthermore, the detonation velocities of the ammonium and hydroxylammonium salts of 4,4′-bis(5-nitro-1,2,3-2*H*-triazolate) and 4,4′-bis(5-nitro-1,2,3-2*H*-triazol-2-olate) are superior to those of the corresponding 1,2,4-triazolate analogues, 5,5′-dinitro-bis(1,2,4-triazole) derivatives (improved by 84–477 $\mathrm{m\,s^{-1}}$; Figure 4). Compounds **6**, **11–13**, **15**, and **16** may be potential replacements for RDX.

Table 1: Physical and detonation properties of compound **4–16** compared with RDX.

Compd	T_m[a] [°C]	T_d[b] [°C]	d[c] [$\mathrm{g\,cm^{-3}}$]	ΔH_f°[d] [$\mathrm{kJ\,mol^{-1}}$ ($\mathrm{kJ\,g^{-1}}$)]	D[e] [$\mathrm{m\,s^{-1}}$]	P[f] [Gpa]	IS[g] [J]	Ω[h] [%]
4	–	155[i]	–	439.3 (1.94)	–	–	–	−7.08
5	–	241	1.71	284.8 (1.10)	8336	26.5	40	−24.6
6·H_2O	107 (H_2O)	180	(1.77)	–	–	–	–	−10.3
6	–	166	1.80	404.4 (1.38)	8954	34.4	16	−12.3
7	139	229	–	396.9 (1.56)	–	–	–	−31.5
8	165	227[j]	1.62	373.3 (1.47)	7563	21.3	> 40	−31.5
9	165	237	1.63	390.5 (1.54)	7626	21.9	> 40	−31.5
10	160	275[j]	1.63 (1.66)	403.1 (1.49)	7642	22.0	> 40	−31.5
11	–	235	1.85	576.3 (2.25)	8884	33.9	10	−12.5
12	–	198	1.85 (1.88)	581.1 (2.27)	8930	34.5	9	−12.5
13	–	191	1.84	578.9 (2.26)	8887	34.0	9	−12.5
15	–	251	1.81	152.2 (0.52)	8744	32.1	> 40	−10.9
16	–	172	1.88	271.9 (0.84)	9171	39.1	–	0
RDX	–	210	1.80	92.6 (0.42)	8795	34.9	7.4	0

[a] Melting point. [b] Thermal decomposition temperature under nitrogen gas (DSC, 5 °C $\mathrm{min^{-1}}$). [c] Density, measured with gas pycnometer (25 °C); crystal density in parentheses. [d] Heat of formation calculated with Gaussian 03 (solid phase). [e] Calculated detonation velocity with EXPLO5 V6.01. [f] Calculated detonation pressure with EXPLO5 V6.01. [g] Impact sensitivity measured with BAM drophammer. [h] Oxygen balance for $C_aH_bO_cN_d$, 1600 (c−a−b/2)/M_w; M_w = molecular weight. [i] Ref. [6]. [j] Sublimation temperature.

In conclusion, a series of new derivatives of 4,4′-bis(5-nitro-1,2,3-2*H*-triazole) (**4**) was synthesized and characterized. The structures of **6**, **10**, and **12** were further confirmed by single-crystal X-ray analysis. The isomers from the methylation and amination reactions were separated and their properties compared. All the nitrogen-rich compounds derived from (**4**) show relatively high thermal stabilities, and high densities and heats of formation. The introduction of N−NH_2 and the N−O group were found to be effective methods to improve the density and detonation properties of the parent ammonium salt. The compounds with substituent groups in the N3 position of 4,4′-bis(5-nitro-1,2,3-2*H*-triazole) system pos-

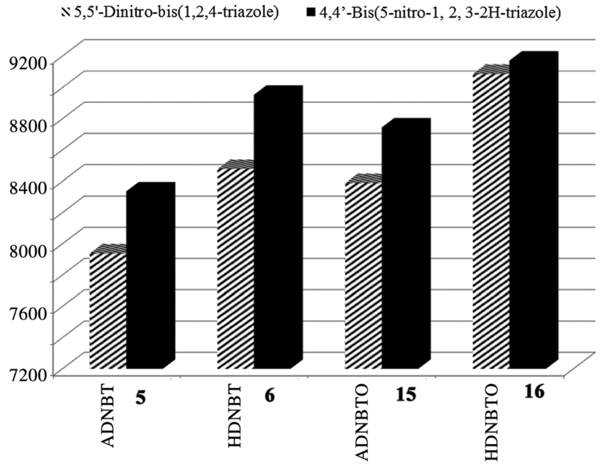


Figure 4. Bar diagram representation of the detonation velocities of isomers (A = ammonium salts, H = hydroxylammonium salts, DNBT = bistriazolate, DNBTO = bistriazololate).

sess slightly better detonation properties than the other isomers with same substituent group at different positions. The detonation properties of compounds in the 4,4′-bis(5-nitro-1,2,3-2*H*-triazole) system are superior to those of the 5,5′-dinitro-4,4′-bis(1,2,4-triazole) system. The derivatives of 4,4′-bis(5-nitro-1,2,3-2*H*-triazole) have the best detonation performance among the reported analogues of fully carbon-nitrated bis(azole) compounds. The calculated detonation properties of compounds **6**, **11**–**13**, **15**, and **16** are comparable to RDX and may make them promising candidates for RDX replacement.

Keywords: amination · bis(1,2,3-triazole) · detonation properties · energetic materials

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 6260–6264
Angew. Chem. **2015**, *127*, 6358–6362

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Received: December 22, 2014