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Synthesis of Benzotriazolo[1,2-*a*]benzotriazole Derivatives as New High Density, Insensitive Energetic Materials

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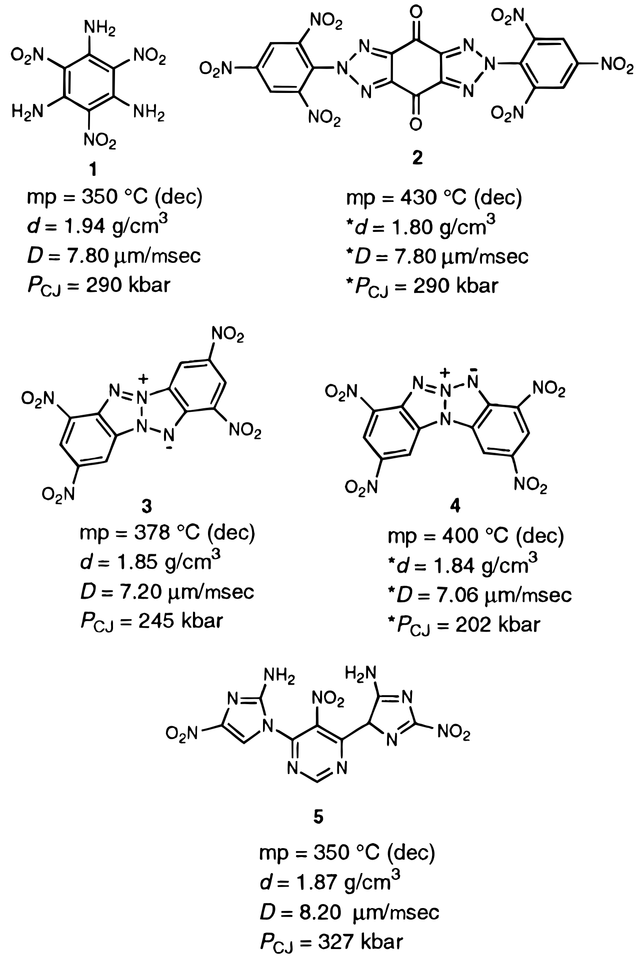
The synthesis of the new high density energetic compound 4,8-dinitro-12*H*-[1,2,5]-oxadiazolo[3,4-*e*][1,2,5]oxadiazolo[3′,4′:4,5]benzotriazolo[1,2-*a*]benzotriazol-13-ium inner salt 1,11-dioxide (**7**) was achieved in three steps (37% yield) from 2,4,8,10-tetranitrobenzotriazolo[1,2-*a*]benzotriazolo-6-ium inner salt (**4**). The compound **7** was found to be thermally stable up to 274 °C and was insensitive to impact (hammer/anvil test).

Introduction

The compounds triaminotrinitrobenzene (**1**, TATB),[1] 2,6-dipicrylbenzo[1,2-*d*][4,5-*d*′]bis-triazole-4,8-dione (**2**),[2] 2,4,8,10-tetranitrobenzotriazolo[2,1-*a*]benzotriazol-6-ium inner salt (**3**, z-Tacot),[3,4] 2,4,8,10-tetranitrobenzotriazolo[1,2-*a*]benzotriazol-6-ium inner salt (**4**, y-Tacot),[5,6] and more recently 5-nitro-4,6-bis(5-amino-3-nitro-1*H*-1,2,4-triazol-1-yl)pyrimidine (**5**, DANTNP)[7] have been developed as insensitive energetic materials for a variety of industrial and military applications (Figure 1). However, despite favorable insensitivity to heat, impact, and electric shock, the density and energetic properties (detonation velocity, *D*; detonation pressure, P_{CJ}) of these compounds are inferior to those observed for the explosives RDX and HMX.[8,9]



1
mp = 350 °C (dec)
d = 1.94 g/cm^3
D = 7.80 μm/msec
P_{CJ} = 290 kbar

2
mp = 430 °C (dec)
*d = 1.80 g/cm^3
*D = 7.80 μm/msec
*P_{CJ} = 290 kbar

3
mp = 378 °C (dec)
d = 1.85 g/cm^3
D = 7.20 μm/msec
P_{CJ} = 245 kbar

4
mp = 400 °C (dec)
*d = 1.84 g/cm^3
*D = 7.06 μm/msec
*P_{CJ} = 202 kbar

5
mp = 350 °C (dec)
d = 1.87 g/cm^3
D = 8.20 μm/msec
P_{CJ} = 327 kbar

Figure 1. Physical and energetic properties of several insensitive energetic compounds. For those compounds in which the energetic properties have not been experimentally determined computed values (*) are indicated (see ref 10).

The design and synthesis of new insensitive energetic compounds with high density and improved energetic properties has been the focus of recent studies in our laboratories.[11−13] Because of the inherent thermal stability of the dibenzotetraazapentalene ring system, **3** and **4** were identified as attractive precursors for the development of new classes of high density insensitive energetic materials. Based on computed densities and energetic properties, the nitro- and furoxano-substituted derivatives **6** and **7** were envisaged as attractive synthetic targets for development of new high density insensitive energetic compounds. The synthesis of 4,11-dinitro[1,2,5]-oxadiazolo[3,4-*e*][1,2,5]oxadiazolo[3′,4′:4,5]benzotriazolo-[2,1-*a*]benzotriazol-6-ium inner salt 1,8-dioxide (**6**, z-DBBD) from **3** has recently been achieved in three steps in 21% overall yield.[11] The z-isomer **6** was found to be thermally stable up to 310 °C and exhibited moderate impact sensitivity (dropweight test (2.5 kg): **6**, 19 cm; RDX$_{std}$, 18 cm).[13] The synthesis of the corresponding y-isomer, 4,8-dinitro-12*H*-[1,2,5]oxadiazolo[3,4-*e*][1,2,5]-oxadiazolo[3′,4′:4,5]benzotriazolo[1,2-*a*]benzotriazol-13-ium inner salt 1,11-dioxide (**7**, y-DBBD) has recently been

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[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1996.

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[4] Carboni, R. A. U.S. Patent 2,904,545, 1959.

[5] Kauer, J. C.; Carboni, R. A. *J. Am. Chem. Soc.* **1967**, *89*, 2633.

[6] Kauer, J. C. U.S. Patent 3,262,943, 1966.

[7] Wartenberg, C.; Charrue, P.; Lavel, F. *Prop. Expl. Pyro.* **1995**, *20*, 23.

[8] Nielsen, A. T. in *Chemistry of Energetic Materials*; Olah, G.; Squire, D. R., Eds., Academic Press Inc.: New York, 1991; pp 95−124.

[9] Meyer, R. in *Explosives*, 3rd ed.; VCH: Weinheim, 1987, pp 150 and 201. [RDX (hexogen); mp 204 °C; d = 1.81 g/cm^3; D = 8.85 mm/s] [HMX (octogen); mp 282 °C; d = 1.9 g/cm^3; D = 9.1 mm/s].

[10] The density d (g/cm^3), detonation velocity D (mm/s), and detonation pressure P_{CJ} (kbar) were computed with a program obtained from the Naval Weapons Center, China Lake, CA.

[11] Subramanian, G.; Boyer, J. H.; Buzatu, D.; Stevens, E. D.; Trudell, M. L. *J. Org. Chem.* **1995**, *60*, 6110.

[12] Subramanian, G.; Boyer, J. H.; Koppes, W.; Sitzmann, M. E.; Nock, L. A.; Gilardi, R.; Russell, T. P.; Trudell, M. L. *J. Org. Chem.* **1996**, *61*, 1898.

[13] Trudell, M. L.; Subramanian, G.; Eck, G.; Boyer, J. H. In *Decomposition, Combustion and Detonation Chemistry of Energetic Materials*; Brill, T. B., Russell, T. P., Tao, W. C., Wardle, R. B., Eds., Materials Research Society Symposium Proceedings: Pittsburgh, PA, 1996; Vol. 418, pp 37−42.

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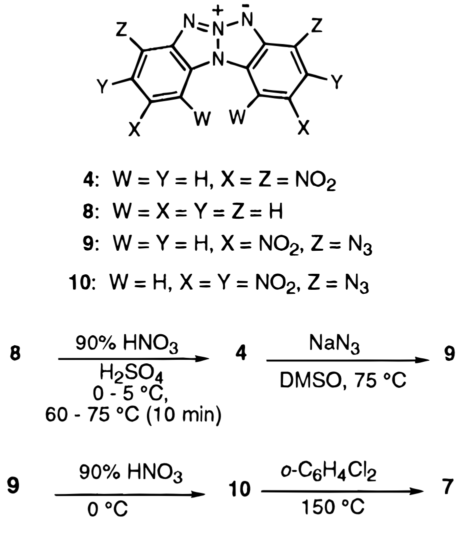
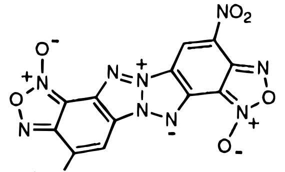
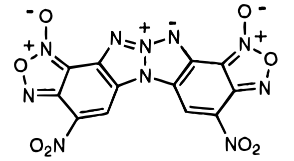
Scheme 1



completed. Herein we wish to describe the synthetic sequence and preliminary insensitivity data for **7**.



6 (z-DBBD)



7 (y-DBBD)

$C_{12}H_2N_{10}O_8$

$^*d = 1.96$ g/cm^3

$^*D = 7.52$ μm/msec

$^*P_{CJ} = 245$ kbar

(*computed values[10])

Results and Discussion

Based on previous studies in the z-isomer system,[11] the synthesis of the target compound **7** was envisaged to proceed from y-Tacot (**4**). The benzotriazolo[1,2-*a*]benzotriazol-6-ium inner salt (**8**) was prepared from *o*-phenylenediamine and 2-chloronitrobenzene according to the procedure developed by Kauer and Carboni.[4] Nitration of **8** was found to proceed cleanly with 90% HNO_3/H_2SO_4 at 0−5 °C, followed by a brief heating period (10 min) at 60−75 °C. This gave the 2,4,8,10-tetranitro derivative **4** as the sole product in 86% yield (Scheme 1). This modified procedure provided **4** in greater yield and in a higher state of purity than the literature nitration conditions.[4] The tetranitro derivative **4** was found to be a strongly fluorescent material [λ_f (acetone) 475 nm, Φ (0.50)]. Although aromatic nitro compounds do not usually possess good luminescent properties, the photophysical properties of **4** are characteristic of nitrated benzotetraazapentalene derivatives.[14] The orientation of the nitro groups in **4** was unequivocally confirmed by X-ray crystallography (Figure 2).[15]

From the X-ray structure, it is readily apparent that one molecule of acetone cocrystallized per molecule of **4**. It is interesting to note that earlier computational studies on simple tetraazapentalenes predicted that a positive electrostatic potential existed above the nitrogen−nitrogen bond of the trivalent nitrogen atoms.[16] In the X-ray structure of **4**·acetone, the electronegative oxygen atoms of the carbonyl of acetone are uniformly oriented throughout the crystal lattice toward this electropositive region of the tetraazapentalene unit of **4**. This is consistent with the computational results and clearly demonstrates for the first time the electronic nature of intermolecular dipolar interactions in a tetraazapentalene system. The stoichiometric cocrystallization of solvent molecules (acetone, DMF) has also been observed (NMR, C,H,N) to take place with other tetraazapentalene derivatives.[11,12]

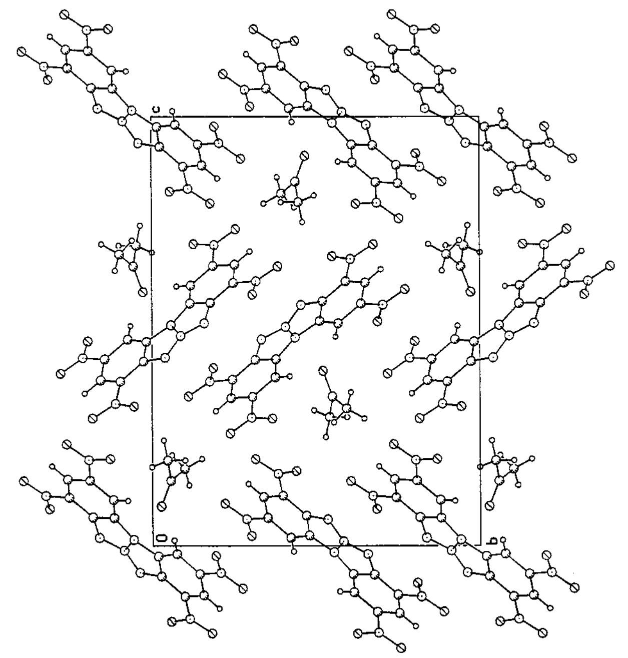


Figure 2.

With multigram quantities of **4** in hand, attention turned toward further functionalization of the benzo rings of **4** for the construction of the furoxan ring systems of the initial target compound **7**. Treatment of **4** with sodium azide in dimethyl sulfoxide furnished a single symmetrical diazido dinitro derivative in 83% yield resulting from nucleophilic substitution of an equivalent pair of nitro groups by the azide anion. The structure of the compound is believed to be that of the symmetrical isomer, 4,8-diazido-2,10-dinitro derivative **9** (Scheme 1). From previous studies with z-Tacot (**3**), nucleophilic substitution of the 4,10-nitro groups (adjacent to the divalent nitrogen atoms of tetraazapentalene moiety) was found to take place regiospecifically.[11] By analogy, the 4,8-nitro groups of **4** are believed to be the site of azide substitution resulting in the formation of **9**.

Nitration of the diazido dinitro derivative **9** proceeded easily to give the 4,8-diazido-2,3,9,10-tetranitro derivative **10** in 76% yield (Scheme 1). The ease of the nitration of **9** stems from activation of the *C(3)*- and *C(9)*-positions toward electrophilic attack by the *ortho*-directing effect of the azido groups.[17] Despite favorable computed density and improved computed energetic properties for **10** ($d = 1.84$ g/cm^3, $D = 8.12$ mm/μs, $P_{CJ} = 301$ kbar),[10] the material was considerably more sensitive than **4**. The diazido tetranitro derivative **10** was found to have good thermal stability (decomposed at 280 °C) but was impact sensitive (violent explosion with flame when struck by a hammer) while **4** was completely stable under these conditions.

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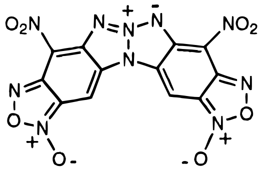
[14] Lu, Q.; Boyer, J. H. *Heteroatom Chem.* **1993**, *4*, 91.

[15] The authors have deposited atomic coordinates for **4**·acetone with the Cambridge Crystallographic Data Center. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

[16] Politzer, P.; Seminario, J. M. *Struct. Chem.* **1990**, *1*, 325.

[17] Biffen, M. E. C.; Miller, J.; Paul, D. B. in *The Chemistry of the Azido Group*; Patai, S., Ed., Wiley and Sons: New York, 1971.

Thermolysis of **10** furnished the new heterocyclic system 4,8-dinitro-12*H*-[1,2,5]oxadiazolo[3,4-*e*][1,2,5]-oxadiazolo[3′,4′:4,5]benzotriazolo[1,2-*a*]benzotriazol-13-ium inner salt 1,11-dioxide (**7**) in 58% yield (Scheme 1). This served to confirm the presence of two sets of contiguous azido and nitro groups and supported the structural assignment of **9**. The structural asignment of **7** was made based on the X-ray structure of z-isomer **6** in which the orientation of the exocyclic oxygen atoms of the furoxan moieties occupied the least sterically hindered site. In addition, the structure of **7** is consistent with the structure of thermodynamically favored 4-nitrobenzofuroxans.[18] However, it should also be noted that without unequivocal confirmation of this structure by X-ray crystallography, the isomer **7′** resulting from the thermal isomerization of **7** must also be considered as a possible structure.[18]



7′

The red microcrystalline material **7** was found to be stable up to temperatures of 274 °C at which point the material decomposed nonexplosively into a tarlike material. In addition, **7** was found to be insensitive to impact (hammer/anvil test). Although no detonation was observed when the material was struck by a hammer, this is a crude test and may not accurately reflect the sensitivity of the compound. We have found a number of moderately sensitive materials to be nonresponsive in this test (*i.e.* **6**, RDX).[11] More accurate experimental measurements have been required to define the sensitivity of these compounds.

Attempts to introduce additional nitro groups at the C(1)- and C(13)-positions of **7** were unsuccessful. Similar to the results obtained in the z-isomer system,[12] attempted nitration of **7** using highly reactive nitration media (100% HNO_3, FSO_3H) resulted in the formation of an intractable mixture of carbonyl-containing compounds. As observed in the z-isomer system, the tetranitro derivatives were very sensitive to moisture and air such that the *o*-dinitro functionality readily decomposed to quinone-like species *via* an unusual hydrolysis/oxidation reaction.[12] In light of the chemical sensitivity of these compounds further attempts to nitrate **7** have been abandoned. The development of new heterocyclic systems which exploit the insensitivity and thermal stability of the tetraazapentalene ring system is currently under investigation.

Experimental Section

All chemicals were purchased from Aldrich Chemical Co., Milwaukee, WI. Reported UV absorptions are restricted to the longest wavelength. Fluorescence quantum yields were determined for solutions in EtOH or DMF with excitation at 460, 540, and 570 nm with sulfarhodamine ($\Phi = 0.68$) and acridine orange ($\Phi = 0.46$) as references. Melting points and decomposition points are uncorrected. Elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, TN, and Midwest Micro Lab, Indianapolis, IN. All reported compounds gave satisfactory carbon and hydrogen analyses. Due to the high nitrogen content and explosive nature of these compounds, some reported microanalytical data for nitrogen were outside the standard acceptable limit of ±0.4%. However, duplicate and triplicate analyses for nitrogen were usually within ±3% of calculated values and corresponded to the empirical formula of the compound. ***Caution*! Compounds 4, 7, 9, and 10 should be handled as potentially explosive materials!**

y-Tacot (4). The dibenzotetraazapentalene **8**[5] (15.6 g, 0.075 mol) was dissolved in sulfuric acid (195 mL), and the mixture was cooled to 10 °C in an ice-bath. Nitric acid (90%, 300 mL) was then added dropwise, keeping the flask temperature below 25 °C. After the addition was complete, the reaction mixture was stirred for 15 min at room temperature and then heated at 60−75 °C for 10 min. The mixture was cooled to 20 °C and poured into ice−water (25 L). The yellow precipitate was filtered, washed with water (3 × 100 mL), and dried. The crude compound (25.8 g) was recrystallized from DMF (550 mL) to give **4** (25.1 g, 86%). An analytical sample was prepared by recrystallization from acetone: mp 398 °C dec [lit.[5] mp 400 °C (dec)]; IR (KBr) ν 3097, 1629, 1586, 1536, 1413, 1377, 726 cm^{-1}; ^1H NMR (DMSO-d_6) δ 10.60 (d, $J = 1.9$ Hz, 2H), 9.31 (d, $J = 1.8$ Hz, 2H); ^{13}C NMR (DMSO-d_6) δ 142.8, 141.2, 135.0, 125.6, 120.7, 116.2; UV (acetone) λ_{max} 452 nm, log ϵ 5.47; λ_f (acetone) 475 nm, Φ 0.50. Anal. Calcd for $C_{12}H_4N_8O_8$: C, 37.12; H, 1.04; N, 28.86. Found: C, 37.02; H, 1.02; N, 27.82.

4,8-Diazido-2,10-dinitrobenzotriazolo[1,2-*a*]benzotriazol-6-ium Inner Salt (9). y-Tacot (**4**) (17.5 g, 45 mmol) and sodium azide (23.4 g, 360 mmol) in dry DMSO (600 mL) were heated at 70−75 °C for 24 h. The mixture was then cooled at 15 °C for 1.5 h, and the yellow-orange solid which separated was collected by filtration and washed with ethyl alcohol (100 mL) and diethyl ether (100 mL) to give **9** (14.3 g, 83%). The crude compound was used directly in the next step without any further purification. A pure sample was prepared for analysis by recrystallization from DMF: mp 175−176 °C dec; IR (KBr) ν 3072, 2123, 1542, 1522, 1337, 1115, 741 cm^{-1}; ^1H NMR (DMSO-d_6) δ 9.82 (d, $J = 1.8$ Hz, 2H), 8.20 (d, $J = 1.7$ Hz, 2H), 2.80 (s, 3H, DMF), 2.72 (s, 3H, DMF). Anal. Calcd for $C_{12}H_4N_{12}O_4{\cdot}C_3H_7NO$: C, 39.76; H, 2.43; N, 40.16. Found: C, 39.71; H, 2.52; N, 39.27.

4,8-Diazido-2,3,9,10-tetranitrobenzotriazolo[1,2-*a*]benzotriazol-6-ium Inner Salt (10). Nitric acid (90%, 47.5 mL) was cooled in an ice-bath, and **9** (12.6 g, 0.033 mol) was added keeping the temperature below 10 °C. Stirring was continued for 2 h at 0−5 °C. The mixture was poured into ice−water (1 L), and the orange-brown precipitate was filtered, washed with water (100 mL), and dried to give **10** (11.9 g, 76%). The crude compound was dissolved in acetone (12.5 mL) at 40 °C. The insoluble material was removed and triturated with hexane (20 mL). The mixture was kept in a freezer overnight, and the precipitate was filtered. The material was then recrystallized from acetone to give **10** (0.9 g, 41%): mp 280 °C dec; IR (KBr) ν 2144, 1558, 1507, 1339, 1320, 1292, 907, 820 cm^{-1}; ^1H NMR (acetone-d_6) δ 10.13 (s, 2H); ^{13}C NMR (acetone-d_6) δ 140.9, 136.8, 133.2, 124.2, 122.1, 108.7. Anal. Calcd for $C_{12}H_2N_{14}O_8{\cdot}C_3H_6O$: C, 34.10; H, 1.53; N, 37.12. Found: C, 33.78; H, 1.58; N, 34.43.

y-BDDB (7). The tetranitrodiazide **10** (10.0 g, 21 mmol) in 1,2-dichlorobenzene (650 mL) was heated for 1 h at 150 °C. The mixture was cooled in an ice-bath for 2 h, and the precipitate was filtered and washed with diethyl ether. The filtrate was triturated with acetonitrile to give **7** (6.0 g, 58%) in pure form: mp 274−275 °C dec; IR (KBr) ν 1654, 1575, 1534, 1414, 1330, 1296, 999, 704 cm^{-1}; ^1H NMR (DMSO-d_6) δ 10.42 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 146.6, 134.6, 132.5, 123.7, 117.2, 107.5. Anal. Calcd for $C_{12}H_2N_{10}O_8$: C, 34.80; H, 0.49; N, 33.82. Found: C, 34.78; H, 0.58; N, 31.23.

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[18] For a relavent review, see: Gasco, A.; Boulton, A. J. *Adv. Heterocycl. Chem.* **1981**, *29*, 251.