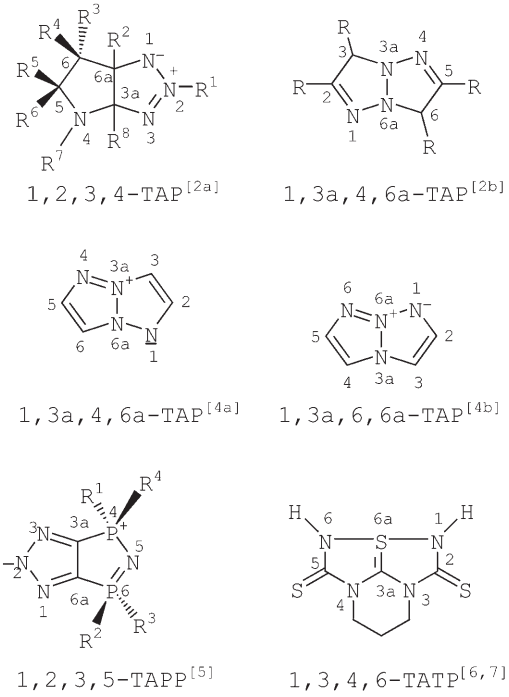

Scheme 1. The structures of tetraazapentalenes (TAPs), tetraazaphosphapentalenes (TAPPs), tetraazathiapentalenes (TATPs), and tetraazaselenapentalenes (TASPs).

Explosives

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Tetraazapentalene Chemistry: Unexpected Intramolecular Electron Rearrangement Induced by Highly Reactive ψ-Dinitroso Substituents**

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Tetraazapentalenes (TAP),[1–4] tetraazaphosphapentalenes (TAPP),[5] tetraazathiapentalenes (TATP),[6–7] tetraazaselenapentalenes (TASP),[8–9] and their derivatives (Scheme 1) are of special interest owing to their unusual electronic structure and chemical behavior which is governed by the striking orientations of the heteroatoms. These heterocyclic systems promise a variety of applications including in organic synthesis, redox chemistry, and in industry, military, and space programs. Some examples of these applications include the derivatization of π-hypervalent heterocyclic TATP,[10–12] the synthesis of versatile heterocyclic compounds,[13–15] exotic metal carbene chemistry,[16–20] shaped charges for downhole penetrators,[21] and thermally stable high-energy materials.[22–26] Much attention has been focused on the preparation (precursors and methods) and properties of the heterocyclic tetraazapentalenes and their derivatives because their applications depend significantly on their thermal stability, performance, and synthetic practicality.

We are interested in the preparation of high-nitrogen-content energetic materials, heterocyclic high-density materials, and green primary explosives for a wide variety of applications through the utilization of tetrazines,[27] tetrazoles,[28] triazines,[29] furazans,[30] triazoles,[31] pyridines,[32] and azetidines.[33] Our interest in heterocyclic tetraazapentalenes was to probe the explosive performance (detonation velocity (V_D) and detonation pressure (P_{CJ})) of previously synthesized, thermally stable high-energy compounds and to

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develop candidates with a better performance for realistic and yet practical applications.

Maquestiau et al. reported the preparation and partial physical characterization (MS: $[M^+] = 389$; IR: $\tilde{\nu} = 1530$ and 1320 cm^{-1}) of **1**, but neither crystal structure, thermal stability, sensitivity, nor explosive performance were provided.[34–35] Herein, we report an improved preparation of **1**, its full characterization, including energetic properties, and its novel reactivity through intramolecular electron rearrangement. The details of the three-step preparation are shown in Scheme 2.

The condensation reaction between benzotriazole and 2-chloro-3-nitropyridine was performed in acetonitrile in the presence of Na_2CO_3, to give regioisomer **1A**, which then underwent ring closure by treatment with $P(OEt)_3$ in refluxing xylene to yield **1B**. After its dissolution in H_2SO_4 (98%) at

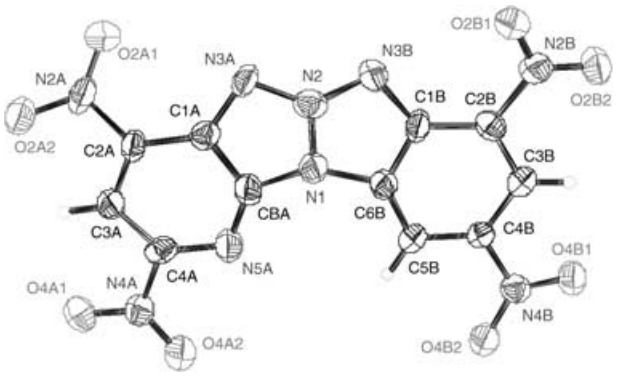
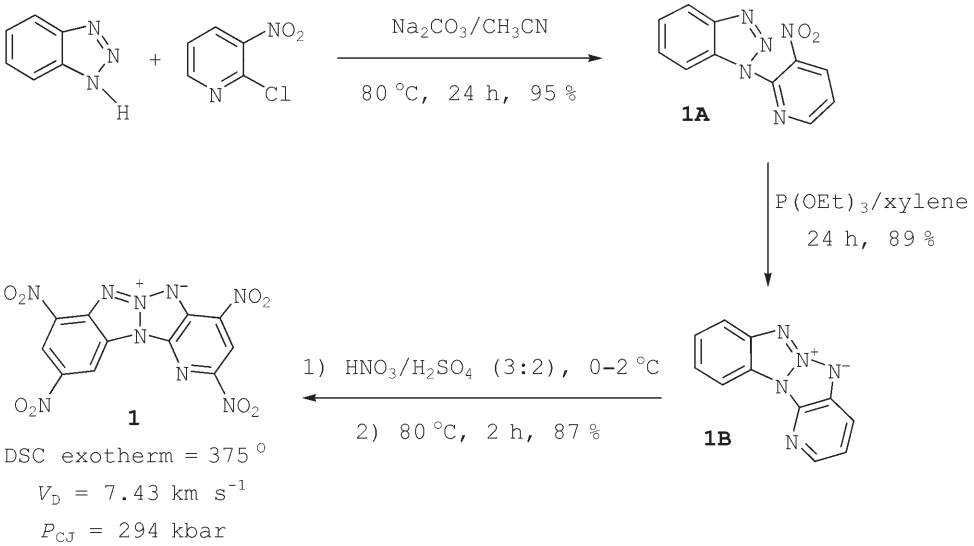


Figure 1. The ORTEP diagram (ellipsoids drawn at the 25% probability level) with labeling scheme for **1**. Selected bond lengths [Å] and angles [°]: N1-N2 1.370(14), N2-N3A 1.337(12), N2-N3B 1.330(13), N1-N2-N3A 114.2(11), N2-N1-C6A 108.3(11), N3A-C1A-C6A 111.5(12).



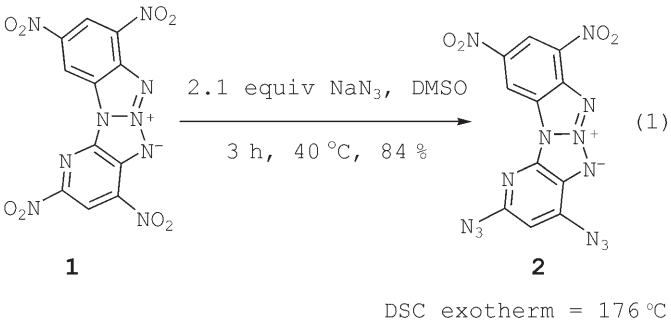
Scheme 2. Detailed preparation of **1**.

5 °C, HNO_3 (90%) was slowly added, while the temperature was maintained below 2 °C. The reaction mixture was stirred vigorously at 80 °C for 2 h, cooled to room temperature, and poured onto crushed ice. Once filtered and washed with cold water, the yellow product was triturated consecutively with a minimum amount of acetone, acetonitrile, and methanol to remove any remaining acids.[21]

Isolated **1** was characterized by X-ray crystallography,[36a] differential scanning calorimetry (DSC, exotherm of fast decomposition), heat of formation, and UV/Vis, IR, and ^1H and ^{13}C NMR spectroscopy.[37] The X-ray crystal structure of **1** (grown through the slow evaporation of a solution in nitromethane), is shown in Figure 1.

Overall, the reaction sequence shown in Scheme 2 gives **1** in 74% yield, which is two and half times greater than that reported by Maquestiau et al.[34–35] Furthermore, the duration of the nitration reaction is much shorter (2 vs 48 h), and both solvents (acetonitrile from the condensation reaction and xylenes from the ring-closure step) are subsequently distilled to allow recovery and reuse. Compound **1** has a thermal stability similar to that of the other well-known thermally stable analogues shown in Scheme 3, but exhibits the highest experimentally measured V_D and P_{CJ}. As a consequence, the combination of better reaction yield, cheaper production cost, and higher performance has made **1** attractive for use in realistic and practical applications.[21]

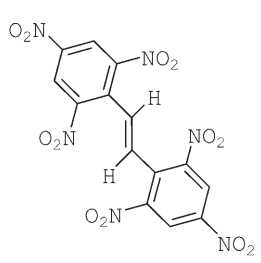
A stoichiometric reaction between **1** and NaN_3 in DMSO at 40 °C gave **2**. After the reaction was cooled to room temperature, water was added to precipitate the analytically pure brown product, which was filtered, washed thoroughly with water, and air-dried, [Eq. (1)].



(1)

Compound **2** was characterized by DSC, elemental analysis, and UV/Vis, IR, and ^1H and ^{13}C NMR spectroscopy.[38] **Caution!** Compound **2** is very sensitive to sparks, friction, and impact,[39] hence, plastic spatulas should be used. This reaction should be performed within a fume hood fitted with a thick blast shield. Grounding straps, thick gloves, and a face shield should be worn at all times.

The reaction shown in Equation (2) exhibits the same nucleophilic disubstitution of the benzopyridotetraazapenta-



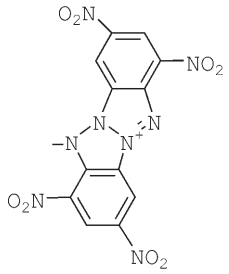
HNS

DSC exotherm = 315 °C

ρ = 1.74 g cm^{-3}

V_D = 7.00 km s^{-1}

P_{CJ} = 199 kbar



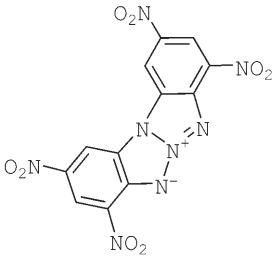
Z-shaped TACOT

DSC exotherm = 378 °C

ρ = 1.85 g cm^{-3}

V_D = 7.20 km s^{-1}

P_{CJ} = 245 kbar



T-shaped TACOT

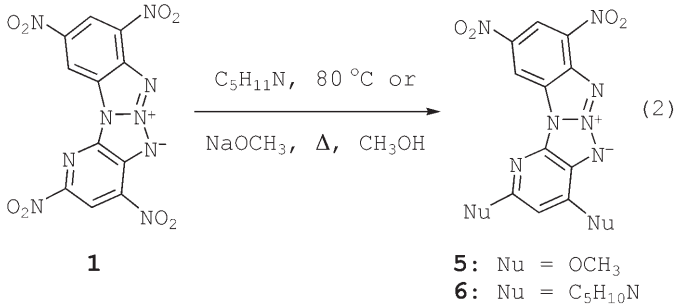
DSC exotherm = 400 °C

ρ = 1.84 g cm^{-3}

V_D = 7.06 km s^{-1}

P_{CJ} = 202 kbar

Scheme 3. Some common thermally stable compounds.



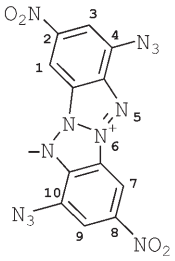
1

5: Nu = OCH_3

6: Nu = $C_5H_{10}N$

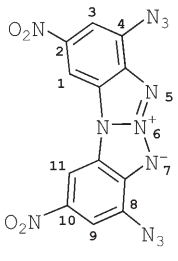
lene (BPTAP) backbone. However, it was necessary to use a large excess of nucleophile (sodium methoxide or piperidine) in the appropriate solvent and to heat the reaction mixtures at reflux or at 80 °C. The isolated product was purified through column chromatography.

The disubstitution pattern of **2**, **5**, and **6** in Equations (1) and (2) is unique when compared to those of the Z-shaped and T-shaped isomers of dibenzotetraazapentalene (BBTAP; **7**) and dipyridotetraazapentalene (PPTAP; **9**).[22–24] As shown in Scheme 4, substitution by the azide group occurred only *ortho* to the N bridgeheads.[22–24] Even with excess NaN_3, higher temperature, and longer reaction time, only one azide group substituted on each side of the BBTAP and PPTAP systems.



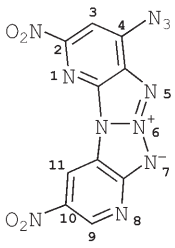
BBTAP (**7**)

DSC exotherm = 187 °C



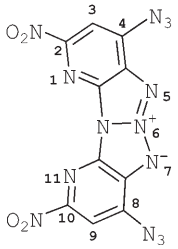
BBTAP (**8**)

DSC exotherm = 176 °C



PPTAP (**9**)

DSC exotherm = 173 °C



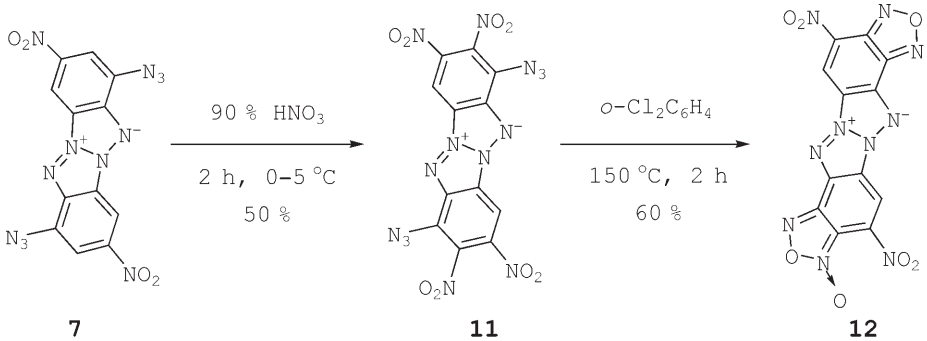
PPTAP (**10**)

DSC exotherm = 157 °C

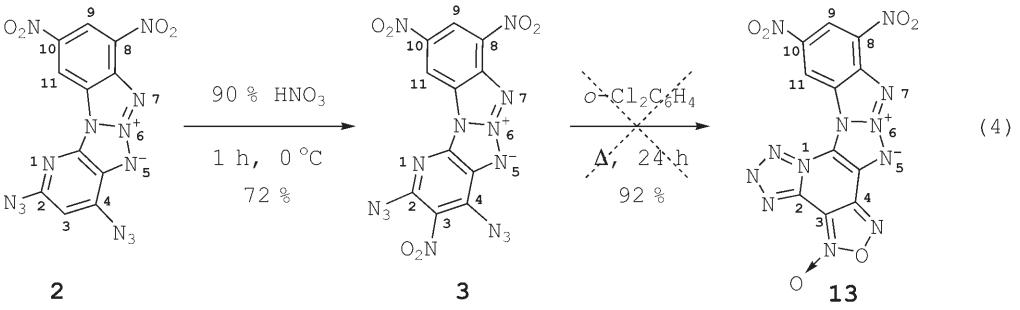
Scheme 4. Diazido-substituted isomeric tetraazapentalenes.

Based on the preparation of **12** (nitrogen atoms form a Z-shaped structure) from **7**[22] [Eq. (3)] or the analogous compound from **8** (the nitrogen atoms in a T-shaped structure),[23] we predicted that the nitration of **2**, followed by azido–nitro ring closure, would give the corresponding furoxano–tetrazolo product **13** as shown in Equation (4).

The reaction shown in Equation (4) did not form **13**, but rather took a substantially different pathway as shown in

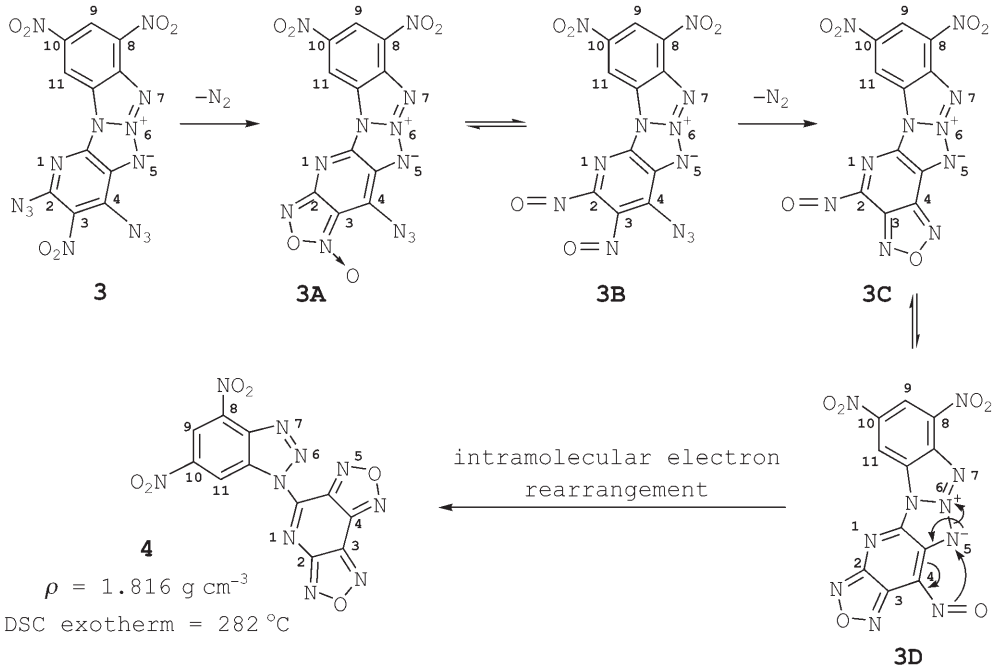


7 **11** **12**



(4)

Scheme 5. The adjacent 2-azido and 3-nitro positioning provoked the elimination of molecular nitrogen followed by ring closure to form the corresponding furazan *N*-oxide compound **3A** or the resonance hybrid ψ-2,3-dinitroso compound **3B**. The presence of the ψ-3-nitroso group triggers the elimination of the second nitrogen molecule and subsequent ring closure to form **3C**, which is the valence isomer of **3D**. The ψ-4-nitroso substituent in **3D** stimulates an intramolecular electron rearrangement to open the T-shaped tetraazapentalene backbone to form **4**. This is the first example of the ring opening of the T-shaped tetraazapentalene isomer. This ring opening is unlike the ring scissions of the Z-shaped TACOT, which was attacked either by oxidation with peracetic acid,[41] reduction with lithium aluminum hydride (or copper(I) cyanide),[41] or nucleophilic substitution with sodium methoxide.[42] The unpredicted product **4** was confirmed through the X-ray crystal structure shown in Figure 2,[36b] and fully characterized by DSC, elemental analysis, and UV/Vis, IR, and ^{1}H and ^{13}C NMR spectroscopy.[43]



Scheme 5. Proposed reaction mechanism for the formation of **4**.

These results are important in demonstrating the improved preparation of **1**, which may lead to a variety of realistic and yet practical applications. Ring scission of the T-shaped tetraazapentalene isomer is novel as it occurs through an unpredicted intramolecular electron rearrangement activated by the highly reactive ψ-dinitroso substituents of **3c**.

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Keywords: azides · nitrogen heterocycles · reactive intermediates · rearrangement · ring opening

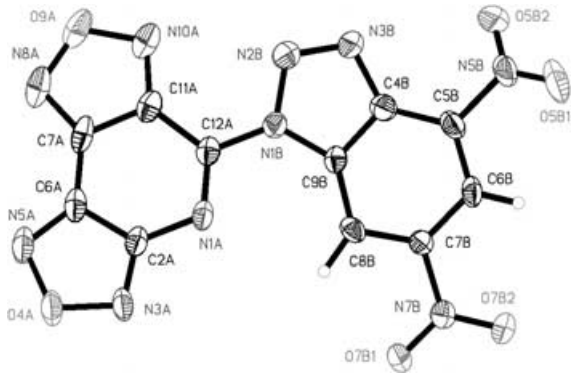

Figure 2. The ORTEP diagram (ellipsoids drawn at the 25% probability level) with labeling scheme for **4**. Selected bond lengths [Å] and angles [°]: N1B–N2B 1.375(4) N2B-N3B = 1.284(3), N1OA-C11A 1.313(4), N1B-N2B-N3B 108.8(2), N2B-N3B-C4B 108.4(3), N2B-N3B-C9B 109.7(2).

[1] a) D. Balachari, M. L. Trudell, *Tetrahedron Lett.* **1997**, *38*, 8607–8610; b) V. Galasso, D. Jones, A. Modelli, M. L. Trudell, *Chem. Phys.* **2000**, *254*, 375–384; c) M. P. Groziak, S. R. Wilson, G. L. Clauson, N. J. Leonard, *J. Am. Chem. Soc.* **1986**, *108*, 8002–8006; d) A. M. Halpern, C. J. Ruggles, X.-K. Zhang, M. P. Groziak, N. J. Leonard, *J. Phys. Chem.* **1987**, *91*, 1366–1367; e) B. Bhat, K. A. Cruickshank, N. J. Leonard, *J. Org. Chem.* **1989**, *54*, 2028–2030.

[2] a) D. Ramaiah, N. P. Rath, M. V. George, *Acta Crystallogr. Sect. C* **1998**, *54*, 872–875; b) M. Brufani, G. Casini, W. Fedeli, F. Mazza, A. Vaciago, *Gazz. Chim. Ital.* **1971**, *101*, 322–343; c) G. Subramanian, M. L. Trudell, J. H. Boyer, *Heteroat. Chem.* **1996**, *7*, 163; d) G. Subramanian, M. L. Trudell, J. H. Boyer, *Heteroat. Chem.* **1995**, *6*, 391–395; e) A. Gunasekaran, T. Jayachandran, J. H. Boyer, M. L. Trudell, *J. Heterocycl. Chem.* **1995**, *32*, 1405–1407; f) A. Gunasekaran, M. L. Trudell, J. H. Boyer, *Heteroat. Chem.* **1994**, *5*, 441–446; g) K. A. Cruickshank, K. Sumoto, N. J.

Leonard, *Tetrahedron Lett.* **1985**, *26*, 2723 – 2726; h) D. E. Pereira, N. J. Leonard, *Tetrahedron Lett.* **1986**, *27*, 4129 – 4132.
[3] a) J. Kalinowski, P. Nantka-Namirski, I. Szczerek, *Pol. Acad. Sci.* **1977**, *34*, 9 – 15; b) P. Nantka-Namirski, J. Kalinowski, *Pol. Acad. Sci.* **1974**, *31*, 125 – 136 and P. Nantka-Namirski, J. Kalinowski, *Pol. Acad. Sci.* **1974**, *31*, 137 – 145; c) P. Nantka-Namirski, J. Kalinowski, *Pol. Acad. Sci.* **1971**, *28*, 219 – 221; d) N. Matsumura, M. Tomura, Y. Tsuchiya, S. Yoneda, M. Nakamura, *Chem. Express* **1986**, *1*, 487 – 490; e) M. D. Bargamova, M. Y. Antipin, L. S. German, Y. T. Struchkov, *Dokl. Akad. Nauk* **1993**, *329*, 44 – 47; f) K. C. V. Ramanaiah, E. D. Stevens, M. L. Trudell, *J. Heterocycl. Chem.* **2000**, *37*, 1597 – 1602.
[4] a) R. A. Carboni, J. E. Castle, *J. Am. Chem. Soc.* **1962**, *84*, 2453 – 2454; b) R. A. Carboni, J. C. Kauer, J. E. Castle, H. E. Simmons, *J. Am. Chem. Soc.* **1967**, *89*, 2618 – 2625; c) J. C. Kauer, R. A. Carboni, *J. Am. Chem. Soc.* **1967**, *89*, 2633 – 2637; d) Y. T. Chia, H. E. Simmons, *J. Am. Chem. Soc.* **1967**, *89*, 2638 – 2643; e) R. J. Harder, R. A. Carboni, J. E. Castle, *J. Am. Chem. Soc.* **1967**, *89*, 2643 – 2647; f) M. E. Grice, P. Politzer, *J. Mol. Struct.* **1995**, *358*, 63 – 69; g) W. Selig, B. J. Mallon, *Explosivstoffe* **1968**, *16*, 266 – 273; h) J. H. Hall, *J. Org. Chem.* **1971**, *36*, 217; i) A. Matsumot, J. H. Lee, M. Yoshida, O. Simamura, *Chem. Lett.* **1973**, 455 – 456; j) G. Norwitz, H. Gordon, *Appl. Spectrosc.* **1975**, *29*, 521 – 523; k) M. B. Laing, R. A. Sparks, M. J. Laing, K. N. Trueblood, *Acta Crystallogr. Sect. B* **1976**, *32*, 2518 – 2520.
[5] S. Trofimenko, A. L. Rheingold, C. D. Incarvito, *Angew. Chem.* **2003**, *115*, 3630 – 3633; *Angew. Chem. Int. Ed.* **2003**, *42*, 3506 – 3509.
[6] a) F. Iwasaki, K. Akiba, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2581 – 2583; b) M. Tomura, O. Mori, H. Chikusa, K. Inazu, A. Ito, N. Matsumura, H. Inoue, *Synthesis* **1991**, 457 – 459.
[7] N. Matsumura, T. Konishi, H. Hayashi, M. Yasui, F. Iwasaki, K. Mizuno, *J. Heterocycl. Chem.* **2002**, *39*, 189 – 202.
[8] N. Matsumura, M. Tomura, H. Inoue, *J. Heterocycl. Chem.* **1989**, *26*, 1655 – 1657.
[9] F. Iwasaki, H. Murakami, N. Yamazaki, M. Yasui, M. Tomura, N. Matsumura, *Acta Crystallogr. Sect. C* **1991**, *47*, 998 – 1003.
[10] a) N. Matsumura, O. Mori, T. Takeguchi, Y. Okumura, K. Mizuno, *J. Heterocycl. Chem.* **2004**, *41*, 873 – 876; b) N. Matsumura, R. Hirase, O. Mori, H. Inoue, *Chem. Lett.* **1993**, *5*, 865 – 868.
[11] a) G. Morel, E. Marchand, S. Sinbandhit, L. Toupet, *Heteroat. Chem.* **2003**, *14*, 95 – 105; b) F. Iwasaki, S. Kakuma, S. Yoshida, S. Murata, M. Yasui, *Phosphorus Sulfur Relat. Elem.* **1994**, *95–96*, 515 – 516.
[12] M. Tomura, O. Mori, N. Matsumura, H. Inoue, *J. Heterocycl. Chem.* **1991**, *28*, 221 – 224.
[13] a) N. Matsumura, A. Ito, M. Tomura, Y. Okumura, K. Mizuno, *J. Heterocycl. Chem.* **2004**, *41*, 99 – 102; b) L. L. Lai, D. H. Reid, R. H. Nicol, J. B. Rhodes, *Heteroat. Chem.* **1994**, *5*, 149 – 157.
[14] M. Tomura, N. Matsumura, O. Mori, H. Chikusa, S. Kamitani, H. Inoue, *J. Heterocycl. Chem.* **1990**, *27*, 2215 – 2217.
[15] G. Labbe, N. Weyns, I. Sannen, P. Delbeke, S. Toppet, *J. Heterocycl. Chem.* **1991**, *28*, 405 – 409.
[16] N. Matsumura, J. Kawano, N. Fukunishi, H. Inoue, M. Yasui, H. Iwasaki, *J. Am. Chem. Soc.* **1995**, *117*, 3623 – 3624.
[17] M. Yasui, S. Yoshida, S. Kakuma, S. Shimamoto, N. Matsumura, F. Iwasaki, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2739 – 2747.
[18] F. Iwasaki, N. Manabe, M. Yasui, N. Matsumura, N. Kamiya, H. Iwasaki, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2749 – 2757.
[19] F. Iwasaki, M. Yasui, S. Yoshida, H. Nishiyama, S. Shimamoto, N. Matsumura, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2759 – 2770.
[20] N. Manabe, M. Yasui, H. Nishiyama, S. Shimamoto, N. Matsumura, F. Iwasaki, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2771 – 2780.
[21] M. H. V. Huynh, M. A. Hiskey, *J. Energ. Mater.* **2004**, *22*, 109 – 115.
[22] G. Subramanian, G. Eck, J. H. Boyer, E. D. Stevens, M. L. Trudell, *J. Org. Chem.* **1996**, *61*, 5801 – 5803, and references therein.
[23] G. Subramanian, J. H. Boyer, D. Buzatu, E. D. Stevens, M. L. Trudell, *J. Org. Chem.* **1995**, *60*, 6110 – 6113, and references therein.
[24] D. Balachari, E. D. Stevens, M. L. Trudell, D. Beardall, C. A. Wight, *Propellants Explos. Pyrotech.* **2000**, *25*, 75 – 80, and references therein.
[25] a) J. Kerth, S. Lobbecke, *Propellants Explos. Pyrotech.* **2002**, *27*, 111 – 118; b) X. N. Diwu, B. Z. Lin, *Theo. Pract. Energ. Mater.* **2003**, *5*, 144 – 148; c) T. B. Brill, H. Ramanathan, R. W. Beal, *Combust. Energ. Mater.* **2002**, 22 – 30; d) Z.-X. Li, Y.-X. Ou, B.-R. Chen, *J. Beijing Inst. Technol. (Engl. Ed.)* **2001**, *10*, 322 – 325; e) A. Hammerl, T. M. Klapotke, H. Noth, M. Warchhold, G. Holl, M. Kaiser, U. Ticmanis, *Inorg. Chem.* **2001**, *40*, 3570 – 3575, and references therein; f) S. F. Son, H. L. Berghout, C. A. Bolme, D. E. Chavez, D. L. Naud, M. A. Hiskey, *Proc. Combust. Inst.* **2000**, *28*, 919 – 924; g) J. R. Stine, *Mater. Res. Soc. Symp. Proc.* **1993**, *296*, 3 – 12; h) R. Haiges, J. A. Boatz, A. Vij, M. Gerken, S. Schneider, T. Schroer, K. O. Christe, *Angew. Chem.* **2003**, *115*, 6027 – 6031; *Angew. Chem. Int. Ed.* **2003**, *42*, 5847 – 5851, and references therein.
[26] M. H. V. Huynh, M. A. Hiskey, **2004**, Patent pending.
[27] M. H. V. Huynh, M. A. Hiskey, J. G. Archuleta, E. L. Roemer, R. D. Gilardi, *Angew. Chem.* **2004**, *116*, 5776 – 5779; *Angew. Chem. Int. Ed.* **2004**, *43*, 5658 – 5661, and references therein.
[28] M. A. Hiskey, N. Goldman, J. R. Stine, *J. Energ. Mater.* **1998**, *16*, 119 – 127.
[29] M. H. V. Huynh, M. A. Hiskey, E. L. Hartline, D. P. Montoya, R. D. Gilardi, *Angew. Chem.* **2004**, *116*, 5032 – 5036; *Angew. Chem. Int. Ed.* **2004**, *43*, 4924 – 4928, and references therein.
[30] D. E. Chavez, L. Hill, M. A. Hiskey, S. Kinkead, *J. Energ. Mater.* **2000**, *18*, 219 – 236.
[31] M. H. V. Huynh, M. A. Hiskey, *J. Energ. Mater.* **2005**, *23*, 27 – 32.
[32] M. D. Coburn, J. L. Singleton, *J. Heterocycl. Chem.* **1972**, *9*, 1039 – 1044.
[33] M. A. Hiskey, M. D. Coburn, M. A. Stinecipher, M. A. Mitchell, B. C. Benicewicz, *J. Heterocycl. Chem.* **1992**, *29*, 1855 – 1856.
[34] A. Maquestiau, M. Flammang-Barbieux, E. Vilain, Pfister- G. Guillouzo, *Bull. Soc. Chim. Belges* **1983**, *92*, 67 – 75.
[35] A. Maquestiau, M. Flammang-Barbieux, E. Vilain, G. Pfister-Guillouzo, *Bull. Soc. Chim. Belges* **1986**, *95*, 1117 – 1122.
[36] CCDC-277008 (**1**) and -277007 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.
[37] Characterization of **1**: DSC: exotherm at 375 °C; heat of formation (ΔH_f): 90.4 kcal mol^{-1}; UV/Vis (DMSO): λ_{max} (ε, M^{-1}cm^{-1}) = 472 (1.55×10^4), 314 (5.86×10^3), and 258 nm (5.65×10^3); IR (nujol): $\tilde{\nu}$ = 1599 (vs), 1589 (vs), 1556 (vs), and 1537 (vs) ($\nu(NO_2)$); 1453 (vs), 1417 (vs), 1372 (vs), 1336 (vs), 1249 (vs), 1178 (vs), 1123 (vs), 1108 (vs), 1056 (vs), 938 (vs), 910 (vs), 896 (vs), 864 (vs), 837 (vs), 782 (vs), 756 (vs), 740 (vs), 727 (vs), 718 (vs), 694 (vs), 612 (vs), 550 (vs), and 481 cm^{-1} (vs) (ν(BPTAP)); ^{1}H NMR (300 MHz, [D$_6$]DMSO, 85 °C): δ = 9.27 (*s*, 1H), 9.30 (*d*, J = 2.0 Hz, 1H), 9.38 ppm (*d*, J = 2.0 Hz, 1H); and ^{13}C NMR (300 MHz, [D$_6$]DMSO, 85 °C): δ = 103.1, 111.2, 118.9, 122.8, 130.9, 132.5, 135.2, 139.6, 140.9, 153.6, 157.8 ppm.
[38] Characterization of **2**: DSC: exotherm at 176 °C; elemental analysis :calcd for $C_{11}H_3N_{13}O_4$: C 34.66, H 0.79, N 47.76; found: C 34.78, H 0.81, N 47.12; UV/Vis (DMSO): λ_{max}(ε, M^{-1}cm^{-1}) = 469 (9.55×10^3), 335 (5.17×10^3), 267 nm (1.51×10^4); IR (nujol): $\tilde{\nu}$ = 2133 (vs) and 2121 (vs) (ν (N_3)); 1586 (vs), 1533 (vs) ($\nu(NO_2)$); 1457 (vs), 1375 (vs), 1333 (vs), 1289 (vs), 1262 (vs), 1243 (vs), 1192 (vs), 1165 (vs), 1109 (vs), 1057 (vs), 938 (vs), 924 (vs), 863 (vs), 844 (vs), 776 (vs), 738 (vs), 718 (vs), 652 (vs), 576

(vs), 535 cm^{-1} (vs) (ν(BPTAP)); ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 7.26$ (*s*, 1H), 9.18 (d, $J = 2.0$ Hz, 1H), 9.06 ppm (d, $J = 2.0$ Hz, 1H); ^{13}C NMR (300 MHz, [D$_6$]DMSO, 80 °C): $\delta = 103.9$, 111.5, 119.5, 122.8, 127.6, 131.8, 136.2, 138.9, 141.4, 141.6, 152.9 ppm.

[39] For explosive sensitivity testing, see: R. T. Paine, W. Koestle, T. T. Borek, E. Duesler, M. A. Hiskey, *Inorg. Chem.* **1999**, *38*, 3738 – 3743.

[40] A. Maquestiau, M. Flammang-Barbieux, E. Vilain, G. Pfister-Guillouzo, *Bull. Soc. Chim. Belges* **1984**, *93*, 973 – 982.

[41] R. A. Carboni, J. C. Kauer, W. R. Hatchard, R. J. Harder, *J. Am. Chem. Soc.* **1967**, *89*, 2626 – 2633.

[42] K. L. Altmann, A. P. Chafin, L. H. Merwin, W. S. Wilson, R. Gilardi, *J. Org. Chem.* **1998**, *63*, 3352 – 3356.

[43] Characterization of **4**: DSC: exotherm. at 282 °C; elemental analysis: calcd for $C_{11}H_2N_{10}O_6$: C 35.69, H 0.54, N 37.84; found: C 35.73, H 0.61, N 38.1; UV/Vis (DMSO): λ_{max} (ε, $M^{-1}cm^{-1}$) = 530 (1.27×10^3), 471 (1.71×10^3), 335 nm (9.47×10^3); IR (nujol): $\tilde{\nu} =$ 1556 (vs), 1541 (vs) ($\nu(NO_2)$); 1498 (vs), 1458 (vs), 1377 (vs), 1347 (vs), 1224 (vs), 1137 (vs), 1058 (vs), 1023 (vs), 995 (vs), 945 (vs), 927 (vs), 880 (vs), 802 (vs), 746 (vs), 724 (vs), 680 (vs), 637 (vs), 611 cm^{-1} (vs) (ν(BPTAP)); ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 9.16$ (d, $J = 2.0$ Hz, 1H), 9.69 ppm (d, $J =$ 2.0 Hz, 1H); ^{13}C NMR (300 MHz, [D$_6$]DMSO, 80 °C): $\delta =$ 116.7, 118.8, 132.9, 136.2, 138.6, 140.5, 143.1, 143.8, 147.2, 148.2, 157.6 ppm.

