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Reactions of Benzotriazolo[2,1-*a*]benzotriazole Derivatives. 1. Synthesis of New Insensitive High-Density Energetic Compounds

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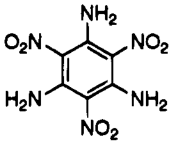
The sequential preference of electrophilic attack on the dibenzotetraazapentalene ring system **6** has unequivocally been shown to be in the order of position 2(8) > 4(10) ≫ 1(7) and 3(9). However, nucleophilic substitution reactions with sodium azide were found to be substrate dependent. Substitution occurred at the 3(9)-position of **9** followed by elimination of hydrogen chloride to give **10** while direct substitution of azide for the 4(10)-nitro group of **2** was found to yield **13**. The reactivity of the dibenzotetraazapentalene derivatives toward electrophiles and nucleophiles was exploited for the synthesis of the new heterocyclic system 14*H*-[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 (**11**). From this study the first of a new class of insensitive energetic materials **4** has been synthesized in a straightforward fashion from **2**.

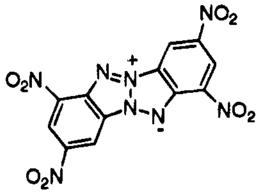
Introduction

There is a need for high-energy, high-density molecules with composition restricted to carbon, hydrogen, nitrogen, and oxygen atoms which possess significant insensitivity to heat, friction, and impact for applications in industry, the military, and the space program.[1–3] Triaminotrinitrobenzene (**1**, TATB),[2] 2,4,8,10-tetranitrobenzotriazolo[2,1-*a*]benzotriazol-6-ium inner salt (**2**, Tacot),[4] and 2,6-dipicrylbenzo[1,2-*d*][4,5-*d*′]bistriazole-4,8-dione (**3**)[5,6] are examples of some of the compounds employed as insensitive energetic materials. However, despite favorable insensitivity, the density and energetic properties (detonation velocity, *D*; detonation pressure, P_{CJ}) of these compounds are inferior to those observed for more conventional explosives.[1,7]



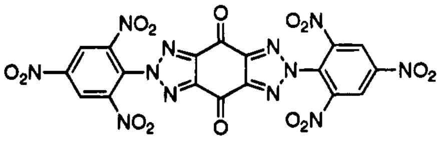
1

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



2

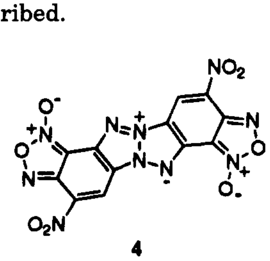
mp = 378 °C (dec)
d = 1.85 g/cm^3
D = 7.20 mm/μsec
P_{CJ} = 245 kbar



3

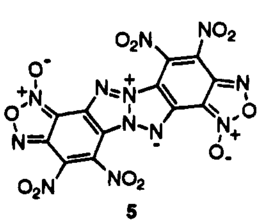
mp = 430 °C (dec)
d = 1.80 g/cm^3
D = 7.80 mm/μsec
P_{CJ} = 290 kbar

Because of the inherent thermal stability of the dibenzotetraazapentalene ring system, **2** was viewed as an attractive starting point for the design of a new class of energetic materials. To increase the density and improve the detonation performance of **2** required the design of compounds with decreased hydrogen content and increased nitrogen and oxygen content. This was best achieved by substitution of hydrogen by nitro or furoxano groups. Using this approach, the derivatives 4,11-dinitro-14*H*-[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 (**4**, DBBD) and 4,5,11,12-tetranitro-14*H*-[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 (**5**, TBBD) were envisaged as potential high-density, thermally stable, shock insensitive materials.[6] Herein two synthetic approaches for the preparation of **4** are described.



4

(DBBD; $C_{12}H_2N_{10}O_8$)
d = 1.96 g/cm^3
D = 7.52 mm/μsec
P_{CJ} = 245 kbar



5

(TBBD; $C_{12}N_{12}O_{12}$)
d = 2.06 g/cm^3
D =8.03 mm/μsec
P_{CJ} = 319 kbar

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(2) Urbanski, T.; Vasudeva, S. K. Heat Resistant Explosives. *J. Sci. Ind. Res.* **1978,** *37,* 250.

(3) Benson, F. R. *The High Nitrogen Compounds*; John Wiley: New York, 1984; pp 6–263.

(4) (a) Carboni, R. A.; Kauer, J. C.; Castle, J. E.; Simmons, H. E. *J. Am. Chem. Soc.* **1967,** *89,* 2618. (b) Carboni, R. A.; Kauer, J. C.; Hatchard, W. R.; Harder, R. J. *J. Am. Chem. Soc.* **1967,** *89,* 2626. (c) Harder, R. J.; Carboni, R. A.; Castle, J. E. *J. Am. Chem. Soc.* **1967,** *89,* 2643. (d) E. I. du Pont de Nemours and Co. U.S. Patent 2,904,544, 1959; *Chem. Abstr.* **1960,** *54,* 11062.

(5) Berlin, J. K.; Coburn, M. D. *J. Heterocycl. Chem.* **1975,** *12,* 235.

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

(7) Meyer, R. *Explosives*, 3rd ed.; VCH: Weinheim; 1987; p 150 (RDX; mp 204 °C; d = 1.81 g/cm^3, D = 8.85 mm/μs, P_{CJ} = 338 kbar).

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Scheme 1

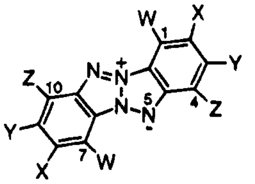
$$\mathbf{6}\xrightarrow[CH_3CO_2H]{Cl_2}\mathbf{8}\xrightarrow[0\ ^\circ C]{HNO_3}\mathbf{9}\xrightarrow[DMSO,\ 130\ ^\circ C]{NaN_3}$$

$$\mathbf{10}\xrightarrow[120\ ^\circ C]{CH_3CO_2H}\mathbf{11}\xrightarrow[0\ ^\circ C]{HNO_3/H_2SO_4}\mathbf{4}$$

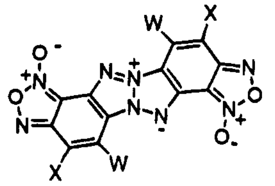
Results and Discussion

Introduction of substituents on the dibenzotetraazapentalene ring system by electrophilic substitution reactions has been reported to proceed with a high degree of regioselectivity. Substitution at the 2(8)-position has been shown to be favored over substitution at the 4(10)-position while electrophilic attack at the 1(7)- and 3(9)-positions is much less favored.[4b] However, prior to the start of this investigation this pattern of reactivity had not been rigorously established and some inconsistancies with regard to the substitution pattern of **2** had been reported in the literature.[8] Therefore, it was felt that the pattern of reactivity of the dibenzotetraazapentalene system had to be unequivocally established prior to proceeding toward the targets **4** and **5**.

The benzotriazolo[2,1-*a*]benzotriazol-6-ium inner salt (**6**) was prepared from *o*-phenylenediamine by the procedure reported by Carboni *et al.*[4a] As illustrated in Scheme 1, electrophilic chlorination (Cl_2, CH_3CO_2H) of **6** produced a mixture of compounds. As expected, chlorination took place at the 2(8)-position regioselectively over other positions to give the new monosubstituted 2-chloro derivative **7** in 28% yield along with the previously reported 2,8-dichloro derivative **8** in 30% yield (Scheme 1).[4b] It was interesting to note that despite the asymmetry of the 2-chloro derivative **7** clearly observed in the ^1H NMR, only six signals were observed in the ^{13}C NMR spectrum.



2: W = Y = H, X = Z = NO_2
6: W = X = Y = Z = H
7: W = X(8) = Y = Z = H, X(2) = Cl
8: W = Y = Z = H, X = Cl
9: W = Y = H, X = Cl, Z = NO_2
10: W = X = H, Y = N_3, Z = NO_2
12: W = Y = H, X = N_3, Z = NO_2
13: W = Y = H, X = NO_2, Z = N_3
14: W = H, X = Y = NO_2, Z = N_3
15: W = Y(9) = H, X = Y(3) = NO_2, Z = N_3



4: W = H, X = NO_2
11: W = X = H

Subsequent nitration (90% HNO_3) of **8** furnished the 2,8-dichloro-4,10-dinitrobenzotriazolo[2,1-*a*]benzotriazol-6-ium inner salt (**9**) in 55% yield (Scheme 1). Similar to **2**, the dichloro dinitro derivative **9** was strongly fluorescent in solution.[9] The structure of **9** was confirmed by X-ray crystallographic analysis.[10] These results unequivocally demonstrate that the sequential preference for electrophilic attack on the dibenzotetraazapentalene ring system is in the order of position 2(8) > 4(10) ≫ 1(7) and 3(9).

With the 2,8-dichloro-4,10-dinitro derivative **9** in hand, attention turned toward the construction of the bisfuroxan ring system of the target compound **4** (Scheme 1). It had been previously reported that **2** easily underwent nucleophilic substitution reactions with azide anion which resulted in direct replacement of a nitro group by an azido group.[4b] However, it was interesting to discover that treatment of **9** with sodium azide in dimethyl sulfoxide did not result in direct substitution of either the chloro or the nitro substituents. Alternatively, the 3,9-diazido-4,10-dinitro derivative **10** was isolated as the sole product in 50% yield (Scheme 1). The formation of **10** must proceed through an addition–elimination sequence in which azide adds to the 3(9)-position followed by elimination of hydrogen chloride.

Thermolysis (CH_3CO_2H, 120 °C) of **10** gave the new heterocyclic system 14*H*-[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 (**11**) in 57% yield (Scheme 1). This served to confirm the structural assignment of **10** as having two sets of contiguous azido and nitro substituents. Finally, nitration (HNO_3/H_2SO_4, 0 °C) of the bisfuroxan **11** afforded **4** in 50% yield as a red amorphous solid (Scheme 1). As expected, electrophilic substitution occurred at the 2(8)-position of **11** despite the proximity of the furoxan rings.[11] The structure of **4** was later confirmed by NMR and X-ray crystallographic analysis of **4**.

In an attempt to develop a more efficient synthesis of **4** for future studies directed toward the synthesis of **5**, an alternative synthetic approach was developed in which **2** could be employed as an early intermediate. On the basis of the results of the study described above, the structure and isomeric composition of **2** was reinvestigated. Nitration (HNO_3/H_2SO_4, 60 °C) of **6** gave a single tetranitro derivative in 75% yield (Scheme 2). From NMR (^1H and ^{13}C) data and on the basis of the observed reactivity of **6**, the structure was unambiguously assigned as the 2,4,8,10-tetranitro derivative **2** originally reported by Carboni *et al.*[4b,12]

As mentioned earlier, it has been reported that treatment of **2** with lithium azide led to the nucleophilic displacement of a pair of nitro groups to yield either the 2,8-diazido-4,10-dinitro derivative **12** or the 4,10-diazido-2,8-dinitro isomer **13**.[4b] Although only one isomer was reportedly obtained, the actual structure was not rigorously confirmed. In fact, the reaction of **2** with sodium azide in dimethyl sulfoxide was found to give the 4,10-diazido-2,8-dinitro derivative **13** as the sole product in 42% yield (Scheme 2). The structure of **13** was supported by spectral data and later confirmed by analysis of products from subsequent synthetic transformations. This result was very surprising since it was shown earlier with **9** (Scheme 2) that attack of a nucleophile occurred regioselectively at the 3(9)-position.

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[8] Chang, M. S.; Orndoff, R. R. U.S. Patent 4,526,980, 1985; *Chem. Abstr.* **1985**, *103*, 141982*d*.

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

[10] The authors have deposited atomic coordinates for compounds **4** and **9** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

[11] Bailey, A. S.; Case, J. R. *Tetrahedron* **1958**, *3*, 113. Nitration of benzofuroxan gave the 4-nitrobenzofuroxan.

[12] Gilardi, R. Naval Research Laboratory, 1994. X-ray crystal structure of Tacot (**2**).

Scheme 2

$$6 \xrightarrow[60\ ^\circ C]{HNO_3/H_2SO_4} 2 \xrightarrow[DMSO,\ 70\ ^\circ C]{NaN_3} 13 \xrightarrow[0\ ^\circ C]{HNO_3}$$

$$14\ (+15) \xrightarrow[150\ ^\circ C]{o\text{-}C_6H_4Cl_2} 4$$

Nitration (90% HNO_3, 0 °C) of **13** afforded the 4,10-diazido-2,3,8,9-tetranitro derivative **14** which resulted from the *ortho*-directing effect of the azido groups.[13] The tetranitro derivative **14** was obtained in 82% yield along with a small amount of the 4,10-diazido-2,3,8-trinitro derivative **15** in 10% yield (Scheme 2). Despite improved computed density and detonation properties for **14** (d = 1.82 g/cm^3, D = 8.12 mm/μs, P_{CJ} = 301 kbar),[6] the material was considerably more sensitive than **2**. The diazido tetranitro derivative **14** has been found to be thermally sensitive (decomposed at 260 °C) and impact sensitive (violent explosion with flame when struck by a hammer) while **2** was stable under these conditions.

Thermolysis (*o*-dichlorobenzene, 150 °C) of **14** furnished **4** in 60% yield (Scheme 2). The amorphous material **4** was crystallized from dry DMF. Subsequent X-ray crystallographic analysis of the red crystalline material unequivocally confirmed the structure of **4** and indirectly confirmed the orientation of the azido groups at position 4(10) in **13**. In addition, X-ray analysis revealed that the material cocrystallized with DMF (1:1).[10] It was interesting to note that the chemical shift of H1(7) in DMSO-d_6 for **4·DMF** (9.70 ppm) was downfield from that observed for the amorphous material **4** (9.50 ppm) prepared from **11**. However, a mixture (1:1) of **4·DMF** and amorphous **4** in DMF-d_6 gave a single signal for H1(7) at 9.70 ppm and a homogenous ^{13}C spectrum. From these results it is clear that both synthetic pathways, conversion of **8** into **4** and **2** into **4**, afforded the same product and same structural isomer.

The amorphous material **4** was found to be thermally stable at temperatures up to 310 °C, at which point the material decomposed. In addition, in these laboratories **4** was found to be stable to impact; no detonation was observed when the material was struck by a hammer. The crystalline material **4·DMF** decomposed at 270 °C and was insensitive to impact.

Summary

In summary, the sequential preference for electrophilic aromatic substitution on the dibenzotetraazapentalene **6** ring system has been unequivocally established to be in the order of position 2(8) > 4(10) ≫ 1(7) and 3(9). However, the pattern of reactivity for the nucleophilic substitution reaction of substituted dibenzotetraazapentalene derivatives appears to be substrate dependent. Further studies are warranted to clearly define the reactivity of the dibenzotetraazapentalene with nucleophiles.

The reactivity of the dibenzotetraazapentalene **6** was exploited for the development of two synthetic approaches for the preparation of **4**. The new insensitive energetic material **4** (d = 1.96 g/cm^3, D = 7.52 mm/μs, P_{CJ} = 245 kbar)[6] was prepared in a straightforward fashion from readily available **2** in 21% overall yield. Studies directed toward the preparation of the tetranitro derivative **5** are currently under investigation.

Experimental Section

All chemicals were purchased from Aldrich Chemical Co., Milwaukee, WI. Reported UV absorptions are restricted to the highest wavelength. Fluorescence quantum yields were determined for solutions in EtOH or DMF with excitation at 460, 540, and 570 nm with sulfarhodamine (Φ = 0.68) and acridine orange (Φ = 0.46) as references. Melting points and decomposition points are uncorrected. All compounds were homogenous by TLC and NMR. 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 (and other heteroatoms) were outside the standard acceptable limit of ±0.4%. However, duplicate and triplicate analyses for nitrogen were usually within ±1% of calculated values and corresponded to the empirical formula of the compound. ***Caution*! Compounds 3, 4, 10, 12, 13, 14, and 15 should be handled as potentially explosive materials!**

Crystal Structure Determination of DBBD (4) and 2,8-Dichloro-4,10-dinitrobenzotriazolo[2,1-*a*]benzotriazol-6-ium Inner Salt (9). Crystals suitable for data collection were recrystallized from DMF. The crystals were attached to glass fibers using silicone vacuum grease and mounted on an Enraf-Nonius CAD4 X-ray diffractometer with graphite monochromator and Mo K radiation. Samples were cooled in a stream of N_2 gas and cell dimensions determined by refinement of the setting angles of 25 reflections with 18° ≤ 2 ≤ 22°. Intensity scans as a function of indicated minimal variation due to absorption and no absorption corrections were applied. Three intensity control reflections were measured at 2 h intervals during data collection, showing fluctuations of less than ±1%. The structures were solved by direct methods using the program MULTAN[14] and refined by full-matrix least-squares techniques. In both cases, the tetraazapentalene ring is located at a crystallographic inversion center. The asymmetric unit thus consists of half of the molecule. In the case of **4**, a molecule of solvent is also present in the asymmetric unit.[10] All computer programs used were from the MolEN package.[15]

2,8-Dichlorobenzotriazolo[2,1-*a*]benzotriazol-6-ium Inner Salt (8).[4b] The benzotriazolobenzotriazole **6**[4a] (1.04 g, 5.0 mmol) was added to a stirred solution of 0.80 g (11.0 mmol) of dry Cl_2 (g) in glacial acetic acid (35 mL). The mixture was heated at 120 °C as half of the solvent was removed by distillation. The cooled concentrate was diluted with water (250 mL), and an insoluble precipitate was isolated. Separation of **7** and **8** by flash chromatography [SiO_2; $CHCl_3$/hexane (40:60)] afforded **8** as a yellow crystalline solid, 0.38 g (28%), mp 298–300 °C, lit.[4b] mp 303–305 °C. ^1H NMR (DMSO-d_6/$CDCl_3$): δ 7.60 (dd, 2H, J = 1.2, 8.5 Hz), 7.25 (d, 2H, J = 1.2 Hz), 7.10 (d, 2H, J = 8.6 Hz).

2-Chlorobenzotriazolo[2,1-*a*]benzotriazol-6-ium Inner Salt (7). Further elution [SiO_2; $CHCl_3$/hexane (60:40)] gave **7** as a yellow crystalline solid, 0.37 g (30%), mp 223–225 °C. ^1H NMR ($CDCl_3$): δ 8.30 (d, 2H, J = 8.3 Hz), 7.60–7.70 (m, 3H), 7.30 (d, 2H, J = 1.5 Hz). ^{13}C NMR ($CDCl_3$): δ 144.23, 132.05, 130.27, 125.80, 121.02, 108.53. Anal. Calcd for $C_{12}H_7N_4Cl$: C, 59.42; H, 2.89; N, 23.09; Cl, 14.62. Found: C, 59.40; H, 2.70; N, 23.02; Cl, 14.00.

2,8-Dichloro-4,10-dinitrobenzotriazolo[2,1-*a*]benzotriazol-6-ium Inner Salt (9). The dichloride **8** (1.10 g, 4.0 mmol) was added in small portions to HNO_3 (90%, 6.50 mL) at 0–5 °C with stirring. The mixture was stirred for 2 h and

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[13] Biffin, M. E. C.; Miller, J.; Paul, D. B. The Directing and Activating Effects of the Azido Group. In *The Chemistry of the Azido Group*; J. Patai, S., Ed.; Wiley and Sons: New York, 1971; pp 209–212. The nitration of aryl azides was discussed.

[14] Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Universities of York, England and Louvain, Belgium.

[15] Fair, C. K. *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*; Enraf-Nonius: Delft, The Netherlands.

poured into ice−water (250 mL). A red precipitate was isolated, dried under vacuum, and recrystallized from DMF to give **9** as a red crystalline solid, 0.80 g (55%), mp 330−335 °C dec. IR (KBr): 1507, 1359 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.30 (d, 2H, J = 1.2 Hz), 8.70 (d, 2H, J = 1.2 Hz). ^{13}C NMR (DMSO-d_6): δ 148.00, 144.00, 137.60, 131.60, 128.92, 125.90 UV (DMF): λ_{max} 480 nm, log ϵ 4.69; λ_f (DMF) 572 nm, Φ 0.69. Anal. Calcd for $C_{12}H_4N_6O_4Cl_2$: C, 39.28; H, 1.09; N, 22.89; Cl, 19.32. Found: C, 39.20; H, 1.00; N, 22.71; Cl, 19.11.

3,9-Diazido-4,10-dinitrobenzotriazolo[2,1-*a*]benzotriazol-6-ium Inner Salt (10). Sodium azide (0.65 g, 10.0 mmol) was added (10 min) to a stirred solution of **9** (1.83 g, 5.0 mmol) in dry DMSO (125 mL) at 25 °C. The reaction mixture was heated at 130 °C for 1 h as the solution became dark brown. The mixture was cooled and poured into ice−water (500 mL). After 24 h a precipitate was isolated, dried under vacuum, and recrystallized from acetone to give **10** as an amorphous brown solid, 0.95 g (50%), mp 192−195 °C dec. IR (KBr): 2127 (N_3), 1508, and 1351 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.20 (d, 2H, J = 6.0 Hz), 8.70 (d, 2H, J = 6.0 Hz). ^{13}C NMR (DMSO-d_6): δ 144.80, 138.10, 137.00, 136.50, 126.00, 122.00. Anal. Calcd for $C_{12}H_4N_{12}O_4$: C, 37.92; H, 1.06; N, 44.20. Found: C, 37.90; H, 1.00; N, 44.00.

14*H*-[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 (11). The dinitro diazide **10** (1.03 g, 2.7 mmol) was added to glacial acetic acid (100 mL), and the mixture was heated at 70 °C until all the material was completely dissolved. The temperature was raised to 120 °C and maintained for 45 min or until nitrogen evolution ceased. After concentration (50%) the solution was diluted with water (200 mL) and filtered. A residue was recrystallized from acetone to give **11** as a light yellow solid, 0.50 g (57%), mp 270−274 °C dec. IR (KBr): 1654 (C=N) cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.10 (d, 2H, J = 4.8 Hz), 8.67 (d, 2H, J = 4.8 Hz). Anal. Calcd for $C_{12}H_4N_8O_4$: C, 44.47; H, 1.24; N, 34.56. Found: C, 44.30; H, 1.20; N, 33.52.

4,11-Dinitro-14*H*-[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 (4). The bisfuroxan **11** (0.52 g, 1.6 mmol) was added slowly to concentrated H_2SO_4 (2 mL) at 0 °C, and after 10 min, a mixture of HNO_3 (70%, 2 mL) and concentrated H_2SO_4 (2 mL) was added slowly at 0−5 °C. The yellow mixture was stirred for 1 h at 0 °C and poured into ice−water (150 mL). The red precipitate was filtered and dried under vacuum to afford **4** as an amorphous solid, 0.33 g (50%), mp 310 °C dec. IR (KBr): 1654 (C=N), 1500, 1357 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.50 (s). ^{13}C NMR (DMSO-d_6): δ 141.00, 138.00, 132.00, 128.13, 128.00, 118.00. Anal. Calcd for $C_{12}H_2N_{10}O_8$: C, 34.80 H, 0.49; N, 33.82. Found: C, 34.52; H, 0.61; N, 32.90.

4,10-Diazido-2,8-dinitrobenzotriazolo[2,1-*a*]benzotriazol-6-ium Inner Salt (13).[4b] Sodium azide (4.00 g, 60 mmol) was added with stirring over a period of 15 min at 25 °C to **2** (6.30 g, 16 mmol) in dry DMSO (ca. 130 mL). The mixture was maintained at 70−80 °C for 1 h as the color deepened. After cooling in ice−water a precipitate was isolated and washed with EtOH (10 mL) and with Et_2O (10 mL) to give **13** as a yellow-orange solid (2.50 g, 42%), mp 187 °C dec [lit.[4b] mp 200 °C dec]. IR (KBr): 2134 (N_3), 1597, 1518, and 1353 cm^{-1}. ^1H NMR (DMSO-d_6): 8.2 (d, 2H, J = 1.5 Hz), 8.9 (d, 2H, J = 1.6 Hz).

4,10-Diazido-2,3,8,9-tetranitrobenzotriazolo[2,1-*a*]benzotriazol-6-ium Inner Salt (14). Nitric acid (90%, 9.50 mL) at 0−5 °C was added to **13** (2.58 g, 6.8 mmol). The mixture was stirred for 2 h at 0−5 °C and poured into ice−water. The crude brown solid precipitate was filtered and purified by flash column chromatography [SiO_2; hexane/acetone (7:3)] to afford **15** as an orange-red solid, 1.60 g (50%), mp 260−261 °C dec. IR (KBr): 2131 (N_3), 1543, and 1361 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.50 (s). ^{13}C NMR (DMSO-d_6): δ 151.80, 131.00, 126.00, 122.22, 117.00, 113.60. UV (EtOH): λ_{max} 457 nm, log ϵ 4.52; λ_f (EtOH) 532 nm, Φ 0.10. Anal. Calcd for $C_{12}H_2N_{14}O_8$: C, 30.65; H, 0.43; N, 41.69. Found: C, 30.47; H, 0.71; N, 40.01.

2,3,8-Trinitro-4,10-diazidobenzotriazolo[2,1-*a*]benzotriazol-6-ium Inner Salt (15). Further elution [SiO_2; hexane/acetone (50:50)] gave **15** as an orange-red amorphous solid, 0.28 g (10%), mp 255−256 °C dec. IR (KBr) 2136 (N_3), 1558, and 1319 cm^{-1}. ^1H NMR (acetone-d_6): δ 9.94 (d, 1H, J = 2.0 Hz), 9.45 (d, 1H, J = 2.0 Hz), 9.40 (s, 1H). ^{13}C NMR (acetone-d_6): δ 150.80, 131.00, 123.00, 117.00, 112.60, 111.07, 109.00. Anal. Calcd for $C_{12}H_3N_{13}O_6$: C, 33.91; H, 0.71; N, 42.81. Found: C, 33.80; H, 1.15; N, 42.01.

DBBD (4). The tetranitro diazide **14** (1.03 g, 2.2 mmol) in *o*-dichlorobenzene (75 mL) was heated at 110 °C for 10 min and at 150 °C for 1 h or until nitrogen evolution ceased. A precipitate was produced by cooling and was triturated with DMF to give **4** as a red amorphous solid, 0.55 g (60%). The amorphous material was crystallized from DMF to give **4·DMF** as an orange-red crystalline solid, mp 274−276 °C dec. IR (KBr): 1654 (C=N), 1533, and 1302 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.70 (s). ^{13}C NMR (DMSO-d_6): δ 140.00, 136.00, 133.00, 130.00, 126.00, 116.00. Anal. Calcd for $C_{12}H_2N_{10}O_8$ (amorphous): C, 34.80; H, 0.49; N, 33.82. Found: C, 34.40; H, 0.71; N, 32.82.

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