Heteroatom Chemistry
Volume 6, Number 5, 1995

Dense Energetic Compounds of Carbon, Hydrogen, Nitrogen, and Oxygen Atoms. V. 1,2,7,8-Bisfuroxano-3,4,9,10-tetranitro-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole (BTBB)

Ganesan Subramanian, Mark L. Trudell, and Joseph H. Boyer*

Department of Chemistry, University of New Orleans, New Orleans, LA 70148

Received August 1994

ABSTRACT

A reaction between 2,8-dichloro-4,10-dinitro-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]-benzotriazole **8** *and sodium azide in dimethyl sulfoxide produced 3,9-diazido-4,10-dinitro-5,11-dehydro-5H,11H-benzotriazolo [2,1-a]benzotriazole* **10** *rather than the 2.8-diazido isomer* **9** *expected by direct displacement. Thermolytic elimination of nitrogen (2 moles) converted the dinitro diazide* **10** *to 3,4,9,10-bisfuroxano-5,11-dehydro-5H, 11H-benzotriazolo[2, 1-a]benzotriazole* **11** *that was subsequently nitrated to give the 2,8-dinitro derivative* **12**. *Similar nitration converted the dinitro diazide* **9** *to the trinitro* **15** *and tetranitro* **14** *derivatives: thermolysis of the latter gave 1,2,7,8-bisfuroxano-4, 10-dinitro-5, 11-dehydro-5H, 11H-benzotriazolo[2,1-a]-benzotriazole* **16**. *Nitration (100% HNO_3, CF_3SO_3H) converted compound* **16** *to the 3,4,10-trinitro derivative* **17**, *whereas a similar nitration (100% HNO_3, FSO_3H) gave the title compound BTBB, an insensitive high-energy, high-density (d 2.03 g/cc) molecule.* © *1995 John Wiley & Sons, Inc.*

INTRODUCTION

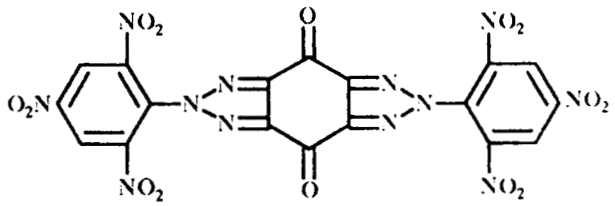
There is a need for high-energy, high-density molecules with composition restricted to carbon, hydrogen, nitrogen, and oxygen atoms and with significant insensitivity to heat, friction, and impact [1,2]. Caged, fused-ring, and other high-nitrogen heterocycles are predominant in the limited number of qualified candidates [1,3]. A review [3] of high-nitrogen heterocycles cited 2,6-dipicrylbenzo[1,2-*d*][4,5-*d*]bistriazole-4,8-dione **1** dec 430°C [4], calculated density [5] *d* 1.8, and 2,4,8,10-tetranitro-5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **2** (Tacot) (Scheme), dec 378°C [6,7], *d* 1.8 g/cc [2] as examples of heat-resistant, high-density derivatives of *vic*-triazole.

Tacot **2**, a commercially available insensitive explosive [7–9] was readily obtained from 5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **5** by nitration. In turn, the benzotriazolobenzotriazole **5** was obtained from *o*-phenylenediamine by a straightforward sequence: oxidation to *o,o'*-diaminoazobenzene, conversion to *o,o'*-diazidoazobenzene, and thermolysis [6]. Later references incorrectly described Tacot as a mixture of isomers [2] and as the 2,3,8,9-tetranitro isomer **3** [9], a compound claimed in a patent [10].

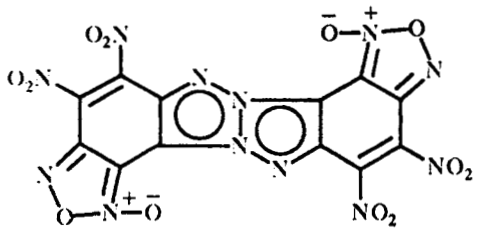
The selection of 1,2,7,8-bisfuroxano-3,4,9,10-tetranitro-5, 11-dehydro-5*H*, 11*H*-benzotriazolo[2,1-*a*]benzotriazole (BTBB) **4** and/or its positional isomers for investigations on syntheses and properties was supported by the calculated *d* 2.06 g/cm^3 [5], partially attributed to zero hydrogen content, and by a favorable oxygen balance revealed by the molecular formula $C_{12}N_{12}O_{12}$ for self-combustion to carbon monoxide (12 CO) and nitrogen (6 N_2). A thermal insensitivity shared with Tacot was predicted.

*To whom correspondence should be addressed.

1042-7163/95/050391-05



1

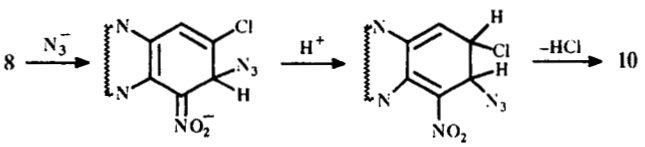


4

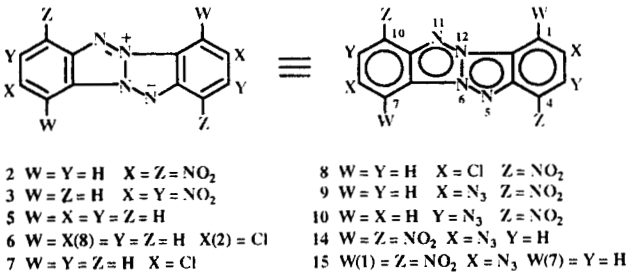
RESULTS AND DISCUSSION

Chlorination of 5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **5** produced the new 2-chloro derivative **6** along with the previously reported 2,8-dichloro derivative **7** [6] with comparable efficiencies. Nitration (nitric acid, 0–5°C) converted the dichloride **7** to 2,8-dichloro-4,10-dinitro-5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **8** (Scheme 1), a structure confirmed by X-ray crystallographic analysis and shown in the **8** Ortep plot [11]. The preference for 4,10 over 1,3,7,9 positions in electrophilic substitution was in agreement with the nitration of benzotriazolobenzotriazole **5** to Tacot **2** [6].

Although the formation of 2,8-diazido-4,10-dinitro-5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]-benzotriazole **9** was previously brought about by treating Tacot **2** with lithium azide [6] and has been reproduced (Scheme 1), a similar treatment of the dinitro dichloride **8** with sodium azide failed to produce the dinitro diazide **9**. Instead, the reaction gave the isomeric 3,9-diazide **10** (Scheme 1), presumably by an addition-elimination sequence:

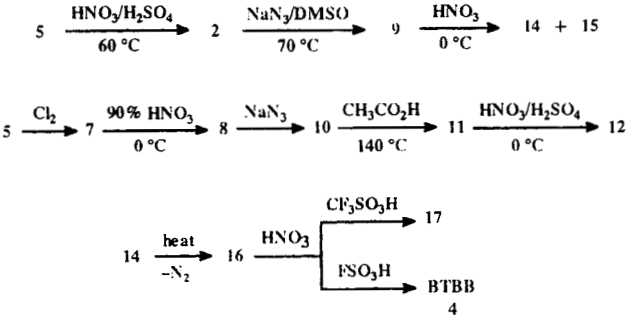


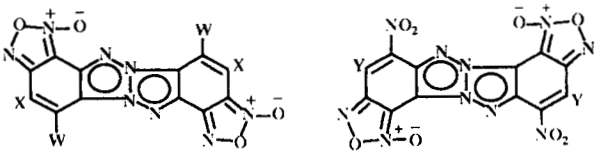
Thermolysis of the dinitro diazide **10** gave 3,4,9,10-bisfuroxano-5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **11**, thereby confirming the structure **10** with two sets of contiguous azido and nitro substituents. Nitration of the bisfuroxan **11** presumably gave 2,8-dinitro-3,4,9,10-bisfuroxano-5,11-dehydro-5*H*,11*H*-benzotriazolo-



2 W = Y = H X = Z = NO_2
3 W = Z = H X = Y = NO_2
5 W = X = Y = Z = H
6 W = X(8) = Y = Z = H X(2) = Cl
7 W = Y = Z = H X = Cl

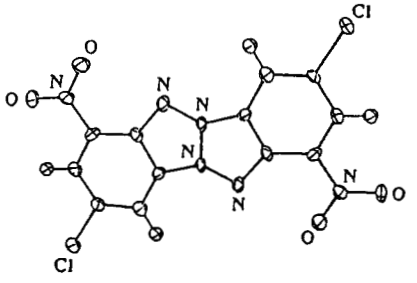
8 W = Y = H X = Cl Z = NO_2
9 W = Y = H X = N_3 Z = NO_2
10 W = X = H Y = N_3 Z = NO_2
14 W = Z = NO_2 X = N_3 Y = H
15 W(1) = Z = NO_2 X = N_3 W(7) = Y = H





11 W = X = H
12 W = H, X = NO_2
13 W = X = NO_2

16 Y = H
17 Y(3) = NO_2, Y(9) = H



8 Ortep Plot

SCHEME 1

[2,1-*a*]benzotriazole **12**. An expected preference for electrophilic substitution at the 2,8 positions in the bisfuroxan **11** was reenforced by the proximity of the 2,8 positions to the furoxan rings [12]. Failure in attempts to bring about further nitration to produce 1,2,7,8-tetranitro-3, 4, 9,10-bisfuroxano-5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **13** was in agreement with resistance toward electrophilic substitution at the 1,7 positions.

In contrast with failure to bring about further nitration in the dinitro bisfuroxano compound **12** a

synthesis of BTBB **4**, an isomer of compound **13**, from the 2,8-diazido-4,10-dinitro derivative **9** was brought about in three steps. A difficulty in nitration at the 1,7 positions, encountered in the attempted nitration of compound **12**, was overcome when nitration [13] of the dinitro diazide **9** gave 1,4,7,10-tetranitro-2, 8-diazido-5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **14** along with a minor amount of the 1,4,10-trinitro derivative **15**. Thermolysis of the tetranitro diazide **14** gave the 1,2,7,8-bisfuroxano-4,10-dinitro derivative **16**. Mononitration of the dinitro derivative **16** was brought about by treatment with a mixture of nitric acid (100%) and trifluoromethanesulfonic acid [14] to give 1,2,7,8-bisfuroxano-3, 4, 10-trinitro-5,11-dehydro-5*H*,11*H*-benzotriazolo[2, 1-*a*]benzotriazole **17**. Dinitration of the dinitro derivative **16** was brought about by treatment with a mixture of nitric acid (100%) and fluorosulfonic acid [14] in nitromethane to give BTBB **4**.

Although the C-nitro substituent was generally regarded as a "killer of fluorescence," [15] luminescence in certain nitro derivatives of benzotriazolo[2,1-*a*]benzotriazoles [16] was extended to the nitro compounds **8**, **14**.

EXPERIMENTAL

Instruments used included the following: Perkin-Elmer 1600 FTIR, Varian Gemini 300 NMR, Hewlett-Packard 5985 (70 eV) GC-MS, Cary 17 (UV), and Perkin-Elmer LS-5B luminescence spectrometers and a Phase-R DLR DL-1100 dye laser with a DL-5Y coaxial flashlamp. Literature procedures were followed to prepare 5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **5** and its derivatives 2,8-dichloro-**7** and 2,4,8,10-tetranitro- **2**[6]. Solvents were removed by rotary evaporation under reduced pressure unless otherwise indicated.

^{1}H NMR spectra were run in DMSO-d_6, acetone-d_6 with tetramethylsilane as an internal standard. ^{1}H NMR (DMSO-d_6) for Tacot **2**: δ 9.32 (d, 2H, J = 2.1 Hz), 10.01 (d, 2H, J = 2.1 Hz). Each recorded UV absorption was restricted to the highest wavelength. Fluorescence quantum yields were determined for solutions in ethanol or dimethylformamide with excitation at 460, 540, and 570 nm with sulfarhodamine, Φ 0.68, and acridine orange, Φ 0.46, as references. Melting and decomposition points were determined on a Mel-Temp II apparatus and are uncorrected. Elemental analyses were obtained from Midwest Micro Lab, Indianapolis, IN, and Galbraith Laboratories, Inc., Knoxville, TN.

2,8-Dichloro-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole 7

The benzotriazolobenzotriazole **5** (1.04 g, 5.0 mmol) was added to a stirred solution of 0.80 g (11.0 mmol) of dry chlorine 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. Flash chromatographic purification [chloroform/hexane (40:60)] yielded the dichloro derivative **7** as a yellow crystalline solid, mp 298–300°C (Ref. [5], mp 303–305°C), 0.38 g (28%). ^{1}H NMR (DMSO/$CDCl_3$): δ 7.60 (d, 2H), 7.25 (d, 2H), 7.10 (d, 2H).

Further elution [chloroform/hexane (60:40)] gave 2-chloro-5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **6** as a yellow crystalline solid, mp 223–225°C, 0.37 g (30%). ^{1}H NMR ($CDCl_3$): δ 8.30 (d, 2H), 7.60–7.70 (m, 3H), 7.30 (d, 2H). ^{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-dinitro-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole 8

The dichloride **7** (1.10 g, 4.0 mmol) was added in small portions to nitric acid (90%, 6.50 mL) at 0–5°C with stirring. The mixture was stored for 2 hours with stirring and then poured into ice water (250 mL). A brick red precipitate was isolated, dried, and recrystallized from dimethylformamide as a red crystalline solid **8**, mp 330–335°C (dec), 0.80 g (55%). IR (KBr) ν/cm^{-1}: 1507, 1359 (NO_2). ^{1}H NMR (DMSO): δ 9.30 (d, 2H), 8.70 (d, 2H). ^{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.

2,8-Diazido-4,10-dinitro-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole 9 *[17]*

Sodium azide (4.00 g, 60 mmol) was added with stirring over a period of 15 minutes at 25°C to the tetranitro derivative **2** (6.30 g, 16 mmol) in dry dimethylsulfoxide (ca. 130 mL). The mixture was maintained at 70–80°C for 1 hour as the color deepened. After the mixture had been cooled in ice water, a precipitate was isolated and washed with ethanol (10 mL) and with ether (10 mL) to give the diazide **9** as a yellow-orange solid (2.50 g, 42%), mp 187°C (dec) [Ref. [2], mp 200°C (dec)]. IR (KBr) ν/cm^{-1}: 2134 (N_3) and 1597, 1518 and 1353 (NO_2).

3,9-Diazido-4,10-dinitro-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole 10

Sodium azide (0.65 g, 10.0 mmol) was added (10 minutes) to a stirred solution of the dichloro dinitro derivative **8** (1.83 g, 5.0 mmol) in dry dimethylsulfoxide (125 mL) at 25°C. The reaction mixture was heated at 130°C for 1 hour as the solution became

dark brown. The mixture was cooled and poured into ice water (500 mL). After 24 hours, a precipitate was isolated, dried, and recrystallized from acetone to give the dinitro diazide **10** as an amorphous brown solid, mp 192–195°C (dec), 0.95 g (50%). IR (KBr) ν/cm^{-1}: 2127 (N_3). 1508 and 1351 (NO_2). ^{1}H NMR (DMSO-d_6): δ 9.20 (d, 2H), 8.70 (d, 2H). ^{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.

3,4,9,10-Bisfuroxano-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole 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 the solution was complete. The temperature was raised to 120°C and maintained there for 45 minutes 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 the bisfuroxan **11** as a light yellow solid, mp 270–274°C (dec), 0.50 g (57%). IR (KBr) ν/cm^{-1}: 1654 (C=N). HNMR (DMSO-d_6): δ 9.10 (d, 2H), 8.67 (d, 2H). 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.

2,8-Dinitro-3,4,9,10-bisfuroxano-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole 12

The bisfuroxan **11** (0.52 g, 1.6 mmol) was added slowly to concentrated sulfuric acid (2 mL) at 0°C, and, after 10 minutes, a mixture of nitric acid (70%, 2 mL) and concentrated sulfuric acid (2 mL) was added slowly at 0–5°C. The yellow mixture was stored for 1 hour at 0°C and poured into ice water (150 mL) to bring about the precipitation of the dinitro derivative **12** as a yellow solid. After isolation and drying, an attempted recrystallization from dimethylformamide gave an amorphous solid, mp 310°C (dec), 0.33 g (50%). IR (KBr) ν/cm^{-1}: 1654 (C=N), 1500 and 1357 (NO_2). ^{1}H 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, 34.81; H, 0.49; N, 33.81. Found: C, 34.52; H, 0.62; N, 32.90.

1,4,7,10-Tetranitro-2,8-diazido-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole 14

Nitric acid (90%, 9.50 mL) was added at 0–5°C to the dinitro diazide **9** (2.58 g, 6.8 mmol). The mixture was stirred for 2 hours at 0–5°C and treated with ice water to bring about the precipitation of a crude brown solid (2.60 g, 81.5%). Purification by column chromatography [hexane/acetone (7:3)] gave the tetranitro diazide **14** as an orange-red solid, mp 260–261°C (dec), 1.60 g (50%). IR (KBr) ν/cm^{-1}: 2131 (N_3), 1543 and 1361 (NO_2). ^{1}H 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 (C_2H_5OH): λ_{max} 457 nm, log ε 4.52; λ_y(C_2H_5OH) 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.

Further elution [hexane/acetone (50:50)] gave 1, 4, 10-trinitro-2, 8-diazido-5, 11-dehydro-5*H*, 11*H*-benzotriazolo[2,1-*a*]benzotriazole **15** as an orange-red amorphous solid, mp 255–256°C (dec), 0.28 g (10%). IR (KBr) ν/cm^{-1}: 2136 (N_3), 1558 and 1319 (NO_2). ^{1}H NMR (acetone-d_6): δ 9.94 (d, 1H), 9.45 (d, 1H), 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.

1,2,7,8-Bisfuroxano-4,10-dinitro-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole 16

The tetranitro diazide **14** (1.03 g, 2.2 mmol) in *o*-dichlorobenzene (75 mL) was heated at 110°C for 10 minutes and then at 150°C for 1 hour or until nitrogen evolution ceased. A precipitate was produced by cooling and was recrystallized from dimethylformamide to give the bisfuroxan **16** as an orange-red crystalline solid, mp 274–276°C (dec), 0.55 g (60%). IR (KBr) ν/cm^{-1}: 1654 (C=N), 1533 and 1302 (NO_2). ^{1}H 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 $C_{12}H_2N_{10}O_8$: C, 34.81; H, 0.49; N, 33.81. Found: C, 34.40; H, 0.71; N, 32.20.

The tetranitro diazide **14** (1.03 g, 2.2 mmol) was added to nitric acid (90%, 2.5 mL) and the mixture was heated at 80°C for 2.5 hours, cooled, combined with ice water (200 mL) and filtered. A precipitate was recrystallized from dimethylformamide to give the bisfuroxan **16** as a red-brown amorphous solid, mp 274–276°C (dec), 0.19 g (21%). IR (KBr) ν/cm^{-1}: 1654 (C=N), 1533 and 1302 (NO_2). ^{1}H NMR (DMSO-d_6): δ 9.70 (s). ^{13}C NMR (DMSO-d_6): δ 140.00, 136.00, 134.00, 128.00, 126.00, 116.00. Anal. calcd for $C_{12}H_2N_{10}O_8$: C, 34.81; H, 0.49; N, 33.81. Found: C, 34.60; H, 0.70; N, 33.50.

1,2,7,8-Bisfuroxano-3,4,10-trinitro-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole 17

Nitric acid (100%, 0.38 g, 0.25 mL, 6 mmol) was added dropwise with stirring to trifluoromethanesulfonic acid (1.80 g, 1.01 mL, 12 mmol) under nitrogen in a flask (25 mL) equipped with a magnetic stirrer, nitrogen inlet tube, and a dropping funnel. A colorless crystalline solid separated [14], and, after 10 minutes, the dinitro bisfuroxano derivative **16** (0.41 g, 1 mmol) was added in one portion. The temperature of the oil bath was raised and maintained at 70–80°C for 2 hours. After the mixture had been cooled and combined with ice water (150 mL), the trinitro bisfuroxan **17** (0.18 g, 40%), mp 310–315°C

(dec), calculated d 2.02 g/cc, D 7.95 mm/μs, and P_{CJ} 286 kbar [5] was isolated and reprecipitated from acetonitrile. Experimental density: 1.97 g/cc (flotation method in methyl iodide). IR (KBr): ν/cm^{-1} 1655 (C=N), 1560, 1534, and 1322 (NO_2). ^{1}H NMR (DMSO-d_6): δ 9.66 (s). ^{13}C NMR (DMSO-d_6): δ 151.07, 140.02, 138.20, 133.02, 131.00, 126.00, 122.22, 118.26, 112.00, 108.32, 104.07, 102.02. Anal. calcd for $C_{12}H_1N_{11}O_{10}$: C, 31.40; H, 0.22; N, 33.55; O, 34.85. Found: C, 31.70; H, 0.36; N, 32.60; O, 34.20. Found: C, 31.20; H, 0.42; N, 32.10; O, 34.60.

BTBB 4

Under an atmosphere of nitrogen, fluorosulfonic acid (1.35 g, 0.80 mL, 13.5 mmol) was placed in an rb flask (25 mL) equipped with a magnetic stirrer and nitrogen inlet tube. Nitric acid (100%, 1.19 g, 0.80 mL, 19 mmol) was added in one portion at 25°C. After 5 minutes, dry nitromethane (5 mL) was added over a period of 10 minutes with stirring. The bisfuroxan **16** (0.35 g, 0.85 mmol) was added in one portion. The temperature was maintained at 80–90°C for 2 hours, nitromethane was removed, and the mixture was cooled and combined with ice water (150 mL) to bring about the precipitation of impure BTBB **4**. It was recrystallized from acetonitrile and was triturated with boiling ether for 15 minutes, then cooled, filtered, and dried to give a red crystalline solid, d 2.03 g/cc (flotation in methyl iodide), calculated D 8.3 mm/μs and P_{CJ} 319 kbar [5], mp 340–341°C (dec) (an irreversible color change from red to yellow was brought about by heating at 180–185°C), 0.084 g (20%). IR (KBr) ν/cm^{-1}: 1654 (C=N), 1560 (NO_2), 1482 (NO_2), 1364 (NO_2), 1072, 1031, 985, 899, 774, 504. ^{13}C NMR (DMSO-d_6): δ 166.65, 163.57, 149.41, 137.51, 113.91, 103.10. Anal. calcd for $C_{12}N_{12}O_{12}$: C, 28.60; H, 0.00; N, 33.33; O, 38.09. Found: C, 28.59; H, 0.00; N, 31.22; O, 39.19. Found: C, 28.58; H, 0.00; N, 31.17; O, 39.67. The values found for N and O were assumed to be in error.

ACKNOWLEDGMENTS

Financial support was received from the ONR and ARO.

REFERENCES

[1] A. T. Nielsen: Polycyclic Amine Chemistry, in G. Olah, D. R. Squire (eds): *Chemistry of Energetic Materials*, Academic Press, Inc., New York, pp. 95–124 (1991).

[2] T. Urbanski, S. K. Vasudeva, *J. Scien. Ind. Res., 37*, 1978, 250.

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

[4] J. K. Berlin, M. D. Coburn, *J. Heterocyclic Chem., 12*, 1975, 235.

[5] A program for the calculation of density d (g/cc), detonation velocity D (mm/μs), and detonation pressure P_{CJ} (kbar) was obtained from the Naval Weapons Center, China Lake, CA.

[6] (a) R. A. Carboni, J. C. Kauer, W. R. Hatchard, R. J. Harder, *J. Am. Chem. Soc., 89*, 1967, 2626; (b) R. J. Harder, R. A. Carboni, J. E. Castle, *J. Am. Chem. Soc., 89*, 1967, 2643; (c) U.S. 2,904,544, E. I. Du Pont de Nemours and Co., Wilmington, DE (1959), *Chem. Abstr., 54*, 1960, 11062.

[7] The compound **2** was initially reported as the tetranitro derivative of dibenzo-1,3*a*,4,6*a*-tetraazapentalene [6,8]. Preferential electrophilic substitution in the 2,4,8, and 10 positions (see Scheme) was established by chemical conversions to known compounds and supported by an approximate charge distribution calculated by molecular orbital methods [6].

[8] B. T. Federoff, O. E. Sheffield: *Encyclopedia of Explosives and Related Items*, Picatinny Arsenal, Dover, NJ, vol. 5, p. D-1184 (1972).

[9] R. Meyer: *Explosives*, 3rd ed., VCH, Weinheim, p. 332 (1987).

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

[11] E. D. Stevens: personal communication. Full details of the X-ray crystallographic analysis will be published elsewhere.

[12] A. S. Bailey, J. R. Case: *Tetrahedron, 3*, 1958, 113. Nitration of benzofuroxan gave the 4-nitro derivative.

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

[14] C. L. Coon, W. G. Blucher, M. E. Hill, *J. Org. Chem., 38*, 1973, 4244.

[15] B. M. Krasovitskii, B. M. Bolotin: *Organic Luminescent Materials*, English Translation by V. G. Vopian, VCH, Weinheim, p. 17 (1988).

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

[17] A treatment of the tetranitro derivative **2** with lithium azide in *N*,*N*-dimethylformamide to give the diazido derivative **9** [6] was repeated.