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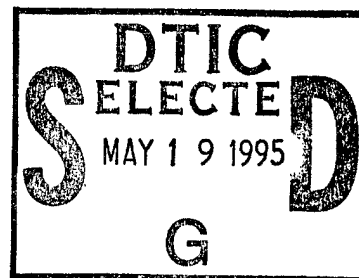
Technical Report No. 2

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

by

Ganesan Subramanian, Joseph H. Boyer, Dan Buzatu, Edwin D. Stevens and Mark L. Trudell*

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13. ABSTRACT (Maximum 200 words) 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 3,4,9,10-bisfuroxano-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole 11. From this study the first of a new class of insensitive energetic materials 4 has been synthesized in a straightforward fashion from 2.			
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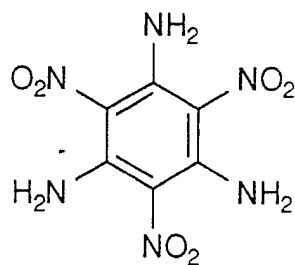
Reactions of Benzotriazolo[2,1-*a*]benzotriazole Derivatives (I). Synthesis of New Insensitive High Density Energetic Compounds.

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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-tetranitro-5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole 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]



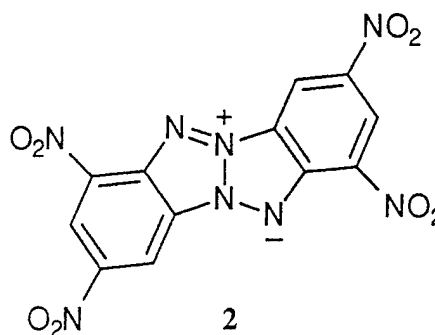
1

mp = 350 °C (dec)

d = 1.94 g/cm³

D = 7.80 mm/μsec

*P*_{CJ} = 290 kbar



2

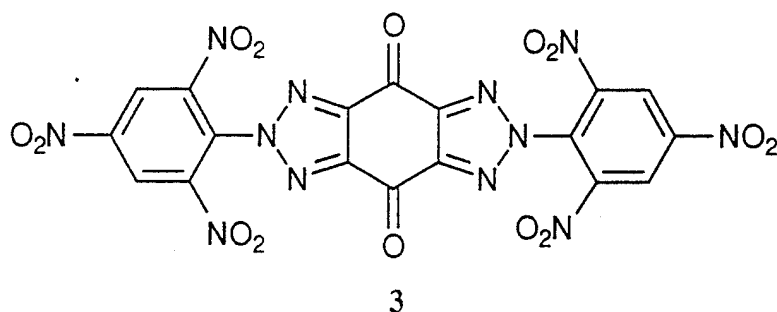
mp = 376 °C (dec)

d = 1.80 g/cm³

D = 7.80 mm/μsec

*P*_{CJ} = 290 kbar

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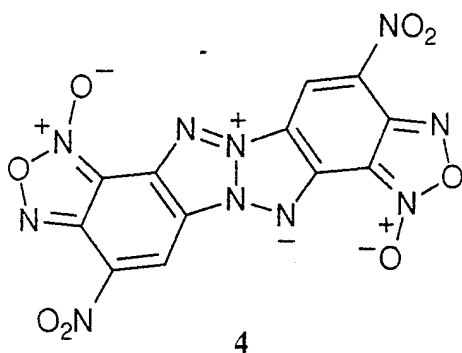
mp = 430 °C (dec)

d = 1.80 g/cm³

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 3,4,9,10-bisfuroxano-2,8-dinitro-5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **4** (BDBB) and 1,2,7,8-tetranitro-3,4,9,10-bisfuroxano-5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **5** (BTBB) were envisaged as potential high density, thermally stable, shock insensitive materials. [6] Herein two synthetic approaches for the preparation of **4** are described.

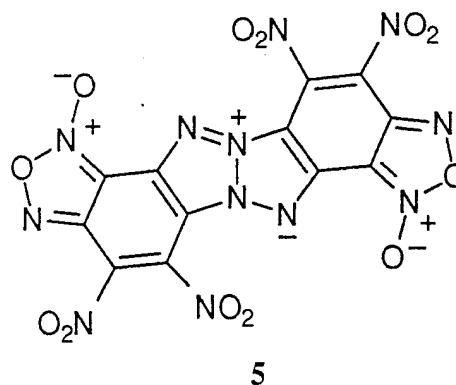


(BDBB; C₁₂H₂N₁₀O₈)

d = 1.96 g/cm³

D = 7.52 mm/μsec

P_{CJ} = 245 kbar



(BTBB; C₁₂N₁₂O₁₂)

d = 2.06 g/cm³

D = 8.03 mm/μsec

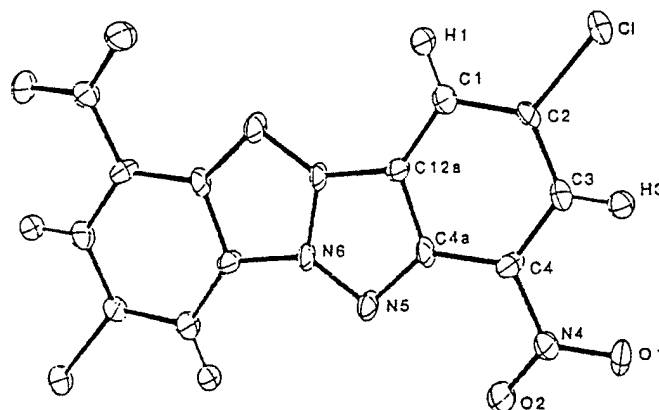
P_{CJ} = 319 kbar

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. [4] However, prior to the start of this investigation this pattern of reactivity had not been rigorously established and some inconsistencies 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 5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **6** was prepared from *o*-phenylenediamine by the procedure reported by Carboni *et al.* [4] Electrophilic chlorination (Cl_2 , $\text{CH}_3\text{CO}_2\text{H}$) 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). [4] Subsequent nitration (90% HNO_3) of **8** furnished the 2,8-dichloro-4,10-dinitro-5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **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 (Figure 1). These results

Figure 1. Ortep Drawing of **9**.

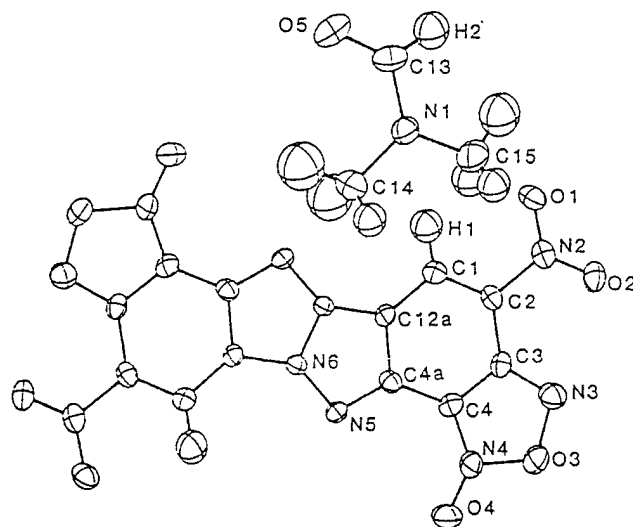


unequivocally demonstrate that the sequential preference for electrophilic attack on the dibenzotetraazapentalene ring system is in the order of position 2(8) > 4(10) >> 1(7) and 3(9).

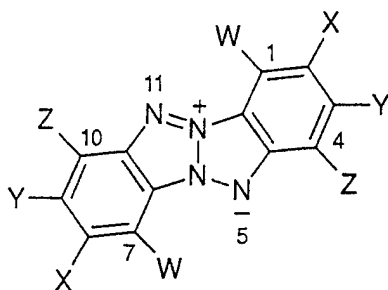
With the 2,8-dichloro-4,10-dinitro derivative **9** in hand, attention turned toward the construction of the bisfuroxan ring system of the target compound **4**. It had been previously reported that **2** easily underwent nucleophilic substitution reactions with azide anion which resulted in direct replacement of a nitro group by an azido group. [4] However, it was interesting to discover that treatment of **9** with sodium azide in dimethylsulfoxide 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 ($\text{CH}_3\text{CO}_2\text{H}$, 140 °C) of **10** gave the new heterocyclic system 3,4,9,10-bisfuroxano-5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **11** in 57% yield (Scheme 1). This served to confirm the structural assignment of **10** having two sets of contiguous azido and nitro substituents. Finally, nitration ($\text{HNO}_3/\text{H}_2\text{SO}_4$, 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** (Figure 2).

Figure 2. ORTEP drawing of BDBB (**4**•DMF).



Scheme 1



2 W = Y = H, X = Z = NO₂

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 = NO₂

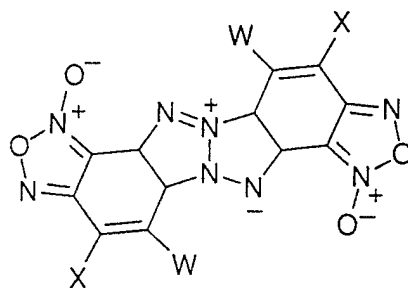
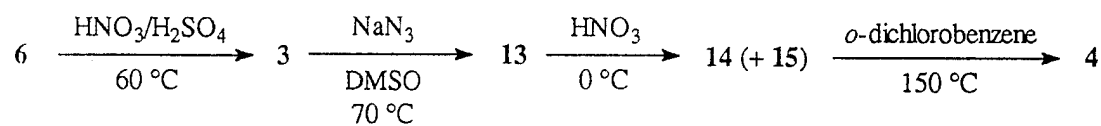
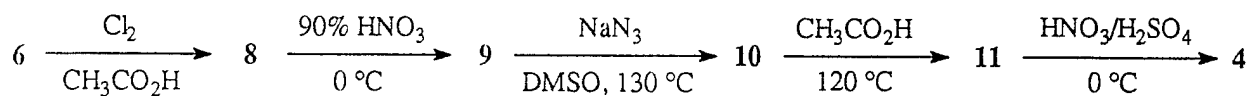
10 W = X = H, Y = N₃, Z = NO₂

12 W = Y = H, X = N₃, Z = NO₂

13 W = Y = H, X = NO₂, Z = N₃

14 W = H, X = Y = NO₂, Z = N₃

15 W = Y(9) = H, X = Y(3) = NO₂, Z = N₃



4 W = H, X = NO₂

11 W = X = H

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. Based on the results of the study described above, the structure and isomeric composition of **2** was reinvestigated. Nitration ($\text{HNO}_3/\text{H}_2\text{SO}_4$, 60°C) of **6** gave a single tetranitro derivative in 75% yield (Scheme 1). From NMR (^1H and ^{13}C) data and based on 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.* [4,11]

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**. [4] Although only one isomer was reportedly obtained, the actual structure was not rigorously confirmed. In fact, the reaction of **2** with sodium azide in dimethylsulfoxide was found to give the 4,10-diazido-2,8-dinitro derivative **13** as the sole product in 42% yield (Scheme 1). 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 1) that attack of a nucleophile occurred regioselectively at the 3(9)-position.

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. [12] 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 1). Despite improved computed density and detonation properties for **14** ($d = 1.82 \text{ g/cm}^3$, $D = 301 \text{ mm}/\mu\text{sec}$, $P_{\text{CJ}} = 8.12 \text{ kbar}$), [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. The 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** (Figure 2). In addition, X-ray analysis

revealed that the material cocrystallized with DMF (1:1). It was interesting to note that the chemical shift of *H*1(7) in DMSO- d_6 for **4•DMF** (δ 9.70 ppm) was downfield from that observed for the amorphous material **4** (δ 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 *H*1(7) at δ 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** ($d = 1.96 \text{ g/cm}^3$, $D = 7.52 \text{ mm}/\mu\text{sec}$, $P_{\text{CJ}} = 245 \text{ kbar}$) 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

All chemicals were purchased from Aldrich Chemical Company, Milwaukee, WI. ^1H and ^{13}C nmr spectra were obtained on a Varian – Gemini Multiprobe 300 MHz nmr spectrometer and ir spectra were recorded on either a Perkin–Elmer 1600 series or 2000 series

infrared spectrometer. Spectra were recorded on a Cary 17 (UV), Perkin – Elmer LS – 5B Luminescence spectrometer and Phase – R DLR DL – 1100 dye laser with DL – 5Y coaxial flashlamp. Reported absorptions are 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 ($\Phi = 0.68$) and acridine orange ($\Phi = 0.46$) as references. Melting points and decomposition points were determined on a Mel – Temp II and are reported uncorrected. Elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, TN and Midwest Micro Lab, Indianapolis, IN. *Caution:* Compounds **3**, **4**, **10**, **12**, **13**, **14**, and **15** should be handled as dangerous explosives.

Crystal Structure Determination of BDBB (4) and 2,8-Dichloro-4,10-dinitro-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole (9).

Crystals suitable for data collection were recrystallized from dimethylformamide. 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 MoK α radiation. Samples were cooled in a stream of N₂ gas and cell dimensions determined by refinement of the setting angles of 25 reflections with $18^\circ \leq 2\theta \leq 22^\circ$. Intensity scans as a function of ψ indicated minimal variation due to absorption and no absorption corrections were applied. Three intensity control reflections were measured at two hour intervals during data collection, showing fluctuations of less than $\pm 1\%$.

The structures were solved by direct methods using the program MULTAN [13] 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 BDBB (**4**), a molecule of solvent is also present in the asymmetric unit. Crystallographic data are summarized in Table I and final atomic coordinates, bond distances and angles are given in Tables II – VII. All computer programs used were from the MolEN package. [14]

2,8-Dichloro-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole (8).

The benzotriazolobenzotriazole **6** (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 **8** as a yellow crystalline solid, 0.38 g (28%), mp 298–300 °C, lit. mp 303–305 °C. [4] ¹H nmr (dimethylsulfoxide-*d*₆/CDCl₃): 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-5H,11H-benzotriazolo[2,1-a]benzotriazole (7)* as a yellow crystalline solid, 0.37 g (30%), mp 223–225 °C; ¹H nmr (CDCl₃): δ 8.30 (d, 2H), 7.60–7.70 (m, 3H), 7.30 (d, 2H). ¹³C nmr (CDCl₃): δ 144.23, 132.05, 130.27, 125.80, 121.02, 108.53.

Anal. calcd for C₁₂H₇N₄Cl: 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 (9).

The dichloride **8** (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 stirred for 2 h and poured into ice-water (250 mL). A brick red precipitate was isolated, dried, and recrystallized from dimethylformamide to give **9** as a red crystalline solid, 0.80 g (55%), mp 330–335 °C (dec); ir (potassium bromide) ν: 1507, 1359 cm⁻¹. ¹H nmr (dimethylsulfoxide-*d*₆): δ 9.30 (d, 2H), 8.70 (d, 2H). ¹³C nmr (dimethylsulfoxide-*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 C₁₂H₄N₆O₄Cl₂: 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-dinitro-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole (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 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, 0.95 g (50%), mp 192–195 °C (dec); ir (potassium bromide) ν : 2127 (N_3), 1508 and 1351 cm^{-1} . ^1H nmr (dimethylsulfoxide- d_6): δ 9.20 (d, 2H), 8.70 (d, 2H). ^{13}C nmr (dimethylsulfoxide- d_6): δ 144.80, 138.10, 137.00, 136.50, 126.00, 122.00.

Anal. calcd for $\text{C}_{12}\text{H}_4\text{N}_{12}\text{O}_4$: 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 min or until nitrogen evolution ceased. After concentration (50%) the solution was diluted with water (200 mL) and filtered. A residue recrystallized from acetone to give the bisfuroxan **11** as a light yellow solid, 0.50 g (57%), mp 270–274 °C (dec); ir (potassium bromide) ν : 1654 ($\text{C} = \text{N}$) cm^{-1} . ^1H nmr (dimethylsulfoxide- d_6): δ 9.10 (d, 2H), 8.67 (d, 2H).

Anal. calcd for $\text{C}_{12}\text{H}_4\text{N}_8\text{O}_4$: 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 (4).

The bisfuroxan **11** (0.52 g, 1.6 mmol) was added slowly to concentrated sulfuric acid (2 mL) at 0 °C and after 10 min, 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 one hour at 0 °C and poured into ice-water (150 mL) to bring about the precipitation of the dinitro derivative **4** as

a red solid. After isolation and drying it recrystallized from dimethylformamide as an amorphous solid, 0.33 g (50%), mp 310 °C (dec); ir (potassium bromide) ν : 1654 (C = N), 1500, 1357 cm^{-1} . ^1H nmr (dimethylsulfoxide- d_6): δ 9.50 (s). ^{13}C nmr (dimethylsulfoxide- d_6): δ 141.00, 138.00, 132.00, 128.13, 128.00, 118.00.

Anal. calcd for $\text{C}_{12}\text{H}_2\text{N}_{10}\text{O}_8$: C, 34.81; H, 0.49; N, 33.81. Found: C, 34.52; H, 0.62; N, 32.90.

4,10-Diazido-2,8-dinitro-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole (13). [4]

Sodium azide (4.00 g, 60 mmol) was added with stirring over a period of 15 min at 25 °C to TACOT 2 (6.30 g, 16 mmol) in dry dimethylsulfoxide (ca. 130 mL). The mixture was maintained at 70 – 80 °C for one hour as the color deepened. After cooling in ice-water a precipitate was isolated and washed with ethanol (10 mL) and with ether (10 mL) to give the diazide **13** as a yellow-orange solid (2.50 g, 42%), mp 187 °C (dec) [lit. mp 200 °C (dec)]; ir (potassium bromide) ν : 2134 (N_3), 1597, 1518 and 1353 cm^{-1} .

4,10-Diazido-2,3,8,9-tetranitro-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole (14).

Nitric acid (90%, 9.50 mL) was added at 0–5 °C to dinitro diazide **13** (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, 82%). Purification by column chromatography [hexane/acetone (7:3)] gave the tetranitro diazide **15** as an orange-red solid, 1.60 g (50%), mp 260 – 261 °C (dec); ir (potassium bromide) ν : 2131 (N_3), 1543 and 1361 cm^{-1} . ^1H nmr (dimethylsulfoxide – d_6): δ 9.50 (s). ^{13}C nmr (dimethylsulfoxide – d_6): δ 151.80, 131.00, 126.00, 122.22, 117.00, 113.60; uv ($\text{C}_2\text{H}_5\text{OH}$): λ_{max} 457 nm, log ϵ 4.52; λ_f ($\text{C}_2\text{H}_5\text{OH}$) 532 nm, Φ 0.10.

Anal. calcd for $\text{C}_{12}\text{H}_2\text{N}_{14}\text{O}_8$: 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 2,3,8-trinitro-4,10-diazido-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole (**15**) as an orange-red amorphous solid, 0.28 g (10%),

mp 255–256 °C (dec); ir (potassium bromide) ν : 2136 (N_3), 1558 and 1319 cm^{-1} . ^1H 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 $\text{C}_{12}\text{H}_3\text{N}_{13}\text{O}_6$: C, 33.91; H, 0.71; N, 42.81. Found: C, 33.80; H, 1.15; N, 42.01.

BDBB (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 one hour 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 (potassium bromide) ν : 1654 ($\text{C}=\text{N}$), 1533 and 1302 cm^{-1} . ^1H nmr (dimethylsulfoxide- d_6): δ 9.70 (s). ^{13}C nmr (dimethylsulfoxide- d_6): δ 140.00, 136.00, 133.00, 130.00, 126.00, 116.00.

Anal. calcd for $\text{C}_{12}\text{H}_2\text{N}_{10}\text{O}_8$: C, 34.81; H, 0.49; N, 33.81. Found: C, 34.40; H, 0.71; N, 32.20.

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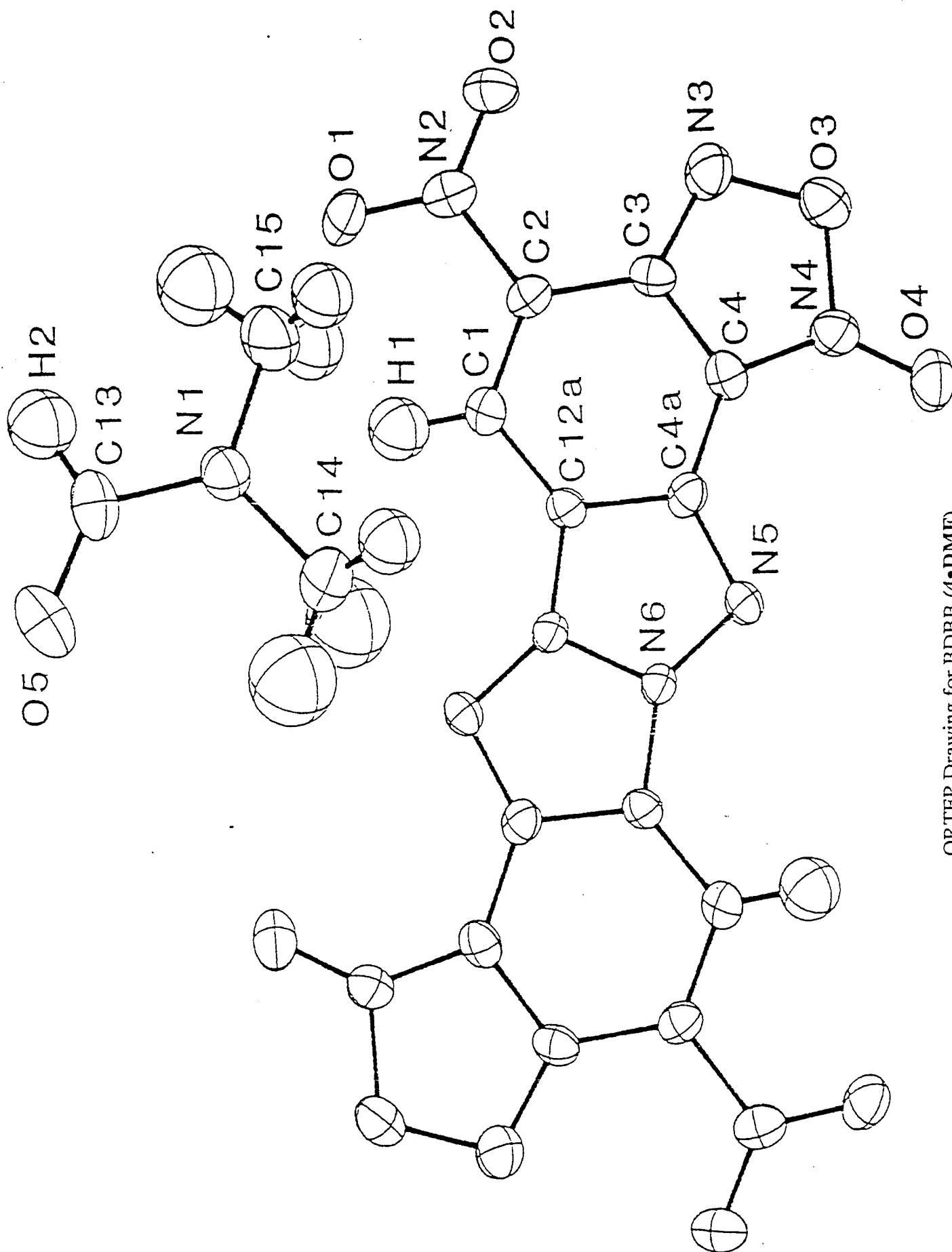
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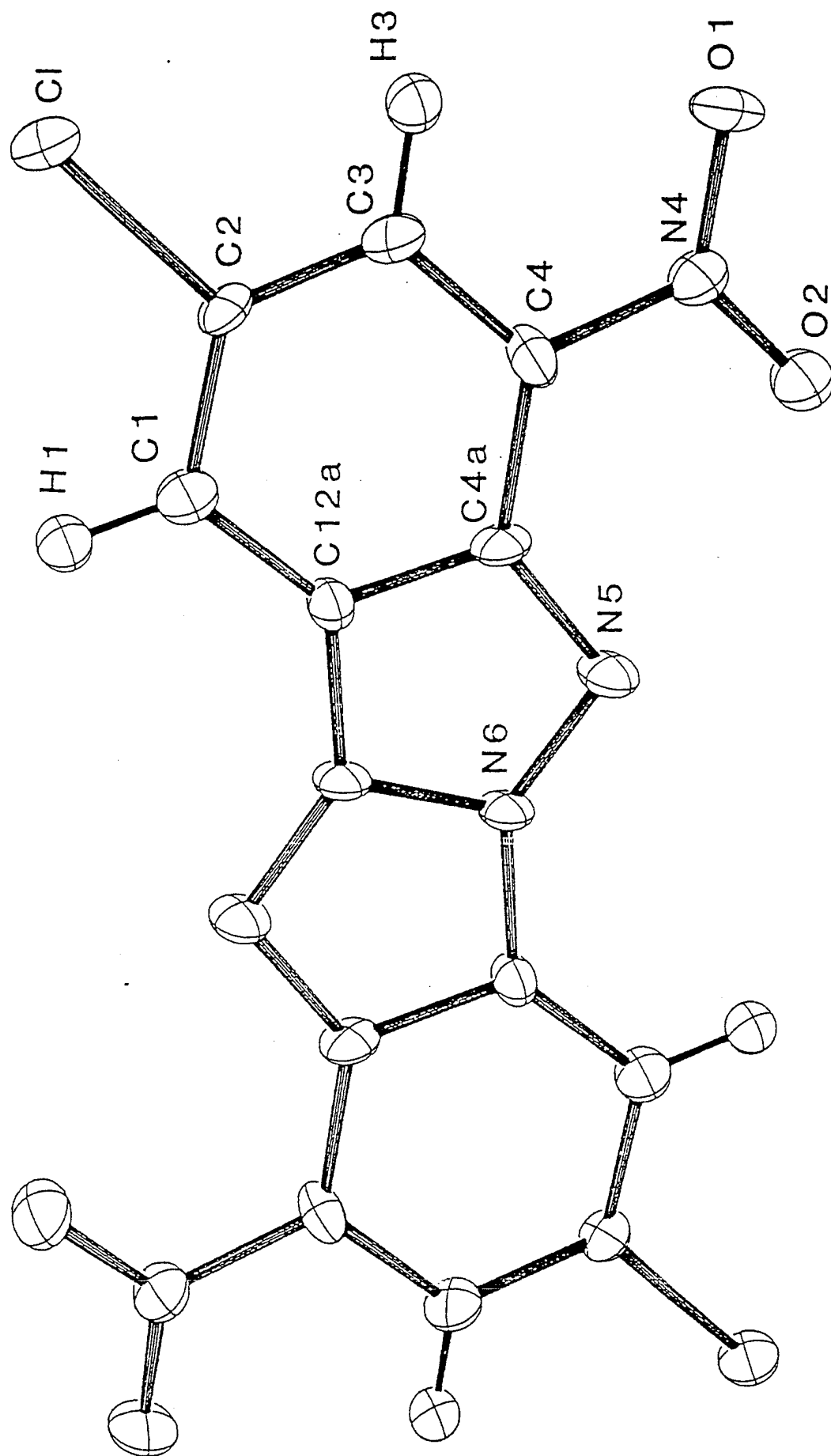
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X-ray Crystallographic Data



ORTEP Drawing for BDBB (4•DMF).



ORTEP Drawing for 9.

Table I. Summary of Crystallographic Data

Compound	4•DMF	9
Formula	$C_{12}H_2N_{10}O_8 \cdot 2C_3H_7NO$	$C_{12}H_4N_6O_4Cl_2$
Space Group	$P\bar{1}$	$P\bar{1}$
Unit Cell Dimensions		
a, Å	6.269 (9)	8.132 (4)
b, Å	9.501 (5)	4.674 (9)
c, Å	9.703 (7)	9.312 (9)
α , deg	94.03 (5)	83.22 (8)
β , deg	97.06 (8)	76.20 (7)
γ , deg	94.13 (7)	66.99 (7)
V, Å ³	570 (2)	316.3 (8)
Z, molecules/cell	1	1
Density (calcd), g/cm ³	1.632	1.927
$\mu(MoK\alpha)$, cm ⁻¹	1.276	5.480
Temperature, K	100	100
2 θ range, deg	4 – 50	2 – 40
Number of measured reflections	2356	575
Number of observed reflections ($I > 3\sigma$)	1252	482
Number of variables	214	109
Agreement factors		
R _F , %	5.78	3.92
R _{WF} , %	6.81	5.58
GOF	2.26	2.34

Table II. Bond Lengths (Å) for BDBB (4•DMF).

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O1	N2	1.237 (3)	N4	C4	1.331 (4)
O2	N2	1.218 (3)	N5	N6	1.340 (3)
O3	N3	1.391 (3)	N5	C4a	1.351 (3)
O3	N4	1.447 (4)	N6	N6	1.372 (4)
O4	N4	1.220 (3)	N6	C12a	1.371 (3)
O5	C13	1.226 (4)	C1	C2	1.362 (4)
N1	C13	1.336 (4)	C1	C12a	1.414 (4)
N1	C14	1.452 (4)	C2	C3	1.451 (4)
N1	C15	1.447 (4)	C3	C4	1.396 (4)
N2	C2	1.456 (4)	C4	C4a	1.413 (4)
N3	C3	1.328 (4)	C4a	C12a	1.405 (4)
C1	H1	1.03 (3)	C14	H5	0.93 (4)
C13	H2	0.99 (4)	C15	H6	0.98 (4)
C14	H3	1.05 (4)	C15	H7	0.91 (5)
C14	H4	0.92 (5)	C15	H8	0.87 (3)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table III. Bond Angles (degrees) for BDBB (4•DMF).

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N3	O3	N4	108.8 (2)	N2	C2	C1	119.4 (2)
C13	N1	C14	120.7 (3)	N2	C2	C3	119.8 (2)
C13	N1	C15	121.5 (3)	C1	C2	C3	120.8 (3)
C14	N1	C15	117.7 (3)	N3	C3	C2	129.0 (3)
O1	N2	O2	124.9 (3)	N3	C3	C4	112.2 (3)
O1	N2	C2	117.1 (2)	C2	C3	C4	119.0 (2)
O2	N2	C2	118.1 (2)	N4	C4	C3	108.1 (2)
O3	N3	C3	105.1 (2)	N4	C4	C4a	129.7 (3)
O3	N4	O4	119.3 (2)	C3	C4	C4a	122.2 (3)
O3	N4	C4	105.8 (2)	N5	C4a	C4	131.2 (2)
O4	N4	C4	134.9 (3)	N5	C4a	C12a	113.7 (2)
N6	N5	C4a	102.2 (3)	C4	C4a	C12a	115.2 (3)
N5	N6	N6	114.0 (3)	N6	C12a	C1	130.9 (2)
N5	N6	C12a	139.6 (2)	N6	C12a	C4a	103.7 (2)
N6	N6	C12a	106.5 (2)	C1	C12a	C4a	125.3 (2)
C2	C1	C12a	117.4 (3)	O5	C13	N1	125.9 (4)
C2	C1	H1	122 (2)	H3	C14	H5	115 (4)
C12a	C1	H1	120 (2)	H4	C14	H5	122 (3)
O5	C13	H2	125 (2)	N1	C15	H6	111 (2)
N1	C13	H2	109 (2)	N1	C15	H7	106 (2)
N1	C14	H3	117 (2)	N1	C15	H8	116 (2)
N1	C14	H4	113 (3)	H6	C15	H7	108 (4)
N1	C14	H5	107 (2)	H6	C15	H8	109 (3)
H3	C14	H4	81 (4)	H7	C15	H8	109 (3)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Positional Parameters and Their Estimated Standard Deviations for BDBB (4•DMF).

Atom	x	y	z	B (Å ²)
O1	0.7990 (4)	0.2567 (3)	0.1289 (3)	2.76 (6)
O2	0.7479 (5)	0.0842 (3)	-0.0345 (3)	2.78 (6)
O3	0.2082 (5)	0.0211 (3)	-0.3179 (3)	3.08 (6)
O4	-0.1165 (5)	0.1178 (3)	-0.3697 (3)	3.28 (7)
O5	0.3681 (5)	0.4618 (3)	0.6845 (3)	3.37 (7)
N1	0.3428 (6)	0.3043 (3)	0.4932 (3)	2.34 (7)
N2	0.6906 (5)	0.1878 (3)	0.0280 (3)	2.27 (7)
N3	0.3902 (6)	0.0502 (4)	-0.2194 (4)	2.95 (8)
N4	0.0543 (6)	0.1237 (3)	-0.2932 (4)	2.49 (7)
N5	-0.1158 (5)	0.3922 (3)	-0.1459 (3)	1.93 (6)
N6	-0.0941 (5)	0.4979 (3)	-0.0449 (3)	1.70 (6)
C1	0.4092 (6)	0.3486 (4)	0.0507 (4)	1.90 (7)
C2	0.4797 (6)	0.2352 (4)	-0.0191 (4)	1.99 (8)
C3	0.3481 (6)	0.1619 (4)	-0.1402 (4)	1.98 (8)
C4	0.1470 (6)	0.2094 (4)	-0.1846 (4)	2.00 (7)
C4a	0.0685 (6)	0.3280 (4)	-0.1170 (4)	1.93 (8)
C12a	0.2053 (6)	0.3926 (4)	-0.0006 (4)	1.76 (7)
C13	0.4432 (7)	0.3723 (4)	0.6114 (4)	2.66 (9)
C14	0.1285 (8)	0.3379 (4)	0.4365 (5)	3.5 (1)
C15	0.4498 (8)	0.2045 (5)	0.4115 (5)	3.3 (1)
H1	0.508 (7)	0.409 (4)	0.127 (5)	4 (1) ^a
H2	0.590 (7)	0.342 (4)	0.629 (5)	4(1) ^a
H3	0.052 (8)	0.410 (5)	0.498 (6)	6 (1) ^a
H4	0.131 (9)	0.413 (5)	0.381 (6)	7 (1) ^a
H5	0.048 (6)	0.253 (4)	0.407 (4)	3.2 (9) ^a
H6	0.483 (7)	0.245 (4)	0.327 (5)	4 (1) ^a
H7	0.577 (7)	0.193 (4)	0.465 (5)	5 (1) ^a
H8	0.381 (6)	0.122 (4)	0.390 (4)	3.3 (9) ^a

^aAtoms were refined isotropically.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

Table V. Bond Lengths (Å) for 9.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
CL	C2	1.737 (3)	C3	C4	1.389 (5)
O1	N4	1.227 (4)	C4	C4a	1.417 (5)
O2	N4	1.226 (4)	C2	C3	1.383 (5)
N6	N6	1.362 (6)	C3	H3	0.96
N5	N6	1.335 (4)	C1	C2	1.374 (6)
N6	C12a	1.375 (5)	C1	C12a	1.387 (5)
N5	C4a	1.365 (4)	C1	H1	0.98
N4	C4	1.439 (6)	C4a	C12a	1.419 (5)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VI. Bond Angles (degrees) for 9.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N6	N6	N5	115.9 (3)	CL	C2	C3	117.0 (3)
N6	N6	C12a	105.9 (3)	CL	C2	C1	119.4 (4)
N5	N6	C12a	138.2 (4)	C1	C2	C3	123.7 (3)
N6	N5	C4a	101.2 (3)	C2	C1	C12a	114.8 (3)
O1	N4	O2	123.2 (3)	C2	C1	H1	122
O1	N4	C4	117.1 (3)	C12a	C1	H1	123
O2	N4	C4	119.7 (4)	N6	C12a	C1	130.9 (4)
N4	C4	C3	118.8 (3)	N6	C12a	C4a	103.7 (4)
N4	C4	C4a	122.2 (3)	C1	C12a	C4a	125.3 (3)
C3	C4	C4a	119.1 (4)	N5	C4a	C4	130.4 (4)
C3	C3	C4	120.8 (3)	N5	C4a	C12a	113.2 (3)
C4	C3	H3	119	C4	C4a	C12a	116.5 (3)
C2	C3	H3	120				

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VII. Positional Parameters and Their Estimated Standard Deviations for **9**.

Atom	x	y	z	B (Å ²)
CL	0.6834 (2)	0.1670 (3)	0.0441 (1)	2.12 (3)
O1	1.2116 (4)	0.3030 (7)	0.2053 (4)	2.40 (9)
O2	1.0976 (4)	0.6835 (7)	0.3553 (4)	2.49 (9)
N4	1.0812 (5)	0.5023 (8)	0.2798 (4)	1.8 (1)
N5	0.7315 (5)	0.9252 (8)	0.4808 (4)	1.8 (1)
N6	0.5512 (5)	1.0485 (8)	0.5322 (4)	1.5 (1)
C1	0.5428 (6)	0.577 (1)	0.2633 (5)	1.7 (1)
C2	0.6995 (6)	0.389 (1)	0.1734 (5)	1.5 (1)
C3	0.8729 (6)	0.364 (1)	0.1792 (5)	1.7 (1)
C4	0.8982 (6)	0.534 (1)	0.2788 (5)	1.6 (1)
C4a	0.7433 (6)	0.7348 (9)	0.3751 (5)	1.5 (1)
C12a	0.5708 (6)	0.744 (1)	0.3626 (5)	1.4 (1)
H1	0.4212	0.5886	0.2582	1.5 ^a
H3	0.9778	0.2275	0.1135	1.5 ^a

^aAtoms were refined isotropically.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

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