Chemistry of Tetraazapentalenes

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2,4,8,10-Tetranitrobenzotriazolo[2,1-*a*]benzotriazole (TACOT), although thermally very stable and insensitive as an explosive, is susceptible to attack by nucleophiles. Reaction with azide ion results in displacement of nitro groups at the 4,10-positions, treatment with methoxide ion effects displacement of the hydrogen atom at the 1-position and scission of the remote triazole ring, while "vicarious nucleophilic amination" displaces all the aromatic hydrogens. 3,5,7-Trinitro-1,2,3-triazolo-[2,1-*a*]benzotriazole and 3,5,7-trinitro-1,2,3-triazolo[1,2-*a*]benzotriazole are prepared readily by nitration of the parent triazolobenzotriazoles. However they are thermally less stable than TACOT and more sensitive to initiation by impact. Furthermore, attempted further nitration and reaction with nucleophiles such as azide and methoxide ions both effect scission of the triazole ring to leave 4,6-dinitrobenzotriazole.

Introduction

The extreme thermal and chemical stability (mp 237−8 °C; sublimes unchanged at atmospheric pressure) of benzotriazolo[2,1-*a*]benzotriazole (**1**; dibenzo-1,3a,4,-6a-tetraazapentalene)[1] (Figure 1) have made this an attractive ring system around which to construct insensitive and thermally stable energetic materials. Thus the tetranitro derivative **2** (TACOT, so-named to reflect the **t**etra**a**za**c**yclo**o**cta**t**etraene core initially assumed for these compounds)[2] is the most thermally stable explosive known,[3] although its explosive performance is modest at best.[4] Attempts to enhance the performance of **2** by further derivatization and improvement of the oxygen balance have formed the basis for a recent series of papers[5] and encouraged us to present the results of our own research into the varied chemistry of tetraazapentalenes.

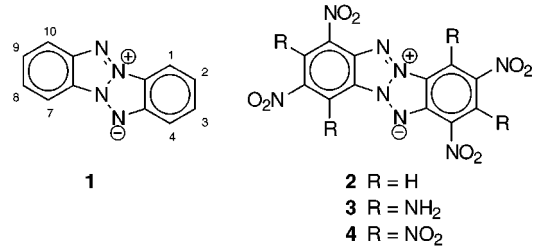

Figure 1. Numbering system for benzotriazolo[2,1-*a*]benzotriazoles.

Two obvious targets for potentially insensitive but powerful tetraazapentalenes are the tetraaminotetranitro derivative (**3**) and the octanitro variant (**4**). The former compound should have increased density and ensured stability and insensitivity, as a consequence of hydrogen bonding between the alternating amino and nitro groups, but improvement in performance would be modest (Table 1). The latter compound should have markedly enhanced density and performance, but stability and insensitivity would be limited to that conferred by the inherent stability of the dibenzotetraazapentalene skeleton, moderated by the chemical lability of the vicinal nitro groups.

Results and Discussion

Carboni originally proposed the structure 2,4,8,10-tetranitrobenzotriazolo[2,1-*a*]benzotriazole (**2**) for TACOT,[2] but more recent authors have clouded the picture with reference to different structures, and even mixtures of positional isomers.[6] We have confirmed that nitration of **1** occurs preferentially at the 2(and 8)-positions followed by the 4(and 10)-positions. Selective mono-, di-, and trinitration may be obtained by careful choice of

(1) Carboni, R. A.; Castle, J. E. *J. Am. Chem. Soc.* **1962**, *84*, 2453. Carboni, R. A.; Kauer, J. C.; Castle, J. E.; Simmons, H. E. *J. Am. Chem. Soc.* **1967**, *89*, 2618.

(2) Carboni, R. A.; Kauer, J. C.; Hatchard, W. R.; Harder, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 2626.

(3) Benson, F. R. *The High Nitrogen Compounds*; Wiley-Interscience: New York, 1984; p 394. Urbanski, T.; Vasudeva, S. K. *J. Sci. Ind. Res.* **1978**, *37*, 250.

(4) (a) Densities (ρ) quoted are those calculated by the method of Cichra, D. A.; Holden, J. R.; Dickinson, C. *Estimation of Normal Densities of Explosive Compounds from Empirical Atomic Volumes*; Silver Spring, MD, Naval Surface Weapons Center report TR 79-273. Available from the National Technical Information Service, U.S. Department of Commerce, Springfield, VA 22161, Feb 1980. (b) Explosive performance (velocity of detonation (D_v) and detonation pressure (P_{CJ})) were calculated using the method of Rothstein, L. R.; Petersen, R. *Propellants Explos.* **1979**, *4*, 56; **1981**, *6*, 91. (c) Impact sensitivity is measured using the Bureau of Mines impact machine with Type 12 tools. A 2.5 Kg weight is dropped onto a 35 mg sample on garnet paper resting on a flat tool steel anvil, and the 50% drop height ($h_{50\%}$) is that at which an explosive event occurs in 50% of tests.

(5) (a) Subramanian, G.; Boyer, J. H.; Buzatu, D.; Stevens, E. D.; Trudell, M. L. *J. Org. Chem.* **1995**, *60*, 6110. (b) Subramanian, G.; Boyer, J. H.; Trudell, M. L.; Koppes, W. M.; Sitzmann, M. E.; Nock, L. A.; Gilardi, R.; Russell, T. P. *J. Org. Chem.* **1996**, *61*, 1898. (c) Subramanian, G.; Eck, G.; Boyer, J. H.; Stevens, E. D.; Trudell, M. L. *J. Org. Chem.* **1996**, *61*, 5801.

(6) Urbanski, T. *Chemistry and Technology of Explosives*, Vol. 4; Pergamon Press: Oxford, 1984; p 211. Meyer, R. *Explosives*, 2nd ed.; Verlag Chemie: Weinheim, 1981; p 323.

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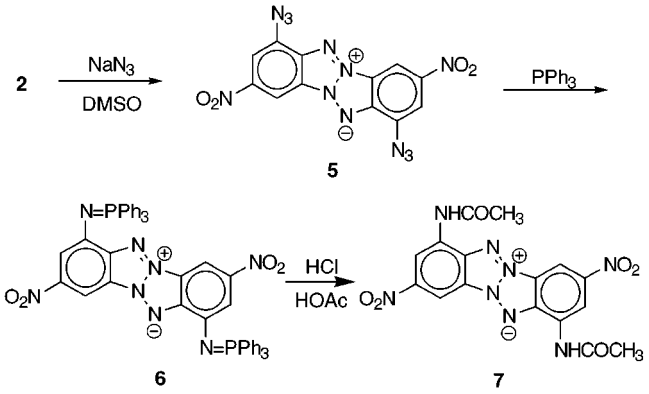
Table 1. Explosive Performance of Benzotriazolo[2,1-*a*]benzotriazoles[4]

	mp (°C)	ρ (g/mL)	D_v (m/s)	P_{CJ} (kbar)	$h_{50\%}$ (cm)
R = H (**2**)	410	1.82	7060	203	>200
R = NH_2 (**3**)		1.86	7570	250	
R = NO_2 (**4**)		2.00	8590	346	

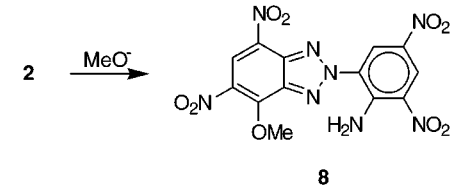
Scheme 1. Nucleophilic Displacement in TACOT



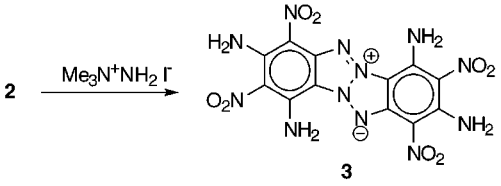
reaction conditions, but duplication of Carboni's mixed acid nitration at 60 °C gave a single pure isomer, fully consistent by ^{1}H and ^{13}C NMR spectroscopy with **2**.[7] The material reproduced in these laboratories was identical in all respects with the commercial product obtained from DuPont. Final confirmation of the structure was afforded by X-ray crystallographic analysis.[8]

Further nitration of **2** to **4** cannot be achieved by direct methods; a more productive approach might be selective reduction of two of the nitro groups to amines, followed by nitration at the now activated positions and finally reoxidation of the amines, in the manner used to prepare polynitroaromatics such as hexanitrobenzene.[9] Unfortunately, selective reduction of the nitro groups in TACOT proved difficult, but a variant of this approach suggested itself. Treatment of **2** with lithium azide in DMF at 80−85 °C was reported to give, by nucleophilic displacement of one pair of nitro groups, a single symmetrical diazidodinitro compound, whose structure could not be assigned unequivocally at that time.[2] Apparently the same compound was obtained using sodium azide in DMSO at 100 °C[5a] and was tentatively assigned the structure **5** (4,10-diazido-2,8-dinitrobenzotriazolo[2,1-*a*]-benzotriazole) on the basis of its ^{1}H NMR spectrum (Scheme 1). Reaction of this material with triphenylphosphine in ethanol or benzene, at ambient temperature or under reflux, gave an exceedingly insoluble purple solid presumed on the basis of infrared and mass spectroscopy to be the bis(triphenylphosphinimine) **6**. Hydrolysis of this phosphinimine required more vigorous conditions than are usually necessary, but concentrated hydrochloric acid in acetic acid under reflux gave 4,10-bis(acetamido)-2,8-dinitrobenzotriazolo[2,1-*a*]benzotriazole (**7**), whose structure was confirmed by X-ray crystallographic analysis of a solvated crystal grown from DMSO,[8] thereby also supporting the structure **5** for the diazidodinitro compound. Surprisingly, **7** proved resistant to both hydrolysis to the 4,10-diamino compound and to further nitration and gave only decomposition under forcing conditions.

Scheme 2. Nucleophilic Scission of Triazole Ring



Scheme 3. Vicarious Nucleophilic Substitution (VNS)



Initial uncertainty regarding the course of the nucleophilic displacement by azide ion prompted us to examine the reaction of **2** at ambient temperature with methanolic sodium methoxide, selected to provide a convenient signal for NMR analysis (Scheme 2). However, the reaction took a substantially different course; instead of displacement of a nitro group, addition of methoxyl occurred at the 1-position, followed by scission of the remote triazole ring to give 2-(2′-amino-3′,5′-dinitrophenyl)-7-methoxy-4,6-dinitrobenzotriazole (**8**). The structure was deduced on the basis of IR, NMR (^{1}H, ^{13}C, and short- and long-range coupling experiments), and mass spectroscopy and was confirmed by X-ray crystallographic analysis.[8] While nucleophilic attack of benzotriazolo[2,1-*a*]benzotriazole and its derivatives at the 1-position has not previously been reported, there is precedent for scission of the triazole ring in the reduction of **1** with lithium aluminum hydride, in its oxidation with peracetic acid and in the reaction of its 2-bromo- and 2,8-dibromo derivatives with cuprous cyanide.[2a] It should also be noted that the methoxyl group in **8** is quite labile and undergoes facile nucleophilic displacement by ammonia, by azide ion, or even by adventitious moisture.[7]

A method frequently convenient for the synthesis of polyaminopolynitroaromatics is the so-called "vicarious nucleophilic substitution" of hydrogen (VNS) on a suitable polynitroaromatic. An early transformation of this type was Meisenheimer's synthesis of 2,4-diamino-1,3-dinitrobenzene by treatment of *m*-dinitrobenzene with hydroxylamine under basic conditions at ambient temperature.[10] More recent VNS reagents have included 4-amino-1,2,4-triazole,[11] sulfenamides,[12] and trimethylhydrazinium iodide,[13] each with a strong base in a polar aprotic solvent at ambient temperature. Subjecting **2** to the VNS conditions using either hydroxylamine or trimethylhydrazinium iodide gave a very insoluble red solid, which melts with decomposition at 350 °C and which was provisionally identified as 1,3,7,9-tetraamino-2,4,8,10-tetranitrobenzotriazolo[2,1-*a*]benzotriazole (**3**) (Scheme

(7) Wilson, W. S. Unpublished results.
(8) The authors have deposited atomic coordinates for structures with the Cambridge Crystallographic Data Centre. The coordinates may be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.
(9) Nielsen, A. T.; Atkins, R. L.; Norris, W. P. *J. Org. Chem.* **1979**, *44*, 1181. Nielsen, A. T.; Atkins, R. L.; Norris, W. P.; Coon, C. L.; Sitzmann, M. E. *J. Org. Chem.* **1980**, *45*, 2341.
(10) Meisenheimer, J.; Patzig, E. *Chem. Ber.* **1906**, *39*, 2533.
(11) Katritzky, A. R.; Laurenzo, K. S. *J. Org. Chem.* **1986**, *51*, 5039.
(12) Makosza, M.; Bialecki, M. *J. Org. Chem.* **1992**, *57*, 4784.
(13) Pagoria, P. F.; Mitchell, A. R.; Schmidt, R. D. *J. Org. Chem.* **1996**, *61*, 2934.

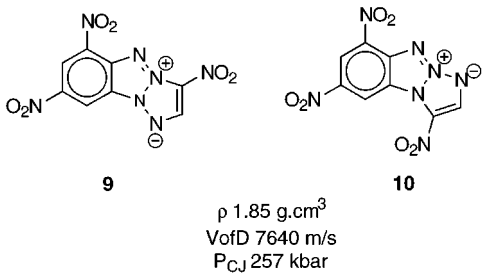
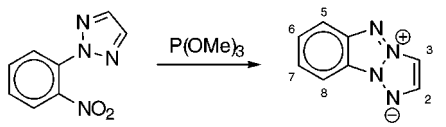
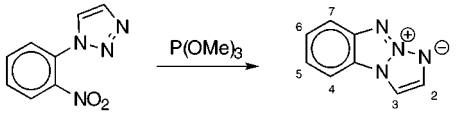


Figure 2. Explosive performance properties of isomeric trinitrobenozotriazoles.

Scheme 4. Synthesis of 1,2,3-Triazolo[2,1-*a*]benzotriazole (12)



Scheme 5. Synthesis of 1,2,3-Triazolo[1,2-*a*]benzotriazole (14)

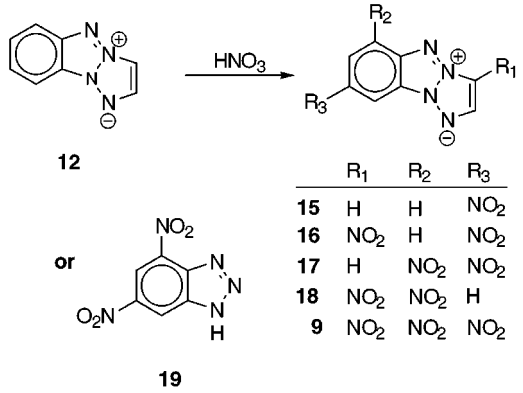


3). The low solubility made purification difficult and recrystallization and solution state NMR spectroscopy impossible, but solid state NMR is consistent with the assigned structure, as is the infrared spectrum which shows the presence of $-NO_2$'s and two distinct $-NH_2$'s, but no CH's. The mass spectrum does not show the expected parent ion at *m*/*z* 448. However, the base peak at *m*/*z* 239 corresponds to diaminodinitrobenzotriazole, a fragment ion expected from **3**. In common with other high nitrogen compounds, and particularly other tetraazapentalenes, elemental analysis for nitrogen is low but carbon and hydrogen are in reasonable agreement with the values expected.

Triazolobenzotriazoles. If the thermal and chemical stability of the dibenzo-1,3a,4,6a-tetraazapentalene (benzotriazolo[2,1-*a*]benzotriazole) ring system were also found in the monobenzo compounds, then the latter may similarly provide appropriate bases from which to design new insensitive energetic materials. For example, the isomeric trinitro compounds **9** and **10** (Figure 2) should be more energetic than TACOT (**2**) as a consequence of a more favorable oxygen balance, and further substitution should lead to even more powerful explosives.

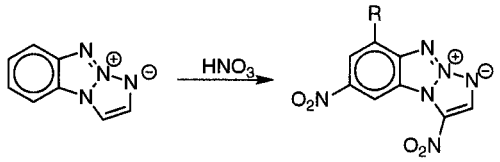
The parent heterocyclic ring systems 1,2,3-triazolo[2,1-*a*]benzotriazole (**12**; 2,3-benzo-1,3a,4,6a-tetraazapentalene) and 1,2,3-triazolo[1,2-*a*]benzotriazole (**14**; 1,2-benzo-1,3a,4,6a-tetraazapentalene) were prepared by heating 2-(2′-nitrophenyl)-1,2,3-triazole (**11**) and 1-(2′-nitrophenyl)-1,2,3-triazole (**13**) respectively in trialkyl phosphite (Schemes 4 and 5). The isomeric aryltriazoles may be prepared in a 3:1 ratio from 1,2,3-triazole and 2-fluoronitrobenzene and separated by vacuum distillation, but **13** is more conveniently obtained by cycloaddition of acetylene to 2-azidonitrobenzene. In contrast to that of **1**, **12** and **14** have melting points of only 108−9 and 121−2 °C.[2a,14]

Scheme 6. Nitration of 1,2,3-Triazolo[2,1-*a*]benzotriazole (12)



	R_1	R_2	R_3
15	H	H	NO_2
16	NO_2	H	NO_2
17	H	NO_2	NO_2
18	NO_2	NO_2	H
9	NO_2	NO_2	NO_2

Scheme 7. Nitration of 1,2,3-Triazolo[1,2-*a*]benzotriazole (14)



Nitration of 1,2,3-triazolo[2,1-*a*]benzotriazole (**12**) can be achieved selectively, occurring first at the 7-position which is followed by nitration at the 3- and 5-positions. Thus, while **12** is unaffected by treatment with 25% nitric acid, 45% nitric acid gives the 7-nitro derivative (**15**, 39%) and the 3,7-dinitro compound (**16**, 58%), and 70% nitric acid yields a mixture of **16** (52%) and the 5,7- and 3,5-isomers **17** (23%) and **18** (ca. 5% by NMR, but not isolated). Clean trinitration to 3,5,7-trinitro-1,2,3-triazolo[2,1-*a*]benzotriazole (**9**) was achieved using 3 equiv of 100% nitric acid in 98% sulfuric acid at ambient temperature. In contrast with the stability of TACOT (**2**) to these conditions, however, nitration of **12** with a 12-fold excess of 100% nitric acid in 98% sulfuric acid resulted in disruption of the triazole ring to leave the previously known[15] 4,6-dinitrobenzotriazole (**19**). The structures of **9**, **15**, **16**, **17**, and **18** (Scheme 6) were assigned on the basis of ^1H and ^{13}C NMR spectroscopy; the structures of **9** and **17** were confirmed unequivocally by X-ray crystallographic analysis.[8]

Nitration of 1,2,3-triazolo[1,2-*a*]benzotriazole (**14**) with 70% nitric acid gave a complex mixture of mono- and dinitro derivatives, from which was isolated the 3,5-dinitro compound (**20**, 47%). Trinitration to 3,5,7-trinitro-1,2,3-triazolo[1,2-*a*]benzotriazole (**10**) was achieved cleanly and in 80% yield using 3 equiv of 100% nitric acid in 98% sulfuric acid at ambient temperature (Scheme 7). In the absence of crystals suitable for X-ray analysis, structural assignment of **20** and **10** was based on ^1H and ^{13}C NMR spectroscopy and on analogy with the related compounds described above.

With melting points (decomposition) of 250−3 °C and 265−6 °C, respectively, the trinitro compounds **9** and **10**

(14) Kauer, J. C.; Carboni, R. A. *J. Am. Chem. Soc.* **1967**, *89*, 2633.
(15) Nietzki, R.; Hagenbach, H. *Ber.* **1897**, *30*, 543.

are thermally quite stable, without however approaching the unprecedented stability of TACOT. On the other hand, **9** and **10** each have a 50% drop height ($h_{50\%}$) of 26 cm in the dropweight impact test, indicating a sensitivity comparable with RDX (cyclotrimethylenetrinitramine). While it is possible that the sensitivity may be a consequence of the asymmetry of the triazolobenzotriazole nuclei, these results suggest that energetic materials based on the triazolo[2,1-*a*]triazole ring system may also be rather sensitive. Finally, attempted nucleophilic attack of either **9** or **10** with azide or methoxide ion also gave 4,6-dinitrobenzotriazole (**19**), although the parent heterocycle **12** was inert to attack by methoxide ion. Clearly the nitrotriazole ring is prone to rupture by either electrophilic (NO_2^+) or nucleophilic (MeO^-) species, and it is probable that the initial processes in impact initiation of **9** and **10** are also localized in this portion of the molecule(s).

Conclusion

Although it is thermally very stable and explosively insensitive, 2,4,8,10-tetranitrobenzotriazolo[2,1-*a*]benzotriazole (TACOT) is surprisingly susceptible to a variety of nucleophilic substitution reactions. Reaction with azide ion results in displacement of the nitro groups at the 4,10-positions. Reaction with methoxide ion affords displacement of the hydrogen atom at the 1(7)-position, followed by scission of the remote triazole ring. Vicarious nucleophilic amination apparently yields the tetraminotetranitro compound.

The trinitrotriazolobenzotriazoles have less thermal stability and are quite sensitive to initiation by impact. Furthermore, they are susceptible to both electrophilic and nucleophilic attack, yielding 4,6-dinitrobenzotriazole on attempted further nitration or when treated with azide or methoxide ion. The annelated nitrotriazole ring appears to be responsible for this thermal, explosive, and chemical reactivity, and triazolobenzotriazoles are probably not a viable source of insensitive explosive ingredients.

Experimental Section

WARNING: Compounds described in this report are potentially explosive and may be subject to accidental initiation by such environmental stimuli as impact, friction, heat, or electrostatic discharge. Appropriate precautions should therefore be taken in their handling and/or use.

4,10-Diazido-2,8-dinitrobenzotriazolo[2,1-*a*]benzotriazole (5). 2,4,8,10-Tetranitrobenzotriazolo[2,1-*a*]benzotriazole (TACOT, **2**) (3.10 g, 8.0 mmol) was added to DMSO (65 mL), and the mixture was heated to 100 °C. Sodium azide (1.95 g, 30.0 mmol) was added slowly and with stirring, and the mixture was heated at 100 °C for 1 h, turning very deep red in color. The mixture was allowed to cool to ambient temperature overnight, and the orange solid was filtered off and washed with ethanol (10 mL) and finally ether (10 mL) to give **5** (1.33 g, 46%), mp 197 °C (dec) (lit.[5a] mp 200 °C (dec)). IR: 2120, 1600, 1525, 1360 cm^{-1}. ^1H NMR (DMSO-d_6, 35 °C): 9.03 (d, J = 1.92 Hz, $H_{1,7}$), 8.15 (d, J = 1.92 Hz, $H_{3,9}$).

4,10-Bis(triphenylphosphinimino)-2,8-dinitrobenzotriazolo[2,1-*a*]benzotriazole (6). Triphenylphosphine (0.80 g, 3.1 mmol) was dissolved in benzene (200 mL) at ambient temperature, and 4,10-diazido-2,8-dinitrobenzotriazolo[2,1-*a*]benzotriazole (**5**) (0.50 g, 1.3 mmol) was added. The reaction mixture was stirred for 48 h to give a purple solution and a dark purple solid. Filtration gave a purple solid (1.00 g, 90%), mp 377 °C (dec). The same product was obtained when the reaction was carried out in ethanol at ambient temperature for 24 h or in benzene solution under reflux for 4 h. This material was too insoluble in the available deuterated solvents (including cloroform, acetone, hot DMSO, hot DMF, and methanol) for measurement of NMR spectra, but the IR spectra displayed clean, sharp signals, with a notable absence of any azide signals around 2100 cm^{-1}. The compound was tentatively identified with the structure **6**. IR: 1600, 1515, 1495, 1440 cm^{-1}. *M*/*z*: 848 (parent ion, discernible), 278, 78 (base peak).

4,10-Bis(acetamido)-2,8-dinitrobenzotriazolo[2,1-*a*]benzotriazole (7). 4,10-Bis(triphenylphosphinimino)-2,8-dinitrobenzotriazolo[2,1-*a*]benzotriazole (**6**) (0.58 g, 0.68 mmol) was added to glacial acetic acid (50 mL), followed by concentrated hydrochloric acid (5 mL), and the mixture was heated under reflux with stirring for 48 h, during which time a brick red solid was formed. The solid was filtered off and washed by heating overnight in ethanol (50 mL) under reflux. Filtration and drying gave 0.23 g (82%). Recrystallization from DMSO gave 4,10-bis(acetamido)-2,8-dinitrobenzotriazolo[2,1-*a*]benzotriazole (**7**)[8] (solvated with 2 mol of DMSO) (0.22 g, 67%), mp 408 °C (dec) (endotherm at ca. 130 °C; loss of DMSO). IR: 3260, 1670, 1605 cm^{-1}. ^1H NMR (DMSO-d_6): 10.63 (br s, 2H, NH's), 9.22 (d, J = 2.06 Hz, $H_{1,7}$), 8.74 (d, J = 2.06 Hz, $H_{3,9}$), 2.53 (s, 12H, $(CH_3)_2SO$), 2.33 (s, 6H, $COCH_3$'s). ^{13}C NMR (DMSO-d_6): 169.6 (CO's), 142.5 ($C_{2,8}$), 140.7 ($C_{1a,7a}$), 128.1 ($C_{4,10}$), 117.3 ($C_{4a,10a}$), 110.4 ($C_{1,7}$), 103.0 ($C_{3,9}$), 39.7 ($(CH_3)_2SO$), 23.5 (CH_3's). (Assignments are not unequivocal.) *M*/*z*: 412 (parent ion), 370, 328 (base peak), 282, 78, 63. DMSO was also separated and detected (78 (parent ion), 63 (base peak)).

2-(2′-Amino-3′,5′-dinitrophenyl)-7-methoxy-4,6-dinitrobenzotriazole (8). 2,4,8,10-Tetranitrobenzotriazolo[2,1-*a*]benzotriazole (TACOT, **2**) (1.00 g, 3.6 mmol) was added to methanolic sodium methoxide (1.00 g sodium metal in 100 mL of methanol) at ambient temperature. The solid appeared to dissolve to give a deep red solution, whereupon an orange solid started to appear. After the reaction mixture was stirred at ambient temperature for 24 h, the solid was filtered off and washed with a little cold methanol (10 mL) to give a dirty orange solid. Suspension in methanol (100 mL) and stirring at ambient temperature for 3 h gave a clean orange solid (1.13 g), probably a Meisenheimer salt. (^1H NMR (DMSO-d_6): 9.04 (br s, NH_2), 9.02 (s, 1H), 8.90 (d, J = 2.76 Hz, 1H), 8.80 (d, J = 2.76 Hz, 1H), 3.07 (s, OCH_3, 6H).) Suspension in water (100 mL) and acidification with 37% hydrochloric acid gave a clean yellow solid (0.85 g), recrystallized from acetone/ethanol to give **8** as ochre/yellow crystals (0.76 g),[8] mp 229−232 °C. IR: 3400, 3280, 3100, 1625, 1580, 1535 cm^{-1}. ^1H NMR (DMSO-d_6): 9.09 (s, H_5), 9.07 (d, J = 2.80 Hz, $H_{4'}$), 8.87 (d, J = 2.80 Hz, $H_{6'}$), 8.45 (br s, NH_2), 4.75 (s, OCH_3). ^{13}C NMR (DMSO-d_6): 152.1 (C_7), 144.3 ($C_{2'}$), 140.8 (C_{3a}), 138.4 (C_{7a}), 133.6 ($C_{5'}$), 132.8 (C_4), 131.9 ($C_{3'}$), 128.7 (C_6), 128.2 ($C_{6'}$), 126.7 ($C_{1'}$), 125.4 ($C_{4'}$), 124.4 (C_5), 63.7 (OCH_3). (Note: NMR spectra should be run on freshly prepared solutions, due to instability of **8** in this solvent.) *M*/*z*: 420 (parent ion and base peak), 406, 405, 333, 328, 239, 209.

1,3,7,9-Tetraamino-2,4,8,10-tetranitrobenzotriazolo-[2,1-*a*]benzotriazole (3). (a) 1,1,1-Trimethylhydrazinium iodide[13] (0.58 g, 2.9 mmol) and sodium methoxide (0.31 g, 5.8 mmol) were added with stirring to dry DMSO (8 mL) at ambient temperature. 2,4,8,10-Tetranitrobenzotriazolo[2,1-*a*]-benzotriazole (TACOT, **2**) (0.23 g, 0.6 mmol) was added, and the mixture was stirred at ambient temperature overnight before being quenched in water (50 mL). The resultant fine precipitate was filtered off and washed with water (2 × 50 mL) and then ethanol (50 mL) before being dried to give a dark red brown solid (0.24 g, 90%), mp 350 °C (dec). IR: 3403, 3366, 3295, 3251, 1619, 1583, 1507 cm^{-1}. *M*/*z*: 239 (base peak), 224, 118, 91, 77, 68, 67. Anal. Calcd for $C_{12}H_8N_{12}O_8$: C, 32.15; H, 1.80; N, 37.50. Found: C, 32.01; H, 2.08; N, 33.35.

(b) Potassium hydroxide (2.00 g, 36 mmol) was dissolved in water (20 mL) and cooled in an ice/water bath. Hydroxylamine hydrochloride (0.20 g, 2.88 mmol) was added in portions, followed by 2,4,8,10-tetranitrobenzotriazolo[2,1-*a*]-benzotriazole (TACOT, **2**) (0.20 g, 0.52 mmol). The reaction

mixture was stirred at ambient temperature overnight to give an orange suspension. Acidification with concentrated hydrochloric acid gave a mustard-colored suspension. Filtration, washing with water (2 × 50 mL) and ethanol (50 mL), and finally drying gave a brown solid (0.20 g, 87%), identical with that described above.

Nitration of 1,2,3-Triazolo[2,1-*a*]benzotriazole (12). (a) Nitration with 45% Nitric Acid. 1,2,3-Triazolo[2,1-*a*]benzotriazole (**12**) (0.316 g, 2 mmol) was added to water (10 mL) and cooled below 5 °C in an ice bath while 70% nitric acid (16 mL) was added. After 1 h below 10 °C, the solution was poured into water (100 mL). The precipitate was filtered off and washed with water and ether to give a brick red solid (0.160 g, 39%), which was recrystallized from acetonitrile (50 mL) to give **7-nitro-1,2,3-triazolo[2,1-*a*]benzotriazole** (**15**) (0.09 g, 25%), mp 245 °C (dec). ^{1}H NMR (DMSO-d_6): 8.95 (d, J = 2.43 Hz, 1H), 8.78 (d, J = 1.41 Hz, 1H), 8.53 (d, J = 1.41 Hz, 1H), 8.33 (dd, J = 2.33, 9.39 Hz, 1H), 7.80 (d, J = 9.03 Hz, 1H). Anal. Calcd for $C_8H_5N_5O_2$: C, 47.30; H, 2.48; N, 34.47. Found: C, 45.65/45.42; H, 1.46/1.30, N, 33.52/33.49. The reaction filtrate was extracted with ether (4 × 50 mL) to give a brown solid (0.29 g, 53%), identified by ^{1}H NMR as mainly 3,7-dinitro-1,2,3-triazolo[2,1-*a*]benzotriazole (**16**).

(b) Nitration with 70% Nitric Acid. 1,2,3-Triazolo[2,1-*a*]benzotriazole (**12**) (0.429 g, 2.7 mmol) was added to 70% nitric acid (15 mL) held below 5 °C in an ice/water bath. After 3 h below 5 °C, the solution was poured into water (100 mL) and extracted with chloroform (2 × 30 mL). The extract was dried over magnesium sulfate and evaporated to dryness to give an orange solid (0.537 g, 80%), shown by ^{1}H NMR to be a mixture of three isomeric dinitro compounds. Purification by column chromatography (silica gel eluted with 40% ethyl acetate/hexanes), followed by crystallization from acetonitrile, gave **3,7-dinitro-1,2,3-triazolo[2,1-*a*]benzotriazole** (**16**) (0.130 g, 19%), mp 250−253 °C. ^{1}H NMR (DMSO-d_6): 9.48 (s, 1H), 9.24 (d, J = 2.02 Hz, 1H), 8.50 (dd, J = 2.16, 9.32 Hz, 1H), 8.31 (d, J = 9.32 Hz, 1H). Anal. Calcd for $C_8H_4N_6O_4$: C, 38.72; H, 1.62; N, 33.87. Found: C, 39.31/39.09; H, 0.90/1.10; N, 34.22/34.30. Further elution gave a yellowish orange solid (0.18 g) which, after recrystallization from 10 mL of CH_3CN, gave red crystals (0.04 g; 6%) identified by ^{1}H and ^{13}C NMR as **5,7-dinitro-1,2,3-triazolo[2,1-*a*]benzotriazole** (**17**).[8] ^{1}H NMR (DMSO-d_6): 9.29 (d, J = 2.08 Hz, 1H), 9.07 (d, J = 1.39 Hz, 1H), 9.04 (d, J = 2.09 Hz, 1H), 8.69 (d, J = 1.37 Hz, 1H). ^{13}C NMR (DMSO-d_6): 142.8, 140.3, 136.6, 130.8, 122.0, 119.6, 113.1, 109.4

(c) Nitration with 100% Nitric Acid (3 equiv) in 98% Sulfuric Acid. 1,2,3-Triazolo[2,1-*a*]benzotriazole (**12**) (6.32 g, 40 mmol) was dissolved in 98% sulfuric acid (100 mL) below 5 °C in an ice bath. Then 100% nitric acid (5 mL, 121 mmol) was added dropwise. The solution was stirred at 5 °C for 3 h and then poured into cold water (700 mL). The precipitate was filtered off, washed with water, and then dried to give an orange solid (10.73 g, 92%). Recrystallization from acetonitrile (1.4 L) gave **3,5,7-trinitro-1,2,3-triazolo[2,1-*a*]benzotriazole** (**9**)[8] (6.38 g, 55%), mp 271−272 °C. The mother liquors were concentrated and cooled to give a further 2.21 g (18%) for a total yield of 73%. IR (KBr): 3103.4 (m), 1544.0 (s), 1329.3 (s), 1144.0 (s) cm^{-1}. ^{1}H NMR (DMSO-d_6): 9.75 (d, J = 2.06 Hz, 1H), 9.65 (s, 1H), 9.21 (d, J = 2.06 Hz, 1H); (CD_3CN): 9.44 (d, J = 2.05 Hz, 1H), 9.28 (d, J = 2.04 Hz, 1H), 9.03 (s, 1H). ^{13}C NMR (DMSO-d_6): 141.3, 141.1, 138.0, 134.2, 121.8, 120.4, 118.0, 115.1. *M*/*z*: 293 (80%, M^+), 277 (10%). Anal. Calcd for $C_8H_3N_7O_6$: C, 32.78; H, 1.03; N, 33.45. Found: C, 33.23; H, 0.54; N, 33.67.

(d) Nitration with Excess 100% Nitric Acid (12 equiv) in 98% Sulfuric Acid. 1,2,3-Triazolo[2,1-*a*]benzotriazole (**12**) (0.316 g, 2 mmol) was dissolved in 98% sulfuric acid (15 mL). After the solution was cooled to below 5 °C in an ice/water bath, 100% nitric acid (1.0 mL, 24 mmol) was added dropwise. The cooling bath was removed and replaced by an oil bath at 45 °C. After 16 h at 45 °C, the mixture was cooled and poured into ice water (100 mL). The clear bright yellow solution was extracted with chloroform (3 × 40 mL) to give an orange solid (0.22 g, 53%) identified by ^{1}H NMR and mass spectrum as 4,6-dinitrobenzotriazole (**19**).[15]

Reaction of 3,5,7-Trinitro-1,2,3-triazolo[2,1-*a*]benzotriazole (9) with Sodium Methoxide. A solution of 3,5,7-trinitro-1,2,3-triazolo[2,1-*a*]benzotriazole (**9**) (0.29 g, 1 mmol) in acetonitrile (35 mL) was added to a solution of sodium methoxide (0.023 g of sodium (1 mmol) in 15 mL of methanol) at 0 °C. After 16 h of stirring at ambient temperature, the solution was evaporated to dryness to give an orange solid. This material was initially insoluble in dichloromethane, but dissolved on addition of 50 mL of 1 N hydrochloric acid. The organic layer was dried over magnesium sulfate and the solvent removed to give an orange glassy solid (0.258 g; solvated) identical to an authentic sample of 4,6-dinitrobenzotriazole (**19**).[15]

3,5-Dinitro-1,2,3-triazolo[1,2-*a*]benzotriazole (20). 1,2,3-Triazolo[1,2-*a*]benzotriazole (**14**) (0.158 g, 1 mmol) was added to 70% nitric acid (7 mL) held below 5 °C in an ice/water bath. After 3 h below 5 °C, the solution was poured into H_2O (50 mL) to give a fine suspension. Extraction with chloroform (3 × 25 mL), drying over magnesium sulfate, and evaporation of the chloroform extract gave an orange solid (0.096 g), shown by ^{1}H NMR to be a complex mixture. Filtration of the aqueous mother liquor gave an orange solid (0.117 g, 47%), identified by ^{1}H NMR as 3,5-dinitro-1,2,3-triazolo[1,2-*a*]benzotriazole. Crystallization from acetonitrile gave 0.075 g of orange crystals (mp 265−266 °C). ^{1}H NMR (DMSO-d_6): 9.44 (s, 1H), 9.31 (d, J = 2.53 Hz, 1H), 8.53 (dd, J m= 2.35, 9.51 Hz, 1H), 8.26 (dd, J = 0.53, 9.49 Hz, 1H); (acetone-d_6): 9.50 (dd, J = 0.60, 2.40 Hz, 1H), 9.14 (s, 1H), 8.59 (dd, J = 2.12, 9.30 Hz, 1H), 8.21 (dd, J = 0.62, 9.45 Hz, 1H). ^{13}C NMR (DMSO-d_6): 146.73, 142.25, 135.49, 122.90, 120.82, 117.92, 111.31. Anal. Calcd for $C_8H_4N_6O_4$: C, 38.72; H, 1.62; N, 33.87. Found: C, 39.22/38.99; H, 0.95/0.83; N, 34.31/34.08.

3,5,7-Trinitro-1,2,3-triazolo[1,2-*a*]benzotriazole (10). Nitric acid (100%) (1.04 mL, 25 mmol) was added dropwise to a solution of 1,2,3-triazolo[1,2-*a*]benzotriazole (**14**) (1.20 g, 7.6 mmol) in 98% sulfuric acid (30 mL) held below 5 °C in an ice/water bath. The solution was allowed to warm to ambient temperature, stirred for 20 min, and then poured into cold water (200 mL). The precipitate was filtered off, washed with water, and dried to give a bright yellow solid (1.78 g, 80%), mp 283−286 °C. Recrystallization from acetonitrile (100 mL) gave a bright yellow solid (1.213 g, 54%), mp 293−294 °C. IR (KBr): 2923, 2852, 1522, 1285 cm^{-1}. ^{1}H NMR (CD_3CN): 9.70 (d, J = 2.06 Hz, 1H), 9.32 (d, J = 2.08 Hz, 1H), 8.93 (s, 1H); (CD_2Cl_2): 9.89 (d, J = 2.07 Hz, 1H), 9.49 (d, J = 2.07 Hz, 1H), 8.82 (s, 1H); (DMSO-d_6): 9.60 (s, 1H), 9.59 (d, J = 1.7 Hz, 1H), 9.26 (d, J = 2.0 Hz, 1H). ^{13}C NMR (CD_2Cl_2): 140.13, 139.96, 135.34, 134.18, 123.13, 120.45, 116.67. Anal. Calcd for $C_8H_3N_7O_6$: C, 32.78; H, 1.03; N, 33.45. Found: C, 32.93; H, 0.38; N, 33.48.

Reaction of 3,5,7-Trinitro-1,2,3-triazolo[1,2-*a*]benzotriazole (10) with Sodium Azide. A mixture of 3,5,8-trinitro-1,2,3-triazolo[1,2-*a*]benzotriazole (**10**) (0.200 g, 0.68 mmol), 18-crown-6 (0.1 g), and finely powdered sodium azide (0.3 g, 4.6 mmol) in acetonitrile (50 mL) was refluxed for 18 h. The solution was cooled and the solvent removed to give 0.29 g of a red solid (clearly solvated), identical to an authentic sample of 4,6-dinitrobenzotriazole.

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Supporting Information Available: Crystal data collection, data reduction and structure solution and refinement for compounds **2**, **7**, **8**, **9**, and **17** (30 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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