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Luminescent Nitro Derivatives of Benzotriazolo[2,1*a*]benzotriazole

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ABSTRACT

Fluorescence was enhanced and laser activity introduced by substitution in 5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole **6** *to give 2-nitro, 2,8-dinitro, 2,4,8-trinitro, and 2,4,8,10-tetranitro derivatives* **9a–d**. *Luminescence for compounds* **6** *and* **9a–d** *and the 2,8-dinitro-3,9-dimethyl and 2,3,8,9-tetramethyl-4,10-dinitro derivatives* **11a,b** *was erratically solvent dependent when examined in ethyl acetate, acetonitrile, and acetone and was most efficient in the 2,8-dinitro derivative* **9b** *[λ_f 479 nm (ethyl acetate) Φ 0.98, λ_f 501 nm (acetonitrile) Φ 0.58, and λ_f 494 nm (acetone) Φ 0.61] and in the tetranitro derivative* **9d** *[λ_f 509 nm (acetonitrile) Φ 0.81 and λ_f 511 nm (acetone) Φ 0.66]. With laser activity at 560–590 nm (acetonitrile) the dye* **9b** *was 30% as efficient as rhodamine 6G (ethanol) in power output. Luminescence was quenched by the reduction of nitro groups to give 2-amino and 2,8-diamino derivatives* **9e,f** *and by the conversion of the tetranitro compound* **9d** *to an unassigned diazido dinitro derivative* **9g**. *Luminescence was not detected in 2,5-dimethyl-3,6-dinitro-1,3a-4,6a-tetraazapentalene* **14** *and ethyl 2,5-dimethyl-1,3a,4,6a-tetraazapentalene-3,6-dicarboxylate* **15**. *Azidoazobenzenes were obtained from 4-methyl- and 4,5-dimethyl-1,2-phenylene diamines via oxidation with lead dioxide to aminoazobenzene derivatives followed by treatment of the diazotized amines with sodium azide and thermolysis of azido intermediates to give 3,9-dimethyl and 2,3,8,9-tetramethyl derivatives* **10a,b** *of the triazolotriazole* **6**. *Nitration converted the triazole* **6** *to the 2,4,8-trinitro derivative* **9c** *and the alkyltriazoles to their dinitro derivatives* **11a,b**.

INTRODUCTION

Rarely has the C-nitro substituent, a "killer of luminescence" [1], been contained in a fluorescent or laser dye. The known laser dyes with nitro substituents included 4-dimethylamino-4'-nitrostilbene **1** [2–4], 1,1'-diethyl-11-nitro-4,4'-quinodicarbocyanine tetrafluoroborate **2** [5], 2-amino-7-nitrofluorene **3** [5], methylene green **4** [5], and 1,3,5,7,8-pentamethyl-2,6-dinitropyrromethene-BF_2 complex **5** [6]. To accommodate fluorescence and laser activity in the stilbene **1** and the absence of luminescence in 4-nitrostilbene, a contribution from electronic interaction between the nitro and amino substituents was proposed [2–4].

A reexamination of the qualitative observation of strong fluorescence in solution for a dinitro derivative of 5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **6** [7] was undertaken. The unsubstituted dibenzotetraazapentalene **6**, a hybrid of mesoionic structures, was a yellow crystalline solid with a very weak yellow-green fluorescence under ultraviolet light and absorption in the electronic spectrum at λ_{max} (ethanol) 402 nm, log ε 4.58 [8]. Its chromophore and luminophor properties were comparable to those reported for isomeric and isosteric dipyrido [1,2-*a*:1',2'-*e*]1,3,4,6-tetraazapentalene **7** with absorption λ_{max} (methanol) 396 nm, log ε 4.00, and λ_f (ethanol) 433 nm, Φ 0.27 [9].

A preparation of the tetraazapentalene **6** from *o*-phenylene diamine **8** (Equation 1); its nitration to the mono, di, and tetranitro derivatives **9a,b,d**; reduction of the mono and dinitro compounds to the corresponding mono and diamino derivatives **9e,f**; and replacement of two nitro groups in compound **9d** with two azido groups to give an unassigned diazido dinitro derivative **9g** were previously reported [7].

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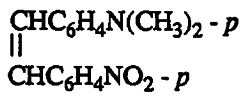

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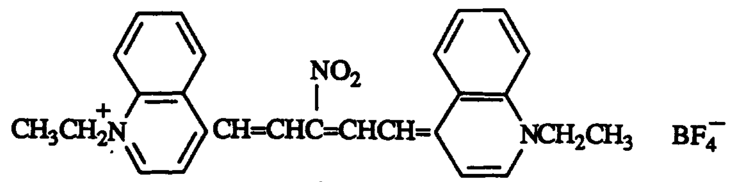

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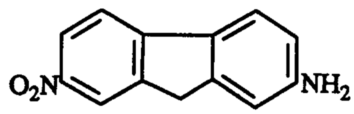

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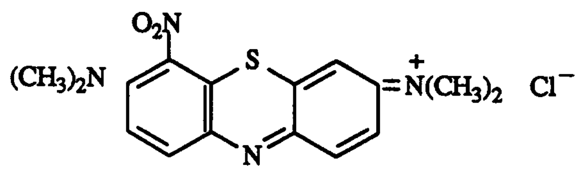

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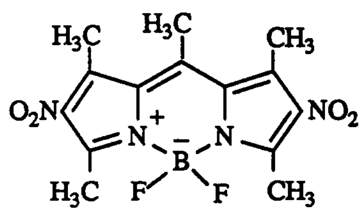

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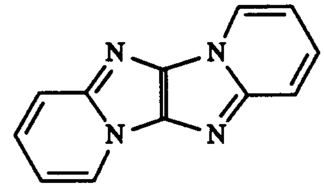

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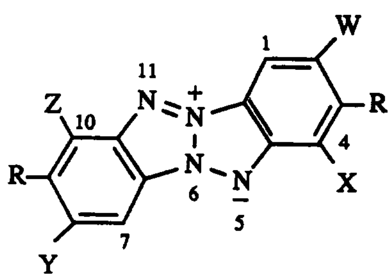
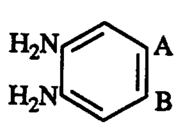
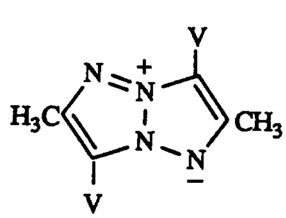


6	W = X = Y = Z = R = H	**9f**	W = Y = NH_2, X = Z = R = H
9a	W = NO_2, X = Y = Z = R = H	**9g**	unassigned diazidodinitro derivative
9b	W = Y = NO_2, X = Z = R = H	**10a**	W = X = Y = Z = H, R = CH_3
9c	W = X = Y = NO_2, Z = R = H	**10b**	W = R = Y = CH_3, X = Z = H
9d	W = X = Y = Z = NO_2, R = H	**11a**	W = Y = NO_2, X = Z = H, R = CH_3
9e	W = NH_2, X = Y = Z = R = H	**11b**	W = Y = R = CH_3, X = Z = NO_2



8 A = B = H
12 A = CH_3, B = H
13 A = B = CH_3



14 V = NO_2
15 V = $CO_2CH_2CH_3$

$$\mathbf{8} \xrightarrow{PbO_2} (o\text{-}H_2NC_6H_4N\!\!=\!)_2 \xrightarrow[2.\ NaN_3]{1.\ HNO_2}$$

16

$$(o\text{-}N_3C_6H_4N\!\!=\!)_2 \xrightarrow[-\ N_2]{heat} \mathbf{6} \qquad (1)$$

17

RESULTS AND DISCUSSION

A suitable variation in the nitration of compound **6** [7,8] gave 2,4,8-trinitro-5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **9c**. The assignment was complementary to the structures of the other nitro derivatives **9a,b,d** and supported by ^{1}H NMR analysis. In straightforward extensions the preparations of 2,8-dinitro-3,9-dimethyl-5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **11a** and 4,10-dinitro-2,3,8,9-tetramethyl-5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **11b** were obtained from 3,4-diaminotoluene **12** and 4,5-dimethyl-1,2-phenylenediamine **13** via the intermediate dimethyl and tetramethyldibenzotetraazapentalenes **10a,b** respectively.

Longest wavelength absorption in the electronic spectrum, fluorescence emission, and laser activity data were obtained for 12 examples of tetraazapentalene derivatives **6,9a–g,11a,b,14**, and **15**. Limited solubilities afforded measurements on each tetraazapentalene in ethyl acetate, acetonitrile, and acetone. Absorption maxima and extinction coefficients were virtually solvent independent and bathochromic shifts progressed from 403 nm for the unsubstituted compound **6** in increments of about 35, 55, 80, and 90 nm as the number of nitro substituents increased from 1 to 4 in compounds **9a–d** (Table). The effect of dinitro substitution was independent of position assignment insofar as the 2,8-dinitro derivatives **9b** and **11a** and the 4,10-dinitro derivative **11b** absorbed at 450 nm (±7), log ε 4.43 ± 0.09.

In comparison with the weak luminophor in dibenzotetraazapentalene **6** fluorescence intensification was brought about by nitro substitution in the derivatives **9a–d** and **11a,b** (Table). Although the quantum yields were erratically solvent dependent dibenzotetraazapentalene **6** and its nitro derivatives **9a–c** and **11a,b** gave highest values in ethyl acetate. The tetranitro derivative **9d** was exceptional with weak fluorescence in ethyl acetate and strong fluorescence in acetonitrile and in acetone (Table). The highest fluorescent quantum yield on record for a nitro compound was observed for 2,8-dinitro-5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **9b**, λ_f (ethyl acetate) 479 nm, Φ 0.98. This high value was not sustained by either the structurally similar 2,8-dinitro-3,9-dimethyl derivative **11a**, Φ 0.46 (ethyl acetate), the 2,3,8,9-tetramethyl-4,10-dinitro derivative **11b**, Φ 0.15 (ethyl acetate), or the unassigned diazido-dinitro derivative **9g** in which fluorescence was not detected. Reduction of nitro groups also led to the disappearance of fluorescence in the monoamino and diamino derivatives **9e,f**. Fluorescence was not detected in either 2,5-dimethyl-3,6-dinitro-1,3a,4,6a-tetraazapentalene **14** or ethyl 2,5-dimethyl-1,3a,4,6a-tetraazapentalene-3,6-dicarboxylate **15**. The simpler tetraazapentalene chromophore in compounds **14** and **15** was shifted to λ_{max} near 380 and 310 nm.

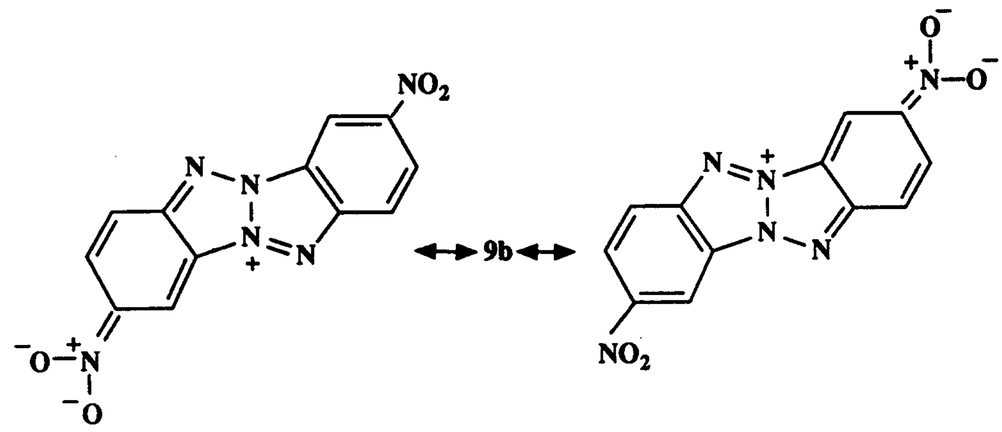
TABLE Absorption and Luminescence in Dibenzotetraazapentalenes

Number	*Solvent*[a]	λ_{max}[b]	log ϵ	λ_f[b]	Φ_f	λ_{las}[c]
6	EA	403	4.68	452	0.02	—
	AN	403	4.68	—	—	—
	A	403	4.85	—	—	—
9a	EA	438	4.40	498	0.53	560
	AN	440	4.42	—	—	—
	A	440	4.42	527	0.18	—
9b	EA	454	4.45	479	0.98	—
	AN	457	4.52	501	0.58	575
	A	457	4.52	494	0.61	562
9c	EA	476	4.50	509	0.61	575
	AN	482	4.39	516	0.27	—
	A	483	4.44	516	0.36	—
9d	EA	497	4.56	512	0.08	—
	AN	493	4.60	509	0.81	560
	A	493	4.71	511	0.66	—
9g	EA	463	4.32	—	—	—
	AN	464	4.32	—	—	—
	A	464	4.37	—	—	—
11a	EA	447	4.34	480	0.46	—
	AN	446	4.36	—	—	—
	A	448	4.42	495	0.10	—
11b	EA	443	4.47	517	0.15	—
	AN	447	4.30	—	—	—
	A	441	4.49	—	—	—

[a]Ethyl acetate (EA); acetonitrile (AN); acetone (A).
[b]6 × 10^{-6} M solutions.
[c]2 × 10^{-4} M solutions.

Laser activity was shown by four nitro derivatives **9a–d** of the dibenzotetraazapentalene **6** but was not detected in the dinitro derivatives **11a,b**. In general the relative efficiency (RE) in power output of a laser dye depended on several factors including a high extinction coefficient of absorption, a high fluorescence quantum yield, and minimal overlap of absorption (singlet-singlet and triplet-triplet) in the fluorescence spectral region. These were presumably operative conditions for the nitro derivatives **9a–d** to show laser activity over the range 530 to 590 nm (Table). Enigmatic results showed the dinitro derivative **9b** with Φ 0.98 in ethyl acetate to be laser inactive and with Φ 0.58 in acetonitrile or Φ 0.61 in acetone to be laser active. A low relative efficiency, RE 30 (on a scale where RE 100 was arbitrarily assigned to laser dye rhodamine 6G), was determined for the dye **9b** in acetonitrile [10]. Photoinstability accounted for its decomposition under flash lamp excitation and precluded an accurate measurement of triplet-triplet absorption [10].

Electronic interaction between conjugated nitro and amino groups was a common feature of laser dyes **1–5** and presumably diminished the role of



(2)

the nitro group as a quencher of luminescence. By extension the laser activity in each dye **9a–d** can tentatively be partially attributed to a charge separated luminophor brought about by electronic interaction between a nitro group in conjugation with an electron rich mesoionic nitrogen atom as illustrated for the 2,8-dinitro compound **9b** (Equation 2). A similar charge separated luminophor failed to bring about laser activity in the 2,8- and 4,10-dinitrodibenzotetraazapentalenes **11a,b** and in 2,5-dimethyl-3,6-dinitro-1,3a,4,6a-tetraazapentalene **14**.

EXPERIMENTAL

Instruments for spectroscopic measurements included: Perkin-Elmer 1600 FTIR, Varian Gemini 300 NMR, Hewlett-Packard 5985 (70 eV) GC-MS, Cary 17 (UV), Perkin-Elmer LS-5B Luminescence spectrometer, and a Phase-R 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 **6**, its mononitro, dinitro, and tetranitro derivatives **9a,b,d**, its 2-amino- and 2,8-diamino derivatives **9e,f** [7,8], 2,5-dimethyl-3,6-dinitro-1,3a,4,6a-tetraazapentalene **14**, and ethyl 2,5-dimethyl 1,3a,4,6a-tetraazapentalene-3,6-dicarboxylate **15** [11,12]. Light absorption, luminescence, and laser activity for the dyes **6,9a–d**, and **11a,b**, are described in the Table.

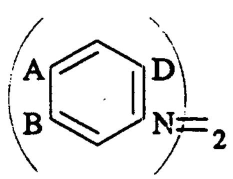
Each recorded UV absorption was restricted to the highest wavelength. ^{1}H NMR spectra were run in $CDCl_3$ with tetramethylsilane as an internal standard. Fluorescence quantum yields of the dyes were determined for solutions in ethyl acetate, acetonitrile, and acetone with excitation at 450 and 460 nm by reference to acridine orange, Φ 0.46 [13]. Melting points were determined on a Thomas Hoover melting point apparatus and were uncorrected. Elemental analyses were obtained from Midwest Micro Lab, Indianapolis, IN, and Galbraith Laboratories, Inc., Knoxville, TN.

2,4,8-Trinitro-5,11-dehydro-5H, 11H-benzotriazolo[2,1-a]benzotriazole 9c

The compound 5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]-benzotriazole **6** (450 mg, 1.5 mmol) was added in small portions to concentrated nitric acid (15 ml) at 5°C with stirring. After stirring was continued for 2 hours, the mixture was poured into ice-water. A precipitate was isolated and recrystallized from dimethylformamide to give 2,4,8-trinitro-5,11-dehydro-5*H*,11*H*-benzotriazolo [2,1-*a*]benzotriazole **9c** as a yellow crystalline solid (460 mg, 62%), mp 282–283°C. ^{1}H NMR ($CDCl_3$): δ 8.24 (d, $J_{10,9}$ 9.6 Hz, H10), 8.66 (dd, $J_{9,10}$ 9.3 Hz, $J_{9,7}$ 2.1 Hz, H9), 8.77 (s, H1), 9.44 (s, H3), 9.54 (d, $J_{7,9}$ 2.1 Hz, H7). IR (KBr): ν 3094, 1617, 1523, 1351, 1325, 1285, 1159, 1108, 819. EI-MS (*m/z*) (%): 343 (30, M), 75 (31), 30 (100). Anal. calcd for $C_{12}H_5N_7O_6$: C, 41.96; H, 1.46; N, 28.55. Found: C, 41.73; H, 1.61; N, 28.21.

General Procedure for the Preparation of Tetraazaplentalenes 10a,b

A straightforward adaptation of the preparation of the dibenzotetraazapentalene **6** from *o*-phenylenediamine **8** was followed. Lead dioxide (1.1 mol) was added to a stirred solution of an *o*-phenylenediamine (0.5 mol) in benzene (1.5 L). After 1 hour at 25°C, the mixture was kept at 80°C for 3 hours. After insoluble lead salts were removed and the deep red mixture was filtered through silica gel (300 g, 230–400 mesh, 60 Å, dichloromethane) and concentrated, recrystallization of the residue from toluene gave a diaminoazobenzene. The 4,4′-dimethyl-2,2′-diaminoazobenzene **18** (37%) was obtained as an orange crystalline solid, mp 142–143°C (Ref. [14], 120°C). IR, MS, and ^{1}H NMR data were in agreement with reported values [14]. Anal. calcd for $C_{14}H_{16}N_4$: C, 69.79; H, 6.68; N, 22.90. Found: C, 69.97; H, 6.17; N, 23.31. The 4,4′,5,5′-tetramethyl-2,2′-diaminoazobenzene **19** (34%) was obtained as red leaf crystals, mp 203–204°C (Ref



18 A = CH_3, B = H, D = NH_2 **20** A = CH_3, B = H, D = N_3
19 A = B = CH_3, D = NH_2 **21** A = B = CH_3, D = N_3

[14], 205°C). IR, MS, and ^{1}H NMR data were in agreement with reported values [14].

An extension of the conversion of the diamine **16** to the diazide **17** afforded the diazides **20** and **21** from the diamines **18** and **19** respectively. The 4,4′-dimethyl-2,2′-diazidoazobenzene **20** (89%) was obtained as orange needles (toluene), mp 122°C (explosive dec). ^{1}H NMR: δ 2.39 (s, 2CH_3), 6.96 (s, H3/H3′), 6.99, 7.63 (d, *J* 8.4 Hz, H5, H6/H5′, H6′). IR (KBr): ν 2117 (N_3), 1603, 1284. EI-MS (*m/z*) (%): 292 (4, M), 236 (78), 192 (19), 39 (100). Anal. calcd for $C_{14}H_{12}N_8$: C, 57.53; H, 4.11; N, 38.36. Found: C, 57.68; H, 4.03; N, 38.11. The 4,4′,5,5′-tetramethyl-2,2′-diazidoazobenzene **21** (63%) was obtained as orange needles (toluene), mp 118°C (explosive dec). ^{1}H NMR: δ 2.25 (s, 2CH_3), 2.29 (s, 2CH_3), 6.92 (s, 2H), 7.51 (s, 2H): IR (KBr): ν 2108 (N_3), 1443, 1378, 1212, 991, 838. Anal. calcd for $C_{16}H_{16}N_8$: C, 59.99; H, 5.03; N, 34.98. Found: C, 59.89; H, 4.92; N, 34.77.

In an extension of the conversion of the diazide **17** to dibenzotetraazapentalene **6**, the diazides 20 and 21 gave the tetraazapentalene derivatives **10a,b**. The 3,9-dimethyl-5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **10a** (99%) was obtained as yellow needles (toluene), mp 197–198°C. ^{1}H NMR: δ 2.60 (s, CH_3), 2.61 (s, CH_3), 7.21 (dd, $J_{8,7}$ 8.7 Hz, $J_{8,10}$ 4.5 Hz, H8), 7.44 (d, $J_{7,8}$ 9.0 Hz, H7), 7.66 (bs, H10), 7.80 (d, $J_{1,2}$ 8.4 Hz, H1), 7.93 (s, H4), 8.03 (d, $J_{2,1}$ 8.4 Hz, H2). IR (KBr): ν 1616, 1496, 1370, 1340, 1102, 798. UV (CH_3CN) λ_{max} 405 (4.54), 387 (4.35), 258 (4.86). EI-MS (*m/z*) (%): 236 (100, M). Anal. calcd for $C_{14}H_{12}N_4$: C, 71.17; H, 5.12; N, 23.71. Found: C, 71.17; H, 5.06; N, 23.52. The 2,3,8,9-tetramethyl-5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*] benzotriazole **10b** (77%) was obtained as a yellow powder (toluene), mp 280°C (dec). ^{1}H NMR: δ 2.28 (s, 2CH_3), 2.46 (s, 2CH_3), 7.69 (s, 2H). IR (KBr): ν 1624, 1595, 1449, 1354, 1271, 999. EI-MS (*m/z*) (%) 264 (47, M). Anal. calcd for $C_{16}H_{16}N_4$: C, 72.73; H, 6.06; N, 21.21. Found: C, 72.61; H, 6.04; N, 20.94.

2,8-Dinitro-3,9-dimethyl-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotrizole **11a**

Nitric acid (25%, 50 ml) at 0–5°C was added to 3,9-dimethyl-5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **10a**, and, after 1.5 hour, the temperature was allowed to rise to room temperature and stored for 4 hours. An orange-red solid was isolated, washed with water, and dried. Purification by column chromatography (silica gel, dichloromethane/light petroleum ether, 1:1) and recrystallization from dimethylformamide and toluene afforded the dinitro derivative **11a** (R_f 0.42) as an orange crystalline solid, mp 260°C (dec). ^{1}H NMR: δ 2.90 (s, CH_3), 7.91 (s, H4 and H10), 9.04 (s, H1 and H7). IR (KBr): ν 1613, 1530, 1331, 1116, 846, 777, 752. EI-MS (*m/z*) (%): 326 (100, M). Anal. calcd for $C_{14}H_{10}N_6O_4$: C, 51.53; H, 3.07; N, 25.77. Found: C, 51.48; H, 3.15; N, 25.53.

4,10-Dinitro-2,3,8,9-tetramethyl-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole **11b**

To a stirred solution of 2,3,8,9-tetramethyl-5,11-dehydro-5*H*, 11*H*-benzotriazolo[2,1-*a*]benzotriazole **10b** (528 mg, 2.0 mmol) in acetonitrile (10 ml) nitronium tetrafluoroborate (531 mg, 4.0 mmol) in acetonitrile (15 ml) was slowly added at 0°C. The mixture was held at 0°C for 1 hour. A yellow precipitate was isolated and recrystallized from toluene to give the dinitro derivative **11b** as a yellow crystalline solid (524 mg, 74%), mp 310°C (dec). ^{1}H NMR: δ 2.59 (s, CH_3), 2.60 (s, CH_3), 8.22 (s, H1 and H7). IR (KBr): ν 1625, 1523, 1359, 1321, 1094, 1027, 865, 813, 769. EI-MS (*m/z*) (%): 354 (100, M). Anal. calcd for $C_{16}H_{14}N_6O_4$: C, 54.24; H, 3.95; N, 23.73. Found: C, 54.04; H, 3.81; N, 23.60.

Spectroscopic data were obtained for 2-amino- and 2,8-diamino-5,11-dehydro-5*H*,11*H*-benzotriazolo[2,1-*a*]benzotriazole **9e,f**, 2,5-dimethyl-3,6-din-itro-1,3a,4,6a-tetraazapentalene **14**, and ethyl 2,5-dimethyl-1,3a,4,6a-tetraazapentalene-3, 6-dicarboxylate **15**. UV absorption [compound, (solvent), λ_{max} nm, log ε] **9e** ($CH_3CO_2C_2H_5$, CH_3CN, or CH_3COCH_3), 436, 4.29; **9f** (CH_3CN or CH_3COCH_3), 477, 4.43; **14** ($CH_3CO_2C_2H_5$), 382, 4.37; **14** (CH_3CN), 384, 4.50; **14** (CH_3COCH_3), 384, 4.61; **15** ($CH_3CO_2C_2H_5$), 310, 4.34; **15** (CH_3CN), 310, 4.61; **15**, 310, 4.35. The diamine **9f** was insoluble in ethyl acetate. Luminescence was not detected in solutions of compounds **9e,f,14**, and **15**.

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