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

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Received ... 

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, 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, [λf 479 nm (ethyl acetate) Φ 0.98, λf 501 nm (acetonitrile) Φ 0.58, and λf 494 nm (acetone) Φ 0.61] and in the tetranitro derivative 9d [λf 509 nm (acetonitrile) Φ 0.81 and λf 511 nm (acetone) Φ 0.66]. With laser activity at 560–590 nm (acetonitrile) the dye 9b was 30 percent 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 10 a,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 11 a,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'-quinodocarbocyanine tetrafluoroborate 2 [5], 2-amino-7-nitrofluorene 3 [5], methylene green 4 [5], and 1,3,5,7,8-pentamethyl-2,6-dinitropyromethene-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].

\[
\begin{align*}
\text{CH}_2\text{C}_6\text{H}_4\text{N}(&\text{CH}_3)_2 - p & \quad \text{CH}_3\text{CH}_2\text{N}^- \\
\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2 - p & \quad \text{CH}_3\text{CH}_2\text{N}^- \\
\text{NO}_2 & \quad \text{NO}_2 \\
\text{CH}=&\text{CH}=&\text{CH}= & \quad \text{CH}=&\text{CH}=&\text{CH}= \\
\text{NCH}_2\text{CH}_3 & \quad \text{NCH}_2\text{CH}_3 \\
\text{BF}_4^- & \quad \text{BF}_4^- \\
\end{align*}
\]
A reexamination of the qualitative observation of strong fluorescence in solution for a dinitro derivative of 5,11-dehydro-5H,11H-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 $\lambda_{\text{max}}$ (ethanol) 402 nm, log $\varepsilon$ 4.58 [8]. Its chromophore and luminophor properties were comparable to those reported for isomeric and isosteric dipyrido [1,2-$\alpha$:1',2'-$\alpha$]1,3,4,6-tetraazapentalene 7 with absorption $\lambda_{\text{max}}$ (methanol) 396 nm, log $\varepsilon$ 4.00, and $\lambda_f$ (ethanol) 433 nm, $\Phi$ 0.27 [9].

![Chemical structure of 6 and 7]
A preparation of the tetraazapentalene 6 from o-phenylene diamine 8, eq (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].

\[
PbO_2 \rightarrow \rightarrow (\text{o-HNC}_6\text{H}_4\text{N}_2)_2 \rightarrow \rightarrow (\text{o-N}_3\text{C}_6\text{H}_4\text{N}_2)_2 \rightarrow \rightarrow \text{heat} \rightarrow 6
\]

\[
\text{16} \quad \text{17}
\]

\text{RESULTS AND DISCUSSION}

A suitable variation in the nitration of compound 6 [7,8] gave 2,4,8-trinitro-5,11-dehydro-5H,11H-benzotriazole[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-5H,11H-benzotriazole[2,1-a]benzotriazole 11a and 4,10-dinitro-2,3,8,9-tetramethyl-5,11-dehydro-5H,11H-benzotriazole[2,1-a]benzotriazole 11b were obtained from 3,4-diaminotoluene 12 and 4,5-dimethyl-1,2-phenylenediamine 13 via the inter-
mediate dimethyl and tetramethyl dibenzotetraazapentalenes 10a,b respectively.

Longest wavelength absorption in the electronic spectrum, fluorescence emission, and laser activity data were obtained for twelve 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-5H,11H-benzotriazolo[2,1-a]benzotriazole 9b, λf (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, 9f. 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 $\lambda_{\text{max}}$ near 380 and 310 nm.

Laser activity was shown by four nitro derivatives 9a–d of the dibenzotetra-
azapentalene 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 in-
cluding a high extinction coefficient of absorption, a high fluorescence quantum yield
and minimal overlap of absorption (singlet-singlet and triplet-triplet) in the fluores-
cence spectral region. These were presumably operative conditions for the nitro deriv-
atives 9a–d to show laser activity over the range 530 to 590 nm (Table). Enigmatic
results showed the dinitro derivative 9b with $\Phi$ 0.98 in ethyl acetate to be laser inac-
tive and with $\Phi$ 0.58 in acetonitrile or $\Phi$ 0.61 in acetone to be laser active. A low rel-
ative 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 com-
mon feature of laser dyes 1–5 and presumably diminished the role of 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 meso-
ionic nitrogen atom as illustrated for the 2,8-dinitro compound 9b, eq (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.

\[ \text{IONIC NITROGEN ATOM AS ILLUSTRATED FOR THE 2,8-DINITRO COMPOUND 9B, EQ (2).} \]

\[ \text{A SIMILAR CHARGE SEPARATED LUMINOPHOR FAILED TO BRING ABOUT LASER ACTIVITY IN THE 2,8- AND 4,10-DINITRODIBENZOTETRAAZAPENTALENES 11A,B AND IN 2,5-DIMETHYL-3,6-DINITRO-1,3A,4,6A-TETRAAZAPENTALENE 14.} \]

**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-5H,11H-benzo-triazolo[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. Fluor-
rescence 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, Ind., and Galbraith Laboratories, Inc., Knoxville, Tenn.

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

The compound 5,11-dehydro-5H,11H-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 h the mixture was poured into ice-water. A precipitate was isolated and recrystallized from dimethylformamide to give 2,4,8-trinitro-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole 9c as a yellow crystalline solid (460 mg, 62%), mp 282–283 °C; ¹H NMR (CDCl₃): 8 8.24 (d, J₁₀,₉ 9.6 Hz, H 10), 8.66 (dd, J₉,₁₀ 9.3 Hz, J₉,₇ 2.1 Hz, H 9), 8.77 (s, H 1), 9.44 (s, H 3), 9.54 (d, J₇,₉ 2.1 Hz, H 7); IR (KBr): v 3094, 1617, 1523, 1351, 1325, 1285, 1159, 1108, 819; EI-MS (m/z) (%): 343 (30, M), 75 (31), 30 (100). Anal. calcd for C₁₂H₈N₇O₆: 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 tetraazapentalenes 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 h at 25 °C the mixture was kept at 80 °C for 3 h. After insoluble lead salts were removed and the deep red mixture was filtered through silica gel (300 g, 230–400 mesh, 60 Å, d-
chloromethane) 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 (lit. [14], 120 °C); IR, MS, and 1H 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 (lit. [14], 205 °C); IR, MS, and 1H NMR data were in agreement with reported values [14].

$\begin{align*}
\begin{array}{c}
A
\end{array}
\begin{array}{c}
D
\end{array}
\begin{array}{c}
N
\end{array}
\begin{array}{c}
B
\end{array}
18 & A = CH_3, B = H, D = NH_2 \\
19 & A = B = CH_3, D = NH_2 \\
20 & A = CH_3, B = H, D = N_3 \\
21 & A = B = CH_3, D = N_3
\end{align*}$

An extension of the conversion of the diamin e 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.); 1H NMR: δ 2.39 (s, 2 CH₃), 6.96 (s, H 3 / H 3'), 6.99, 7.63 (d, J 8.4 Hz, H 5, H 6 / H 5', H 6'); IR (KBr): ν 2117 (N₃), 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.); 1H NMR: δ 2.25 (s, 2 CH₃), 2.29 (s, 2 CH₃), 6.92 (s, 2 H), 7.51 (s, 2 H); IR (KBr): ν 2108 (N₃), 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-5H,11H-benzotriazolo[2,1-a]benzotriazole 10a (99%) was obtained as yellow needles (toluene) mp 197-198 °C; \( {^1}H \) NMR: \( \delta 2.60 (s, CH_3) \), 2.61 (s, CH_3), 7.21 (dd, \( J_{8,7} \) 8.7 Hz, \( J_{8,10} \) 4.5 Hz, H 8), 7.44 (d, \( J_{7,8} \) 9.0 Hz, H 7), 7.66 (bs, H 10), 7.80 (d, \( J_{1,2} \) 8.4 Hz, H 1), 7.93 (s, H 4), 8.03 (d, \( J_{2,1} \) 8.4 Hz, H 2); IR (KBr): v 1616, 1496, 1370, 1340, 1102, 798; UV (CH_3CN) \( \lambda_{max} \) 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-tetranethyl-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole 10b (77%) was obtained as a yellow pow. (toluene), mp 280 °C (dec); \( {^1}H \) NMR: \( \delta 2.28 (s, 2 CH_3) \), 2.46 (s, 2 CH_3), 7.69 (s, 2 H); IR (KBr): v 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]benzotriazole 11a

Nitric Acid (25%, 50 ml) at 0–5 °C was added to 3,9-dimethyl-5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole 10a and after 1.5 h, the temperature was allowed to rise to room temperature and stored for 4 h. An orange-red solid wa 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: \( \delta 2.90 (s, CH_3) \), 7.91 (s, H 4 and H 10), 9.04 (s, H 1 and H 7); IR (KBr): v 1613, 1530, 1331, 1116, 846, 777, 752; EI–MS (m/z) (%): 326 (100,
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-5H,11H-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 h. 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); ^1H NMR: δ 2.59 (s, CH₃), 2.60 (s, CH₃), 8.22 (s, H 1 and H 7); IR (KBr): v 1625, 1523, 1359, 1321, 1094, 1027, 865, 813, 769; EI-MS (m/z) (%): 354 (100, M). Anal. calcd for C₁₁₄H₁₄N₆O₄: 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-5H,11H-benzotriazolo[2,1-a]benzotriazole 9e,f, 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: UV absorption [compound, (solvent), λ_{max} nm, log ε]: 9e (CH₃CO₂C₂H₅, CH₃CN, or CH₃COCH₃), 436, 4.29; 9f (CH₃CN or CH₃COCH₃), 477, 4.43; 14 (CH₃CO₂C₂H₅), 382, 4.37; 14 (CH₃CN), 384, 4.50; 14 (CH₃COCH₃), 384, 4.61; 15 (CH₃CO₂C₂H₅), 310, 4.34; 15 (CH₃CN), 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.
ACKNOWLEDGMENTS

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REFERENCES


[3] Fluorescence for the stilbene 1, $\lambda_f$ 590 nm, $\Phi$ 0.7 (benzene) [2] did not agree with the more recently reported $\lambda_f$ 600 nm, $\Phi$ 0.085 (benzene); $\lambda_f$ 502 nm, $\Phi$ 0.46 (cyclohexane); $\lambda_f$ 678 nm, $\Phi$ 0.38 (tetrahydrofuran); $\lambda_f$ 772 nm, $\Phi$ 0.0006 (acetonitrile) [4].


[12] We are indebted to Dr. A. Natesh for the preparation of compounds 14 and 15.


# Absorption and Luminescence in Dibenzotetrazapentalenes

<table>
<thead>
<tr>
<th>No.</th>
<th>Solvent&lt;sup&gt;a&lt;/sup&gt;</th>
<th>( \lambda_{\text{max}}^b )</th>
<th>( \log \varepsilon )</th>
<th>( \lambda_f^b )</th>
<th>( \Phi_f )</th>
<th>( \lambda_{\text{las}}^c )</th>
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<tbody>
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<td>EA</td>
<td>403</td>
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<sup>a</sup> Ethyl acetate (EA); acetonitrile (AN); acetone (A).  
<sup>b</sup> 6 x 10\(^{-6}\) M solutions.  
<sup>c</sup> 2 x 10\(^{-4}\) M solutions.