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

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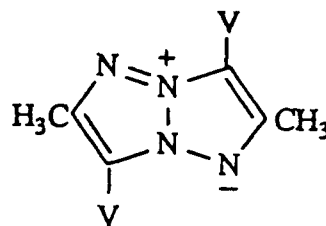
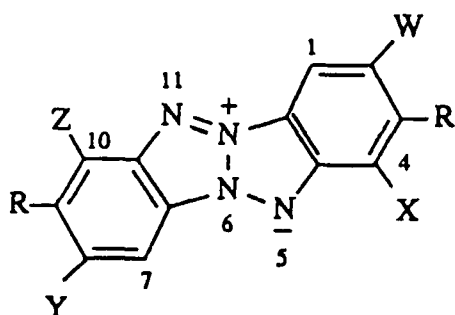


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Luminescent Nitro Derivatives of Benzotriazolo[2,1-a]benzotriazole

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**, [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 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**.



14 V = NO₂

15 V = CO₂CH₂CH₃

6 W = X = Y = Z = R = H

9a W = NO₂, X = Y = Z = R = H

9b W = Y = NO₂, X = Z = R = H

9c W = X = Y = NO₂, Z = R = H

9d W = X = Y = Z = NO₂, R = H

9e W = NH₂, X = Y = Z = R = H

9f W = Y = NH₂, X = Z = R = H

9g unassigned diazidodinitro derivative

10a W = X = Y = Z = H, R = CH₃

10b W = R = Y = CH₃, X = Z = H

11a W = Y = NO₂, X = Z = H, R = CH₃

11b W = Y = R = CH₃, X = Z = NO₂

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