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

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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, [λₐ 479 nm (ethyl acetate) Φ 0.98, λₐ 501 nm (acetonitrile) Φ 0.58, and λₐ 494 nm (acetone) Φ 0.61] and in the tetranitro derivative 9d [λₐ 509 nm (acetonitrile) Φ 0.81 and λₐ 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 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.