# Red- and Near-infrared-luminescent Benzazole Derivatives

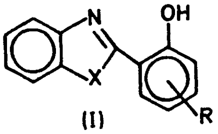
By C. M. ORLANDO, JUN.,* J. G. WIRTH, and D. R. HEATH

(*General Electric Research and Development Center, Schenectady, New York* 12301)

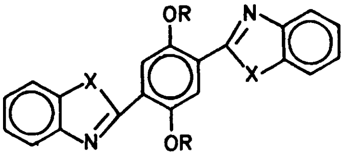
*Summary* Bis-2,5-(2-benzazolyl)hydroquinones, a new class of luminescent benzazoles, possess unusually long wavelength luminescence between 630 and 730 nm.

MOST luminescent organic compounds provide emission in the u.v. and shorter-wavelength region of the visible spectrum. Red and near-i.r. luminescence is less common among simple organic compounds but has been observed for some complex organic dyes.[1] Recent studies of the luminescent properties of 2-(2-hydroxyphenyl)benzazoles (I) described the emission wavelength range of the parent benzazoles (I; R = H, X = S, O, NH) between 462 and

517 nm.[2] Structural variation of R and X in (I) extends this range to 575 nm. We now describe a new class of luminescent benzazole derivatives, the bis-2,5-(2-hydroxyphenyl)benzazoles (IIa); X = S, O, NH) which display emission at wavelengths considerably red-shifted relative to the simple benzazoles (I).



(I)



(IIa; R = H)
(IIb; R = Me)

The bis-2,5-(benzazolyl)hydroquinones were prepared by the standard methods used in the synthesis of the benzazoles (I):[3] (IIa; X = S), m.p. 344—346° from 2,5-dihydroxyterephthalaldehyde and *o*-aminothiophenol; (IIa; X = O), m.p. 376—378° from 2,5-dihydroxyterephthalic acid and *o*-aminophenol; and (IIa; X = NH), m.p. >380° from the bisulphite adduct of 2,5-dihydroxyterephthalaldehyde and *o*-phenylenediamine. The u.v. spectra of the bis-benzazoles in dimethylformamide (IIa; X = S, O, NH) possess intense absorption from 320 to 410 ($\epsilon$ 26,000 to 43,000). The luminescence spectra were determined in the solid state using excitation wavelengths between 360 and 460 nm from a xenon lamp source and are shown in the Figure. The characteristic feature of the luminescence spectra of these compounds is the very broad band emission near the red end of the visible and in the near-i.r. region with extensive tailing to 1000 nm. Only the bisbenzimidazole derivative (IIa; X = NH) possesses a maximum in the near-i.r. region at 730 nm, while both the benzoxazole (IIa; X = O) and the benzothiazole derivatives (IIa; X = S) display maxima in the visible at 615 and 680 nm, respectively. A comparison of the emission maxima of the 2-(2-hydroxyphenyl)benzazoles (I) and the corresponding bis-(2,5-benzazolyl)hydroquinones (IIa) in the Table illustrates the dramatic differences in luminescence properties between the two classes of compounds.

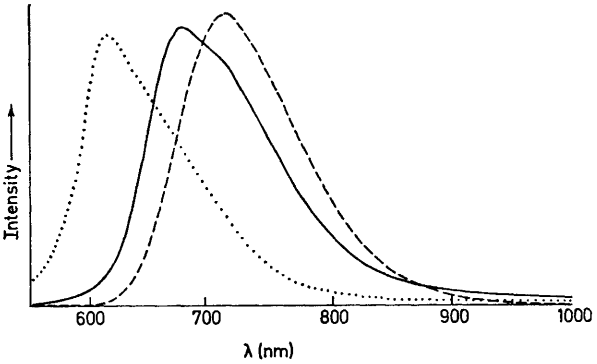


FIGURE. *Solid-state luminescence spectra of bis-2,5-(2-benzazolyl)-hydroquinones* (IIa). *Curves:* ------, (X = NH); · · · · · ·, (X = O); ———, (X = S).

TABLE

*Luminescence wavelengths (nm) of benzazole* (I) *and bis-benzazole* (II) *compounds*

| X | (I; R = H) | (IIa) | (IIb) |
|---|---|---|---|
| S | 517 | 680 | 595, 640 |
| O | 506 | 615 | 455 |
| NH | 462 | 730 | 430, 450 |

The replacement of the *o*-hydroxy-group in compounds (I) by an *o*-methoxy-group renders these benzazoles non-luminescent.[2] However, the analogous methoxy-substituted bis-benzazoles (IIb; X = S, O, NH) are luminescent. A hypsochromic shift of the emission band relative to those of the corresponding hydroxy-derivatives is observed for all the (IIb) compounds. Unusually large blue shifts (160—300 nm) are observed for both the bis-benzimidazole (IIb; X = NH) and the bis-benzoxazole (IIb; X = O).

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[2] D. L. Williams and A. Heller, *J. Phys. Chem.*, 1970, **74**, 4473.

[3] (a) H. W. Hofmann, *Ber.*, 1880, **13**, 7236; (b) H. P. Lankelina and P. X. Sharnoff, *J. Amer. Chem. Soc.*, 1931, **53**, 2654; (c) H. F. Ridley, R. G. W. Spickett, and G. M. Timnus, *J. Heterocyclic Chem.*, 1965, **2**, 453; (d) D. Jerchel, H. Fisher, and M. Krocht, *Annalen*, 1952, **575**, 162; (*e*) D. W. Hein, R. J. Alheim, and J. J. Leavitt, *J. Amer. Chem. Soc.*, 1957, **79**, 427; U.S Patent 2,985,661.