Novel Syntheses of Quinone-type I.R. Dyes for Optical Recording Media

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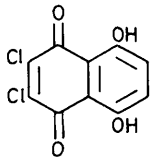
New routes to quinone-type i.r. dyes for optical recording media have been developed by the ring-closure reaction of halogenoquinones with potassium 2-aminobenzenethiolate or zinc 2-aminobenzeneselenate.

There is interest in the development of a suitable dye medium for use in diode-laser optical storage. Syntheses of functional dyes which absorb i.r. light in the 700—800 nm region are at present being sought for diode-laser high density recording and laser printing.[1] Recently, i.r. dyes such as squarylium and pentamethine cyanine dyes have been reported but these ionic dyes must be applied using a solvent-coating method.[2] Disperse-type dyes which can be applied by sublimation techniques under reduced pressure can produce thin films of desired thickness on a polymer surface.[3] We have previously reported that 5-amino-8-arylamino-2,3-dicyano-1,4-naphthoquinones, which absorb i.r. light at 750—800 nm, have superior properties as a dye medium.[4] In this paper, we report the novel syntheses of phenothiazinequinone and phenoselenazinequinone i.r. dyes by the ring-closure reaction of halogenoquinones (**1**) with potassium 2-aminobenzenethiolate (**2a**) or zinc 2-aminobenzeneselenate (**2b**). The reaction of (**1a**) with (**2a**) gives the 1,4-bis-ring-closure product (**4a**) in 86% yield together with a small amount of (**3a**). Dye (**4a**) is green in colour and absorbs i.r. light at 727 nm.[5] Similar reaction of the tetrabromo species (**1b**) with (**2a**) gives the corresponding 1,5-bis-ring-closure product (**5b**), which absorbs i.r. light at 780 nm, *i.e.* at a longer wavelength than (**4a**). Dye (**5a**) was synthesised by the reaction of (**1c**)

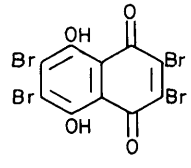
Table 1. Some properties of i.r. dyes (**3**)—(**7**).[a]

Dye	M.p./°C	Yield/% [b]	$\lambda_{max.}$/nm ($\varepsilon \times 10^{-4}$)[c]	
(**3a**)	>300	trace	616 (0.68)[d]	642 (0.46)[d]
(**3b**)	275	25	664 (0.97)[d,e]	719 (0.99)[d,e]
(**4a**)	>300	86	665 (1.22)	725 (1.52)
(**4b**)	212	78	670 (1.21)	727 (1.36)
(**5a**)	>300	12	685 (1.83)	750 (3.20)
(**5b**)	>300	49	715 (1.82)[e]	780 (2.37)[e]
(**6a**)	259—261	93	635 (1.10)	690 (0.86)
(**6b**)	272	12	645 (1.27)	705 (1.15)
(**7a**)	246—247	74	655 (1.77)	712 (1.50)
(**7b**)	>300	8.4	665 (1.42)	720 (1.27)
(**7c**)	235	75	700 (1.24)	770 (1.56)
(**7d**)	>300	8.1	725 (1.31)	780 (1.48)

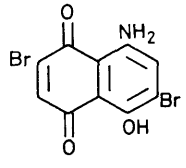
[a] General procedure; halogenoquinone (**1**) (0.1 mmol) and 2-aminobenzene-thiolate (**2a**) (0.22 mmol) or -selenate (**2b**) (0.11 mmol) in EtOH (30 ml) were heated at 20—80 °C for 5 h. [b] Isolated yield. All compounds gave spectral data in agreement with the proposed structures and satisfactory analytical data. [c] Measured in $CHCl_3$ unless otherwise stated. [d] Quinone–quinoneimine tautomerism was observed. [e] Measured in dimethylformamide.



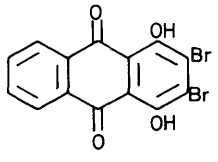
(**1a**)



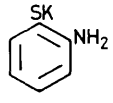
(**1b**)



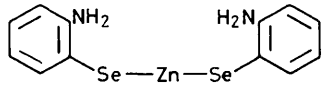
(**1c**)



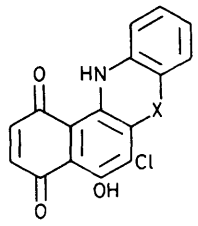
(**1d**)



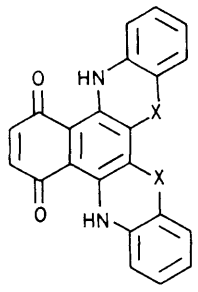
(**2a**)



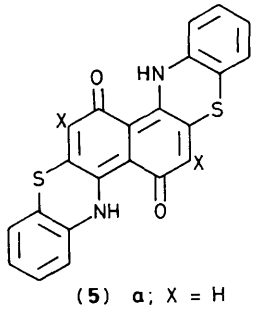
(**2b**)



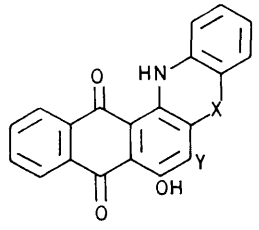
(**3**) **a**; X = S
b; X = Se



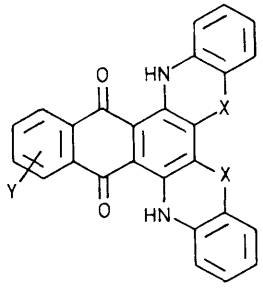
(**4**) **a**; X = S
b; X = Se



(**5**) **a**; X = H
b; X = Br



(**6**) **a**; X = S, Y = H
b; X = Se, Y = Br



(**7**) **a**; X = S, Y = H
b; X = Se, Y = H
c; X = S, Y = F_4
d; X = Se, Y = F_4

with (**2a**) in 12% yield. The anthraquinone analogue (**7a**) could be synthesised by the reaction of (**1d**) with (**2a**) in 74% yield. Phenoselenazinequinone dyes could be synthesised by the reaction of (**1a**) with zinc 2-aminobenzeneselenate (**2b**). In the reaction, the mono-ring-closure product (**3b**), and the bis-ring-closure product (**4b**) were obtained. The anthraquinone analogues (**6b**) and (**7b**) could be synthesised by the reaction of (**1d**) with (**2b**). Phenoselenazinequinone dyes generally absorb at much longer wavelength than the corresponding phenothiazinequinone dyes. The results are summarized in Table 1. The experimental details will be published elsewhere.[6]

The new organic material developed by using these i.r. dyes, with a single layer structure, can be recorded and played back by a laser diode through a substrate, and shows long-term stability.

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References

1 M. Umehara, M. Abe, and H. Oba, *J. Synth. Org. Chem. Jpn.*, 1985, **43**, 334.
2 D. J. Gravesteijn, C. Steenbergen, and J. Van der Veen, 'Optical Storage Media,' SPIE-420, eds. A. E. Bell and A. A. Jamberdino, 1983, p. 327.
3 M. Itoh, S. Esho, K. Nakagawa, and M. Matsuoka, in ref. 2, 1983, p. 332.
4 S. Esho, M. Itoh, and M. Matsuoka, *Japan Kokai Tokkyo Koho*, 1984, **59**, 5096.
5 K. Takagi, M. Kawabe, M. Matsuoka, and T. Kitao, *Dyes and Pigments*, 1985, **6**, 177.
6 S. H. Kim, M. Matsuoka, Y. Kubo, T. Yodoshi, and T. Kitao, *Dyes and Pigments*, submitted for publication.