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Convenient Synthesis and Dichroic Properties of Heterocyclic Quinone Dyes, 3-(Dialkylamino)benzo[b]naphtho[2,3-d]furan-6,11-diones

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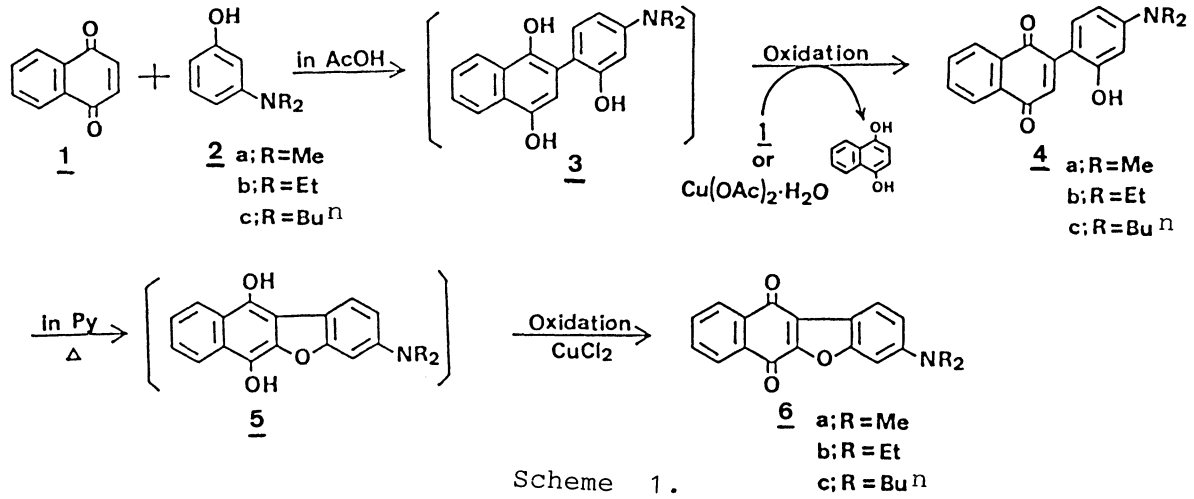
New heterocyclic quinone dyes, 3-(dialkylamino)benzo-[b]naphtho[2,3-d]furan-6,11-diones, were conveniently prepared from 1,4-naphthoquinone and m-(dialkylamino)phenols. These dyes show dichroic properties and good solubility in a nematic liquid crystalline system.

Dichroic dyes have attracted considerable attention in recent years, since these dyes are available as guest molecules in the system of guest-host liquid crystal displays. A variety of dye structures such as azo dyes, anthraquinone dyes, and quinophthalone dyes etc., have already been investigated from the standpoint of practical use in the system.[1] Heterocyclic quinone dyes are expected to have good properties as guest molecules, however, few works have been carried out from these viewpoints. We have developed a convenient synthetic method of new heterocyclic quinone dyes, 3-(dialkylamino)benzo[b]naphtho[2,3-d]furan-6,11-diones 6, which show appropriate dichroism and solubility in a nematic liquid crystalline system. The results are described herein.

The synthetic route of the dyes 6 is outlined in Scheme 1. The intermediate compounds, 2-[4-(dialkylamino)-2-hydroxyphenyl]-1,4-naphthoquinones 4, were conveniently obtained by the reaction of 1,4-naphthoquinone 1 with m-(dialkylamino)phenols 2.[2] The reaction conditions and yields are



Scheme 1.

Table 1. Reaction of 1 with m-(Dialkylamino)phenols 2a-2c[a)]

Run	Reactant 2	Molar ratio [2]/[1]	[Cu-salt]/[1]	Time h	Product (4)	Yield/%[b)]
1	2a	1.0	none[c)]	8.0	4a	51
2	2a	0.5	none[c)]	2.0	4a	41 (82)[d)]
3	2a	1.0	0.5	5.5	4a	77
4	2b	1.0	0.5	7.5	4b	76
5	2c	1.0	0.5	7.5	4c	79

a) To a solution of 1 (6.0 g, 38 mmol) and $Cu(OCOCH_3)_2 \cdot H_2O$ (19 mmol) in 200 ml of acetic acid was added 2 (19 or 38 mmol) with stirring at 50 °C. b) Isolated yield after column chromatography. c) Absence of $Cu(OCOCH_3)_2 \cdot H_2O$. d) Yield based on 2.

Table 2. Intramolecular Ring Closure of 4 in Refluxing Pyridine[a)]

Run	Reactant 4	Molar ratio [Cu-salt]/[4]	Time h	Product (6)	Yield/%[b)]
1	4a	none[c)]	80	6a	42
2	4a	0.5	12	6a	69
3	4a	1.0	12	6a	76
4	4b	1.0	13	6b	62
5	4c	1.0	13	6c	56

a) A mixture of 4 (6.82 mmol) and $CuCl_2$ (3.41 mmol or 6.82 mmol) in pyridine (50 ml) was heated to reflux. b) Isolated yield after column chromatography. c) Absence of $CuCl_2$.

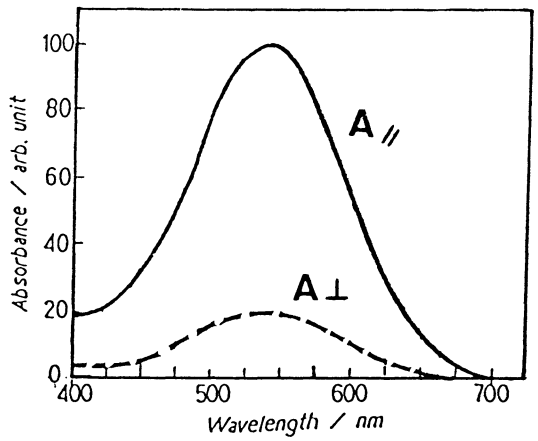


Fig. 1. Absorption spectra of the dye(6a) for parallel(A //) and perpendicular(A ⊥) modes.

summarized in Table 1. The reaction was initiated by nucleophilic conjugate addition of 2 to 1 to form the adduct 3 which was subsequently oxidized by the starting quinone 1 giving the arylation product 4.[3] Use of a moderate oxidizing agent[4] such as copper(II) acetate was especially effective to save quinone 1. The intermediates 4 then underwent cyclization into 6 [5] by refluxing in pyridine through intramolecular 1,4-addition and tautomerism. As shown in Table 2, this reaction was remarkably promoted by the addition of $CuCl_2$ and resulted in higher yields of 6.

Dichroic properties of the dyes 6 were investigated in the nematic liquid crystals (ZLI-1840, Merck). Figure 1 shows a typical example of the spectral changes for parallel and perpendicular modes in the liquid crystalline system. The dyes have one broad absorption band in visible region of 400-700 nm and show an appropriate dichroism. The spectral properties, order parameters, and solubility of 6a-6c are summarized in Table 3. The order parameters of the three dyes were almost the same

Table 3. The Spectral Properties, Solubility, and Order Parameters of Dyes 6

Dyes	In benzene		In ZLI-1840		
	λmax/nm	εmax	λmax/nm	Solubility/%wt[a]	Order parameter[b]
6a	531	7210	544	0.7	0.58
6b	547	7560	572	1.2	0.56
6c	551	7620	576	2.8	0.58

a) A maximum dye concentration was shown by %wt. b) The order parameter (S) was determined from the formula: $S=(A_{//}-A_{\perp})/(2A_{//}-A_{\perp})$.

value (ca. 0.58). The solubility of the dyes increased remarkably with the introduction of longer alkyl chains to the 3-dialkylamino group, a small bathochromic shift of λmax with increse in εmax being also observed. These data support that the heterocyclic quinone skeleton is a useful structure for the design of dichroic dyes with high solubility and order parameter. Further synthesis of the related compounds and the correlation between the structure and dichroic properties are now under investigation.

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References

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2) The reaction of 1 with N,N-dialkylanilines in acetic acid is known to give 2-[p-(dialkylamino)phenyl]-1,4-naphthoquinones: C. Blackburn and J. Griffiths, J. Chem. Res.(S), 1982, 320.

3) 2-[4-(Dimethylamino)-2-hydroxyphenyl]-1,4-naphthoquinone (4a): mp 200-201 °C; IR (KBr) 3200 (OH), 1661 and 1634 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.02 (6H,s), 6.34 (1H, d, J=2.6 Hz), 6.37 (1H, dd, J=2.6, 9.4 Hz), 6.97 (1H, s), 7.19 (1H, d, J=9.4 Hz), 7.6-7.9 (2H, m), 8.0-8.3 (2H, m), 8.53 (1H, b). Found:C; 73.83, H; 4.88, N; 4.53%. Calcd for $C_{18}H_{15}NO_3$: C; 73.70, H; 5.15; N; 4.78%.

4) Since m-(dialkylamino)phenols 2 are very susceptible to oxidation, especially mild oxidizing agents are needed.

5) 3-(Dimethylamino)benzo[b]naphtho[2,3-d]furan-6,11-dione (6a): mp 228-229 °C; IR (KBr) 1664 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ= 3.09 (6H, s), 6.79 (1H, d, J=2.2 Hz), 6.92 (1H, dd, J=2.2, 9.0 Hz), 7.6-7.9 (2H, m), 8.04 (1H, d, J=9.0 Hz), 8.1-8.6 (2H, m). Found:C; 73.97, H; 4.38, N; 4.71%. Calcd for $C_{18}H_{13}NO_3$: C; 74.21, H; 4.50, N; 4.81%.

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