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# The synthesis and properties of naphthodifuranones and naphthofuranonepyrrolidones

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**Abstract**

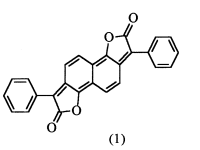
Benzodifuranones were modified by the replacement of central benzene nucleus with naphthalene moiety. Such modified structures offer the possibility of extension into the blue colour shade range. Symmetrically disubstituted naphthodifuranones were synthesised by the reaction of 1,5-dihydroxynaphthalene with an appropriate mandelic acid. Asymmetrically mono and disubstituted naphthodifuranones were synthesised by the reaction of the half-condensed intermediates with appropriate mandelic acids. Symmetrical naphthofuranonepyrrolidones were synthesised by the reaction of 1-amino-5-hydroxynaphthalene with an appropriate mandelic acid. © 2001 Published by Elsevier Science Ltd. All rights reserved.

*Keywords:* Naphthodifuranone; Naphthofuranonepyrrolidone; 1,5-Dihydroxynaphthalene

## 1. Introduction

Commercial benzodifuranones show good dyeing properties, but provide red shades only. Therefore attempts have been made to produce more bathochromic benzodifuranones by replacing alkoxy groups by alkylamino groups and by replacing the central benzene nucleus with a naphthalene moiety [1–3]. The replacement of an alkoxy group by an alkylamino group gives rise to bathochromism due to the increased electron donating strength of the substituents, whereas the central nucleus with the naphthalene gives rise to bathochromism due to the increase in conjugation.

Researchers at ICI prepared the symmetrical naphthodifuranone (**1**) which was synthesised from 1,5-dihydroxynaphthalene and mandelic acid in an inert high-boiling point solvent [3]. Recently, Smith prepared symmetrically disubstituted naphthodifuranones (**2**) using a similar synthetic method [4]. The synthesis of asymmetrically substituted naphthodifuranones (**3**) which are prepared from the half-condensed benzofuranone intermediates and appropriate mandelic acids are discussed in the present paper.

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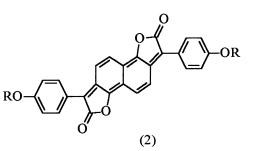


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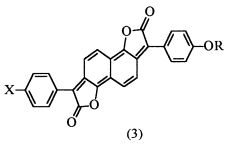
In this study, symmetrically disubstituted naphthofuranonepyrrolidones (**4**) were also prepared by condensation of 1-amino-5-hydroxynaphthalene with appropriate mandelic acids.

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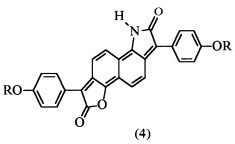


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## 2. Experimental

Melting points were determined using an electrothermal melting point apparatus. Thermal analyses were carried out using a Du Pont 2000 differential scanning calorimeter. Thin layer chromatography was performed on aluminium-backed silica gel plates (DC Alufolien Kieselgel 60 $F_{254}$, Merck), this type having a layer thickness of 0.2 mm. The purity of almost all compounds synthesised in this study was checked by TLC except for very insoluble compounds. Microanalyses were carried out in the Department of Chemistry, University of Leeds. Mass spectral analyses were carried out at the LG Chemical Institution, South Korea. The $\lambda_{max}$ values of the dyes synthesised were measured using Philips spectrophotometer variously in, DMF, acetone, chloroform and toluene.

### *2.1. Preparation of the half-condensed intermediates*

#### *2.1.1. 6-Hydroxy-2-oxo-3-phenyl-2,3-dihydronaphtho[1,2-*b*]furan* (**5**)

1,5-Dihydroxynaphthalene (99%, 3.2 g, 0.02 mol), DL-mandelic acid (99%, 3.0 g, 0.02 mol) and 1,2,4-trichlorobenzene (30 ml) were charged into a reaction vessel. The mixture was heated to 200°C, and was stirred for 1 h at this temperature. During the heating, nitrogen gas was used in order to remove water and to prevent contact with air. The mixture was allowed to cool to room temperature. The product began to precipitate during cooling and was stirred for a further 1 h at room temperature. The product was filtered off and washed with a small amount of toluene and hexane, respectively, giving a light-brown solid contaminated with a dilactone compound and unreacted 1,5-dihydroxynaphthalene. The crude yield was 2.8 g (50.7%). The crude product was suspended in 1,2,4-trichlorobenzene, heated to 200°C to dissolve, and was then cooled to room temperature. The precipitated product was filtered off and washed with toluene. The product was dried in the air. The dried product was dissolved in DMF and precipitated by water. The series of purification procedures was repeated two or three times in order to achieve enough purity, giving a pale yellow solid (1.50g; 27.2% yield, m.p. 232–235°C).

Microanalysis found C, 77.5%; H, 4.3% ($C_{18}H_{12}O_3$ requires C, 78.3%; H, 4.3%). DSC showed a sharp peak at 236.7°C. Mass spectrum gave the $M^+$ peak at 276.

#### *2.1.2. 6-Hydroxy-2-oxo-3-(4-chlorophenyl)-2,3-dihydronaphtho[1,2-*b*]furan* (**6**)

The preparation of the half-condensed intermediate (**5**) was followed except that 4-chloromandelic acid (3.7 g, 0.02 mol) was used instead of mandelic acid, giving a brown solid contaminated with a dilactone compound and unreacted 1,5-dihydroxynaphthalene. The crude yield was 1.9 g (30.4%). The same purification procedures for the half-condensed intermediate (**5**) were used, giving a pale yellow solid (0.8 g; 12.9% overall yield, m.p. 211–215°C).

Microanalysis found C, 69.1%; H, 3.3%; Cl, 11.8% ($C_{18}H_{11}ClO_3$ requires C, 69.6%; H, 3.5%; Cl, 11.4%).

#### *2.1.3. 6-Hydroxy-2-oxo-3-(4-methylphenyl)-2,3-dihydronaphtho[1,2-*b*]furan* (**7**)

The preparation of the half-condensed intermediate (**5**) was followed except that 4-methylmandelic acid (3.3 g, 0.02 mol) was used instead of mandelic acid, giving a brown solid contaminated with a dilactone compound and unreacted 1,5-dihydroxynaphthalene. The crude yield was 3.6 g (62.1%). The same purification procedures for the half-condensed intermediate (**5**) were used, giving a pale yellow solid (2.1 g; 36.2% overall yield, m.p. 241–245°C).

Microanalysis found C, 79.1%; H, 4.3% ($C_{19}H_{14}O_3$ requires C, 78.6%; H, 4.8%).

*2.1.4. 6-Hydroxy-2-oxo-3-(4-methoxyphenyl)-2,3-dihydronaphtho[1,2-*b*]furan* (**8**)

The preparation of the half-condensed intermediate (**5**) was followed except that 4-methoxylmandelic acid (3.6 g, 0.02 mol) was used instead of mandelic acid, giving a brown solid contaminated with a dilactone compound and unreacted 1,5-dihydroxynaphthalene. The crude yield was 3.5 g (57.1%). The same purification procedures for the half-condensed intermediate (**5**) were used, giving a pale yellow (2.1 g; 34.3% overall yield, m.p. 223–225°C).

Microanalysis found C, 74.1%; H, 4.3% ($C_{19}H_{14}O_4$ requires C, 74.5%; H, 4.6%).

*2.2. Preparation of the symmetrical naphthodifuranones*

*2.2.1. 3,8-Diphenylnaphtho[1,2-*b*:5,6-*b′*]difuran-2,7-dione* (**1**)

1,5-Dihydroxynaphthalene (99%, 1.6 g, 0.01 mol), DL-mandelic acid (99%, 3.04 g, 0.02 mol) and 1,2,4-trichlorobenzene (20 ml) were stirred for 6 h at 200°C, allowing formed water to distil off, before cooling to room temperature. Nitrobenzene (1.0 g) was added and the mixture was stirred for a further hour at 200°C, then allowed to cool. The precipitate was filtered off and washed with toluene. The crude product was dissolved in 1,2,4-trichlorobenzene at 200°C, precipitated at room temperature, and digested in hot acetic acid. The product obtained was refluxed in methanol, giving a brown solid (1.6 g, 41% yield, m.p. >300°C).

Microanalysis found C, 79.3%; H, 3.6% ($C_{26}H_{14}O_4$ requires C, 80.0%; H, 3.6%). DSC showed a sharp peak at 405.1°C with decomposition.

*2.2.2. 3,8-Di(4-propoxyphenyl)naphtho[1,2-*b*:5,6-*b′*]difuran-2,7-dione* (**2-1**)

1,5-Dihydroxynaphthalene (99%, 1.6 g, 0.01 mol), 4-propoxymandelic acid (4.2 g, 0.02 mol) and 1,2,4-trichlorobenzene (20 ml) were stirred for 2 h at 200°C, allowing formed water to distill off. The mixture was cooled to room temperature, and nitrobenzene (1.0 g) was added. The mixture was stirred for a further hour at 200°C, then allowed to cool. The precipitate was filtered off and washed with toluene. The crude product was dissolved in 1,2,4-trichlorobenzene at 200°C, precipitated at room temperature, and digested in hot acetic acid. The product obtained was refluxed in methanol, giving a bright green-coloured solid (3.1 g, 61% yield, m.p. >300°C).

Microanalysis found C, 75.1%; H, 5.2% ($C_{32}H_{26}O_6$ requires C, 75.9%; H, 5.1%). DSC showed a peak at 367.5°C with decomposition.

*2.2.3. 3,8-Di(4-butoxyphenyl)naphtho[1,2-*b*:5,6-*b′*]difuran-2,7-dione* (**2-2**)

1,5-Dihydroxynaphthalene (99%, 1.6 g, 0.01 mol), 4-butoxymandelic acid (4.3 g, 0.02 mol) and 1,2,4-trichlorobenzene (20 ml) were stirred for 2 h at 200°C, allowing formed water to distill off. The mixture was cooled to room temperature, and nitrobenzene (1.0 g) was added. The mixture was stirred for a further hour at 200°C, then allowed to cool. The precipitate was filtered off and washed with toluene. The crude product was dissolved in 1,2,4-trichlorobenzene at 200°C, precipitated at room temperature, and digested in hot acetic acid. The product obtained was refluxed in methanol, giving a green-coloured solid (3.5 g, 61% yield, m.p. 281–285°C).

Microanalysis found C, 75.8%; H, 5.9% ($C_{34}H_{30}O_6$ requires C, 76.4%; H, 5.6%). DSC showed a sharp peak at 279.5°C.

*2.3. Preparation of the asymmetrical naphthodifuranones*

*2.3.1. 3-Phenyl-8-(4-propoxyphenyl)naphtho[1,2-*b*:5,6-*b′*]difuran-2,7-dione* (**3-3**)

6-Hydroxy-2-oxo-3-phenyl-2,3-dihydronaphtho [1,2-*b*]furan (1.4 g, 0.005 mol), 4-propoxy-mandelic acid (1.1 g, 0.005 mol) and 1,2,4-trichlorobenzene (20 ml) were stirred for 2 h at 200°C, allowing formed water to distil off. The mixture was cooled to room temperature, and nitrobenzene (0.5 g) was added. The mixture was stirred for a further hour at 200°C, then allowed to cool. The precipitate was filtered off and washed with toluene. The crude product (0.65 g; 29% crude yield) was dissolved in

1,2,4-trichlorobenzene at 200°C, precipitated at room temperature, and digested in hot acetic acid. These purification processes were repeated two or three times. The product obtained was refluxed in methanol, giving a green solid (m.p. > 300°C).

Microanalysis found C, 77.2%; H, 4.4% ($C_{29}H_{20}O_5$ requires C, 77.7%; H, 4.5%). DSC showed a sharp peak at 342.8°C with decomposition. Mass spectrum gave the $M^+$ peak at 448.

*2.3.2. 3-Phenyl-8-(4-ethoxyphenyl)naphtho[1,2-b:5,6-b′]difuran-2,7-dione* (**3-2**)

The preparation of the naphthodifuranone dye (**3–3**) was followed except that 4-ethoxymandelic acid (1.0 g, 0.005 mol) was used instead of 4-propoxymandelic acid. The crude product (0.45 g; 21% crude yield) obtained was purified by the above process, giving a dark green solid (m.p. > 300°C).

Microanalysis found C, 76.4%; H, 4.4% ($C_{28}H_{18}O_5$ requires C, 77.4%; H, 4.1%). DSC showed a sharp peak at 345.9°C with decomposition.

*2.3.3. 3-Phenyl-8-(4-methoxyphenyl)naphtho[1,2-b:5,6-b′]difuran-2,7-dione* (**3-1**)

The preparation of the naphthodifuranone dye (**3-3**) was followed except that 4-methoxymandelic acid (0.9 g, 0.005 mol) was used instead of 4-propoxymandelic acid. The crude product (0.5 g; 24% crude yield) obtained was purified by the above process, giving a green solid (m.p. > 300°C).

Microanalysis found C, 77.5%; H, 3.9% ($C_{27}H_{16}O_5$ requires C, 77.1%; H, 3.8%). DSC showed a sharp peak at 366.1°C.

*2.3.4. 3-Phenyl-8-(4-isopropoxyphenyl)naphtho-[1,2-b:5,6-b′]-difuran-2,7-dione* (**3-4**)

The preparation of the naphthodifuranone dye (**3-3**) was followed except that 4-isopropoxymandelic acid (1.1 g, 0.005 mol) was used instead of 4-propoxymandelic acid. The crude product (0.60 g; 27% crude yield) obtained was purified by the above process, giving a green solid (m.p. > 300°C).

Microanalysis found C, 76.8%; H, 4.5% ($C_{29}H_{20}O_5$ requires C, 77.7%; H, 4.5%). DSC showed a sharp peak at 321.4°C with decomposition.

*2.3.5. 3-Phenyl-8-(4-butoxyphenyl)naphtho[1,2-b:5,6-b′]difuran-2,7-dione* (**3-5**)

The preparation of the naphthodifuranone dye (**3-3**) was followed except that 4-butoxymandelic acid (1.1 g, 0.005 mol) was used instead of 4-propoxymandelic acid. The crude product (0.7 g; 31% crude yield) obtained was purified by the above process, giving a dark green solid (m.p. > 300°C).

Microanalysis found C, 76.9%; H, 5.1% ($C_{30}H_{22}O_5$ requires C, 77.9%; H, 4.8%). DSC showed a sharp peak at 337.1°C with decomposition.

*2.3.6. 3-Phenyl-8-(4-(2-ethoxyethoxy)phenyl)-naphtho[1,2-b:5,6-b′]difuran-2,7-dione* (**3-6**)

The preparation of the naphthodifuranone dye (**3–3**) was followed except that 4-(2-ethoxyethoxy) mandelic acid (1.20 g, 0.005 mol) was used instead of 4-propoxymandelic acid. The crude product (0.51 g; 21.5% crude yield) obtained was purified by the above process, giving a green solid (m.p. > 300°C).

Microanalysis found C, 75.6%; H, 4.2% ($C_{30}H_{22}O_6$ requires C, 75.3%; H, 4.6%). DSC showed a sharp peak at 328.6°C with decomposition.

*2.3.7. 3-(4-Methylphenyl)-8-(4-propoxyphenyl)-naphtho[1,2-b:5,6-b′]difuran-2,7-dione* (**3-7**)

6-Hydroxy-2-oxo-3-(methylphenyl)-2,3-dihydronaphtho[1,2-*b*]furan (1.5 g, 0.005 mol), 4-propoxymandelic acid (0.9 g, 0.005 mol) and 1,2,4-trichlorobenzene (20 ml) were charged into a reaction vessel. The mixture was heated to 200°C and stirred for 2 h. The mixture was cooled to room temperature, and nitrobenzene (0.5 g) was added. The mixture was stirred for a further hour at 200°C, then allowed to cool. The precipitate was filtered off and washed with toluene. The crude product (0.62 g, 26.8% crude yield) was dissolved in 1,2,4-trichlorobenzene at 200°C, precipitated at room temperature, and digested in hot acetic acid. These purification processes were repeated two or three times. The product obtained was refluxed in methanol, giving a dark green solid (m.p. > 300°C).

Microanalysis found C, 77.1%; H, 4.6% ($C_{30}H_{22}O_5$ requires C, 77.9%; H, 4.8%). DSC showed a sharp peak at 320.3°C with decomposition.

*2.3.8. 3-(4-Methylphenyl)-8-(4-ethoxyphenyl)-naphtho[1,2-*b*:5,6-*b′*]difuran-2,7-dione* (**3-10**)

The preparation of the naphthodifuranone dye (**3-7**) was followed except that 4-ethoxymandelic acid (0.98 g, 0.005 mol) was used instead of 4-propoxymandelic acid. The crude product (0.57 g; 25.5% crude yield) obtained was purified by the above process, giving a dark green solid (m.p. $>300^{\circ}$C).

Microanalysis found C, 75.8%; H, 4.7% ($C_{29}H_{20}O_5$ requires C, 77.7%; H, 4.5%). DSC showed a sharp peak at 309.4°C with decomposition.

*2.3.9. 3-(4-Methylphenyl)-8-(4-(2-ethoxyethoxy)-phenyl)naphtho-[1,2-*b*:5,6-*b′*]difuran-2,7- dione* (**3-11**)

The preparation of the naphthodifuranone dye (**3-7**) was followed except that 4-(2-ethoxyethoxy)mandelic acid (1.20 g, 0.005 mol) was used instead of 4-propoxymandelic acid. The crude product (0.62 g; 27.6% crude yield) obtained was purified by the above process, giving a dark green solid (m.p. $>300^{\circ}$C).

Microanalysis found C, 75.3%; H, 5.0% ($C_{31}H_{24}O_6$ requires C, 75.6%; H, 4.8%). DSC showed a sharp peak at 301.6°C with decomposition.

*2.3.10. 3-(4-Chlorophenyl)-8-(4-propoxyphenyl)-naphtho[1,2-*b*:5,6-*b′*]difuran-2,7-dione* (**3-8**)

The preparation of the naphthodifuranone dye (**3-3**) was followed except that 6-hydroxy-2-oxo-3-(chlorophenyl)-2,3-dihydronaphtho[1,2-*b*]furan (1.6 g, 0.005 mol) was used instead of 6-Hydroxy-2-oxo-3-phenyl-2,3-dihydronaphtho[1,2-*b*]furan. The crude product (0.5 g; 21% crude yield) obtained was purified by the above process, giving a dark green solid (m.p. $>300^{\circ}$C).

Microanalysis found C, 72.3%; H, 4.2%; Cl, 7.2% ($C_{29}H_{19}ClO_5$ requires C, 72.1%; H, 3.9%; Cl, 7.4%). DSC showed a sharp peak at 312.8°C.

*2.3.11. 3-(4-Methoxyphenyl)-8-(4-propoxyphenyl)-naphtho[1,2-*b*:5,6-*b′*]difuran-2,7-dione* (**3-9**)

The preparation of the naphthodifuranone dye (**3-3**) was followed except that 6-hydroxy-2-oxo-3-(methoxyphenyl)-2,3-dihydronaphtho[1,2-*b*] furan (1.53 g, 0.005 mol) was used instead of 6-hydroxy-2-oxo-3-phenyl-2,3-dihydronaphtho[1,2-*b*]furan. The crude product (0.54 g; 22.5% crude yield) obtained was purified by the above process, giving a dark green solid (m.p. $>300^{\circ}$C).

Microanalysis found C, 75.1%; H, 4.7% ($C_{30}H_{21}O_6$ requires C, 75.5%; H, 4.4%). DSC showed a sharp peak at 358.3°C with decomposition.

*2.4. Preparation of naphthofuranonepyrrolidones*

*2.4.1. 3,8-Di(4-propoxyphenyl)naphtho[1,2-*b*:5,6-*b′*]furan-2-onepyrrole-7-one* (**4-3**)

1-Amino-5-hydroxynaphthalene (99%, 1.59 g, 0.01 mol), 4-propoxymandelic acid (6.30 g 0.03 mol) and 1,2,4-trichlorobenzene (30 ml) were stirred for 2 h at 200°C. After cooling to room temperature, nitrobenzene (1.0 g) was added and the mixture was stirred for further 30 min at 200°C. After cooling, the solid was filtered off, washed with toluene and dried in the air. The crude product (0.78 g, 15.4% crude yield) was dissolved in 1,2,4-trichlorobenzene at 200°C, precipitated at room temperature, and digested in hot acetic acid. These purification processes were repeated two or three times. The product obtained was refluxed in methanol, giving a dark green solid (m.p. 290–294°C).

Microanalysis found C, 76.0%; H, 5.3%; N, 2.7% ($C_{32}H_{27}NO_5$ requires C, 76.0%; H, 5.3%; N, 2.8%). DSC showed a sharp peak at 366.9°C with decomposition.

*2.4.2. 3,8-Di(4-methoxyphenyl)naphtho[1,2-*b*:5,6-*b′*]furan-2-onepyrrole-7-one* (**4-1**)

The preparation of the naphthodifuranone dye (**4-3**) was followed except that 4-methoxymandelic acid (5.46 g 0.03 mol) was used instead of 4-propoxymandelic acid. The crude product (0.66 g, 14.7% crude yield) obtained was purified by the above process, giving a dark green solid (m.p. $>300^{\circ}$C).

Microanalysis found C, 74.7%; H, 4.4%; N, 3.1% ($C_{28}H_{19}NO_5$ requires C, 74.8%; H, 4.2%; N, 3.1%). DSC showed a sharp peak at 375.0°C with decomposition.

*2.4.3. 3,8-Di(4-ethoxyphenyl)naphtho[1,2-*b*:5,6-*b′*]furan-2-onepyrrole-7-one* (**4-2**)

The preparation of the naphthodifuranone dye (**4-3**) was followed except that 4-ethoxymandelic

acid (5.88 g 0.03 mol) was used instead of 4-propoxymandelic acid. The crude product (0.86 g, 18.0% crude yield) obtained was purified by the above process, giving a dark green solid (m.p. $>300^{\circ}C$).

Microanalysis found C, 73.4%; H, 4.8%; N, 2.7% ($C_{30}H_{23}NO_5$ requires C, 75.4%; H, 4.8%; N, 2.9%). DSC showed a sharp peak at 370.5°C with decomposition.

#### *2.4.4. 3,8-Di(4-isopropoxyphenyl)naphtho[1,2-b:5,6-b′]furan-2-onepyrrole-7-one* (**4-4**)

The preparation of the naphthodifuranone dye (**4-3**) was followed except that 4-isopropoxymandelic acid (6.30 g 0.03 mol) was used instead of 4-propoxymandelic acid. The crude product (0.74 g, 14.8% crude yield) obtained was purified by the above process, giving a dark green solid (m.p. $>300^{\circ}C$).

Microanalysis found C, 75.5%; H, 5.4%; N, 2.5% ($C_{32}H_{27}NO_5$ requires C, 76.0%; H, 5.3%; N, 2.8%). DSC showed a sharp peak at 357.1°C with decomposition.

#### *2.4.5. 3,8-Di(4-butoxyphenyl)naphtho[1,2-b:5,6-b′]furan-2-onepyrrole-7-one* (**4-5**)

The preparation of the naphthodifuranone dye (**4-3**) was followed except that 4-butoxymandelic acid (6.72 g 0.03 mol) was used instead of 4-propoxymandelic acid. The crude product (0.89 g, 16.7% crude yield) obtained was purified by the above process, giving a dark green solid (m.p. $>300^{\circ}C$).

Microanalysis found C, 76.6%; H, 6.0%; N, 2.4% ($C_{34}H_{31}NO_5$ requires C, 76.5%; H, 5.8%; N, 2.6%). DSC showed a sharp peak at 363.8°C with decomposition.

## 3. Results and discussion

As mentioned in the introduction, synthetic routes to the parent symmetrically disubstituted naphthodifuranone dyes are outlined in the literature [3]. The literature describes two ways of using 1,5-dihydroxynaphthalene, giving rise to entirely different products. Under the first set of reaction conditions, condensation of 1 mol of 1,5-dihydroxynaphthalene with 2 mol of mandelic acid in a high-boiling point solvent such as 1,2,4-trichlorobenzene in the absence of an acid catalyst is followed by subsequent oxidation to give the violet naphthodifuranone dye (**1**). Alternatively, heating 1,5-dihydroxynaphthalene with mandelic acid in molten p-toluenesulphonic acid, followed by oxidation step gives rise to a *peri*-cyclised dilactone isomer which is blue. Under strongly acidic conditions, it can be seen that protonation of mandelic acid, followed by loss of water, generates a carbonium ion, leading to electrophilic substitution at the 4-position of 1,5-dihydroxynaphthalene. In the absence of a strong acid catalyst at 200°C esterification takes place first between a hydroxy group of 1,5-dihydroxynaphthalene and the carboxyl group of mandelic acid. This ester intermediates can undergo intramolecular *ortho*-cyclisation, giving the desired naphthodifuranone dye (**1**).

Symmetrically disubstituted naphthodifuranones (**2**) can be synthesised easily using alkoxymandelic acids instead of mandelic acid in the absence of a strong acid catalyst at 200°C. The reaction of using alkoxymandelic acid is energetically favourable, because the presence of an electron donating group such as alkoxy at the *para* position leads to resonance stabilisation of the carbonium ion.

Smith synthesised several symmetrically substituted naphthodifuranones and examined their properties [4]. He reported that such dyes have quite low solubility in solvents, so that these dyes showed very poor build up on polyester fibre. Consequently, the introduction of asymmetry into naphthodifuranone dyes is essential in order to improve solubility and build up as in the case of structurally modified benzodifuranones [7]. Asymmetrical benzodifuranones show greatly improved build up on polyester than do the corresponding symmetrical benzodifuranones. The asymmetry of the dyes decreases high crystallinity, so that solubility is improved significantly [1].

### *3.1. Synthesis of the half-condensed intermediates for asymmetrical naphthodifuranones*

The synthesis of naphthodifuranones developed in this study needs several reaction steps, the preparation of appropriate mandelic acid, half-condensed intermediates and the condensation.

The preparation of various mandelic acid derivatives was discussed in the previous paper [5]. The half-condensed intermediates that can be obtained from the condensation of 1,5-dihydroxynaphthalene with appropriate mandelic acids are much more difficult to prepare than corresponding half-condensed intermediates for benzodifuranones. There are several reasons for this difficulty in synthesis. Firstly, competitive reaction between *ortho* and *para* positions of 1,5-dihydroxynaphthalene leads to low yields of product and generates many kinds of by-products. Secondly, the higher reaction temperatures needed, due to absence of acid catalyst, bring about decomposition of the half-condensed intermediate. Consequently, these half-condensed intermediates were generally impure and were obtained only in low yields. Two synthetic methods were used to prepare the half-condensed intermediates. The first involved the use of acetic acid as solvent with a small amount of sulphuric acid catalyst at a temperature between 100 and 110°C (Scheme 1).

As shown in Scheme 1, the reaction of *p*-alkoxymandelic acid with 1,5-dihydroxy-naphthalene under these reaction conditions gave the half-condensed intermediates, but they were too impure for isolation. Interestingly, the reaction of mandelic acid with 1,5-dihydroxy-naphthalene gave only by-product, due to the low reactivity of mandelic acid itself.

The other synthetic method (Scheme 2) employed for preparing the half-condensed intermediates involved the use of 1,2,4-trichlorobenzene as a solvent. The reaction of 1 mol of substituted or non-substituted mandelic acid with 1 mol of 1,5-dihydroxynaphthalene at a higher temperature (200°C) gave the desired products. Under these reaction conditions, nitrogen gas was used to expel water generated and to prevent air oxidation, leading to relatively good yields of the product.

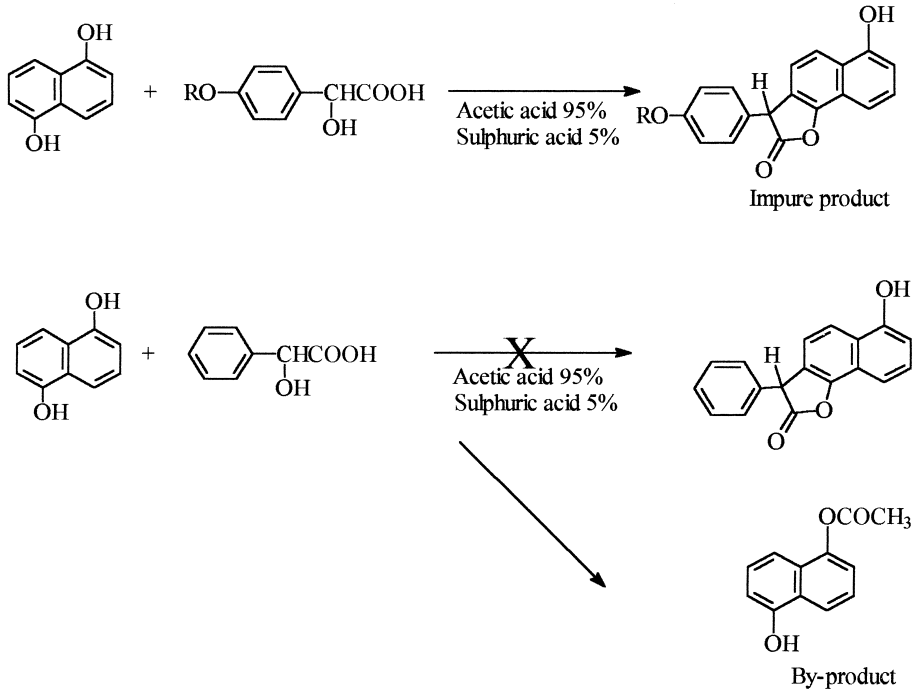
The half-condensed intermediates, mono-naphthofuranone thus obtained also contained unreacted 1,5-dihydroxynaphthalene and dicyclised by-products, so that intensive purification methods were needed. To remove the non-polar dicyclised by-products, the crude products were dissolved in a high-boiling point solvent, such as 1,2,4-trichlorobenzene, and precipitated again. The unreacted 1,5-dihydroxynaphthalene was removed by dissolution in DMF and subsequent precipitation by water. This series of purification methods was repeated two or three times to achieve enough purity. The resulting products obtained by this purification procedure were very pure, but the yields were low. The mass spectrum of the half-condensed intermediate synthesised from 1,5-dihydroxy-naphthalene and mandelic acid, is consistent with its structure. The mass spectrum shows the $M^+$ peak of the half-condensed intermediate (6-hydroxy-2-oxo-3-phenyl-2,3-dihydronaphthofuranone) at 276.

### *3.2. Synthesis of asymmetrically substituted naphthodifuranones*

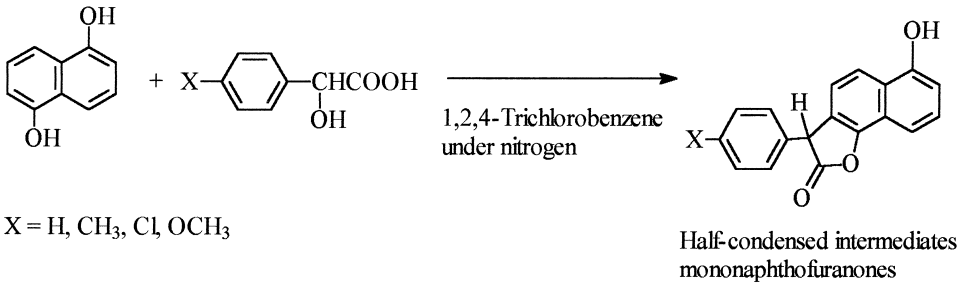
Asymmetrically substituted naphthodifuranones were synthesised by reaction of 1 mol of the half-condensed intermediate with 1 mol of the appropriate mandelic acid in 1,2,4-trichlorobenzene at 200°C (Scheme 3). The reaction mixture was allowed to cool to room temperature, nitrobenzene was added to oxidise the product, and then the mixture was heated to 200°C and stirred for a further hour. This procedure gave low yields (20–30%) of impure products.

To obtain the pure asymmetrical naphthodifuranones, purification was carried out three or four times. Unfortunately, the asymmetrical naphthodifuranones are too insoluble for successful recrystallisation and column chromatography. However, the impurities could be removed by digesting the impure products in a range of hot solvents, leaving the required products undissolved. Another useful purification method for the asymmetrical naphtho-difuranones was to dissolve the impure products in 1,2,4-trichlorobenzene at 200°C and then reprecipitated at room temperature. A combination of several purification methods had often to be used. For example, the naphthodifuranone dye was purified by twice dissolving and precipitating in hot 1,2,4-trichlorobenzene, digestion in hot acetic acid, boiling in water and refluxing in methanol.

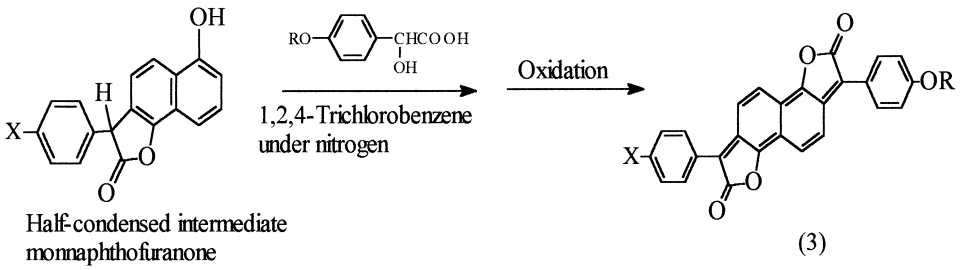
The mass spectrum of the typical naphthodifuranone dye (**3-3**) is consistent with its structure, showing clearly the $M^+$ peak at 448.




Scheme 1.




Scheme 2.




Scheme 3.

### 3.3. Synthesis of symmetrically disubstituted naphthofuranonepyrrolidones

Structurally symmetrically substituted naphthofuranonepyrrolidones were synthesised by reaction of 1 mol of 1-amino-5-hydroxynaphthalene with 3 mol of a 4-substituted mandelic acid in 1,2,4-trichlorobenzene at 200°C (Scheme 4). This process was best achieved by employing nitrogen gas to remove water and to avoid contact with air. The mixture was cooled and a small amount of nitrobenzene was added for oxidation.

The crude products obtained were relatively impure so that intensive purification methods were needed. Similarly, these products were quite insoluble in solvents. The purification methods used for naphthodifuranones were thus employed to purify the crude naphthofuranonepyrrolidones. The resulting purified dyes were obtained in low yield. The result of microanalysis was consistent with its structure.

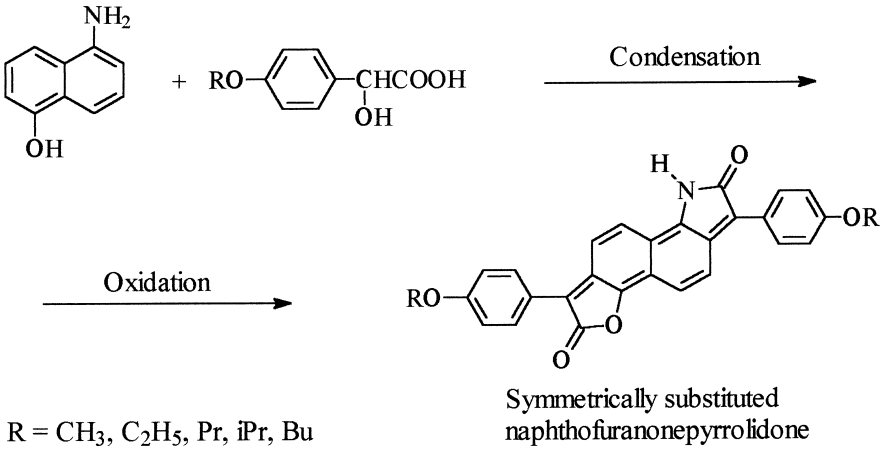
Interestingly, as shown in Scheme 5, reaction of 1-amino-5-hydroxynaphthalene with mandelic acid did not give product, presumably, due to the low reactivity of mandelic acid.

A synthesis of asymmetrically substituted naphthofuranonepyrrolidone was also attempted by using the method developed for the naphthodifuranones. Firstly, preparation of a half-condensed intermediate was attempted by condensation of 1 mol of 1-amino-5-hydroxynaphthalene with 1 mol of mandelic acid in 1,2,4-trichlrobenzene at reflux temperature. Scheme 6 shows route to the desired product. But, the desired half-condensed intermediate could not be prepared, only tar and unidentified side products were obtained.

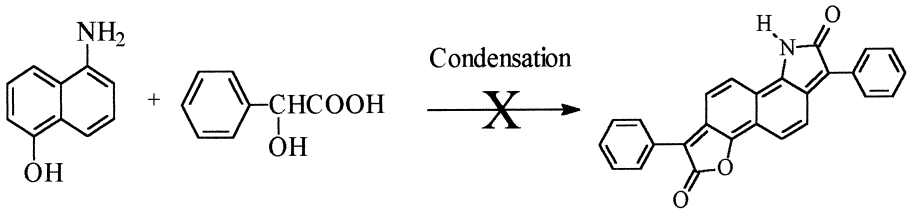
Mandelic acid was then structurally modified to improve the reactivity. The hydroxy group in mandelic acid was replaced with better leaving groups such as chlorine or acetate, as shown in Fig 1. α-Chlorophenylacetyl chloride was prepared in chloroform by reaction of 1 mol of mandelic acid with 3 mol of thionyl chloride at reflux temperature [6]. Excess thionyl chloride, sulphur dioxide, hydrogen chloride and solvent were evaporated to purify the product. Acetylmandelic acid was prepared in chloroform by reaction of 1 mole of mandelic acid with 2 mol of acetyl chloride at reflux temperature [6]. Excess acetyl chloride, hydrogen chloride and solvent were removed by evaporation. Unfortunately, the desired half-condensed intermediate still could not be obtained by using even these modified compounds.

### 3.4. Absorption spectra

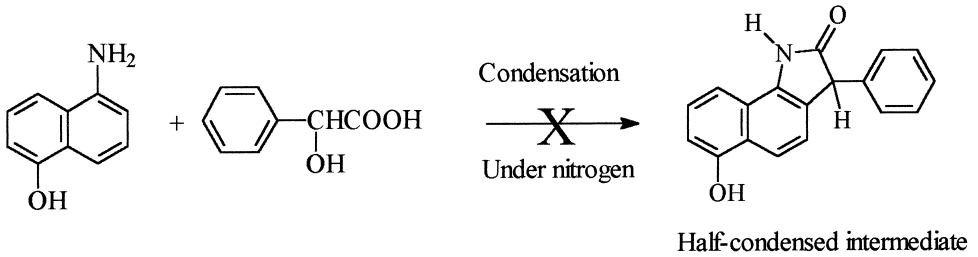
The $\lambda_{max}$ values of the dyes synthesised in this study were measured variously in toluene, chloroform, acetone and DMF. But $\epsilon_{max}$ values could not be measured due to their extreme insolubility. As expected, asymmetrically monosubstituted naphthodifuranones are more hypsochromic than




Scheme 4.




Scheme 5.




Scheme 6.

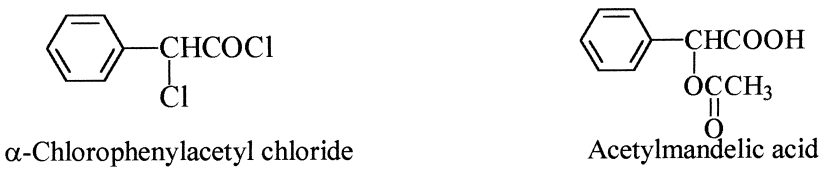
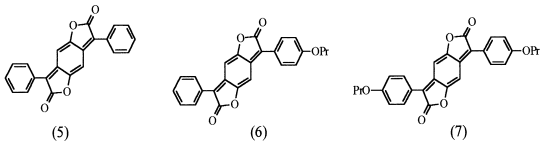



Fig. 1. Modification of mandelic acid by introducing better leaving group.

symmetrically disubstituted naphthodifuranones. Symmetrically substituted naphthofuranonepyrrolidones are slightly more hypsochromic than symmetrical naphthodifuranones. Spectral data of the dyes synthesised are listed in Tables 1 and 2.

A large bathochromic effect is achieved in the benzodifuranone system when the central benzene moiety is replaced with naphthalene. Thus, non-substituted benzodifuranone dye (**5**) has $\lambda_{max}$ at 466 nm in chloroform [7], whereas dye (**1**) has $\lambda_{max}$ at 555 nm in the same solvent. Likewise, substituted naphthodifuranones show similar trends to substituted benzodifuranones when substituent groups are introduced. Naphthodifuranone dye (**3-3**), with one propoxy group, has $\lambda_{max}$ at 583 nm in DMF; naphthodifuranone dye (**2-1**), with two propoxy groups, has $\lambda_{max}$ at 609 nm in DMF; benzodifuranone dye (**6**), with one propoxy group, has $\lambda_{max}$ at 505 nm in DMF; benzodifuranone dye (**7**), with two propoxy groups, has $\lambda_{max}$ at 536 nm in DMF. These spectral data show that the bathochromic effect of an alkoxy group is greater than in naphthodifuranone. It is generally true that the introduction of a second alkoxy group gives rise to a smaller bathochromic shift than the first.




An interesting result was obtained where a 2-ethoxyethoxy group was introduced into the naphthodifuranone system. Thus, dye (**3-6**) has $\lambda_{max}$ at 589 nm in toluene; dye (**3-5**) with a butoxy group, has $\lambda_{max}$ at 604 nm in toluene. The relative

Table 1
Spectral data ($\lambda_{max}$ values) of naphthodifuranone dyes (nm)

| Dye No. | $R_1$ | $R_2$ | Toluene | Chloroform | Acetone | DMF |
|---|---|---|---|---|---|---|
| **1** | H | H | 561 | 555 | 551 | 554 |
| **2-1** | $O(CH_2)_2CH_3$ | $O(CH_2)_2CH_3$ | 613 | 613 | 598 | 609 |
| **2-2** | $O(CH_2)_3CH_3$ | $O(CH_2)_3CH_3$ | 615 | 614 | 596 | 610 |
| **3-1** | H | $OCH_3$ | 587 | 586 | 575 | 582 |
| **3-2** | H | $OCH_2CH_3$ | 596 | 596 | 577 | 590 |
| **3-3** | H | $O(CH_2)_2CH_3$ | 594 | 589 | 571 | 583 |
| **3-4** | H | $OCH(CH_3)_2$ | 600 | 593 | 579 | 592 |
| **3-5** | H | $O(CH_2)_3CH_3$ | 604 | 590 | 575 | 580 |
| **3-6** | H | $O(CH_2)_2OC_2H_5$ | 589 | 600 | 577 | 601 |
| **3-7** | $CH_3$ | $O(CH_2)_2CH_3$ | 598 | 595 | 579 | 593 |
| **3-8** | Cl | $O(CH_2)_2CH_3$ | 599 | 601 | 579 | 590 |
| **3-9** | $CH_3O$ | $O(CH_2)_2CH_3$ | 612 | 610 | 596 | 606 |
| **3-10** | $CH_3$ | $OCH_2CH_3$ | 598 | 601 | 580 | 593 |
| **3-11** | $CH_3$ | $O(CH_2)_2OC_2H_5$ | 598 | 595 | 580 | 593 |

Table 2
Spectral data ($\lambda_{max}$ values) of naphthofuranonepyrrolidone dyes (nm)

| Dye No. | $R_1$ | $R_2$ | Toluene | Chloroform | Acetone | DMF |
|---|---|---|---|---|---|---|
| **4-1** | $OCH_3$ | $OCH_3$ | 597 | 601 | 588 | 597 |
| **4-2** | $OCH_2CH_3$ | $OCH_2CH_3$ | 602 | 601 | 592 | 601 |
| **4-3** | $O(CH_2)_2CH_3$ | $O(CH_2)_2CH_3$ | 599 | 604 | 590 | 602 |
| **4-4** | $OCH(CH_3)_2$ | $OCH(CH_3)_2$ | 605 | 607 | 593 | 605 |
| **4-5** | $O(CH_2)_3CH_3$ | $O(CH_2)_3CH_3$ | 602 | 600 | 592 | 602 |

hypsochromic effect of 2-ethoxyethoxy group can be attributed to electron withdrawal by the ether linkage. Adversely, the relative bathochromic effect was observed in polar solvent such as chloroform, acetone and DMF due to the interaction between the ether linkage and solvent molecules.

Methyl and chlorine substituents in the naphthodifuranone system also increase the bathochromism as in the case of the benzodifuranone system [5].

Symmetrical naphthofuranonepyrrolidone dyes are slightly hypsochromic compared with the corresponding naphthodifuranone dyes, so that the nitrogen atom in the central system does not play a special role in relation to the overall bathochromic shift.

Naphthodifuranone and naphthofuranonepyrrolidone dyes do not undergo strong solvatochromism depending solvent polarity as shown in Tables 1 and 2.

## 4. Conclusions

The asymmetrically substituted naphthodifuranones synthesised and examined in this paper show bright blue colour. As expected, the asymmetrically substituted naphthodifuranones have a less hypsochromic colour shade compared with symmetrically substituted ones. The symmetrically substituted naphthofuranonepyrrolidones exhibited a green blue colour. Synthesis of asymmetrical naphthodifuranones was quite difficult due to generation of many by-products by two competitive reactions, low yield and difficulty of purification. Syntheses of naphthofuranonepyrrolidones were carried out by reaction of 1-amino-5-hydroxynaphthalene with an appropriate mandelic acid. Reactivity of 1-amino-5-hydroxynaphthalene is lower than that of 1,5-dihydroxynaphthalene so that half-condensed intermediates for asymmetrically substituted naphthofuranonepyrrolidones could not be prepared.

Purification processes were essential for preparing these dyes. Column chromatography and recrystallisation could not be used due to their extremely low solubility. Alternatively, digestion in hot acetic acid and precipitation in high boiling point solvents were used for purification. Naphthodifuranone and naphthofuranonepyrrolidone dyes synthesised in this study do not show strong solvatochromism.

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