ELSEVIER

Dyes and Pigments 48 (2001) 107–119

DYES and PIGMENTS

The synthesis and properties of red and blue benzodifuranones

G. Hallas [a], Chun Yoon [b,*]

[a] *Department of Colour Chemistry, University of Leeds, Leeds LS2 9JT, UK*
[b] *LG Chemical Research Park, Yusung-Gu, Taejon, South Korea*

Received 2 May 2000; received in revised form 17 July 2000; accepted 12 September 2000

Abstract

Benzodifuranones were developed by ICI researchers twenty years ago. Red benzodifuranones are one of the most successful new classes of commercial dyes due to their bright colours and excellent wash and sublimation fastness properties. In this study, red and blue benzodifuranones have been synthesised and their physical properties measured. Red benzodifuranones were synthesised from the half-condensed intermediates and alkoxymandelic acid derivatives. Blue benzodifuranones were synthesised from the half-condensed intermediates and phenyltartronic acid derivatives.

Keywords: Benzodifuranone; Alkoxymandelic acid; Monobenzofuranone

1. Introduction

Currently, some benzodifuranones (**1**) are used as commercial dyes for high quality textile dyeing in the red colour shade range. However, in the 1970s, the only important classes used to colour polyester fibres were the azo and anthraquinone dyes; azo dyes were far more important than any other dye class due to full colour range and high tinctorial strength [1]. Anthraquinone dyes provided valuable bright red and blue colours with good light fastness and relatively good dyeing properties [1]. Unfortunately, owing to their low tinctorial strength and difficulty of manufacturing, anthraquinone dyes are still expensive, so that it is difficult to compete with other dye classes. For these reasons, researchers at ICI developed the benzodifuranone chromogen which has high tinctorial strength and brightness [2]. All the commercial dyes are red, alkoxy derivatives, and in the present study, blue benzodifuranone dyes were prepared by replacing the alkoxy groups by stronger electron donor groups, i.e. alkylamino substituents [3].

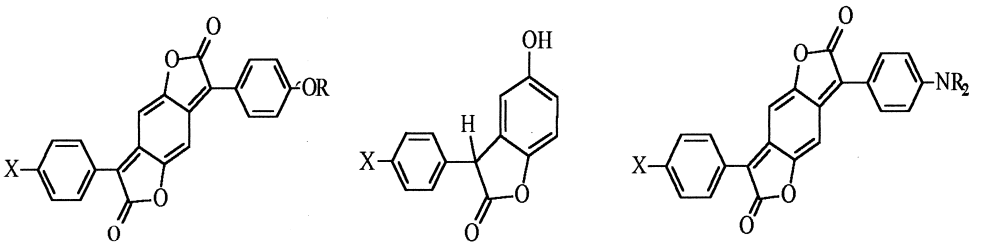
Researchers at ICI reported that symmetrical benzodifuranones have much poorer build up properties on polyester fibre than asymmetrical benzodifuranones, the poor substantivity being due to the high degree of symmetry and crystallinity of the molecule [2].

1.1. Asymmetrical red benzodifuranones

In this study, asymmetrical red benzodifuranones have been synthesised by using the methods which had been developed by ICI [4]. The synthetic route to asymmetrical red benzodifuranones is outlined in Scheme 1. Asymmetrical red benzodifuranones

* Corresponding author. Fax: +82-42-861-2585.

0143-7208/01/$ - see front matter
PII: S0143-7208(00)00092-9



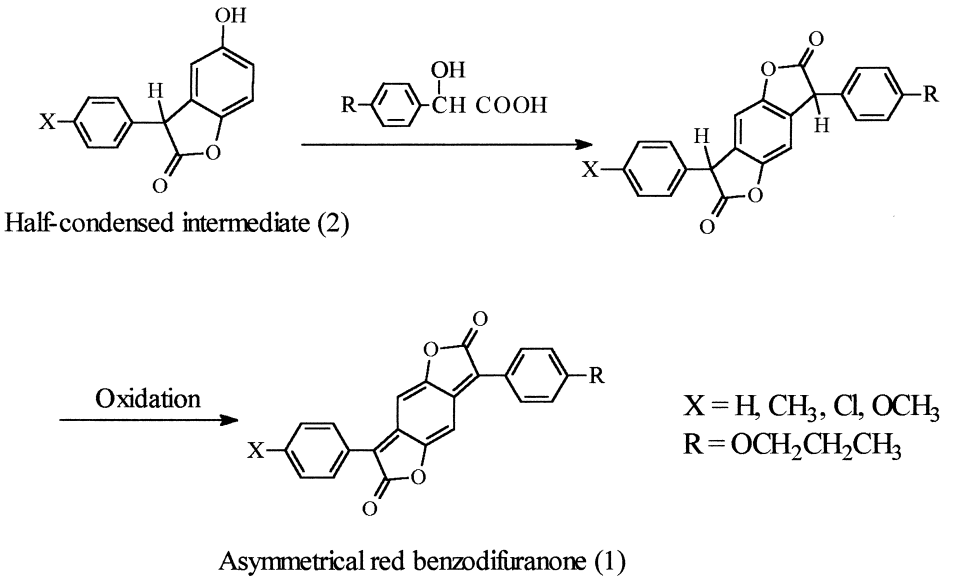
were synthesised from 1 mol of the relevant half-condensed intermediate and 1 mol of *p*-alkoxy-mandelic acid under acid catalyst. Two types of solvents were employed for this reaction, inert solvents such as chlorobenzene with a small amount of *p*-toluenesulphonic acid, and acetic acid with a small amount of sulphuric acid. Chloranil and ammonium persulphate were employed as oxidising agents, but the latter compound was effective in acetic acid.

1.2. Half-condensed intermediates for the red and blue benzodifuranones

The half-condensed intermediates (**2**) (benzofuranones) were prepared by two synthetic methods: the first synthetic method, which was a reaction of hydroquinone with the corresponding mandelic acids in 73% sulphuric acid [5]. The second method which was developed in this study, was a reaction of hydroquinone with the corresponding substituted mandelic acids in acetic acid with small amount of sulphuric acid. Scheme 2 shows synthetic routes to the half-condensed intermediates.

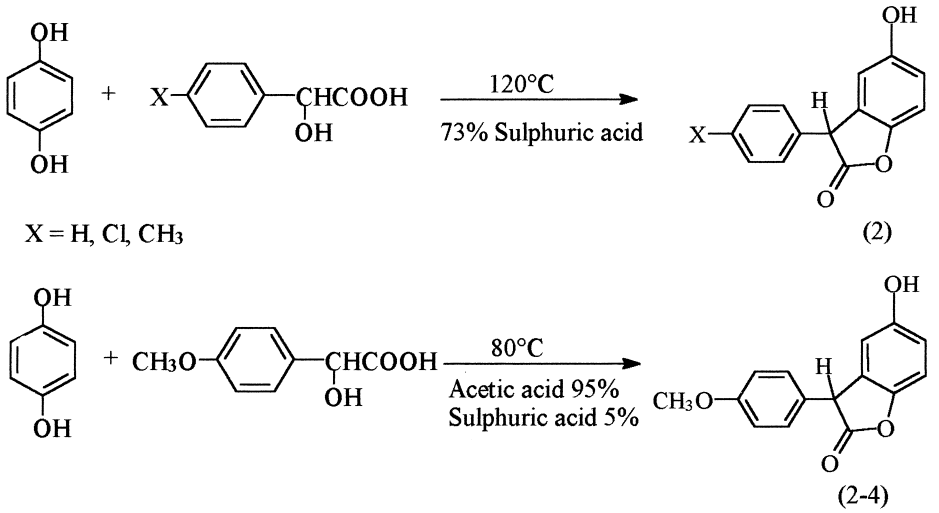
1.3. Mandelic acids for the benzodifuranones and relevant half-condensed intermediates

Mandelic acid derivatives are key intermediates to synthesise red and blue benzodifuranones. *p*-Chloromandelic acid and *p*-methylmandelic acid were prepared by hydrolysis of mandelonitriles

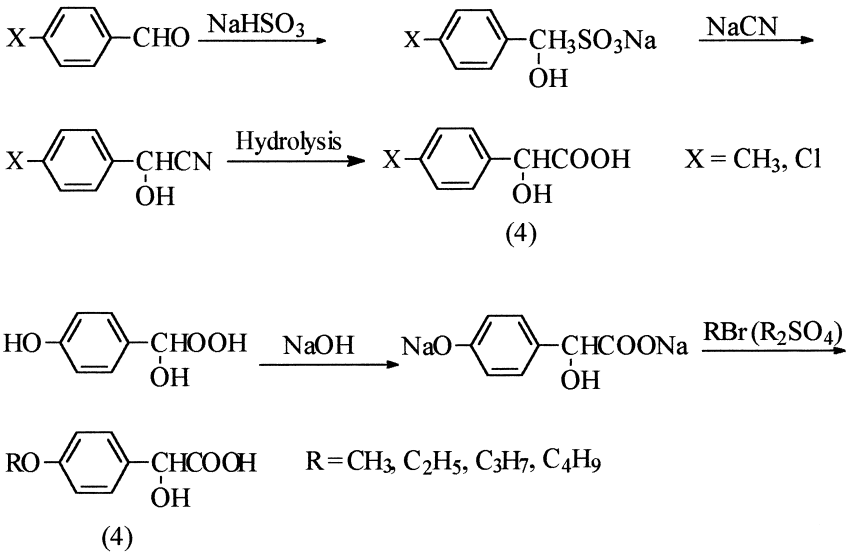


Scheme 1.

which were obtained from the corresponding benzaldehydes, sodium cyanide and sodium bisulphite. This synthetic method is shown in Scheme 3 [6]. The mandelonitriles need to be hydrolysed on separation from the aqueous reaction medium in order to prevent a rapid conversion into the aldehyde acetals [6]. *p*-Alkoxymandelic acid derivatives can be prepared by alkylation of *p*-hydroxymandelic acid in the aqueous medium (Scheme 3). ICI developed and patented this much simpler synthetic method which is suitable for laboratory scale [7]. The reaction involves the treatment of an aqueous solution of an alkali metal salt of 4-hydroxymandelic acid with an alkylating agent, such as propyl bromide and dimethyl sulphate, at pH 12, followed by acidification.



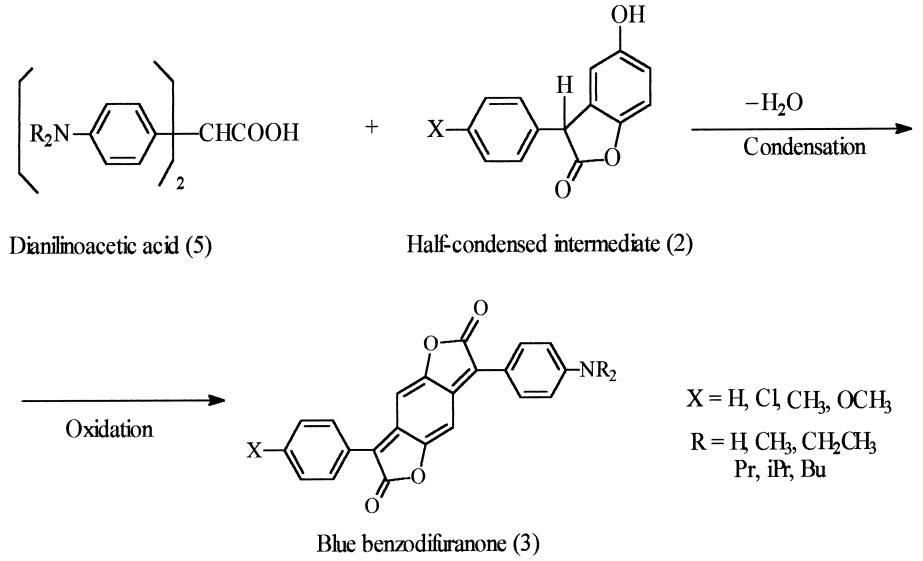
Scheme 2.



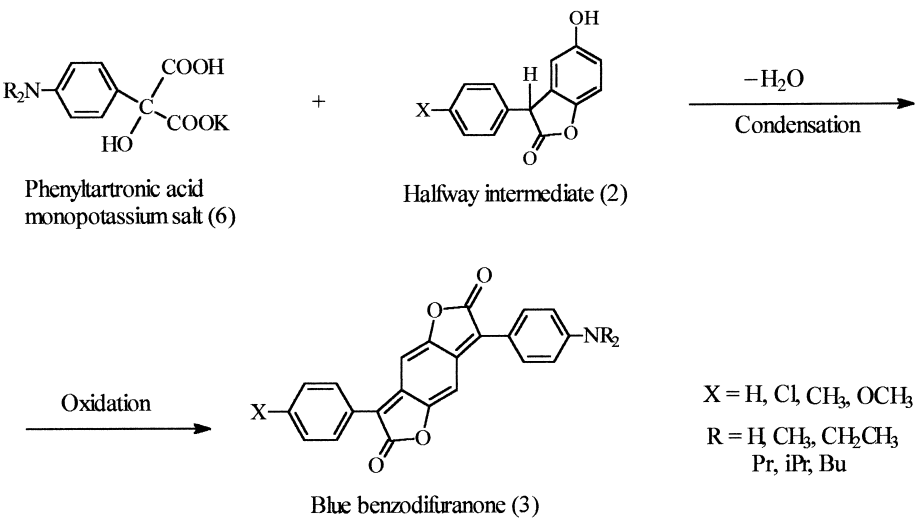
Scheme 3.

1.4. Asymmetrical blue benzodifuranones

Blue benzodifuranones can be synthesised by two synthetic methods: the first synthetic method [8] was condensation of 1 mol of the half-condensed intermediates (2) with 1 mol of dianilinoacetic acid derivatives in *o*-dichlorobenzene at reflux temperature for one or two days, followed by oxidation using nitrobenzene or chloranil (Scheme 4). The second synthetic method [3,9] was condensation of 1 mol of half-condensed intermediates (**2**) with 1.5 mol of phenyltartronic acid derivative in acetic acid at 110°C for 5 h and followed by oxidation using ammonium persulphate (Scheme 5).



Scheme 4.



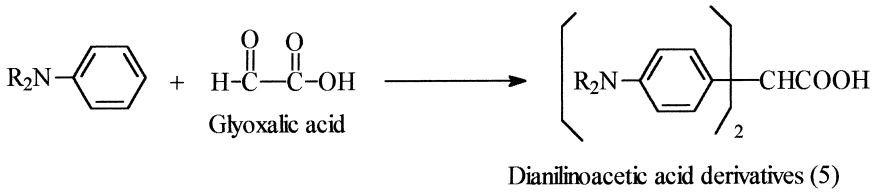
Scheme 5.

1.5. Dianilinoacetic derivatives for blue benzodifuranones

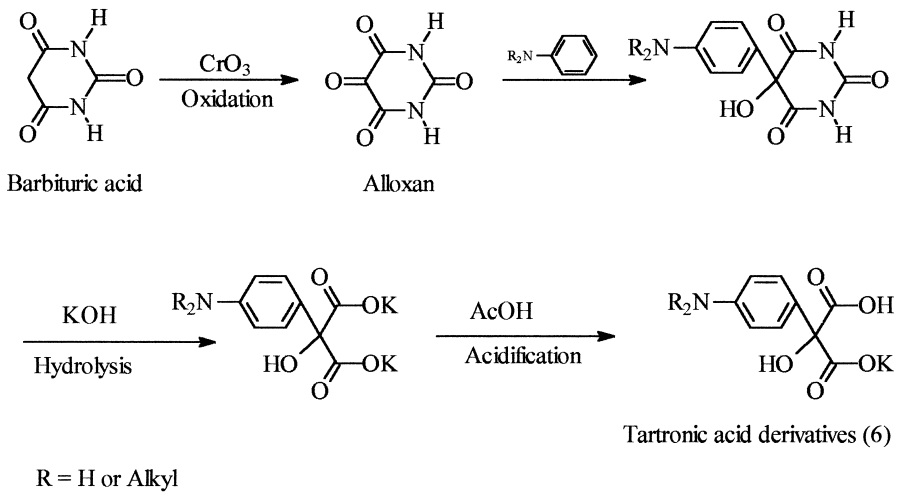
The formation of dianilinoacetic acid derivatives is outlined in a patent which was disclosed by ICI [8]. Reaction of 1 mol of glyoxalic acid with 2 mol of appropriate aniline in aqueous methanol gave dianilinoacetic acid derivatives in good yield. After the reaction was complete, the product was precipitated by cooling and sufficiently pure for use in next step. Scheme 6 shows the formation of dianilinoacetic acid derivatives.

1.6. Phenyltartronic acid derivatives for blue benzodifuranones

Phenyltartronic acid derivatives are very useful for preparing blue benzodifuranone dyes. They are much more reactive than mandelic acid derivatives, so that lactonisation can take place without acid catalyst in good yield. Phenyltartronic acid derivatives were prepared from barbituric acid. Synthetic routes to phenyltartronic acid derivatives are outlined in the literature [10], but in this study the reaction conditions for each step were based on the known synthetic method and adapted for the experimental conditions used in this study. A synthetic route to phenyltartronic acid derivatives is outlined in Scheme 7. The synthesis of alloxan is described in the literature [11]. Barbituric acid can be easily converted into the alloxan monohydrate by oxidation with chromium trioxide in acetic acid. Alloxan monohydrate reacts with anilines via electrophilic substitution with a trace of acid catalyst in the aqueous medium. The resulting substituted alloxan derivatives can be converted into dipotassium salts of the tartronic acid derivatives by hydrolysis under strongly alkaline conditions.



Scheme 6.



Scheme 7.

Subsequent acidification of the dipotassium salt by acetic acid gives the corresponding monopotassium salt.

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. The λ_{max} values of the dyes synthesised were measured using Philips spectrophotometer variously in ethanol, DMF, acetone, chloroform and toluene. ε_{max} values were measured in acetone.

2.1. Preparation of mandelic acid derivatives

2.1.1. 4-Propoxymandelic acid (**4-1**)

4-Hydroxymandelic acid monohydrate (99%, 18.6 g, 0.1 mol), sodium hydroxide (8.0 g, 0.2 mol) and 1-bromopropane (99%, 18.4 g, 0.15 mol) in water (50 g) were charged into a reaction vessel and heated to a temperature between 60 and 65°C. The pH at this stage was 11.5. The mixture was stirred for 24 h at that temperature. After cooling to room temperature, the pH was adjusted to 1.5 by the addition of concentrated hydrochloric acid. The precipitated product was filtered off and washed with ice water. The filtered product was suspended in water (50 g), extracted with ethyl acetate and evaporated, giving a white-coloured powder (m.p. 135–138°C, 12.5 g; 59% yield).

Microanalysis found C, 62.5%; H, 6.6% ($C_{11}H_{14}O_4$ requires C, 62.9%; H, 6.6%).

2.1.2. 4-Methoxymandelic acid (**4-2**)

4-Hydroxymandelic acid monohydrate (99%, 18.6 g, 0.1 mol) and sodium hydroxide (8.0 g, 0.2 mol) in water (50 g) were charged into a reaction vessel. The pH at this stage was 11.5. Dimethyl sulphate (99%, 18.9 g, 0.15 mol) was added by dropwise addition to the mixture which was cooled the mixture during the addition. After the addition was completed, the reaction mixture was heated to a temperature between 60 and 65°C and stirred for 24 h at that temperature. After cooling to room temperature, the pH was adjusted to 1.5 by the addition of concentrated hydrochloric acid. The precipitated product was filtered off and washed with ice water. The filtered product was suspended in water (50 g), extracted with ethyl acetate and evaporated, giving a white-coloured powder (m.p. 100–102°C, 12.2 g; 48.5% yield).

Microanalysis found C, 59.2%; H, 5.5% ($C_9H_{10}O_4$ requires C, 59.3%; H, 5.5%).

2.1.3. 4-Chloromandelic acid (**4-3**)

A saturated solution of sodium metabisulphite was prepared by stirring 250 g of finely powdered sodium metabisulphite with 335 ml of water for half an hour and then filtered to remove the excess of salt. Finely crushed 4-chlorobenzaldehyde (14.1 g, 0.1 mol, m.p. 48°C) and a solution of sodium cyanide (5.0 g, 0.1 mol) in 20 ml of water were charged into a reaction vessel. The saturated sodium metabisulphite solution (120 g) prepared was added dropwise to the mixture. During the addition, 50 g of ice was added to the mixture in several portions to maintain the temperature between 20 and 30°C. After the addition was completed, the mixture was stirred for a further 30 min. The oily layer was extracted several times with ethyl acetate. The solution was evaporated to remove the ethyl acetate and mixed with 15 ml of concentrated hydrochloric acid. The hydrochloric acid solution was heated for several hours for hydrolysis at 60°C and was extracted with ethyl acetate. The solution was evaporated, giving a white solid (9.2 g; 49.2% crude yield). The white solid was recrystallised in water, giving a white coloured product (m.p. 117°C).

Microanalysis found C, 51.8%; H, 3.9%; Cl, 19.0% ($C_8H_7ClO_3$ requires C, 51.5%; H, 3.8%; Cl, 19.0%). DSC showed a sharp peak at 118.3°C.

2.1.4. 4-Methylmandelic acid (**4-4**)

The procedure of compound (**4-3**) was followed except that *p*-tolualdehyde (12.0 g, 0.1 mol) was

used instead of 4-chlorobenzaldehyde, giving a white-coloured product (m.p. 144°C).

Microanalysis found C, 65.3%; H, 6.3% ($C_9H_{10}O_3$ requires C, 65.1%; H, 6.0%). DSC showed a sharp peak at 145.1°C.

2.2. Preparation of half-condensed intermediates

2.2.1. Hydroxy-2-oxo-3-phenyl-2,3-dihydrobenzo-[1,2-b]furan (**2-1**)

Hydroquinone (99%, 27.5 g, 0.25 mol), DL-mandelic acid (99%, 15.2 g, 0.1 mol) and 73% sulphuric acid (50 g) were stirred and heated slowly to 120°C. The mixture was left at this temperature for 5 min then allowed to cool to 60°C. The mixture was poured carefully into ice water (100 g); the resulting white solid was filtered off and washed with water until the washings were acid-free. The product was dried in the air, giving a white crystalline powder (14 g; 61.9% crude yield). Recrystallisation from toluene gave a white needle-shaped solid (m.p. 165°C).

Microanalysis found C, 73.9%; H, 4.7% ($C_{14}H_{10}O_3$ requires C, 73.7%; H, 4.9%).

2.2.2. Hydroxy-2-oxo-3-(4-chlorophenyl)-2,3-dihydrobenzo[1,2-b]furan (**2-2**)

Hydroquinone (99%, 6.6 g, 0.06 mol), 4-chloromandelic acid (3.7 g, 0.02 mol) and 73% sulphuric acid (20 g) were stirred and heated slowly to 120°C. The mixture was left at this temperature for 10 min then allowed to cool to 60°C. The mixture was poured carefully into ice-water (50 g); the resulting white solid was filtered off and washed with water until the washings were acid-free. The product was dried in the air, giving a white crystalline powder (4.0 g; 76.8% crude yield). Recrystallisation from toluene gave a white solid (m.p. 163°C).

Microanalysis found C, 63.8%; H, 3.5%; Cl, 13.5% ($C_{14}H_9ClO_3$ requires C, 64.5%; H, 3.5%; Cl, 13.6%).

2.2.3. Hydroxy-2-oxo-3-(4-methylphenyl)-2,3-dihydrobenzo[1,2-b]furan (**2-3**)

The procedure of compound (**2-2**) was followed except that 4-methylmandelic acid (3.3 g, 0.02 mol) was used instead of 4-chloromandelic acid, giving a pale pink crystalline powder (3.7 g; 76.8% crude yield). Recrystallisation from toluene gave a white solid (m.p. 175°C).

Microanalysis found C, 74.5%; H, 5.0% ($C_{15}H_{12}O_3$ requires C, 75.6%; H, 5.0%).

2.2.4. Hydroxy-2-oxo-3-(4-methoxyphenyl)-2,3-dihydrobenzo[1,2-b]furan (**2-4**)

Hydroquinone (99%, 2.2 g, 0.02 mol), 4-methoxymandelic acid (3.6 g, 0.02 mol) and concentrated sulphuric acid (0.5 g) were dissolved in acetic acid (20.0 g). The mixture was heated to 80°C and was stirred at this temperature for 2 h then allowed to cool to 40C. Water (10.0 g) was added to the mixture to precipitate the product. The resulting pale pink solid was filtered off and washed with water until the washings were acid-free. The product was dried in the air, giving a pale pink crystalline powder (3.9 g; 76.2% crude yield). Recrystallisation from toluene gave a pale pink solid (m.p. 168°C).

Microanalysis found C, 69.5%; H, 4.7% ($C_{15}H_{12}O_4$ requires C, 70.3%; H, 4.6%).

2.3. Preparation of red benzodifuranones

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

5-Hydroxy-2-oxo-3-phenyl-2,3-dihydrobenzo-[1,2-*b*]furan (1.1 g, 0.005 mol), 4-propoxymandelic acid (1.1 g, 0.005 mol) and *p*-toluenesulphonic acid (1.0 g) were stirred in chlorobenzene (20 ml). The mixture was heated to 80°C and stirred for 5 h at this temperature. The mixture was allowed to cool to 40°C, and chloranil (1.2 g) was then added. The temperature of the mixture was raised to 60°C, and stirring was continued for further a further hour at this temperature. Methanol (30 ml) was added to precipitate the product. The mixture was stirred for 1 h at 15°C, filtered off and washed with methanol then water. The crude product (1.2 g), 1-bromopropane (0.4 g) and potassium carbonate (0.3 g) were dissolved in sulpholane (20 ml). This mixture was heated to 100°C and stirred for 1 h. Water (10 ml) was added to precipitate the product. The precipitated product was filtered off, washed with methanol and water. The product was refluxed in methanol, giving a red-coloured solid (0.7 g, 35.2%, m.p. 240–242°C).

Microanalysis found C, 74.8%; H, 4.5% ($C_{25}H_{18}O_5$ requires C, 75.4%; H, 4.5%). DSC showed a sharp peak at 242.2°C.

2.3.2. *3-(4-Chlorophenyl)-7-(4-propoxyphenyl)-benzo[1,2-b:4,5-b]difuran-2,6-dione* (**1-2**)

The procedure for compound (**1-1**) was followed except that 5-hydroxy-2-oxo-3-(4-chlorophenyl)-2,3-dihydrobenzo[1,2-*b*]furan (1.3 g, 0.005 mol) was used instead of 5-hydroxy-2-oxo-3-phenyl-2,3-dihydrobenzo[1,2-*b*]furan, giving a red-coloured solid (0.9 g, 41.6%, m.p. 300–303°C).

Microanalysis found C, 68.8%; H, 3.9%; Cl, 8.1% ($C_{25}H_{17}ClO_5$ requires C, 69.3%; H, 3.9%; Cl, 8.2%). DSC showed a sharp peak at 300.9°C.

2.3.3. *3-(4-Methylphenyl)-7-(4-propoxyphenyl)-benzo[1,2-b:4,5-b′]difuran-2,6-dione* (**1-3**)

The procedure of compound (**1-1**) was followed except that 5-hydroxy-2-oxo-3-(4-methylphenyl)-2,3-dihydrobenzo[1,2-*b*]furan (1.2 g, 0.005 mol) was used instead of 5-hydroxy-2-oxo-3-phenyl-2,3-dihydrobenzo[1,2-*b*]furan, giving a red coloured solid (0.8 g, 38.8%, m.p. 251–255°C).

Microanalysis found C, 75.0%; H, 4.9% ($C_{26}H_{20}O_5$ requires C, 75.7%; H, 4.9%). DSC showed a sharp peak at 251.1°C.

2.3.4. *3-(4-Methoxylphenyl)-7-(4-propoxyphenyl)-benzo[1,2-b:4,5-b′]difuran-2,6-dione* (**1-4**)

5-Hydroxy-2-oxo-3-(4-methoxyphenyl)-2,3-dihydrobenzo[1,2-*b*]furan (1.2 g, 0.005 mol), 4-propoxymandelic acid (1.1 g, 0.005 mol) and *p*-toluenesulphonic acid (1.0 g) in chlorobenzene (20 ml) were heated to 80°C and stirred for 6 h at this temperature. The mixture was allowed to cool to 40°C, and chloranil (1.2 g) was then added. The temperature of the mixture was raised to 60°C, and the stirring was continued for a further 1 h at 60°C. Methanol (30 ml) was added to precipitate the product. The precipitate was filtered off and washed with methanol then water. The crude product was recrystallised twice from toluene, giving a red coloured solid (m.p. 245–247°C).

Microanalysis found C, 71.9%; H, 4.7% ($C_{26}H_{20}O_6$ requires C, 72.9%; H, 4.7%). DSC showed a sharp peak at 247.8°C.

2.3.5. *3,7-Di(4-propoxyphenyl)benzo[1,2-b:4,5-b′]difuran-2,6-dione* (**1-5**)

Hydroquinone (99%, 1.1 g, 0.01 mol), 4-propoxymandelic acid (4.2 g 0.02 mol) and 1,2,4-trichlorobenzene (25 ml) were stirred for 1 h at 200°C. After cooling to room temperature, nitrobenzene (2.0g) was added and the mixture was stirred for a further hour at 200°C. After cooling, the solid was filtered off, washed with toluene and dried in the air. The product obtained was a dark red solid (3.7 g; 80% crude yield). Recrystallisation from toluene gave red crystals (m.p. 278°C).

Microanalysis found C, 71.1%; H, 5.4% ($C_{28}H_{24}O_6$ requires C, 73.4%; H, 5.3%). DSC showed a sharp peak at 278.1°C.

2.4. *Preparation of dianilinoacetic acid and phenyltartronic acid derivatives*

2.4.1. *Di(4-N-ethylaminophenyl)acetic acid*

A mixture of *N*-ethylaniline (30 g) and methanol (100 g) was stirred with glyoxalic acid 50% solution (16.5 g) at reflux temperature for 24 h. The mixture was cooled down to the room temperature. The precipitated product was filtered and dried, giving a light brown solid (30 g).

2.4.2. *Alloxan monohydrate (5,5-dihydroxy-barbituric acid)*

Glacial acetic acid (99%, 280 g) and chromium trioxide (99%, 47.3 g) were charged into a reaction vessel. The solution was stirred for 15 min at room temperature for activation. Barbituric acid (99%, 38.4 g) was added in the course of about 25 min in portions approximating 5 g. The temperature of the mixture rose from room temperature at the beginning of the reaction to 50°C and was held at that value until all the barbituric acid had been added. During the addition, alloxan monohydrate began to crystallise. After the addition was completed, the temperature of the mixture was kept at 50°C for 30 min. The precipitated solid was filtered off and washed with a small amount of acetic acid and diethyl ether, giving a pale yellow solid [38.0 g; 79.1% crude yield, m.p. 254°C (decomposed)]. The product obtained was very pure so that further purification was unnecessary.

Microanalysis found C, 30.0%; H, 2.6%; N, 17.6% ($C_4H_4N_2O_5$ requires C, 30.0%; H, 2.5%; N, 17.5%).

2.4.3. Propylaminophenyltartronic acid (**6-1**)

Alloxan monohydrate (3.2 g, 0.02 mol), *N*-propylaniline (2.7 g, 0.02 mol), ethanol (6.0 g), acetic acid (2.0 g) and water (10.0 g) were charged into a reaction vessel. The mixture was heated to 60°C and was stirred for 3 h at that temperature. During the heating, the product began to precipitate. The precipitated product was filtered off and washed with a small amount of water, giving a pale yellow, 5-hydroxy-5-(4-propylaminophenyl) barbituric acid (4.6 g; 83.0% crude yield). The crude intermediate obtained was pure and was used in the next reaction without purification. The 5-hydroxy-5-(4-propylaminophenyl)barbituric acid (4.6 g, 0.017 mol) was dissolved in a solution of potassium hydroxide (3.0 g) in 40 ml water. The basic aqueous solution was stirred for 4 h at 30°C. The pH of the solution was adjusted to 7 using acetic acid. The product was filtered off, giving a pale yellow solid, propylaminophenyltartronic acid mono potassium salt (3.3 g; 56% overall yield).

The product obtained was used in the next stage without analysis except for a TLC purity check.

2.4.4. Ethylaminophenyltartronic acid (**6-2**)

The procedure of compound (**6-1**) was followed except that *N*-ethylaniline (2.4 g, 0.02 mol) was used instead of *N*-propylaniline, giving a pale yellow solid, ethylaminophenyltartronic acid mono potassium salt (3.0 g; 54.1% overall yield).

2.4.5. Isopropylaminophenyltartronic acid (**6-3**)

The procedure of compound (**6-1**) was followed except that *N*-isopropylaniline (2.7 g, 0.02 mol) was used instead of *N*-propylaniline, giving a pale yellow solid, isopropylaminophenyltartronic acid mono potassium salt (3.7 g; 63.8% overall yield).

2.4.6. Methylaminophenyltartronic acid (**6-4**)

The procedure of compound (**6-1**) was followed except that *N*-methylaniline (2.1 g, 0,02 mol) was used instead of *N*-propylaniline, giving a pale yellow solid, methylaminophenyltartronic acid mono potassium salt (2.9 g, 56% overall yield).

2.4.7. Butylaminophenyltartronic acid (**6-5**)

The procedure of compound (**6-1**) was followed except that *N*-butylaniline (3.0 g, 0,02 mol) was used instead of *N*-propylaniline, giving a light-brown solid, butylaminophenyltartronic acid mono potassium salt (3.4 g; 55.7% overall yield).

2.4.8. Dipropylaminophenyltartronic acid (**6-6**)

The procedure of compound (**6-1**) was followed except that *N,N*-dipropylaniline (3.5 g, 0,02 mol) was used instead of *N*-propylaniline, giving a light-brown solid, dipropylaminophenyltartronic acid mono potassium salt (4.1 g; 61.5% overall yield).

2.5. Preparation of blue benzodifuranones

*2.5.1. 3-Phenyl-7-(4-propylaminophenyl)-benzo[1,2-*b*:4,5-*b′*]difuran-2,6-dione* (**3-1**)

5-Hydroxy-2-oxo-3-phenyl-2,3-dihydrobenzo-[1,2-*b*]furan (1.1 g, 0.005 mol) and propyl-aminophenyltartronic acid mono potassium salt (2.2 g, 0.0075 mol) were stirred in acetic acid (20 ml). The mixture was heated to 110°C and stirred for 5 h at this temperature. Ammonium persulphate (1.0 g) was added in ten portions at 80°C. The mixture was allowed to cool to room temperature, and was stirred for a further hour at room temperature. The precipitate was filtered, washed with a small amount of acetic acid then with methanol and water. The crude product was refluxed in methanol, giving a dark green-coloured solid (0.9 g, 45.3%, m.p. 240–242°C).

Microanalysis found C, 75.4%; H, 4.8%; N, 3.5% ($C_{25}H_{19}NO_4$ requires C, 75.6%; H, 4.8%; N, 3.5%). DSC showed a sharp peak at 241.9°C.

*2.5.2. 3-Phenyl-7-(4-ethylaminophenyl)benzo[1,2-*b*:4,5-*b′*]difuran-2,6-dione* (**3-2**)

The procedure of compound (**3-1**) was followed except that ethylaminophenyltartronic acid mono potassium salt (2.1 g, 0.0075 mol) was used instead of propylaminophenyltartronic acid mono potassium salt, giving a dark green-coloured solid (0.85 g, 44.3%, m.p. 283–286°C).

Microanalysis found C, 74.9%; H, 4.6%; N, 3.6% ($C_{24}H_{17}NO_4$ requires C, 75.2%; H, 4.4%; N, 3.7%). DSC showed a sharp peak at 283.9°C.

2.5.3. 3-Phenyl-7-(4-isopropylaminophenyl)-benzo[1,2-b:4,5-b′]difuran-2,6-dione (**3-3**)

The procedure of compound (**3-1**) was followed except that isopropylaminophenyltartronic acid mono potassium salt (2.2 g, 0.0075 mol) was used instead of propylaminophenyltartronic acid mono potassium salt, giving a dark green-coloured solid (0.95 g, 47.8%, m.p. 264–268°C).

Microanalysis found C, 75.3%; H, 4.9%; N, 3.5% ($C_{25}H_{19}NO_4$ requires C, 75.6%; H, 4.8%; N, 3.5%). DSC showed a sharp peak at 264.3°C.

2.5.4. 3-Phenyl-7-(4-methylaminophenyl)-benzo[1,2-b:4,5-b′]difuran-2,6-dione (**3-4**)

The procedure of compound (**3-1**) was followed except that methylaminophenyltartronic acid mono potassium salt (2.0 g, 0.0075 mol) was used instead of propylaminophenyltartronic acid mono potassium salt, giving a dark green-coloured solid (0.78 g, 42.3%, m.p. 292–295°C).

Microanalysis found C, 74.6%; H, 4.2%; N, 3.9% ($C_{23}H_{15}NO_4$ requires C, 74.8%; H, 4.1%; N, 3.8%). DSC showed a sharp peak at 293.8°C.

2.5.5. 3-Phenyl-7-(4-butylaminophenyl)benzo[1,2-b:4,5-b′]difuran-2,6-dione (**3-5**)

The procedure of compound (**3-1**) was followed except that butylaminophenyltartronic acid mono potassium salt (2.3 g, 0.0075 mol) was used instead of propylaminophenyltartronic acid mono potassium salt, giving a dark green coloured solid (0.95 g, 47.8%, m.p. 238°C).

Microanalysis found C, 75.7%; H, 5.2%; N, 3.2% ($C_{26}H_{21}NO_4$ requires C, 75.9%; H, 5.1%; N, 3.4%). DSC showed a sharp peak at 238.8°C.

2.5.6. 3-Phenyl-7-(4-dipropylaminophenyl)-benzo[1,2-b:4,5-b′]difuran-2,6-dione (**3-6**)

The procedure of compound (**3-1**) was followed except that dipropylaminophenyltartronic acid mono potassium salt (2.5 g, 0.0075 mol) was used instead of propylaminophenyltartronic acid mono potassium salt, giving a dark green-coloured solid (1.05 g, 47.8%, m.p. 219°C).

Microanalysis found C, 76.4%; H, 5.9%; N, 3.1% ($C_{28}H_{25}NO_4$ requires C, 76.5%; H, 5.7%; N, 3.2%). DSC showed a sharp peak at 217.6°C.

2.5.7. 3-(4-Chlorophenyl)-7-(4-propylaminophenyl)-benzo[1,2-b:4,5-b′]difuran-2,6-dione (**3-7**)

The procedure of compound (**3-1**) was followed except that 5-hydroxy-2-oxo-3-(4-chlorophenyl)-2,3-dihydrobenzo[1,2-*b*]furan (1.3 g, 0.005 mol) were used instead of 5-hydroxy-2-oxo-3-phenyl-2,3-dihydrobenzo[1,2-*b*]furan, giving a dark green coloured solid (0.86 g, 40.0%, m.p. 258°C).

Microanalysis found C, 69.6%; H, 4.3%; Cl, 8.1%; N, 3.0% ($C_{25}H_{18}ClNO_4$ requires C, 69.5%; H, 4.2%; Cl, 8.2%; N, 3.2%). DSC showed two sharp peaks at 251.8 and 259.8°C.

2.5.8. 3-(4-Methylphenyl)-7-(4-propylaminophenyl)-benzo[1,2-b:4,5-b′]difuran-2,6-dione (**3-8**)

The procedure of compound (**3-1**) was followed except that 5-hydroxy-2-oxo-3-(4-methylphenyl)-2,3-dihydrobenzo[1,2-*b*]furan (1.2 g, 0.005 mol) were used instead of 5-hydroxy-2-oxo-3-phenyl-2,3-dihydrobenzo[1,2-*b*]furan, giving a dark green-coloured solid (0.82 g, 40.0%, m.p. 255°C).

Microanalysis found C, 75.8%; H, 5.1%; N, 3.3% ($C_{26}H_{21}NO_4$ requires C, 75.9%; H, 5.1%; N, 3.4%). DSC showed a sharp peak at 255.4°C.

2.5.9. 3-(4-Methoxyphenyl)-7-(4-propylamino-phenyl)benzo[1,2-b:4,5-b′]difuran-2,6-dione (**3-9**)

The procedure of compound (**3-1**) was followed except that 5-hydroxy-2-oxo-3-(4-methoxyphenyl)-2,3-dihydrobenzo[1,2-*b*]furan (1.3 g, 0.005 mol) were used instead of 5-hydroxy-2-oxo-3-phenyl-2,3-dihydrobenzo[1,2-*b*]furan, giving a dark green coloured solid (0.92 g, 43.1%, m.p. 247°C).

Microanalysis found C, 73.0%; H, 5.0%; N, 3.3% ($C_{26}H_{21}NO_4$ requires C, 73.1%; H, 4.9%; N, 3.3%). DSC showed two sharp peaks at 224.1 and 248.2°C.

3. Results and discussion

Asymmetrical red benzodifuranones were synthesised in relatively good yields (35–45%). During this reaction, a significant preparation of the hydroxy compound was formed (ca. 10–20% by TLC analysis) (Fig. 1). This can be attributed to acid-catalysed dealkylation.

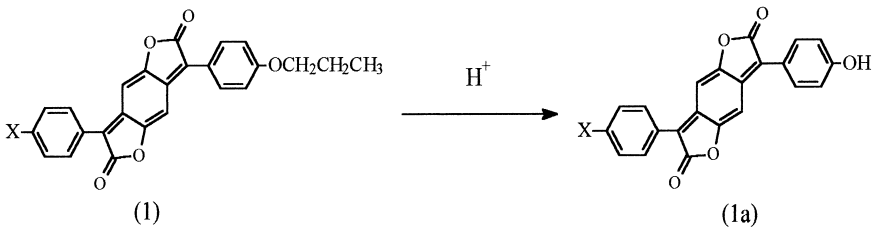


Fig. 1. Dealkylation of the alkoxy derivatives.

The dealkylated product (**1a**) present in the reaction mixture was converted into the required product (**1**) without isolation by alkylation with the appropriate bromoalkane and potassium carbonate in the sulpholane. After the alkylation was completed, the final product of greater purity was precipitated by the addition of water.

Blue benzodifuranones can be synthesised by condensation of dianilinoacetic acid derivatives. However this process gave the desired blue benzodifuranone dyes as impure material in very low yield. The use of phenyltartronic acid derivatives instead of the dianilinoacetic acid derivatives was found to be a good method for preparing blue benzodifuranones. Dianilinoacetic acid derivatives have low reactivity because aniline is not good leaving group. In contrast, phenyltartronic acid derivatives are more reactive than mandelic acid derivatives due to decarboxylation, so that reactions of phenyltartronic acid derivatives gave the pure products in quite good yields (about 50%).

3.1. Absorption spectra

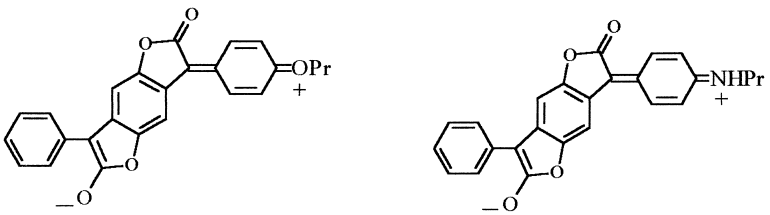
The λ_{max} values of the dyes synthesised in this study were measured variously in toluene, chloroform, acetone, ethanol and DMF. ε_{max} values were measured in acetone. The benzodifuranone dye without substituents exhibits λ_{max} at 466 nm in chloroform [2]. Dye (**1-1**) with only one propoxy group shows λ_{max} at 507 nm, and dye (**1-5**) with two propoxy groups has λ_{max} at 539 nm in chloroform. This trend means that an alkoxy group at 4-position in the pendant phenyl ring stabilises the excited of the dye, resulting in a bathochromic shift. Weak eletron donating group, such as methyl can give rise to bathochromism. Thus, symmetrically and asymmetrically disubstituted benzodifuranones are more bathochromic than asymmetrically monosubstituted benzodifuranones. Trends in the observed ε_{max} values are difficult to discern. The ε_{max} values for each range of dyes with the same central nucleus are similar and lie within the limits of experimental error. However, the more heavily substituted benzodifuranones tend to have the higher ε_{max} values, and red benzodifuranones have generally higher ε_{max} values than blue benzodifuranones. For example, blue benzodifuranone (**3-4**) with one methylamino group has an ε_{max} value of 41,100, whereas that of corresponding dipropylamino derivatives is 48,300. Chlorine plays a peculiar role in the benzodifuranone system in terms of ε_{max} values. Thus, the ε_{max} value decreases when chlorine is present in a blue benzodifuranone, but increases on substitution into a red benzodifuranone. Spectral data for the dyes synthesised are listed in Table 1.

An alkylamino group is a more powerful electron donor than an alkoxy group, and consequently, the replacement of alkoxy by alkylamino increase the bathochromism dramatically, so that the resultant dyes are blue. Valence Bond theory readily predicts the large bathochromism caused by the introduction of an amino group [12], as shown in Fig. 2.

Blue benzodifuranones with groups, such as alkoxy, methyl and chlorine, behave differently compared with the corresponding red benzodifuranones. Thus, in particular, chlorine produces a bigger bathochromic shift than methoxy in blue benzodifuranone, even though it is a net electron withdrawing group. It appears that the presence of a very strong donating group, such alkylamino, prevents relatively weak donors, such as alkoxy and alkyl, from functioning normally in the benzodifuranone system. For example, methoxy group in red

Table 1
Spectral data (λ_{max} values) of benzodifuranone dyes (nm)

Dye no.	R_1	R_2	Toluene	Chloroform	Acetone	Ethanol	DMF	ε_{max} $(l/(mol^{-1}\ cm))^{-1}$
1-1	H	$O(CH_2)_2CH_3$	509	507	497	502	505	49,100
1-2	Cl	$O(CH_2)_2CH_3$	520	517	501	507	509	55,000
1-3	CH_3	$O(CH_2)_2CH_3$	517	517	504	508	511	54,500
1-4	OCH_3	$O(CH_2)_2CH_3$	539	538	520	534	530	54,100
1-5	OPr	OPr	540	539	528	531	533	54,900
3-1	H	$NH(CH_2)_2CH_3$	612	617	627	645	652	47,100
3-2	H	$NHCH_2CH_3$	610	613	625	643	652	41,700
3-3	H	$NHCH(CH_3)_2$	613	620	628	649	654	43,500
3-4	H	$NHCH_3$	606	611	627	639	645	41,100
3-5	H	$NH(CH_2)_3CH_3$	614	620	630	650	655	45,800
3-6	H	$N(CH_2CH_2CH_3)_2$	657	673	658	662	667	48,300
3-7	Cl	$NH(CH_2)_2CH_3$	628	628	636	654	661	39,600
3-8	CH_3	$NH(CH_2)_2CH_3$	613	615	627	645	652	48,600
3-9	CH_3O	$NH(CH_2)_2CH_3$	615	619	628	645	650	48,000



(1-1a) (3-1a)

Fig. 2. Donor–acceptor interactions in a red and blue benzodifuranone.

benzodifuranone increases λ_{max} considerably, whereas methoxy group in blue benzodifuranone increases λ_{max} very little, as shown in Table 2.

It follows that the bathochromic effect of chlorine is affected very little by the counterpart substituent. Additionally, the values of the electron density changes confirm that the donating effect of chlorine is much smaller than that of methoxy. Thus, the bathochromic effect of chlorine is different from that of an alkoxy group.

3.2. Solvatochromism

Red benzodifuranones did not show solvatochromism depending on solvent polarity. Only blue benzodifuranones were sensitive to solvent

Table 2
Changes in absorption maxima by substituents in benzodifuranones

Red benzodifuranones				Blue benzodifuranones			
Dye no.	Substituent X	λ_{max} (nm) in toluene	$\Delta\lambda_{max}$ (nm)	Dye no.	Substituent X	λ_{max} (nm) in toluene	$\Delta\lambda_{max}$ (nm)
1-1	H	509	–	**3-1**	H	612	–
1-2	Cl	520	+11	**3-7**	Cl	628	+16
1-3	CH_3	517	+8	**3-8**	CH_3	613	+1
1-4	CH_3O	540	+31	**3-9**	CH_3O	615	+3

Table 3
Observed absorption maxima of benzodifuranones in various solvents

Dye no.	λ_{max} (nm)					$\Delta\lambda_{max}$ between ethanol and toluene
	Toluene (2.39)[a]	Chloroform (4.81)[a]	Acetone (20.7)[a]	Ethanol (25.0)[a]	DMF (38.3)[a]	
1-1	509	507	497	502	505	−7 nm
3-1	612	617	627	645	652	+33 nm
3-6	657	673	658	662	676	+5 nm

[a] Dielectric constant at 20°C [13].

polarity, especially, dyes with monoalkylamino substituents showed strong solvatochromism.

In the case of the blue benzodifuranones, the excited states of these dyes are more polar than the ground states. The bathochromic shifts observed in polar solvents can be attributed to the fact that the polar excited states are easily stabilised by interactions, such as hydrogen bonding, van der Waals forces or dipole–dipole electrostatic attractions between dye molecule and solvent molecules. Hydrogen bonding is one of the most important interactions in the solvatochromism of blue benzodifuranones. Dye (**3-1**), with a monopropylamino group, undergoes strong solvatochromism, but dye (**3-6**), with a dipropylamino group, undergoes weak solvatochromism. This comparison is shown in Table 3.

4. Conclusions

The benzodifuranones synthesised and examined in this study show a wide range of colour from yellowish red to bluish green. Synthesis of asymmetrical red and blue benzodifuranones can be carried out in relatively good yields and purity. Spectral properties of the dyes could be anticipated by qualitative examination, but various exceptions were noted. The observed extinction coefficients were relatively good (approximately 50,000) compared with ordinary disperse dyes. Only blue benzodifuranone dyes showed positive solvatochromism due to the presence of substituted amino groups. Red benzodifuranones were not sensitive to solvent polarity.

References

[1] Annen O, Egli R, Hasler R, Henzi B, Jakcob H, Matzinger P. Rev Prog Coloration 1987;17:72.
[2] Greenhalgh CW, et al. JSDC 1994;110:178.
[3] ICI, EP 0450765 (1991).
[4] ICI, BP 2103231 (1982); BP 2068402 (1980); EP 023080 (1979).
[5] Bystrzycki A, Flatau J. Chem Ber 1897;30:124.
[6] Corson BB, Dodge RA. Organic Syntheses 1941;1:336.
[7] ICI, BP 2101988 (1981).
[8] ICI, EP 0502278 (1992).
[9] Sumitomo, EP 0484962 (1992).
[10] Gry G. Hebd Seances Acad Sci 1909;148:929.
[11] Holmgren AV, Wenner W. Organic Syntheses 1963;4:23.
[12] Gordon PF, Gregory P. Organic chemistry in colour. Berlin: Springer-Verlag, 1987. p. 121–30.
[13] Dean JA. Handbook of organic chemistry. New York: McGraw-Hill, 1987. p. 45 [Chapter 4].