

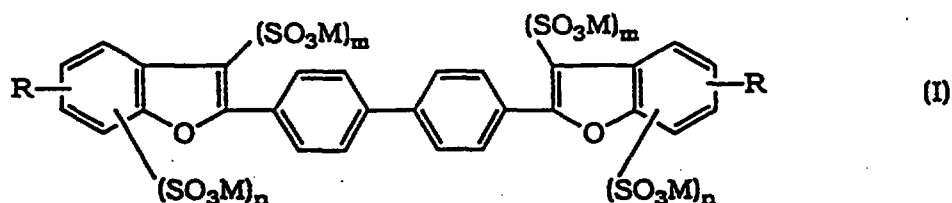
WK12-17052/-

The present application relates to sulfonated benzofuranylbi-phenyl compounds and to their preparation and their use as fluorescent whitening agents.

Mixtures of sulfonated benzofuranylbi-phenyl compounds of an undefined composition and structure and their use as optical brighteners have been known for a long time (DE-A 2,238,734, DE-A 2,238,628, DE-A 2,361,338 and DE-A 2,843,850). Hitherto, however, it has not been possible to prepare individual compounds having a single structure.

It has now been found, surprisingly, that sulfonated benzofuranylbi-phenyl compounds of a definite structure can be prepared selectively by specific processes and that these individual compounds have outstanding whitening properties, for example for whitening textiles and paper.

The application therefore relates to benzofuranylbi-phenyl compounds of the formula (I)

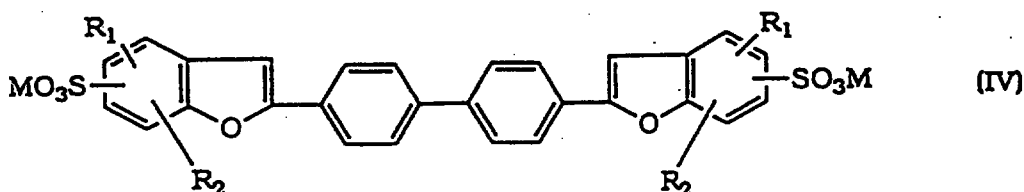
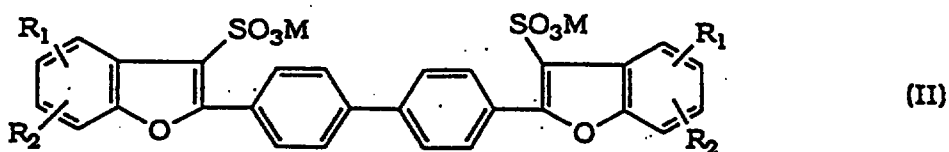


which is unsubstituted or polysubstituted by radicals R = hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy, halogen, phenoxy and benzyloxy and in which M is hydrogen and/or one equivalent of a non-chromophoric cation and n is the number zero or 1 and m is the number zero or 1, subject to the condition that n and m are not both zero or 1.

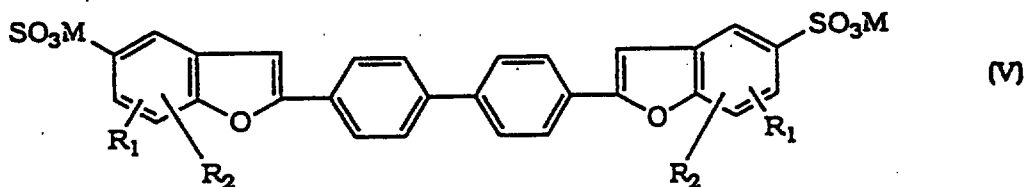
As a non-chromophoric cation, M is, for example, an alkaline earth metal, such as magnesium and calcium, but is preferably an alkali metal, such as lithium, sodium and potassium and also substituted or unsubstituted ammonium, such as ammonium, mono-, di- or tri-

ethanolammonium, mono-, di- or tri-propanolammonium or trimethylammonium or tetramethylammonium.

Preferred compounds are those of the formula (II) and IV)

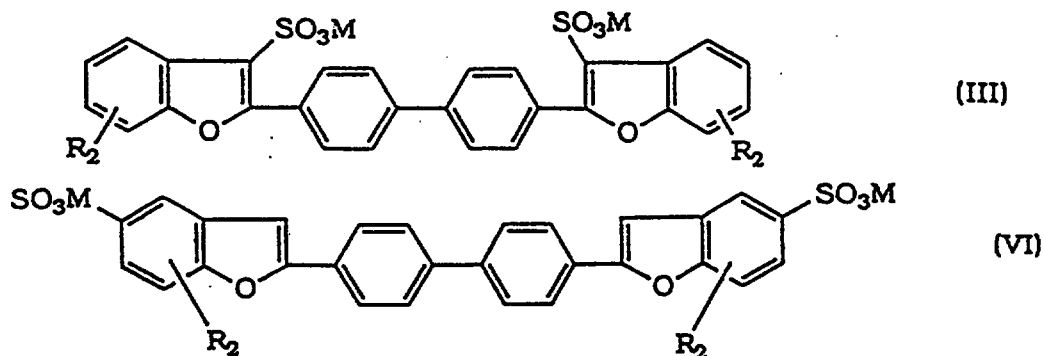


in which R_1 is hydrogen, C_1 - C_4 alkyl, chlorine, C_1 - C_4 alkoxy, phenoxy or benzyloxy, R_2 is hydrogen, C_1 - C_4 alkyl, chlorine or C_1 - C_4 alkoxy and M is hydrogen and/or one equivalent of a non-chromophoric cation and, in particular, compounds of the formula (V)



in which R_1 , R_2 and M are as defined above.

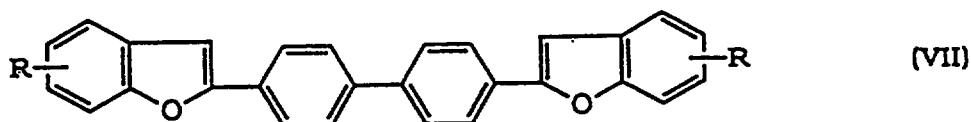
Compounds of particular interest are, however, those of the formula (III) and (VI)



in which R_2 and M are as defined above. R_2 is preferably hydrogen.

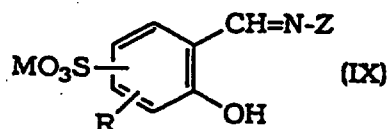
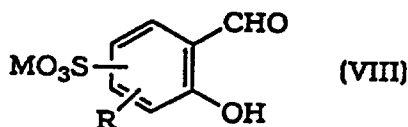
This application also relates to processes for the preparation of the compounds of the formula (I), which comprise

a) reacting one mole of a compound of the formula (VII)

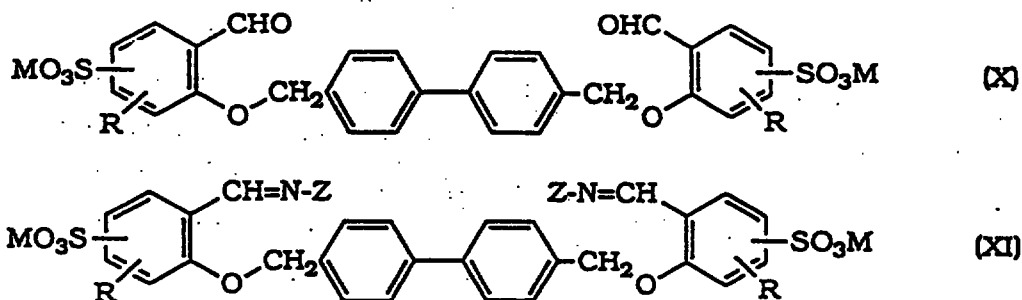


which is unsubstituted or polysubstituted by radicals R = hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, halogen, phenoxy and benzyloxy, with at least stoichiometric amounts of an SO_3 /base complex in an inert organic solvent, at temperatures from $20^\circ C$ up to the boiling point of the solvent used, or

b) etherifying one mole of bis(halomethyl)biphenyl with at least 2 moles of salicylaldehyde or anils thereof of the formula (VIII) or (IX)



which are unsubstituted or polysubstituted by radicals R = hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy, halogen, phenoxy and benzyloxy and in which M is hydrogen and/or one equivalent of a non-chromophoric cation and Z is phenyl or chlorophenyl, and cyclizing by means of bases the resulting bisphenyl ethers of the formula (X) or (XI)



The starting compounds of the formula (VII), (VIII) and (IX) are known and can be prepared by known methods. The intermediates of the formula (X) and (XI) are novel and can be isolated. However, it is advantageous to carry out the process b) as a one-pot process without isolating the intermediates (X) and (XI).

Specifically, the compounds of the formula (II) and (III) are prepared by process a).

SO₃/base complexes are to be understood as meaning addition compounds of SO₃ with organic bases, for example dioxane, preferably nitrogen-containing bases, for example triethylamine, N-ethyldiisopropylamine, dimethylformamide (DMF) and especially pyridine. The stability of these addition compounds is a decisive factor in this reaction for the degree of sulfonation. Thus, for example, if 2 to 6, in particular 3 to 5, moles of SO₃/pyridine complex (based on the SO₃ content) are used per mole of the compound of the formula (VII), compounds of the formula (II) and (III) are prepared. SO₃/base complexes are known and can be prepared by known methods (E.E. Gilbert, E.P. Jones, Ind. Engng. Chem. 49, No. 9, Part II, pages 1553 et seq. (1957); Beilstein 20, III/IV, 2232).

Examples of the inert organic solvent used in process a) are saturated aliphatic hydrocarbons, such as gasoline, petroleum ether and ligroin, halogenated, aliphatic hydrocarbons, such as chloroform, carbon tetrachloride, dichloroethane, trichloroethane, tetrachloroethane, dichloropropane, trichloropropane, dichlorodifluoromethane and dichlorotetrafluoroethane, chlorobenzenes, such as mono-, di- and tri-chlorobenzene, nitrobenzenes, such as nitrobenzene and nitrotoluene, and bicyclic hydrocarbons, such as cyclohexane, methylcyclohexane and decalin.

The compounds of the formula (IV) and, in particular, the compounds of the formula (V) and (VI) are prepared by process b).

The etherification is carried out at temperatures from 60°C to 140°C, in particular 100° to 120°C, in a known manner by means of one equivalent of a base, such as a tertiary amine or a base mentioned in the cyclization below, or by employing the compounds of the formula (VIII) or (IX) already converted into the phenate of this base. The reaction is carried out in a polar, aprotic solvent or solvent mixture, for example dimethylformamide, N-methylpyrrolidone, hexamethylphosphoric triamide, tetramethylurea or, preferably, dimethyl sulfoxide.

The cyclization is similarly carried out in a polar, aprotic solvent, preferably in the same solvent in which the etherification is also carried out, at slightly higher temperatures compared with the etherification and in the presence of a base, for example quaternary ammonium bases, alkaline earth metal hydroxides, alkali metal amides, alkali metal hydrides, alkali metal carbonates and, preferably, alkali metal alcoholates, such as potassium t-butyrate and sodium methylate, and also, in particular, alkali metal hydroxides, such as sodium hydroxide, potassium hydroxide and lithium hydroxide. The basic condensation agents are employed in at least stoichiometric amounts, preferably in excess. It is advantageous to carry out the reaction with the exclusion of atmospheric oxygen and under an inert gas atmosphere.

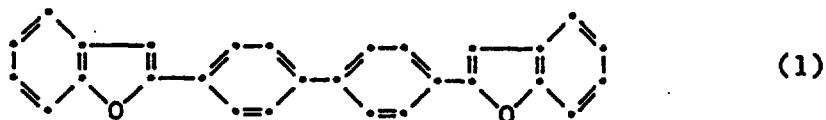
The benzofuranylbiphenyl compounds according to the invention are used for the fluorescent whitening of textiles, for example fabrics

containing cellulose and/or polyamide, and also paper. The benzofuranylbiphenyl compounds according to the invention are preferably incorporated into bleaching agents containing, for example, hypochlorite or, in particular, into detergents.

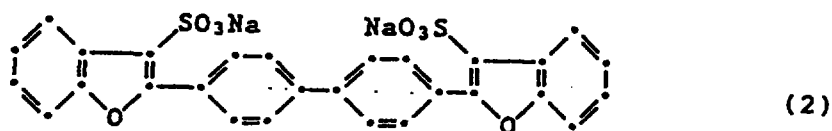
The benzofuranylbiphenyl compounds according to the invention are distinguished by their very good stability, associated with excellent whitening properties.

The following examples illustrate the invention; parts and percentages are by weight.

Example 1: 11.8 g (0.03 mol) of the compound of the formula (1)

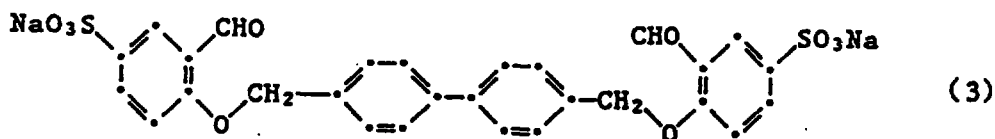


together with 21 g (0.12 mol of SO_3) of sulfur trioxide/pyridine complex (containing approx. 45 % of SO_3), in 50 ml of nitrobenzene are heated at 125°C for 15 hours, with stirring. The nitrobenzene is then removed by means of steam, the resulting suspension is rendered alkaline with sodium hydroxide solution and the product is filtered off with suction and recrystallized from a mixture of 150 ml of water and 150 ml of ethanol. This gives 4.7 g of the compound of the formula



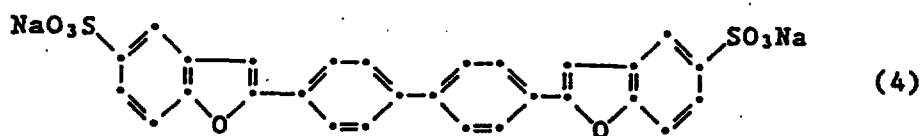
Example 2: 27.1 g (0.11 mol) of disodium salicylaldehyde-5-sulfonate are stirred in 200 ml of dimethyl sulfoxide at 100°C . A solution, preheated to 60° , of 13.4 g (0.05 mol) of 94 % 4,4'-bis-(chloromethyl)-biphenyl is added dropwise to the resulting suspension in the course of one hour. The salicylaldehyde derivative goes into solution meanwhile and a little

bisbenzyl ether of the formula



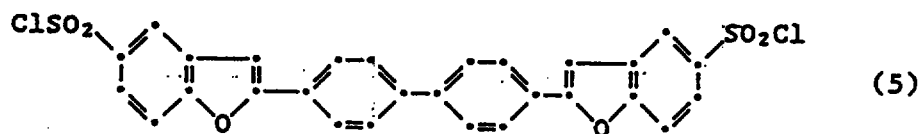
is precipitated. If it is desired to isolate the ether completely, the solvent is removed by vacuum distillation, the residue is stirred with 250 ml of water and the product is filtered off and washed with water, methanol and acetone. The prior isolation of the compound of the formula (3) is not necessary for the subsequent cyclization reaction.

8.2 g (0.2 mol) of finely powdered sodium hydroxide are introduced, with nitrogen blanketing, into the hot reaction mixture previously described and stirring is continued for one hour at 100°C and for 16 hours at 120°C. In the course of this the end product is partially precipitated. Approx. 180 ml of solvent are removed by vacuum distillation at 120°C, the residue is allowed to cool and the precipitate is filtered off with suction. After repeated washing with dimethyl sulfoxide, methanol and water and drying in vacuo, 13.1 g of the compound of the formula



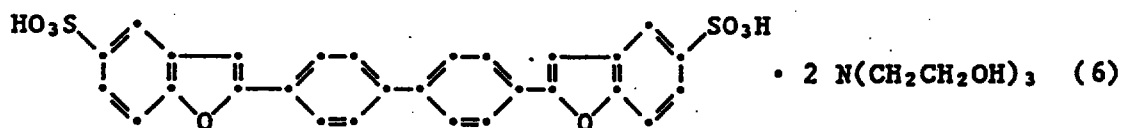
are obtained.

Example 3: A suspension of 11.8 g of the compound of the formula (4) in 240 ml of chlorobenzene, 10 ml of thionyl chloride and 0.3 ml of dimethylformamide is stirred for 2 hours at reflux temperature. A little more thionyl chloride and dimethylformamide are added in order to complete the reaction and stirring is continued at reflux temperature. The resulting cloudy solution is clarified by hot filtration, concentrated greatly and cooled. The precipitated product is filtered off with suction, washed with chlorobenzene and dried. This gives the disulfochloride of the formula



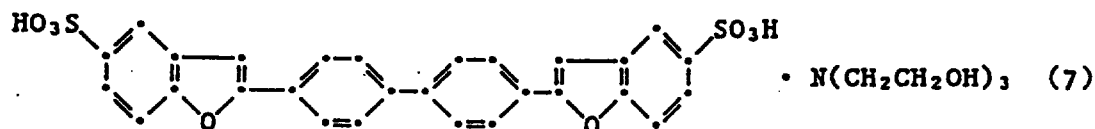
and this is recrystallized from chlorobenzene.

A suspension of 3.7 g of the sulfochloride of the formula (5) in 15 g of triethanolamine and 3 g of water is stirred at 150° for one hour. The excess solvent is substantially removed in vacuo at 120-150°C, and 50 ml of isopropanol are added to the viscous residue. The precipitated product is filtered off with suction, washed repeatedly with isopropanol and taken up in approx. 40 ml of water. The cloudy solution is clarified by filtration with 0.2 g of active charcoal through a pressure filter. This gives an aqueous solution of the bistriethanolamine salt of the formula



which still contains triethanolamine hydrochloride.

If excess concentrated hydrochloric acid is added to such a solution at 95°C, with stirring, the monotriethanolamine salt of the formula



is precipitated. This salt is filtered off with suction, washed with dilute hydrochloric acid and a little water and dried.

Example 4: A piece of polyamide 66 (nylon woven tricot) is heated from 40°C to 98°C in the course of 30 minutes at a liquor ratio of 1:20 in soft water containing 0.1 % of the compound of the formula (2) (percentage by weight based on the textile material) and 3 g/l of stabilized hydrosulfite and 1 ml/l of 80% acetic acid, and is then treated at 98°C for 30 minutes, cooled again to 40°C in the course of 15 minutes, rinsed under cold conditions and dried at 60°C in a drying cabinet.

A high and brilliant degree of whiteness results. When exposed to light in a Xenotest apparatus by the customary standard method, this white effect displays an excellent fastness to light.

Example 5: 1 g of the compound of the formula (2) is dissolved in 1 l of soft water containing 2 g/l of polyphosphate and 5 ml of 80 % acetic acid. A piece of polyamide 6 (Perlon woven tricot) is padded under cold conditions with this liquor, at a liquor pick-up of 110 %, and is then thermofixed for 40 seconds at 190°C. After this treatment the textile material has a high degree of whiteness with very good fastness to light.

Example 6: Detergent granules having a residual moisture of approx. 5 % are prepared by spray-drying a slurry consisting of 1 part of water and 1 part of detergent of the following composition:

8.4 g of linear dodecylbenzenesulfonate,
3.1 g of tallow alcohol tetradecane ethylene glycol ether (14 EO),
3.7 g of Na soap (consisting mainly of behenic acid and C₁₄-C₂₀ acids),
45.8 g of Na tripolyphosphate,
7.9 g of Na silicate,
2.0 g of Mg silicate,
1.2 g of carboxymethylcellulose,
0.2 g of ethylenediamine tetraacetate,
22.2 g of Na sulfate and
0.15 g of the compound (2).

4 g of this detergent are dissolved in 1 l of water (12° of German

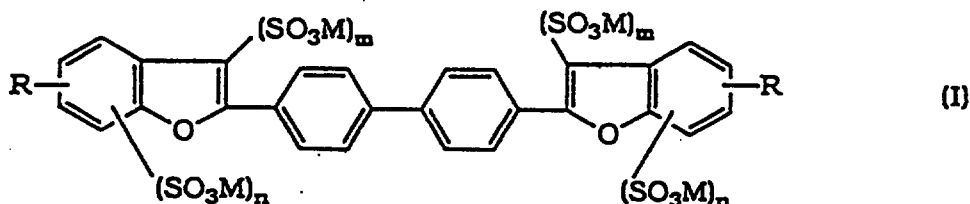
hardness) at a temperature of 30°C. Five pieces of bleached cotton, each 10 g, are washed in this bath for 15 minutes at 30°C, then rinsed under cold, running water and centrifuged for 30 seconds in a swinging machine at a speed of revolution of approx. 1,000 r.p.m. This washing process is repeated 3 times and the pieces of cotton are then dried and their degree of whiteness is determined by the method of Ganz using a photometer (Zeiss RFC 3).

Example 7: Detergents are prepared in accordance with Example 6, but containing 0.1 g of the compound (4) or (7) instead of the compound (2). The 3-fold washings are carried out as described in Example 6, but at a temperature of 90°C. The degrees of whiteness obtained are all above 145.



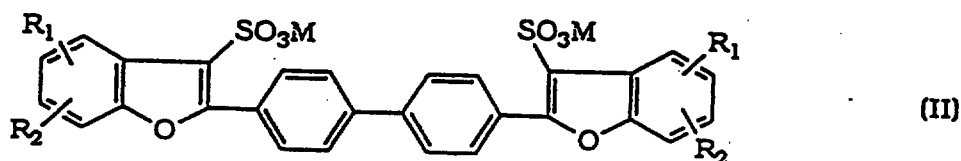
Patent claims

1. A benzofuranylbiaryl compound of the formula (I)



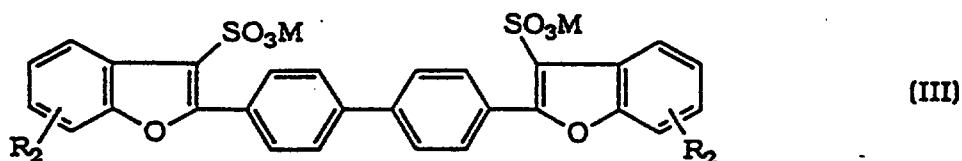
which is unsubstituted or polysubstituted by radicals R = hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy, halogen, phenoxy and benzyloxy and in which M is hydrogen and/or one equivalent of a non-chromophoric cation and n is the number zero or 1 and m is the number zero or 1, subject to the condition that n and m are not both zero or 1.

2. A benzofuranylbiaryl compound of the formula (II) according to claim 1



in which R₁ is hydrogen, C₁-C₄alkyl, chlorine, C₁-C₄alkoxy, phenoxy or benzyloxy, R₂ is hydrogen, C₁-C₄alkyl, chlorine or C₁-C₄alkoxy and M is hydrogen and/or one equivalent of a non-chromophoric cation.

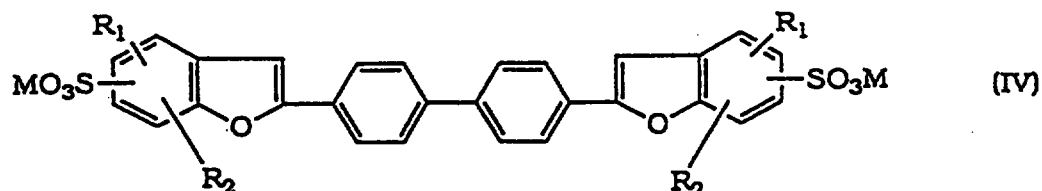
3. A benzofuranylbiaryl compound of the formula (III) according to claim 2



in which R₂ is hydrogen, C₁-C₄alkyl, chlorine or C₁-C₄alkoxy and M is hydrogen and/or one equivalent of a non-chromophoric cation.

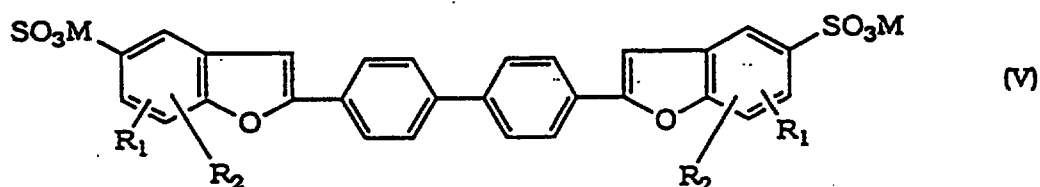


4. A benzofuranylbiaryl compound of the formula (IV) according to claim 1



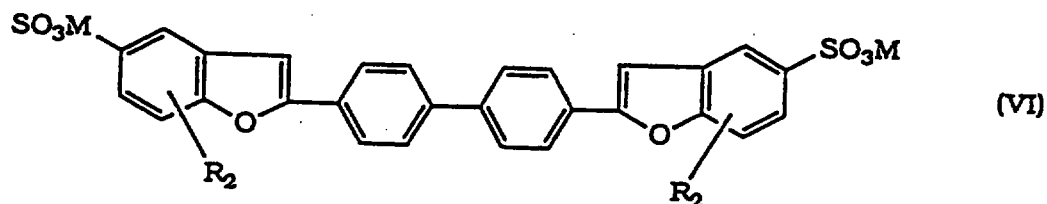
in which R_1 is hydrogen, C_1 - C_4 alkyl, chlorine, C_1 - C_4 alkoxy, phenoxy or benzyloxy, R_2 is hydrogen, C_1 - C_4 alkyl, chlorine or C_1 - C_4 alkoxy and M is hydrogen and/or one equivalent of a non-chromophoric cation.

5. A benzofuranylbiaryl compound of the formula (V) according to claim 4



in which R_1 is hydrogen, C_1 - C_4 alkyl, chlorine, C_1 - C_4 alkoxy, phenoxy or benzyloxy, R_2 is hydrogen, C_1 - C_4 alkyl, chlorine or C_1 - C_4 alkoxy and M is hydrogen and/or one equivalent of a non-chromophoric cation.

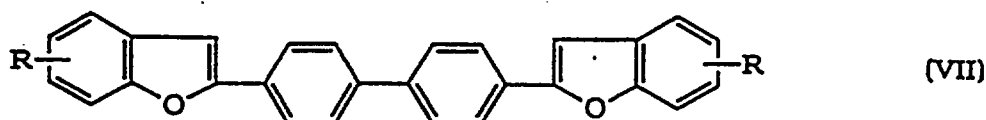
6. A benzofuranylbiaryl compound of the formula (VI) according to claim 5



in which R_2 is hydrogen, C_1 - C_4 alkyl, chlorine or C_1 - C_4 alkoxy and M is hydrogen and/or one equivalent of a non-chromophoric cation.

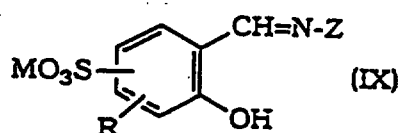
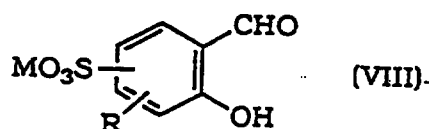
7. A process for the preparation of a compound of the formula (I), which comprises

a) reacting one mole of a compound of the formula (VII)

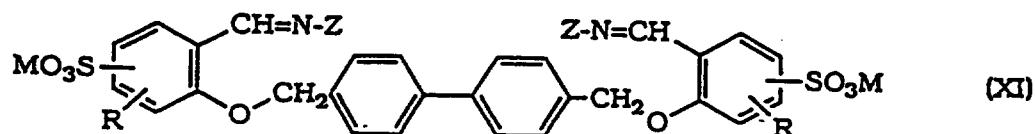
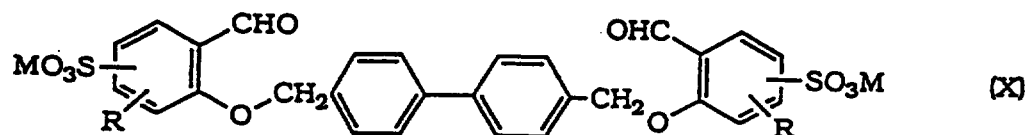


which is unsubstituted or polysubstituted by radicals R = hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy, halogen, phenoxy and benzyloxy, with at least stoichiometric amounts of an SO₃/base complex in an inert organic solvent, at temperatures from 20°C up to the boiling point of the solvent used, or

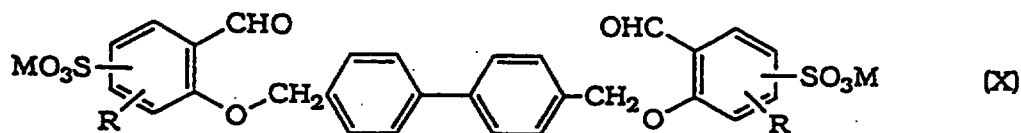
b) etherifying one mole of bis(halomethyl)biphenyl with at least 2 moles of salicylaldehyde or anils thereof of the formula (VIII) or (IX)



which are unsubstituted or polysubstituted by radicals R = hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy, halogen, phenoxy and benzyloxy and in which M is hydrogen and/or one equivalent of a non-chromophoric cation and Z is phenyl or chlorophenyl, and cyclizing by means of bases the resulting bisphenyl ethers of the formula (X) or (XI)

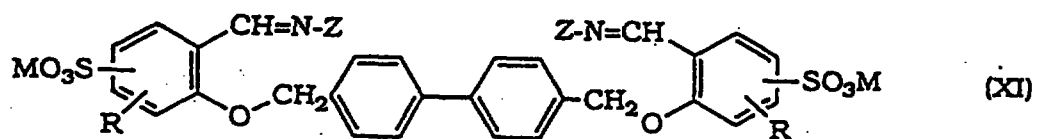


8. A bisbenzyl ether of the formula





or



in which R, M and Z are as defined in claim 7.

9. The use of the compounds claimed in claims 1 to 6 for fluorescent whitening.

10. The use of the compounds according to claim 9 in bleaching agents containing hypochlorite and in detergents.