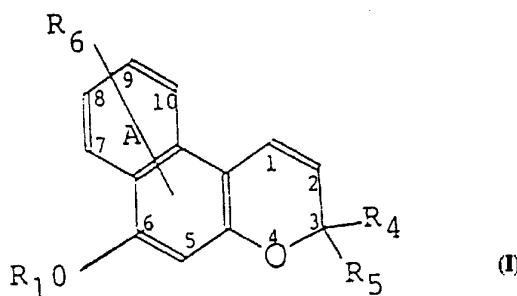




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(54) Title: PHOTOCROMIC NAPHTHO(2,1-B)PYRANS



(57) Abstract

A naphthopyran compound of general formula (I) wherein R₁ represents an alkyl group or an aryl group; each of R₄ and R₅, which may be the same or different, independently represents an alkyl, alkenyl, carbocyclic or heterocyclic group, or R₄ and R₅ taken together with the carbon atom to which they are attached form a carbocyclic ring or a heterocyclic ring; and R₆ represents a hydrogen atom or a substituent selected from alkyl, alkoxy, aryl, aryloxy, heteroaryl, halogen, amino, substituted amino, azo, imino, amide, carboxylate, ester, cyano, trifluoromethyl or nitro, and in addition R₆ may represent a carbocyclic or heterocyclic ring fused to ring A. The naphthopyran compounds of the invention are useful as photochromic materials in lenses, e.g. sunglasses, and photochromic transparencies for cars and aircrafts.

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PHOTOCHROMIC NAPHTHO (2,1-B)PYRANS

The present invention relates to certain novel photochromic naphthopyran compounds, and to articles and compositions containing them.

Photochromism is a well-known physical phenomenon which is observed with certain classes of chemical compounds. A detailed discussion of this phenomenon can be found in "Photochromism : Molecules and Systems", Studies in Organic Chemistry 40, edited by H. Durr and H. Bouas-Laurent, Elsevier 1990.

Naphthopyran compounds as a class of compounds are known to be capable of exhibiting a photochromic effect. For example, U.S. Patent No. 4980089 describes a series of photochromic naphthospiropyran compounds containing a norcamphor group or a tricyclodecane group at the 2-position of the naphthospiropyran ring (This 2-position corresponds to the 3-position of the ring in the numbering system used in the present specification).

A series of novel reversible photochromic naphthopyran compounds carrying an acetoxy group (or analogues thereof) at the 5-position of the naphthopyran ring is described in WO 92/09503.

U.S. Patent No. 5106998 describes a variety of photochromic compounds including various naphthopyran compounds of different structures.

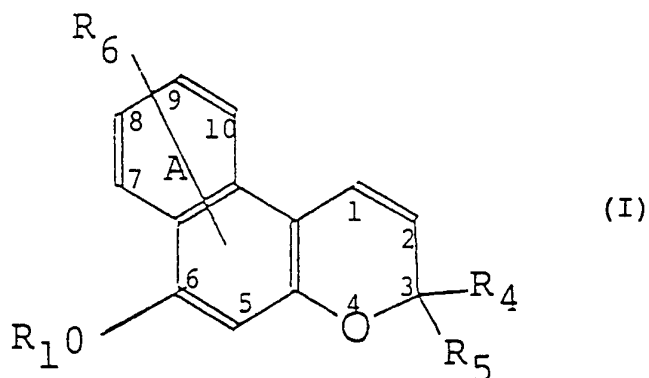
U.S. Patent No. 5066818 describes a group of novel reversible photochromic naphthopyran compounds having at least one ortho-substituted phenyl group at the 3-position of the pyran ring.

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In our earlier U.K. patent application No. 9306587 we describe naphthopyran compounds which provide substantially greater induced optical density in their darkened state than other known naphthopyran compounds. The common characteristic of the novel naphthopyran compounds described in our earlier U.K. patent application is that they carry a substituted amino group in the 6-position of the molecule.

We have now discovered that a similar enhanced induced optical density in the darkened state can be achieved with a group of naphthopyran compounds which carry an alkoxy or an aryloxy group in the 6-position of the molecule instead of the 6-amino substituent described in our earlier U.K. patent application. The 6-alkoxy or 6-aryloxy compounds of the present invention have a less intense induced optical density than the corresponding 6-amino compounds described in our U.K. patent application No. 9306587 but nevertheless exhibit deeper colouration in the darkened state than other known photochromic naphthopyran materials.

Accordingly, the present invention provides a naphthopyran compound of general formula (I)



wherein R_1 represents an alkyl group or an aryl group;

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each of R_4 and R_5 , which may be the same or different, independently represents an alkyl, alkenyl, carbocyclic or heterocyclic group, or R_4 and R_5 taken together with the carbon atom to which they are attached form a carbocyclic ring or a heterocyclic ring; and

R_6 represents a hydrogen atom or a substituent selected from alkyl, alkoxy, aryl, aryloxy, heteroaryl, halogen, amino, substituted amino, azo, imino, amide, carboxylate, ester, cyano, trifluoromethyl or nitro, and in addition R_6 may represent a carbocyclic or heterocyclic ring fused to ring A.

Throughout this specification, unless stated otherwise, the term "alkyl" is to be taken to mean an alkyl group having from 1 to 6 carbon atoms. Similarly, the term "alkoxy" is to be taken to mean an alkoxy group having from 1 to 6 carbon atoms.

Furthermore, in the definitions of R_4 , R_5 and R_6 above, whenever reference has been made to a carbocyclic or heterocyclic ring (or group), unless specified otherwise it is to be understood that such carbocyclic or heterocyclic rings (or groups) may be unsubstituted or may carry one or more substituents chosen from halogen atoms, alkyl, alkoxy, aryl, aryloxy, heteroaryl, amino, substituted amino, azo, imino, amide, carboxylate, ester, cyano, trifluoromethyl or nitro groups, or, further, such rings may have one or more further rings which are fused thereto.

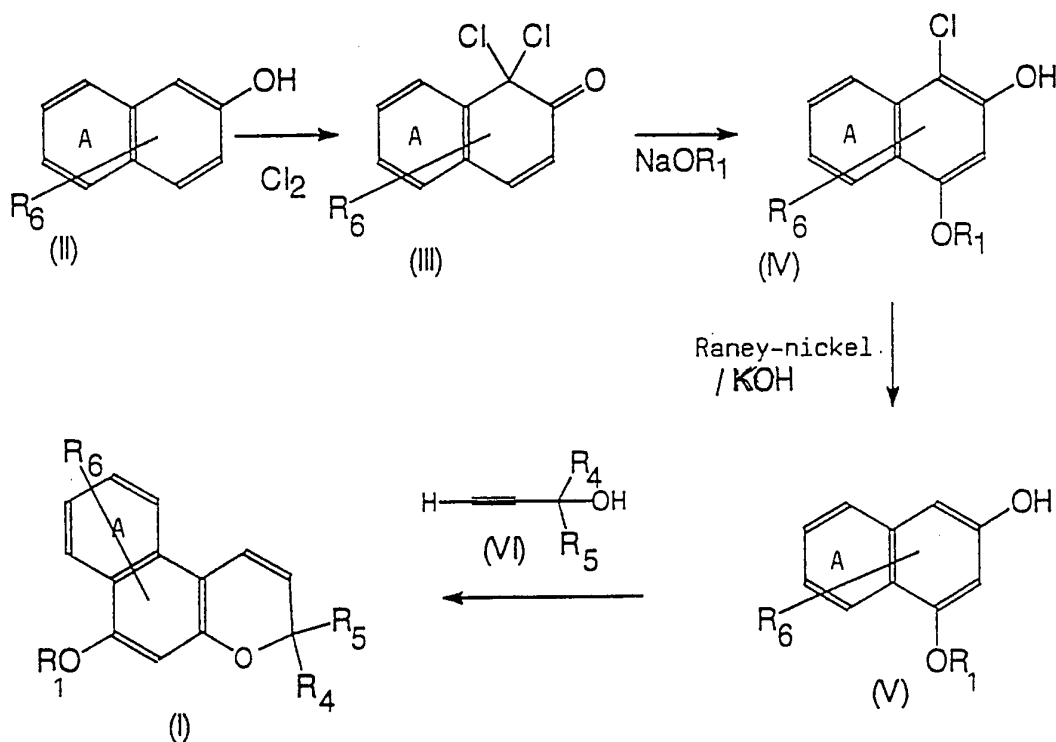
In the compounds of formula (I), ring A may carry more than one substituent R_6 .

In a group of preferred compounds in accordance with the invention, the R_1 0- substituent is a methoxy group.

Preferably, the substituents R_4 and R_5 on the pyran ring are chosen from a phenyl group, a 4-trifluoromethyl-phenyl group, a 4-alkoxyphenyl group (preferably 4-methoxyphenyl), a 2,4-di(alkoxy)phenyl group (preferably 2,4-dimethoxyphenyl) or a 4-dialkylamino-phenyl group (preferably 4-dimethylamino-phenyl).

It is also envisaged that the advantageous properties of the compounds of the present invention will be obtained with a compound of general formula (I) in which the R_4 and R_5 substituents together with the carbon atom to which they are attached form a spiro-adamantylidene group.

The naphthopyran compounds of the present invention may be prepared by a general preparative method which is based on the following reaction scheme:-



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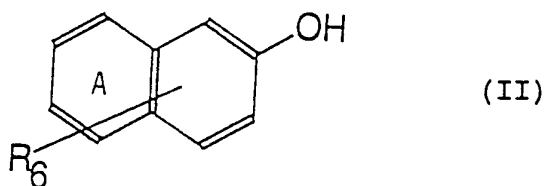
In the preparative process shown above, the 4-alkoxy/aryloxy-2-naphthol compound of formula (V) is prepared from the 2-naphthol compound of formula (II) via a series of reaction steps. Firstly, gaseous chlorination of the 2-naphthol compound of formula (II) in glacial acetic acid and an excess of sodium acetate gives the 1,1-dichloronaphth-2-one compound of formula (III) which is then reacted with sodium alkoxide/aryloxy (e.g. sodium methoxide) at 0°C to give the 1-chloro-4-alkoxy/aryloxy-2-naphthol compound of formula (IV). Subsequent hydrodehalogenation of the chloro-naphthol (IV) with Raney-nickel in aqueous potassium hydroxide affords the 4-alkoxy/aryloxy-2-naphthol compound of formula (V). These process steps are described in more detail in a paper by G.M. Iskander et al., J. Chem. Soc. (C), 1970, 1701-3.

The final step in the preparative process is the condensation of the 4-alkoxy/aryloxy-2-naphthol compound of formula (V) with a propargyl alcohol of formula (VI) in the presence of acidic alumina (e.g. Brockmann 1 alumina), trifluoroacetic acid or other like acidic catalyst. Such condensation reactions are well known in the preparation of naphthopyran compounds and are described in detail by, for example, L. Merlini in Advances in Heterocyclic Chemistry, 1975, 18, 159 and in a number of patents, such as U.S. 5066818, U.S. 4990287, U.S. 4980089 and WO 92/09593.

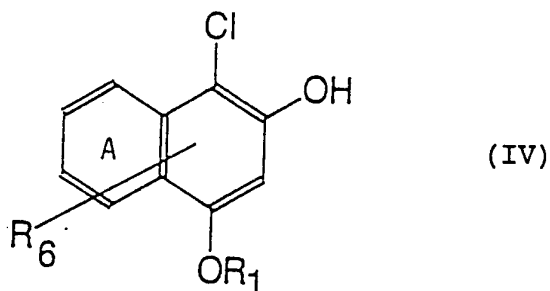
Accordingly, the present invention also provides a process for preparing a naphthopyran compound of general formula (I) as defined above, which process comprises

(a) chlorinating a solution of a 2-naphthol compound of general formula (II):-

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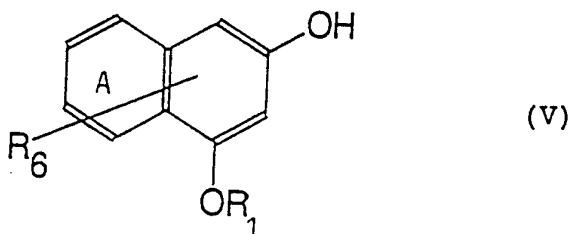


wherein A and R_6 are as defined above, in an organic solvent to produce the corresponding 1,1-dichloronaphth-2-one which is reacted with a sodium alkoxide/aryloxide of general formula $NaOR_1$, wherein R_1 is as defined above, to generate a chloro-naphthol of general formula (IV):-



wherein A, R_1 and R_6 are as defined above,

(b) subjecting the chloro-naphthol of general formula (IV) to a hydrodehalogenation reaction to produce a substituted naphthol of general formula (V):-

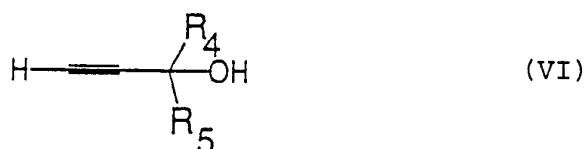


wherein A, R_1 and R_6 are as defined above,

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and then:

(c) condensing the substituted naphthol of general formula (V) with a propargyl alcohol of general formula (VI):-



wherein R_4 and R_5 are as defined above, in the presence of acidic alumina, trifluoroacetic acid or another like acidic catalyst.

The novel naphthopyran compounds of the present invention are found to be particularly useful as photochromic materials to be incorporated into polymeric host materials so as to impart photochromic properties to the said polymeric host materials.

The photochromic naphthopyran compounds of the present invention are incorporated into the plastics host material in known manner, for example as described in European Patent No. 0245020 or U.S. Patent No. 5066818.

The naphthopyran compounds of the invention exhibit substantially greater induced optical density (IOD) than prior art materials of comparable structure. As a result, the amount of photochromic material required to impart a useful degree of photochromism to a polymeric host material or to a solution is greatly reduced when compared to the amount required to obtain an equivalent photochromic effect with prior art photochromic materials. The use of reduced quantities of the photochromic materials of the invention provides a saving in cost.

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The colour range of the naphthopyrans of the present invention is 410 to 500 nm; thus, the materials of the present invention impart a yellow or orange or red colouration in their darkened state. In the faded or bleached condition the materials exhibit a colourless or pale colouration.

Typical polymeric host materials are optically clear polymer materials, such as polymers of polyol(allyl carbonate)-monomers, polyacrylates such as polymethylmethacrylates, cellulose acetate, cellulose triacetate, cellulose acetate propionate, cellulose acetate butyrate, poly(vinyl acetate), poly(vinyl alcohol), polyurethanes, polycarbonates, polyethylene terephthalate, polystyrene, styrene/methylmethacrylate copolymers, styrene/acrylonitrile copolymers, and polyvinylbutyral. Transparent copolymers and blends of the transparent polymers are also suitable as host materials. Polymers of the type described in EP 0294056 and EP 0453149 are also suitable.

Preferably, the polymeric host material is an optically clear polymerized organic material such as a polyurethane or a polymer of diethylene glycol bis(allyl carbonate) (sold under the trade name CR-39), or SPECTRALITE - a material sold by Sola Optical USA.

Usually, the amount of photochromic naphthopyran compound incorporated in the polymeric host material ranges from 0.01 to 0.5 wt%, based on the weight of the polymeric host material.

In some applications, it may be desirable or advantageous to combine the naphthopyran compounds of the present invention with other photochromic materials to obtain an aggregate colour effect. For example, spiro-oxazine materials may have a colour range of 530 to 680 nm which means that in the darkened condition the spiro-oxazines impart a red-purple or

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purple or blue or blue-green or green colouration to a host material. Thus, the present naphthopyran compounds are complementary to known spiro-oxazine materials such as those described in our European Patent No. 0245020, or in our UK Patent Applications Nos. 92/25346, 92/25347 and 92/25348, or to the spiro (indolino) naphthoxazines, spiro (indolino) pyrido benzoxazines and spiro (indolino) benzoxazines described in U.S. Patents Nos. 4637698, 3562172, 3578602, 4816584, 4215010 and 4342668, and can be combined with such other photochromic materials.

Typically, when used in combination, the further additional photochromic material is present in an amount of from 0.001 to 0.5 weight %, based on the weight of the polymeric host material.

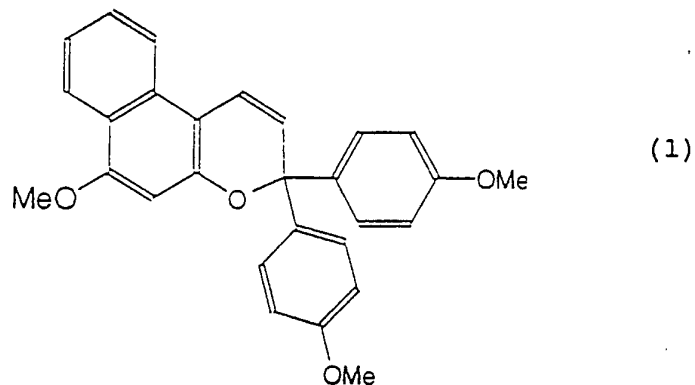
Examples of suitable uses of the photochromic plastic articles incorporating the naphthopyran compounds of the invention are in the manufacture of plano lenses, e.g. for sunglasses, and ophthalmic lenses and as photochromic transparencies for vehicles such as cars and aircraft.

The following Examples illustrate the present invention.

Example 1

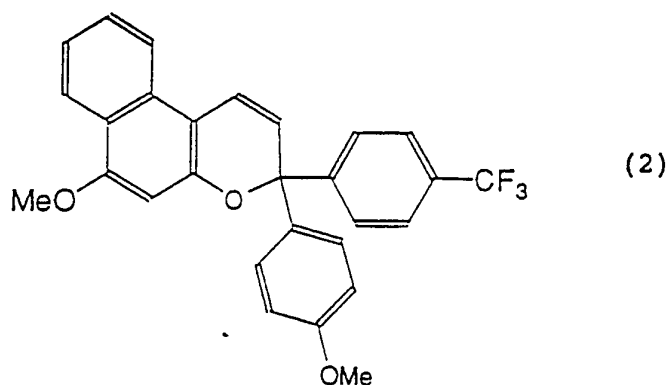
3,3-Dianisyl-6-methoxy-3H-naphtho[2,1-b]pyran.

A mixture of 4-methoxy-2-naphthol (0.26g; 0.015mol), 1,1-dianisylprop-2-yn-1-ol (0.40g; 0.0015mol), acidic alumina Brockmann 1 (3.5g) and toluene (40.0 ml) was heated and stirred for 1.5h, cooled, filtered. The filtrate was washed with 2M NaOH then water, dried and evaporated to give an orange gum. Trituration with hexane yielded 3,3-dianisyl-6-methoxy-3H-naphtho[2,1-b]pyran of formula (1) below as an off-white solid (41%). Crystallisation from hexane and ethylacetate gave the pyran as white micro-platelets, m.pt. 158-160°C.

Example 2

3-Anisyl-3-(p-trifluoromethyl)phenyl-6-methoxy-3H-naphtho
[2,1-b]pyran.

A mixture of 4-methoxy-2-naphthol (0.19g; 0.0011mol), 1-anisyl-1-(p-trifluoromethyl)phenylprop-2-yn-1-ol (0.33g; 0.0011mol), acidic alumina Brockmann 1 (3.5g) and toluene (40.0ml) was heated and stirred for 1h, cooled then filtered. The filtrate was washed with 2M NaOH then water, dried and evaporated to give a thick orange oil. Trituration with hexane followed by recrystallisation with hexane gave 3-anisyl-3-(p-trifluoromethyl)phenyl-6-methoxy-3H-naphtho[2,1-b]pyran of formula (2) below as a white solid (20% yield), m.pt. 149-151°C.



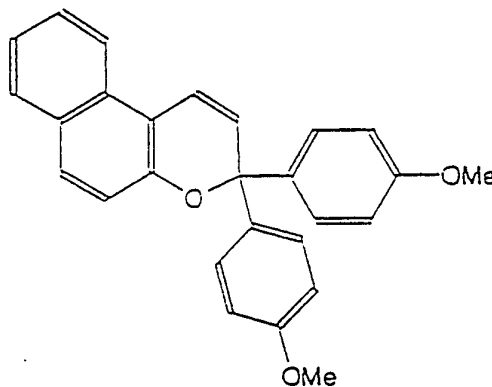
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For the purposes of comparison a number of corresponding compounds having no substitution at the 6-position were also prepared. The preparation of these compounds is described in the following Comparative Examples.

Comparative Example 1

3,3-Dianisyl-3H-naphtho[2,1-b]pyran.

A mixture of 2-naphthol (3.23g;0.0224 mol), 1,1-dianisylprop-2-yn-1-ol (6.00g;0.0224mol), acidic alumina Brockmann 1(6g) and toluene (250ml) was heated and stirred for 1.5h, cooled, filtered and the solid washed with toluene. The filtrate was evaporated to give a pale purple tacky solid which was washed with pet. ether (40-60)/diethyl ether to yield crude product (7.07g). Purification of the solid by crystallisation from ethylacetate gave 3,3-dianisyl-3H-naphtho[2,1-b]pyran as a white solid (5.52g;66% yield), m.pt 176-177°C.



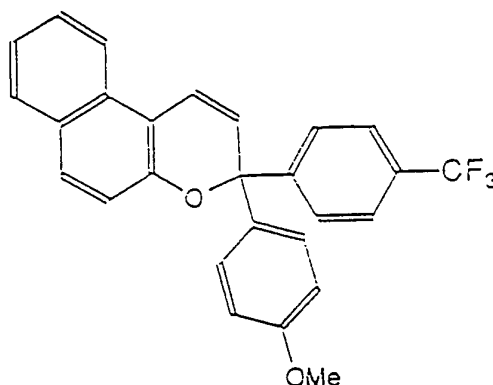
Comparative Example 2

3-Anisyl-3-(p-trifluoromethyl)phenyl-3H-naphtho[2,1-b]pyran.

A mixture of 2-naphthol (1.44g;0.010mol), 1-anisyl-1-(4-trifluoromethyl)phenylprop-2-yn-1-ol (3.22g;0.0105mol), acidic alumina Brockmann 1 (8g) and benzene (40.0ml) was heated and stirred for 3h, cooled, filtered

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and the solid washed with toluene. The filtrate was evaporated to give an orange oil which was chromatographed over silica (eluent: 10% ethylacetate in pet. ether (40-60)) to give a pale yellow oil which solidified on trituration with diethyl ether to yield 3-anisyl-3-(4-trifluoromethyl)phenyl-3H-naphtho[2,1-b]pyran as a white solid (1.60g; 37% yield), m.pt. 136-137.5°C.



The photochromic properties of the naphthopyran compounds of the present invention were tested by preparing, in conventional manner, by a direct casting process, 2.4 mm plates of a U.V. curable plastics host material (made and sold as SPECTRALITE by Sola Optical USA) incorporating the photochromic naphthopyran in a concentration of 0.05% w/w.

Similar plates were made with samples of the comparative compounds.

The resultant plates were illuminated under standard solar simulation conditions at Air Mass 2 at 21°C (see Parry Moon, J. Franklin Inst. 230, (1940), p 583-617). The measurements which were made on the samples in the darkened condition were taken when the samples had reached a steady state; this steady state was deemed to have been reached after 10 minutes in the darkened condition.

The results obtained are shown in Table 1 below.

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TABLE 1

Examples	Bleached IVT	Darkened IVT	IOD $\lambda_{\max}$	$\lambda_{\max}$ nm
1	81.2	59.1	1.42	455
2	89.3	76.0	1.62	425

Comparative
Examples

1	91.2	79.9	0.12	490
2	91.2	84.0	0.15	450

The results in Table 1 show the integrated visible transmission (IVT) measured in both the bleached condition and the darkened condition. These values show, for each material, the typical visual photochromic range which can be achieved.

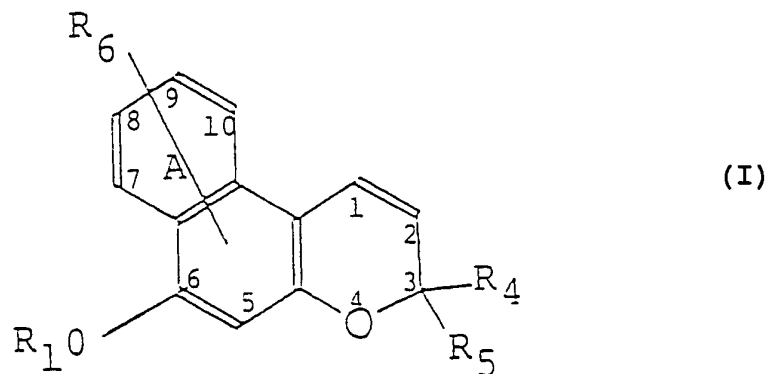
The induced optical density at the point of maximum adsorption of the chromophore (IOD at $\lambda_{\max}$) is deduced by means of the following relationship:-

$$\text{IOD at } \lambda_{\max} = \log_{10} \frac{\text{Bleached } (\lambda_{\max})}{\text{Darkened } (\lambda_{\max})}$$

The IOD values set out in Table 1 show that the naphthopyran compounds of the present invention exhibit in their darkened condition a very much greater depth of colour than the corresponding structures in which the 6-alkoxy substituent is absent (IOD of 1.42 as compared to IOD of 0.12; and IOD of 1.62 as compared to IOD of 0.15).

Claims

1. A naphthopyran compound of general formula (I)



wherein R_1 represents an alkyl group or an aryl group;

each of R_4 and R_5 , which may be the same or different, independently represents an alkyl, alkenyl, carbocyclic or heterocyclic group, or R_4 and R_5 taken together with the carbon atom to which they are attached form a carbocyclic ring or a heterocyclic ring; and

R_6 represents a hydrogen atom or a substituent selected from alkyl, alkoxy, aryl, aryloxy, heteroaryl, halogen, amino, substituted amino, azo, imino, amide, carboxylate, ester, cyano, trifluoromethyl or nitro, and in addition R_6 may represent a carbocyclic or heterocyclic ring fused to ring A.

2. A naphthopyran compound according to claim 1, wherein the R_{10} - substituent is a methoxy group.

3. A naphthopyran compound according to claim 1 or 2, wherein the R_4 and R_5 substituents are chosen from a phenyl group, a 4-trifluoromethylphenyl group, a 4-alkoxyphenyl group, a 2,4-di(alkoxy)phenyl group or a 4-dialkylaminophenyl group.

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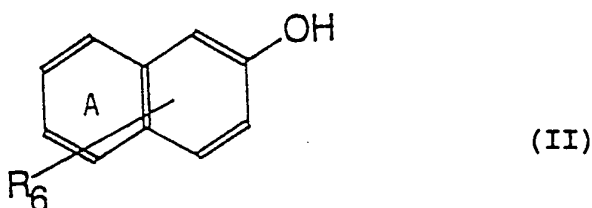
4. A naphthopyran compound according to claim 3, wherein the R_4 and R_5 substituents are chosen from a 4-methoxyphenyl group, a 2,4-dimethoxyphenyl group or a 4-dimethylaminophenyl group.

5. 3,3-Dianisyl-6-methoxy-3H-naphtho[2,1-b]pyran.

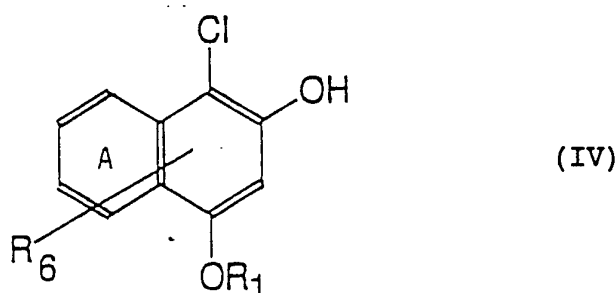
6. 3-Anisyl-3-(p-trifluoromethyl)phenyl-6-methoxy-3H-naphtho[2,1-b]pyran.

7. A process for preparing a naphthopyran compound of general formula (I) as defined in claim 1, which process comprises

(a) chlorinating a solution of a 2-naphthol compound of general formula (II):-



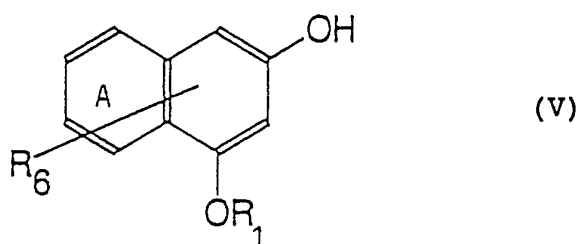
wherein A and R_6 are as defined in claim 1, in an organic solvent to produce the corresponding 1,1-dichloronaphth-2-one which is reacted with a sodium alkoxide/aryloxide of general formula NaOR_1 , wherein R_1 is as defined in claim 1, to generate a chloro-naphthol of general formula (IV):-



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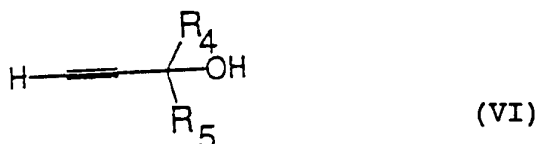
wherein A, R₁ and R₆ are as defined in claim 1,

(b) subjecting the chloro-naphthol of general formula (IV) to a hydrodehalogenation reaction to produce a substituted naphthol of general formula (V):-



wherein A, R₁ and R₆ are as defined in claim 1, and then:

(c) condensing the substituted naphthol of general formula (V) with a propargyl alcohol of general formula (VI):-



wherein R₄ and R₅ are as defined in claim 1, in the presence of acidic alumina, trifluoroacetic acid or another like acidic catalyst.

8. A photochromic article comprising a polymeric host material having a naphthopyran compound as defined in any one of claims 1 to 6 incorporated therein or applied thereto.

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9. A photochromic article according to claim 8, wherein the polymeric host material is selected from polymers of polyol (allyl carbonate) monomers, polyacrylates, poly(alkylacrylates), cellulose acetate, cellulose triacetate, cellulose acetate propionate, cellulose acetate butyrate, poly(vinyl acetate), poly(vinyl alcohol), polyurethanes, polycarbonates, polyethylene terephthalate, polystyrene, styrene/methylmethacrylate copolymers, styrene/acrylonitrile copolymers, and polyvinylbutyral.

10. A photochromic article according to claim 9, wherein the polymeric host material is a polyurethane, or a polymer of diethyleneglycol bis (allyl carbonate).

11. A photochromic article according to claim 8, 9 or 10, wherein the amount of naphthopyran compound is from 0.01 to 0.5% by weight, based on the weight of the polymeric host material.

12. A photochromic article according to any one of claims 8 to 11, comprising a further photochromic compound selected from spiro(indoline)naphthoxazines, spiro(indolino)pyrido benzoxazines, and spiro(indolino)benzoxazines.

13. A photochromic article according to claim 12, wherein the further photochromic compound is present in an amount of from 0.001 to 0.5% by weight, based on the weight of the polymeric host material.

14. A photochromic article according to any one of claims 8 to 13, which is in the form of a lens.

15. A photochromic article according to claim 14, wherein the lens is an ophthalmic lens.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 94/01759

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07D311/92

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 246 114 (THE PLESSEY COMPANY PLC) 19 November 1987 see page 4, column 59 - page 5, column 5; claims 1-15	1-15
Y	WO,A,92 01959 (PPG INDUSTRIES, INC.) 6 February 1992 see page 7, line 1 - page 8, line 31; claims 1-17	1-15
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

5 October 1994

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