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Bi-or terthienyl substituted photochromic naphtho[2,1-b]pyran compounds

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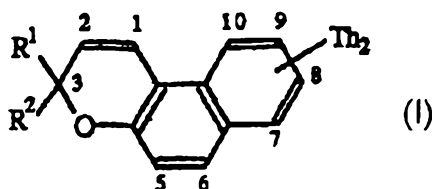
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(54) Title: BI-OR TERTHIENYL SUBSTITUTED PHOTOCHROMIC NAPHTHO[2,1-B]PYRAN COMPOUNDS

(54) Titre: COMPOSES PHOTOCHROMIQUES NAPHTHO(2,1-B)PYRANES A SUBSTITUTIONS BI OU TERTHIENYLE



(57) Abstract: The invention concerns photochromic compounds corresponding to the formula (I) wherein: Th₂ represents a bithienyl group in one among positions 5, 6, 8-10 of the naphthenic cycle; R¹ represents a bithienyl or trithienyl group; and R² represents a bithienyl, trithienyl, aryl, naphthyl, thienyl, furanyl, pyrrolyl or N-alkyl pyrrolyl group. The invention is useful for making glazing for buildings, windscreen, helmet visor and glasses for spectacles.

(57) Abrégé: Les composés photochromiques de l'invention répondent à la formule (I) dans laquelle Th₂ représente un groupement bithiényle dans l'une des positions 5, 6, 8-10 du cycle

naphthénique. R¹ désigne un groupement bithiényle ou trithiényle, et R² désigne un groupement bithiényle, trithiényle, aryle, naphtyle, thiényle, furanyle, pyrrolyle ou N-alkyl pyrrolyle. Application: à la fabrication de vitrages de bâtiment, pare-bris, visières de casques et verres de lunettes.

WO 01/04233 A1

Bi- or terthienyl substituted photochromic naphtho[2,1-b]pyran compounds

5 The object of the present invention is photochromic compounds, more particularly heterocyclic compounds of the naphtho[2,1-b]pyran family substituted by bi- or terthienyl groups, as well as their use in the field of materials and articles with variable optical transmission.

10 When photochromic compounds are subjected to irradiation containing ultraviolet radiation (sunlight, xenon or mercury lamps), they undergo a reversible colour change. When the radiation ceases, they return to their original colour.

15 Much research has been carried out in recent years on organic materials for optical applications. Particular attention has been paid to ophthalmic lenses, glazing for buildings, windscreens for cars or aircraft, and helmet visors whose transparence in the visible may be modified by photochromic molecules. For this type of application using sunlight (heliochromism), the active photochromic compound must satisfy a number of criteria, including :

- 20 - a strong colorability in the visible after light excitation (colorability is the measure of the capacity of a photochromic compound to give an intense colour);
- an absence of coloration (or very slight coloration) in its initial state;
- rapid kinetics of thermal decoloration at ambient temperature;
- low decoloration by visible light; and
- high coloration speed.

25 One of the major difficulties encountered with photochromic compounds is obtaining a compromise between strong colorability and rapid discoloration kinetics. Under continuous solar irradiation, a photostationary equilibrium is established between those molecules which are colouring under the action of ultraviolet light and those which are discolouring under the combined action of
30 temperature and visible light. Thus an increase in the speed of discoloration frequently causes a reduction in colorability.

The applicant company has discovered a new family of naphtho[2,1-b]pyrans substituted with bithienyl or terthienyl groups which have particularly advantageous photochromic properties.

35 The compounds according to the invention, in comparison with naphtho[2,1-b]pyrans of the prior art, show an at least equivalent colorability for

higher coloration speeds and discoloration speeds. Other properties observed for these compounds are :

- an absence of coloration or very slight coloration in the original state;
- particularly long lifetime;
- 5 - sensitivity to low-energy ultraviolet radiation (wavelengths greater than 380 nm);
- an absorption of the coloured forms at long wavelength (539 nm and higher).

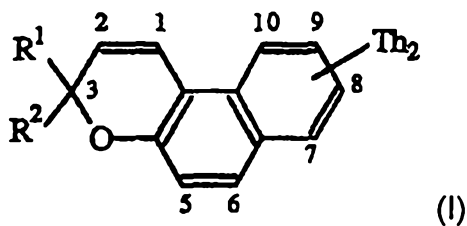
These properties overall render these compounds particularly
10 advantageous for the manufacture of photochromic materials, in particular those comprising a transparent polymer substrate such as organic glasses with variable optical transmission (lenses for sunglasses, glazing for buildings, windscreens for cars or aircraft, and helmet visors).

The photochromic compounds may be directly incorporated into the
15 organic glass substrate or dissolved in a polymer film joined to the organic glass substrate.

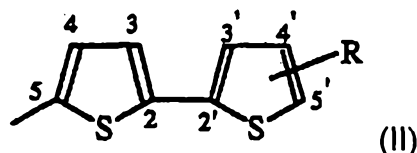
The photochromic compounds according to the invention contain a [3H]naphtho[2,1-b]pyran structure and are characterized by the fact that they contain at least one bithienyl group, substituted or not, in one of positions 5 to
20 10 of the naphthalene ring of the [3H]naphtho[2,1-b]pyran structure and at least one bithienyl or terthienyl group, substituted or not, in position 3 of said structure and excluding compounds of [3H]naphtho[2,1-b]pyran structure containing a single bithienyl group in position 3 of said structure and a bithienyl group in position 7 of the naphthalene ring.

25 The photochromic compounds according to the invention preferably contain a bithienyl group in position 5, 6, 8-10 of the naphthalene ring.

More particularly, the compounds of the invention correspond to the following general formula :

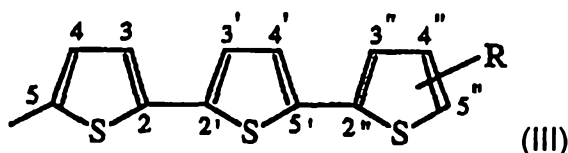


where Th₂ represents the formula (II) :



in which :

R represents a substituent occupying one of the positions 3, 3', 4, 4' or 5, preferably 5', and is selected from a hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group, an OR^3 , SR^3 , COR^3 or $COOR^3$ group where R^3 represents a hydrogen atom, an alkyl or cycloalkyl group, an aryl group, an amino group, an NO_2 , CN or SCN group, a halogen atom, a mono- or polyhaloalkyl group, R^1 designates a Th_2 group as represented by the formula (II) or a terthienyl group (Th_3) as represented by the formula (III) :



where R is a substituent as defined above occupying one of the positions 3, 3', 3'', 4, 4', 4'', 5'', preferably 5'', and

R^2 may be a Th_2 group as defined by formula (II), a Th_3 group as defined by the formula (III), an aryl group, a naphthyl group, a thienyl group, a furanyl group, a pyrrolyl or N-alkylpyrrolyl group.

In this definition of R^2 , an aryl group represents a phenyl, a phenyl mono- or polysubstituted by one or more alkyl, cycloalkyl, phenyl, amino, halogen, or OR^3 , SR^3 , COR^3 or $COOR^3$ substituents (where R^3 has the same definition as above); the R^2 of the naphthyl type may be substituted with the same substituents.

The heterocyclic groups (thiophene, furan, pyrrole) may be benzo-condensed and the benzo group may carry alkyl, cycloalkyl, aryl, OR^3 , SR^3 , COR^3 or $COOR^3$ (where R^3 has the same definition as above) amino, NO_2 , CN or SCN, or mono (or poly)haloalkyl substituents.

R^1 preferably represents a Th_3 group.

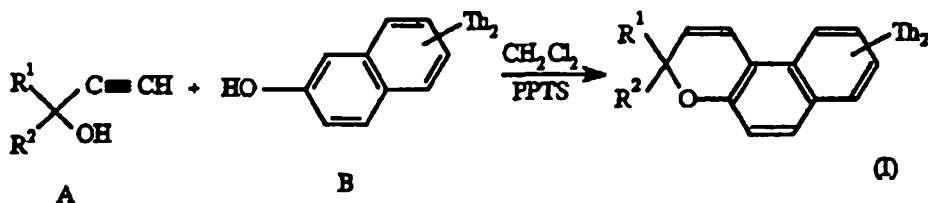
In the bithienyl and terthienyl substituents, the alkyl groups are preferably C_1 - C_6 alkyl groups, for example methyl, ethyl, propyl, butyl, pentyl and hexyl; the cycloalkyl groups are preferably C_5 - C_7 cycloalkyl groups, for example cyclopentyl, cyclohexyl and cycloheptyl; the aryl groups preferably represent a

phenyl, a phenyl mono- or polysubstituted by one or more C₁-C₆ alkyl, C₅-C₇ cycloalkyl, phenyl and amino substituents; the halogens preferably represent Br, Cl, and F; and the mono (or poly) haloalkyl groups are preferably mono (or poly) chloro or fluoro C₁-C₆ alkyl groups, for example CF₃.

- 5 The compounds represented by formula (I) may be prepared by the coupling reaction of an appropriately substituted propargylic alcohol (A) with a 2-naphthol carrying a bithienyl group (B) (scheme 1).

This reaction is performed in dichloromethane in the presence of an acid catalyst (PPTS : pyridinium paratoluenesulfonate) :

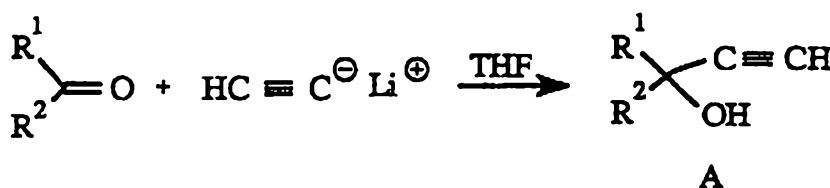
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where R¹, R² and Th₂ have the definitions above.

Scheme 1

- 15 The propargylic alcohols may be prepared as described in scheme 2, by the action of lithium acetylide on an appropriately substituted ketone.



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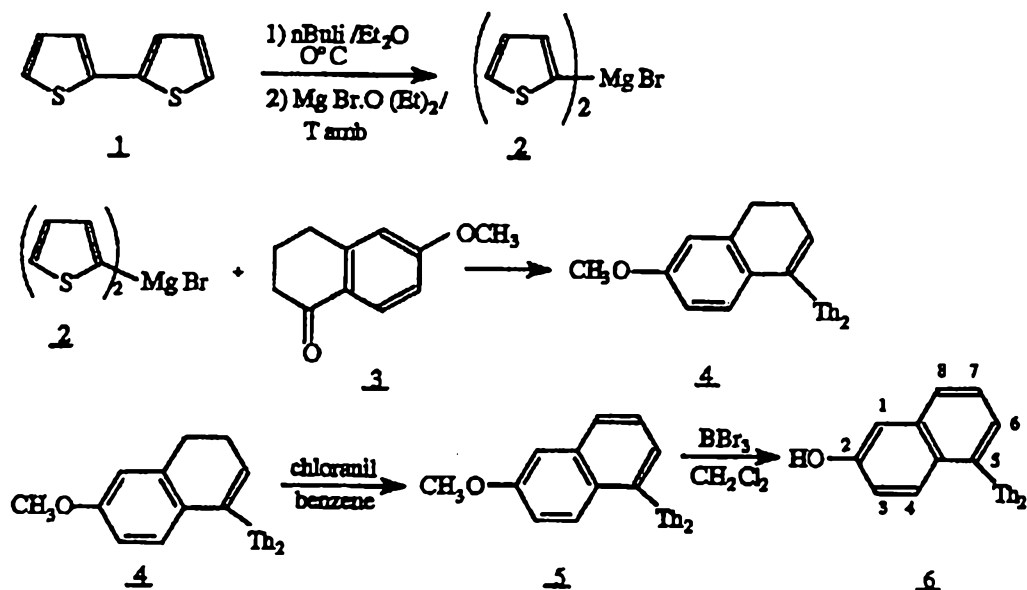
Scheme 2

The preparation of the naphthols (B) may be performed in two different ways depending on whether the bithienyl group will occupy the 7 position or the other positions (5, 6, 8-10) on the target molecule (I).

- 25 The preparation of 5-(2,2'-bithien-5-yl)-2-hydroxynaphthalene 6 (precursor of the naphthopyrans (I) substituted in position 7 by the Th₂ group) is performed in four stages as shown in scheme 3. Bithienyl magnesium bromide 2 (obtained by a transmetalation reaction starting from 2,2'-bithiophene 1) reacts with 6-methoxy-1-tetralone (3) to give the derivative 4. After an oxidation reaction in the presence of chloranil (2,3,5,6-tetrachlorobenzoquinone), the resulting compound 5 is demethylated by boron tribromide in dichloromethane

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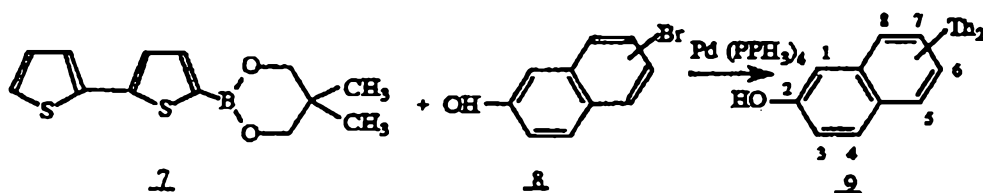
to give the desired naphthol 6.



5

Scheme 3

The naphthols of type 9 (used to produce naphthopyrans (I) substituted in the 5, 6, 8, 9 or 10 position by a Th₂ group) are prepared by a coupling reaction catalysed by a palladium catalyst such as Pd(PPh₃)₄ between the boron derivative 7 of bithiophene and a bromo-2-naphthol (scheme 4) or a 2-naphthol substituted by a triflate group, the bromo substituent or triflate group occupying one of positions 3, 4, 6-8 of the naphthalene ring.



15

Scheme 4

The naphthopyrans of the present invention show particularly advantageous photochromic properties compared to those of molecules of the same family of the prior art and in particular to [3H]naphtho[2,1-b]pyrans having a bithienyl substituent in position 7 of the naphthalene ring. A toluene solution of the compounds of formula (I) colours and discolours very rapidly at ambient temperature. The major advantage of these new compounds is that the rapid responses to coloration and discoloration do not cause the significant reduction

20

in colorability which might be expected, and may even sometimes be accompanied by an increase in colorability.

Another advantage of the compounds according to the invention is that they colour under the action of ultraviolet light with a wavelength greater than
5 380 nm, whereas the majority of similar compounds from the prior art colour little or not at all under the same conditions. This property makes possible the use of this type of photochromic compound in the manufacture of transparent articles from organic glass absorbing ultraviolet radiation of shorter wavelength (glazing for buildings, aircraft or car windscreens), in particular for the
10 manufacture of spectacle lenses or helmet visors.

The compounds according to the invention may be directly introduced into the transparent polymer matrix or incorporated in a composition intended to be applied to a transparent organic polymer material. In this case, the compounds object of the invention are dissolved in an appropriate solvent (for
15 example chloroform, ethyl acetate, acetone, acetonitrile, dichloromethane, benzene) and incorporated into a polymer solution (for example polyurethane, polyacrylate, polymethacrylate) in the same solvent.

The compositions are then applied in the form of a film of a few micrometres in thickness onto a transparent polymer substrate (such as
20 polycarbonate, cellulose acetate, poly(alkyl acrylate), to obtain a photochromic material which can colour in the presence of ultraviolet radiation and return rapidly to the colourless and transparent state in the absence of the light source.

The compounds according to the invention have the advantage of
25 allowing this colour change a large number of times at close to ambient temperatures.

More precisely, the compounds according to the invention may be introduced into a composition intended to be applied to or introduced into a transparent organic polymer material to obtain a transparent photochromic
30 article. They may also be introduced into solid compositions such as plastic films, plates and lenses to produce materials usable in particular as ophthalmic lenses, sunglasses, viewfinders, camera optics and filters, glazing for buildings, aircraft or car windscreens and helmet visors.

The liquid compositions which are an object of the invention are
35 essentially characterized by the fact that they contain the compounds according to the invention in dissolved or dispersed form in a medium based on solvents

suitable to be applied to or introduced into a transparent polymer material.

Solvents which may particularly be used are organic solvents selected from benzene, toluene, chloroform, dichloromethane, ethyl acetate, methyl ethyl ketone, acetone, ethyl alcohol, methyl alcohol, acetonitrile, tetrahydrofuran, dioxane, ethylene glycol methyl ether, dimethylformamide, dimethyl sulfoxide, methylcellosolve, morpholine and ethylene glycol.

When the compounds according to the invention are dispersed, the medium may also contain water.

According to another embodiment, the compounds according to the invention may be introduced into and preferably dissolved in colourless or transparent solutions prepared from polymers, copolymers or mixtures of transparent polymers in an appropriate organic solvent.

These polymers and copolymers may include the polyurethanes, the poly(meth)acrylates, the polyallyl(meth)acrylates, the cellulose derivatives, such as nitrocellulose, cellulose acetate and ethylcellulose, polyvinyl chloride, polystyrene, poly(alkyl)styrene, and polyvinylpyrrolidone.

Examples of such solutions are, amongst others, solutions of nitrocellulose in acetonitrile, polyvinyl acetate in acetone, polyvinyl chloride in methyl ethyl ketone, polymethyl methacrylate in acetone, cellulose acetate in dimethylformamide, polyvinylpyrrolidone in acetonitrile, polystyrene in benzene, ethylcellulose in methylene chloride.

These compositions may be applied to transparent substrates such as polyethylene glycol terephthalate, borax paper, cellulose triacetate and dried to obtain a photochromic material which can colour in the presence of ultraviolet radiation, and which returns to the colourless and transparent state in the absence of the radiation source.

The photochromic compounds according to the invention or the compositions containing them described above may be applied to or incorporated into a solid transparent organic polymer material suitable for transparent articles such as ophthalmic lenses or materials which may be used in sunglasses, viewfinders, camera optics and filters, glazing for buildings, aircraft or car windscreens and helmet visors.

Suitable transparent solid materials which may be used to produce ophthalmic lenses according to the invention include the polyol (allyl carbonate) polymers, the polyacrylates, the poly(alkyl acrylates) such as the polymethyl methacrylates, cellulose acetate, cellulose triacetate, cellulose propionate

acetate, cellulose butyrate acetate, poly(vinyl acetate), poly(vinyl alcohol), the polyurethanes, the polycarbonates, the polyethylene terephthalates, the polystyrenes, the (polystyrene-methyl-methacrylates), the styrene acrylonitrile copolymers, the polyvinyl butyrates.

5 Transparent copolymers or mixtures of transparent polymers are also suitable to produce such materials.

 Examples of these are materials prepared from polycarbonates such as poly(4,4'-dioxydiphenol-2,2-propane), polymethyl methacrylate, the polyol (allyl carbonates) such as in particular diethylene glycol bis(allyl carbonate) and its
10 copolymers such as for example with vinyl acetate. Suitable materials are in particular the copolymers of diethylene glycol bis(allyl carbonate) and vinyl acetate (80-90/10-20) and also the copolymer of diethylene glycol bis(allyl carbonate) and vinyl acetate, cellulose acetate and cellulose propionate, cellulose butyrate (80-85/15-20).

15 The polyol (allyl carbonates) are prepared by using the allyl carbonates of aliphatic or aromatic, linear or branched, liquid polyols, such as the aliphatic glycol bis(allyl carbonates) or the alkylene bis(allyl carbonates). Among the polyol (allyl carbonates) which may be used to prepare the solid transparent materials usable according to the invention are ethylene glycol bis(allyl
20 carbonate), diethylene glycol bis(2-methylallyl carbonate), diethylene glycol bis(allyl carbonate), ethylene glycol bis(2-chloroallyl carbonate), triethylene glycol bis(allyl carbonate), 1,3-propanediol bis(allyl carbonate), propylene glycol bis(2-ethylallyl carbonate), 1,3-butanediol bis(allyl carbonate), 1,4-butanediol bis(2-bromoallyl carbonate), dipropylene glycol bis(allyl carbonate), trimethylene
25 glycol bis(2-ethylallyl carbonate), pentamethylene glycol bis(allyl carbonate), isopropylene bisphenol bis(allyl carbonate). The most important product is ethylene glycol bis(allyl carbonate), also known under the name CR39.

 The quantity of photochromic compounds to be used according to the invention, either in composition, or at the time of its introduction into the solid
30 substrate, is not critical and generally depends on the intensity of the colour which the composition may impart to the material after exposure to radiation. In general, the more the photochromic compound added, the greater the coloration under irradiation.

 According to the invention, a sufficient quantity is used to impart to the
35 treated material the property of changing colour on exposure to radiation. This quantity of photochromic compound is generally between 0.01 and 20% by

weight and preferably between 0.05 and 10% by weight with respect to the total weight of the optical material or composition.

The photochromic compounds according to the invention may also be introduced into a temporary transfer substrate (such as a varnish forming a coating on a substrate) and subsequently transferred thermally into the substrate as disclosed in particular in the patents US-4 286 957 or US-4 880 667.

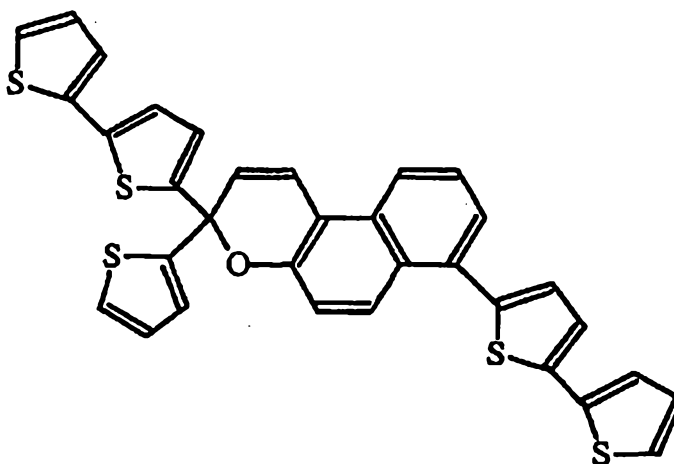
These compounds may be used with other photochromic compounds, such as the photochromic compounds giving different colours such as blue, green known in the state of the art. The spiro(indoline-oxazines), well known in the art, may thus be used.

The following examples are intended to illustrate the invention without in any way being limiting.

In the examples, except where stated otherwise, all percentages and parts are by weight.

Comparative example 1

Synthesis of 3,7-di(2,2'-bithien-5-yl)-3-(thien-2-yl)-[3H]-naphtho[2,1-b]pyran.



Step 1

0.072 mole of 2-bromothiophene and 2 g of [1,3-bis(diphenylphosphino)propane]dichloronickel (II) previously dissolved in 100 ml of anhydrous ethyl ether were introduced into a two-necked 250 ml round-bottomed flask fitted with a stirring system and surrounded with a coolant. Freshly prepared 2-thienyl magnesium bromide (0.072 mole) was added at 0°C over about 40 minutes. The reaction mixture was stirred for 3 hours. The

mixture was cooled in an ice bath and a 10% aqueous solution of sulfuric acid was added slowly until two clear phases were obtained. After decantation, the aqueous phase was extracted with ethyl ether (3 x 100 ml). The combined organic phases were dried over magnesium sulfate.

5 After evaporation of the solvent under reduced pressure, the crude product was purified by chromatography on a silica column, eluted with pure pentane.

The 2,2'-bithiophene was obtained in 95% yield

Molecular formula : $C_8H_6S_2$

10 Molecular weight : 166.220

Melting point : 32°C.

Step 2

A mixture under argon of 6 mmoles of 4-methoxybenzoyl chloride, 6 mmoles of the 2,2'-bithiophene prepared in step 1 and 15 ml of anhydrous benzene was cooled in ice-water. 6 mmoles of $SnCl_4$ were added slowly. The mixture was stirred for 30 minutes. The formation of a precipitate was observed, 30 ml of benzene, then 15 ml of an aqueous 10% hydrochloric acid solution were added. When the precipitate had completely dissolved, the aqueous phase was extracted with benzene. The resulting organic phase was washed with water until a neutral pH was reached, dried over magnesium sulfate then concentrated under reduced pressure. The resulting (2,2'-bithienyl) (thien-2-yl) ketone was washed with pentane then filtered.

Molecular formula : $C_{13}H_8S_3$

Molecular weight : 276.404

25 Yield : 83%

Melting point : 98°C.

Step 3

A mixture under argon of lithium acetylide (15 mmoles) and 200 ml of anhydrous THF was cooled to 0°C in an ice-water bath. 1.5 mmole of the ketone prepared in step 2 were added in a single step. The reaction mixture was allowed to return to ambient temperature and stirred for 3 hours. The reaction was monitored by thin-layer chromatography on silica. The solution was then hydrolysed with a saturated aqueous solution of ammonium chloride. The water-THF mixture was extracted with ethyl ether.

35 The resulting organic phases were combined, dried over magnesium sulfate, then concentrated under reduced pressure. The crude product was

chromatographed on silica gel with pentane/dichloromethane mixtures of increasing polarity (50 : 50 to 0 : 100). The 1-(2,2'-bithien-5-yl)-1-(thien-2-yl)prop-2-yn-1-ol was isolated in the form of an oil.

Yield : 81%

5 Molecular formula : $C_{15}H_{10}OS_3$

Molecular weight : 302.441.

Step 4

0.018 Mole of the bithiophene prepared in step 3 dissolved in 90 ml of anhydrous ethyl ether were introduced into a three-necked 250 ml round-bottomed flask fitted with a stirring system and surrounded with a coolant. The reaction mixture was cooled to 0°C, then 0.021 mole of n-butyl lithium 1.6 M in hexane were added slowly.

The reaction proceeded under argon. After an hour, 0.018 mole of $MgBr.O(Et)_2$ were added to the lithium derivative.

15 The reaction mixture was left for two hours at ambient temperature, then 18 mmoles of 6-methoxy-2-tetralone dissolved in 15 ml of anhydrous ether were added. The mixture was refluxed for 5 hours. The reaction mixture was allowed to return to ambient temperature, then cooled (ice bath). A 10% aqueous solution of sulfuric acid was slowly added until two clear phases formed. After decantation, the aqueous phase was extracted with ethyl ether (3 x 100 ml).

20 After evaporation of the solvent under reduced pressure, the crude product was purified by chromatography on a silica column and eluted with pentane/ethyl ether mixtures of increasing polarity (100 : 0 to 80 : 20). The 1-(2,2'-bithien-5-yl)-3,4-dihydro-6-methoxynaphthalene was isolated in the form of an oil.

Yield : 60%

Molecular formula : $C_{19}H_{16}OS_2$

Molecular weight : 324.467.

Step 5

30 27 mmoles of chloranil and 50 ml of anhydrous benzene were introduced into a two-necked 250 ml flask fitted with a stirring system and surrounded with a coolant. The reaction proceeded under argon. 9.2 mmoles of the cycloalkene obtained from step 4, dissolved in 20 ml of benzene, were added drop by drop using a dropping funnel, and the reaction mixture was then refluxed for 5 hours.

35 The cooled solution was filtered over silica under vacuum and then rapidly eluted with ethyl ether. After evaporation of the solvent under reduced pressure,

the crude product was purified by chromatography on a silica column and eluted with pentane/ethyl ether mixtures of increasing polarity (100 : 0 to 80 : 20).

The oily residue was 1-(2,2'-bithien-5-yl)-6-methoxynaphthalene.

Yield : 93%

5 Molecular formula : $C_{19}H_{14}OS_2$

Molecular weight : 322.451.

Step 6

8.6 mmoles of the compound obtained from step 5 and 15 ml of freshly distilled CH_2Cl_2 were introduced into a three-necked 50 ml flask fitted with a stirring system and surrounded with a coolant. The reaction mixture was cooled to 0°C, then 11.2 ml (11 mmoles) of a 1 M solution of BBr_3 in CH_2Cl_2 were added. The addition lasted about 20 minutes. The reaction proceeded under argon. The mixture was then refluxed for 15 hours. The reaction mixture was then allowed to return to ambient temperature, then neutralized with a saturated solution of Na_2CO_3 until a pH of 7 was reached. The mixture obtained was filtered over celite. After decantation, the aqueous phase was extracted with CH_2Cl_2 (3 x 10 ml). The organic phases were combined, washed, with water, then dried over magnesium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by chromatography on a silica column and eluted with pentane/ethyl ether mixtures of increasing polarity (100 : 0 to 50 : 50). The 1-(2,2'-bithien-5-yl)-6-hydroxynaphthalene was isolated in a yield of 24%.

Molecular formula : $C_{18}H_{12}OS_2$

Molecular weight : 308.424

25 Melting point : 133°C.

Step 7

A mixture under argon of 1 mmole of the propargylic alcohol prepared in step 3, 1 mmole of the naphthol prepared in step 6 and 20 ml of CH_2Cl_2 were stirred.

30 A catalytic quantity of pyridinium paratoluenesulfonate was added at ambient temperature. The reaction mixture was stirred for 6 to 8 hours. The reaction was monitored by analytical thin-layer chromatography. The mixture was poured onto an iced 5% soda solution. The aqueous phase was extracted three times with dichloromethane. The organic phases were combined, dried over magnesium sulfate, then concentrated under reduced pressure. The residue was purified by chromatography on a silica column eluted with

pentane/dichloromethane mixtures of increasing polarity (100 : 0 to 50 : 50). The 3,7-di(2,2'-bithien-5-yl)-3-(thien-2-yl)[3H]naphtho[2,1-b]pyran was isolated in a yield of 30%.

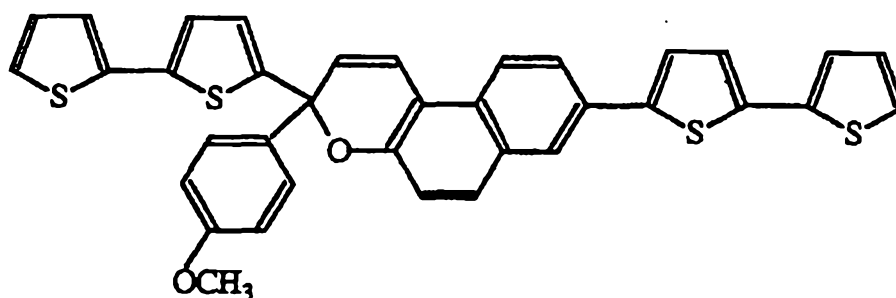
Molecular formula : $C_{33}H_{20}OS_5$

5 Melting point : 98°C.

Example 1

Synthesis of 3,8-di(2,2'-bithien-5-yl)-3-(4-methoxyphenyl)-[3H]-naphtho[2,1-b]pyran.

10



Step 1

15 The (2,2'-bithien-5-yl) (4-methoxyphenyl) ketone was prepared according to the same procedure as that described in step 2 of comparative example 1. The precursors in this case were 4-methoxybenzoyl chloride and 2,2'-bithiophene.

Yield : 85%

Molecular formula : $C_{16}H_{12}O_2S_2$

20 Molecular weight : 300.402

Melting point : 119-120°C.

Step 2

25 The 1-(2,2'-bithien-5-yl)-1-(4-methoxyphenyl)prop-2-yn-1-ol was prepared according to the same procedure as that described in step 3 of comparative example 1. The precursor in this case was the ketone described above (step 1, example 1).

Yield : 87%

Molecular formula : $C_{18}H_{14}O_2S_2$

Molecular weight : 326.441

30 Oily product.

Step 3

6 mmoles of 2'2'-bithiophene dissolved in 30 ml of anhydrous THF were introduced into a three-necked round-bottomed flask under argon. The mixture was cooled to -40°C. 2.65 ml (1.05 mmole) of a 2.5 M solution of nBuLi in
 5 hexane were then added slowly. The resulting mixture was stirred for 1 hour at -40°C, then cooled to -90°C. 4 ml (18 mmoles) of B(OBu)₃ were then added as quickly as possible. The mixture was allowed to return to ambient temperature, then 30 mmoles of 2,2-dimethylpropane-1,3-diol were added. The resulting mixture was stirred for 10 minutes, then hydrolysed with 30 ml of water. The
 10 water-THF mixture was extracted with benzene (3 x 30 ml). The resulting organic phase was washed several times with a saturated aqueous solution of NaCl, dried over magnesium sulfate, then concentrated under reduced pressure. The crude product was chromatographed on a silica column eluted with pentane/dichloromethane mixtures of increasing polarity (100 : 0 to 70 : 30)
 15 giving 5,5-dimethyl-2-(2,2'-bithien-2-yl)[1,3,2]dioxaborinane.

Yield : 46%

Molecular formula : C₁₃H₂₅O₂S₂B

Molecular weight : 278.20.

Step 4

20 A mixture of 3.59 mmoles of the boronic ester prepared in step 3 (example 1), 3 mmoles of 6-bromo-2-hydroxynaphthalene, a catalytic quantity of Pd(PPh₃)₄ and 9 ml of DMF was brought to 100°C for 24 hours. The reaction mixture was allowed to return to ambient temperature, then diluted with 20 ml of THF. The solution was filtered over celite. The THF was evaporated under
 25 reduced pressure. The organic products precipitated on addition of water. These were filtered off and recrystallized from a heptane/THF mixture.

The 2-(2,2'-bithien-5-yl)-6-hydroxynaphthalene was obtained in 78% yield.

Molecular formula : C₁₈H₁₂OS₂

30 Molecular weight : 308.329

Melting point : 231°C.

Step 5

The 3,8-di(2,2'-bithien-5-yl)-3-(4-methoxyphenyl)-[3H]-naphtho[2,1-b]pyran was obtained according to the procedure described in step 7 of comparative example 1. The precursors in this case were the propargylic
 35 alcohol and the naphthol described in steps 2 and 4 respectively of example 1.

The final product was recrystallized from toluene.

Yield : 72%

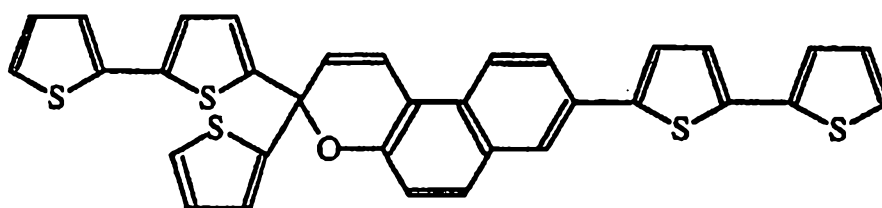
Molecular formula : $C_{36}H_{24}O_2S_4$

Molecular weight : 616.658

5 Melting point : 210°C.

Example 2

Synthesis of 3,8-di(2,2'-bithien-5-yl)-3-(thien-2-yl)-[3H]-naphtho[2,1-b]pyran.



10

Step 1

The (2,2'-bithien-5-yl) (thien-2-yl) ketone was prepared from 2-thiophenecarboxylic acid chloride and 2,2'-bithiophene according to the same
15 procedure as that described in step 2 of comparative example 1.

Yield : 83%

Molecular formula : $C_{13}H_8OS_4$

Molecular weight : 276.404

20 Melting point : 98°C.

Step 2

The 1-(2,2'-bithien-5-yl)-1-(thien-2-yl)prop-2-yn-1-ol was prepared from the ketone described in step 1 (example 2) according to the same procedure as that described in step 3 of comparative example 1.

Yield : 81%

25 Molecular formula : $C_{35}H_{10}OS_3$

Molecular weight : 302.441

Oily product.

Step 3

The 3,8-di(2,2'-bithien-5-yl)-3-(thien-2-yl)-[3H]-naphtho[2,1-b]pyran was
30 obtained according to the procedure described in step 7 of comparative example 1. The precursors in this case were the propargylic alcohol described in step 2 above (example 2) and the naphthol described in step 4 of example 1. The final product was recrystallized from toluene.

Yield : 67%

Molecular formula : $C_{33}H_{20}OS_5$

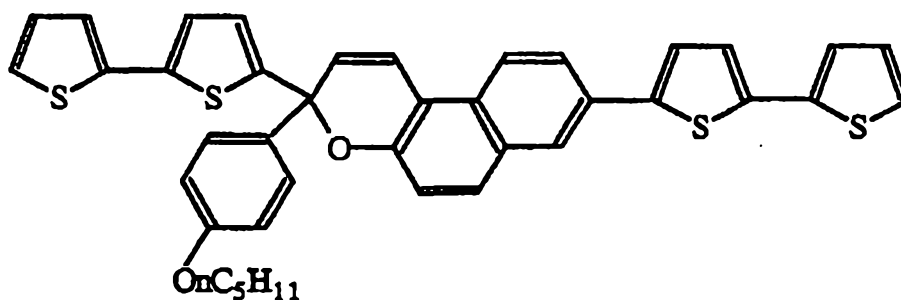
Molecular weight : 592.692

Melting point : 213°C.

5

Example 3

Synthesis of 3,8-di(2,2'-bithien-5-yl)-3-(4-pentyloxyphenyl)-[3H]-naphtho[2,1-b]pyran.



10

Step 1

The (2,2'-bithien-5-yl) (4-pentyloxyphenyl) ketone was prepared from 4-pentyloxybenzoyl chloride and 2,2'-bithiophene according to the same procedure as that described in step 2 of comparative example 1.

15

Yield : 93%

Molecular formula : $C_{20}H_{20}O_2S_2$

Molecular weight : 356.350

Melting point : 114°C.

20

Step 2

The 1-(2,2'-bithien-5-yl)-1-(4-pentyloxyphenyl)prop-2-yn-1-ol was prepared from the ketone described in step 1 (example 3) according to the same procedure as that described in step 3 of comparative example 1.

Yield : 81%

25

Molecular formula : $C_{15}H_{10}OS_3$

Molecular weight : 302.441

Oily product.

Step 3

The 3,8-di(2,2'-bithien-5-yl)-3-(4-pentyloxyphenyl)-[3H]-naphtho[2,1-b]pyran was obtained according to the procedure described in step 7 of comparative example 1. The precursors in this case were the propargylic

30

alcohol described in step 2 above (example 3) and the naphthol described in step 4 of example 1. The final product was recrystallized from heptane.

Yield : 78%

Molecular formula : $C_{40}H_{32}O_2S_4$

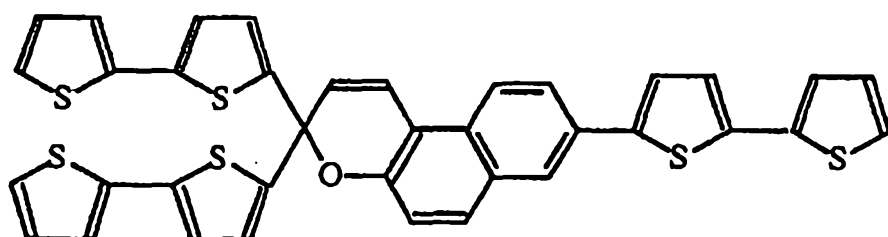
5 Molecular weight : 672.702

Melting point : 147°C.

Example 4

Synthesis of 3,3,8-tri(2,2'-bithien-5-yl)-[3H]-naphtho[2,1-b]pyran.

10



Step 1

15 The di(2,2'-bithien-5-yl) ketone was prepared from 5-(2'-thienyl)-2-thenoic acid chloride and 2,2'-bithiophene according to the same procedure as that described in step 2 of comparative example 1. The purification was performed by chromatography on a silica column using pentane/ CH_2Cl_2 mixtures of increasing polarity (0 : 100 to 50 : 50) as eluents. A recrystallization was carried out from benzene.

20 Yield : 66%

Molecular formula : $C_{17}H_{10}OS_4$

Molecular weight : 358.450

Melting point : 181°C.

Step 2

25 The 1,1-di(2,2'-bithien-5-yl)prop-2-yn-1-ol was prepared from the ketone described in step 1 (example 4) according to the same procedure as that described in step 3 of comparative example 1. It was used without purification for the following step, as chromatography on silica or alumina degraded this compound.

30 Molecular formula : $C_{19}H_{12}OS_4$

Molecular weight : 384.472

Oily product.

Step 3

The 3,3,8-tri(2,2'-bithien-5-yl)-[3H]-naphtho[2,1-b]pyran was obtained according to the procedure described in step 7 of comparative example 1. The precursors in this case were the propargylic alcohol described in step 2 above (example 4) and the naphthol described in step 4 of example 1. The final product was recrystallized from toluene.

Yield : 44% (steps 2 + step 3)

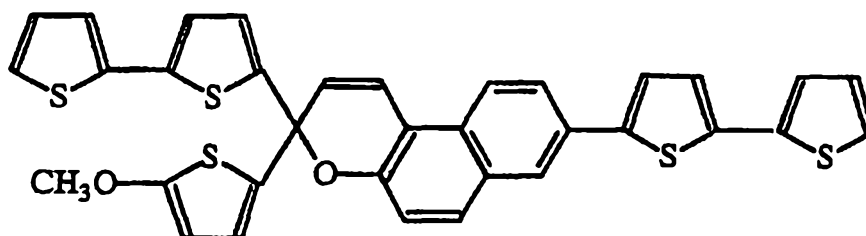
Molecular formula : $C_{37}H_{22}OS_6$

Molecular weight : 674.802

Melting point : 223°C.

Example 5

Synthesis of 3,8-di(2,2'-bithien-5-yl)-3-(5-methoxythien-2-yl)-[3H]-naphtho[2,1-b]pyran.



Step 1

The (2,2'-bithien-5-yl) (5-methoxythien-2-yl) ketone was prepared from 5-methoxythienoic acid chloride and 2,2'-bithiophene according to the same procedure as that described in step 2 of comparative example 1. The purification was performed by chromatography on a silica column using pentane/ CH_2Cl_2 mixtures of increasing polarity as eluents.

Yield : 72%

Molecular formula : $C_{14}H_{10}O_2S_3$

Molecular weight : 306.350

Melting point : 106°C.

Step 2

The 1-(2,2'-bithien-5-yl)-1-(5-methoxythien-2-yl)prop-2-yn-1-ol was prepared from the ketone described in step 1 (example 5) according to the same procedure as that described in step 3 of comparative example 1. It was used without purification for the following step, as chromatography on silica

degraded the compound.

Molecular formula : $C_{16}H_{12}O_2S_3$

Molecular weight : 322.374

Oily product.

5

Step 3

The 3,8-di(2,2'-bithien-5-yl)-3-(5-methoxythien-2-yl)-[3H]-naphtho[2,1-b]pyran was obtained according to the procedure described in step 7 of comparative example 1. The precursors in this case were the propargylic alcohol described in step 2 (example 5) and the naphthol described in step 4 of example 1. The final product was recrystallized from toluene.

10

Yield : 52% (step 2 + step 3)

Molecular formula : $C_{34}H_{22}O_2S_5$

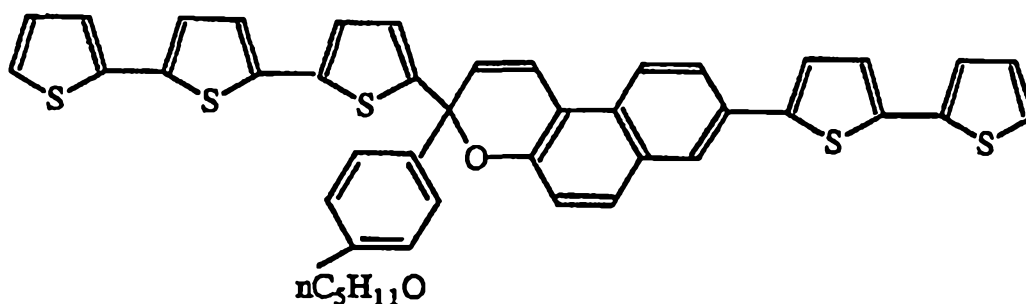
Molecular weight : 622.702

Melting point : 204°C.

15

Example 6

Synthesis of 8-(2,2'-bithien-5-yl)-3-(4-pentyloxyphenyl)-3-(2,2'-5',2''-terthien-5-yl)-[3H]-naphtho[2,1-b]pyran.



20

Step 1

The (4-pentyloxyphenyl) (2,2'-5',2''-terthien-5-yl) ketone was prepared from 4-pentyloxybenzoyl chloride and 2,2'-5',2''-terthiophene according to the same procedure as that described in step 2 of comparative example 1. The purification was performed by chromatography on a silica column using pentane/ CH_2Cl_2 mixtures of increasing polarity as eluents.

25

Yield : 53%

Molecular formula : $C_{24}H_{22}O_2S_3$

30

Molecular weight : 438.460

Melting point : 174°C.

Step 2

The 1-(4-pentyloxyphenyl)-1-(2,2'-5',2''-terthien-5-yl)prop-2-yn-1-ol was prepared from the ketone described in step 1 (example 6) according to the same procedure as that described in step 3 of comparative example 1.

5 Yield : 73%

Molecular formula : $C_{27}H_{24}O_2S_3$

Molecular weight : 478.275

Oily product.

Step 3

10 The 8-(2,2'-bithien-5-yl)-3-(4-pentyloxyphenyl)-3-(2,2'-5',2''-terthien-5-yl)[3H]-naphtho[2,1-b]pyran was obtained according to the procedure described in step 7 of comparative example 1. The precursors in this case were the propargylic alcohol described in step 2 above (example 6) and the naphthol described in step 4 of example 1. The final product was recrystallized from
15 toluene.

Yield : 63%

Molecular formula : $C_{44}H_{35}O_2S_5$

Molecular weight : 755.812

Melting point : 158°C.

20 Comparative example 2

3,3'-Diphenyl[3H]naphtho[2,1-b]pyran was prepared as follows :

10 mmoles of 1,1-diphenyl-2-propyn-1-ol and 11 mmoles of 2-naphthol were dissolved in anhydrous toluene (20 ml) with heating. A catalytic quantity of paratoluenesulfonic acid was added. The mixture was brought to reflux under
25 argon for 2 hours 30 minutes. It was allowed to return to ambient temperature and 20 ml of a 5% aqueous solution of NaOH was added. The aqueous phase was continuously extracted with methylene chloride. The organic phases were combined and dried over magnesium sulfate. The solvent was evaporated under reduced pressure. The resulting product was purified by washing with
30 hexane.

Yield : 62%

Molecular formula : $C_{24}H_{18}O$

Molecular weight : 334.42

Melting point : 158°C

35 Comparative example 3

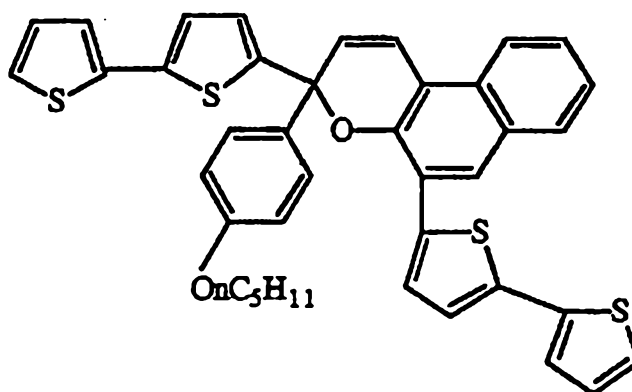
3,3'-Di(4-methoxyphenyl)[3H]naphtho[2,1-b]pyran was prepared as

follows :

The procedure was the same as that for comparative example 2, except that the precursor was 1,1-di(4-methoxyphenyl)-2-propyn-1-ol.

5 Example 7

Synthesis of 3,5-di(2,2'-bithien-5-yl)-3-(4-pentyloxyphenyl)-[3H]-naphtho[2,1-b]pyran.



10

Step 1

The (2,2'-bithien-5-yl) (4-pentyloxyphenyl) ketone was prepared according to the same procedure as that described in step 1 of example 3.

Step 2

15 The 1-(2,2'-bithien-5-yl)-1-(4-pentyloxyphenyl)prop-2-yn-1-ol was prepared according to the same procedure as that described in step 2 of example 3.

Step 3

20 12 mmoles of dihydroxynaphthalene and 25 ml of pyridine under argon were stirred for 20 minutes at ambient temperature. The mixture was cooled to 0°C and 2.1 ml (12 mmoles) of trifluoromethanesulfonic anhydride were added slowly.

25 The mixture was allowed to return to ambient temperature and stirred overnight. The solution was then poured onto iced water (25 ml), then extracted with ethyl ether (3 x 30 ml). The resulting organic phase was washed with water (2 x 20 ml), then with a saturated aqueous salt solution (20 ml). The organic phase was dried over magnesium sulfate. After evaporation under reduced pressure, a brown oil was isolated. The crude product was chromatographed on a silica column, eluted with pentane/ether mixtures of increasing polarity (100/0

to 70/30) to give 2-hydroxy-3-trifluoromethane sulfonate naphthalene.

Yield : 20%

Molecular formula : $C_{11}H_7O_3SF_3$

Molecular weight : 292.230

5 Melting point : 62-63°C.

Step 4

The 5,5-dimethyl-2-(2,2'-bithien-2-yl)[1,3,2]dioxaborinane was obtained according to the procedure of step 3 of example 2.

Step 5

10 The 2-(2,2'-bithien-5-yl)-3-hydroxynaphthalene was obtained according to the same experimental procedure as that described in step 4 of example 2.

11.34 mmoles of the boronic ester (step 4 above), 9.45 mmoles of the naphthol prepared in step 3 above, 14.17 mmoles of K_3PO_4 , a catalytic quantity of $Pd(PPh_3)_4$ and 13 ml of DMF were used.

15 Yield : 74%

Molecular formula : $C_{18}H_{12}OS_2$

Molecular weight : 308.329

Melting point : 174°C.

Step 6

20 The 3,5-di(2,2'-bithien-5-yl)-3-(4-pentyloxyphenyl)-[3H]-naphtho[2,1-b]pyran was obtained according to the procedure described in step 7 of example 1.

The precursors in this case were the propargylic alcohol and the naphthol described in steps 2 and 5 respectively of example 7.

25 Yield : 76%

Molecular formula : $C_{40}H_{32}O_2S_4$

Molecular weight : 672.702

Melting point : 77°C.

30 Example 8

10^{-4} M solutions in toluene of the photochromic compounds obtained from the examples and the comparative examples were prepared.

The photochromic properties were determined at 20°C on a Beckmann DU 700 electronic absorption spectrophotometer. An external irradiation, perpendicular to the analysis beam, was supplied by a 150 W xenon arc lamp fitted with a water filter, a diaphragm and a light guide. The luminous flux was

35

maintained constant during all the recordings.

In an initial experiment, the absorption spectrum of the coloured form obtained after 2 minutes of irradiation was recorded to determine the maximum absorption wavelength in the visible (λ_{max}).

- 5 In a second experiment, the variation of the absorbance of the solution at the absorption λ_{max} as a function of the irradiation time was recorded, the absorbance maximum obtained after a few seconds to several tens of seconds of irradiation was measured (A_{∞}). The irradiation was then stopped. The decrease of the absorbance as a function of time was then recorded, giving a
- 10 measure of the thermal decoloration constant ($k\Delta$).

The results are given in table I below.

TABLE I

Solvent toluene	(A_{∞})	$k\Delta$ (s^{-1})	λ_{max} (nm)
T = 20°C			
Example 1	0.43	0.19	549
Example 2	0.36	0.18	549
Example 3	0.38	0.19	548
Example 4	0.35	0.29	564
Example 5	0.21	0.55	560
Example 6	0.50	0.19	564
Comp. example 1	0.15	0.60	520
Comp. example 2	0.23	0.06	423
Comp. example 3	0.13	0.24	480

- 15 The results show that the photochromic compounds according to the invention have a maximal absorption wavelength (λ_{max}) very substantially shifted towards high wavelengths (bathochromic shift) and a high absorbance maximum combined with rapid kinetics.

20 Example 9

10^{-4} M solutions in toluene of the photochromic compounds obtained in example 1 and in comparative example 2 were irradiated under the conditions of example 8. This time the coloration times (time necessary to reach photostationary equilibrium) and the percentage discoloration 10 s after the end

of irradiation were measured.

Compound	<u>Coloration</u>	<u>Discoloration</u>
	Time necessary to reach photostationary equilibrium (s)	% discoloration at 10 s
Example 1	14	83%
Comparative example 2	26	50%

Example 10

5 10^{-4} M solutions in toluene of the photochromic compounds obtained in example 1 and in comparative example 2 were irradiated under the conditions of example 8, but with a GG400 (Schott) filter, which cut out all UV radiation with wavelength less than 380 nm, placed in the light beam.

10 The solution prepared from comparative example 2 did not develop any coloration, but the solution prepared from the photochromic compound of example 1 retained its photochromic properties.

Example 11

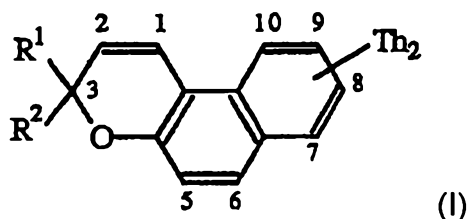
15 A polyurethane film (thickness 15 μm) containing $2 \cdot 10^{-5}$ ml/g of the naphthopyran of example 1 was prepared. Under the same conditions of irradiation as those described in example 8, this sample showed excellent photochromic properties :

$$A_{\infty} = 0.1, \lambda_{\text{max}} = 344 \text{ nm}, k_{\Delta} = 0.14 \text{ s}^{-1}$$

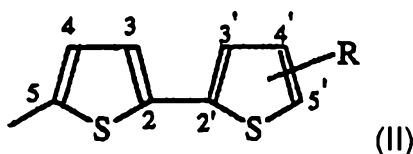
20 Although slower in comparison with the toluene solution of example 8, the discoloration speed remained very rapid.

CLAIMS

1. Photochromic compound containing a [3H]naphtho[2,1-b]pyran structure, characterized in that it contains at least one bithienyl group, substituted or not, in one of positions 5 to 10 of the naphthalene ring of the [3H]naphtho[2,1-b]pyran structure and at least one bithienyl or terthienyl group, substituted or not, in position 3 of said structure and excluding compounds of [3H]naphtho[2,1-b]pyran structure containing a single bithienyl group in position 3 of said structure and a bithienyl group in position 7 of the naphthalene ring.
2. Compound according to claim 1, characterized in that it contains a bithienyl group in one of positions 5, 6, 8-10 of the naphthalene ring.
3. Photochromic compound according to claim 1 or 2, characterized in that it corresponds to the formula :



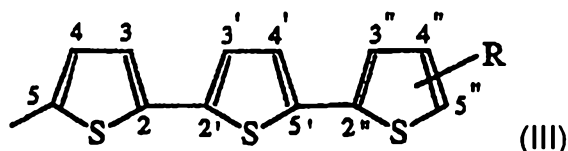
in which Th₂ represents the a bithienyl group corresponding to the formula :



in which :

R represents a substituent in positions 3, 3', 4, 4' or 5', selected from a hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group, an OR³, SR³, COR³ and COOR³ group, where R³ represents a hydrogen atom, an alkyl group, an aryl group, an amino group, an NO₂, CN or SCN group, a halogen atom, or a mono- or polyhaloalkyl group;

R¹ designates a Th₂ group as defined above or a Th₃ group of formula :



where

R is a substituent as defined above which may occupy one of the positions 3, 3', 3'', 4, 4', 4'', 5'', and

R² designates a Th₂ group, a Th₃ group, an aryl group, a naphthyl group, a thienyl group, a furanyl group, a pyrrolyl group or an N-alkylpyrrolyl group.

4. Photochromic compound according to claim 3, characterized in that the alkyl groups are C₁-C₆ alkyl groups, the cycloalkyl groups are C₅-C₇ cycloalkyl groups, the aryl groups comprise phenyl and (C₁-C₆ alkyl)phenyl, and the halogens are bromine, chlorine and fluorine.

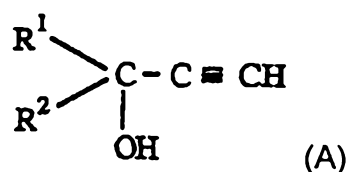
10 5. Photochromic compound according to claim 3 or 4, characterized in that the substituent R is in position 5' in the Th₂ group.

6. Photochromic compound according to any of claims 3 to 5, characterized in that the substituent R is in position 5'' in the Th₃ group.

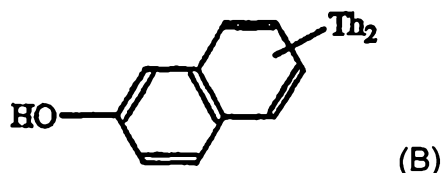
15 7. Photochromic compound according to any of claims 3 to 6, characterized in that the Th₂ group is in position 8 of the naphthalene ring.

8. Photochromic compound according to any of claims 3 to 7, characterized in that R¹ is a Th₃ group.

20 9. Method of preparing a photochromic compound according to claim 3, characterized in that it comprises the reaction, in the presence of an acid catalyst, of a propargylic alcohol of formula :



where R¹ and R² are defined as in claim 3, with a 2-naphthol of formula :

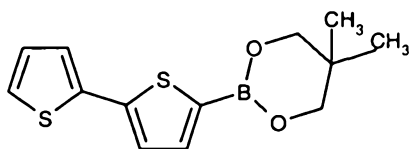


where Th₂ is defined as in claim 3 and occupies one of positions 3, 4, 6-8 of the naphthalene ring.

30 10. Method according to claim 9, characterized in that the 2-naphthol of formula (B) is prepared by the coupling reaction catalysed by a palladium

catalyst between a boron derivative of bithiophene and a 2-naphthol substituted in one of positions 3, 4, 6-8 of the naphthalene ring by a bromine atom or a triflate group.

11. Method according to claim 10, characterised in that the boron derivative of
5 bithiophene corresponds to the formula:

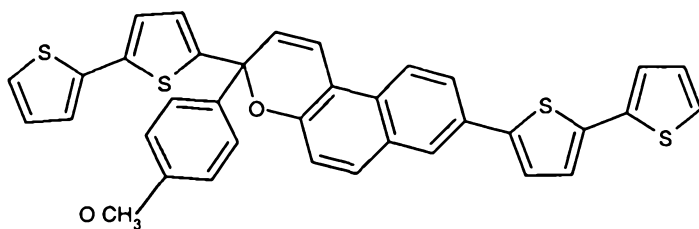


12. Transparent article comprising a transparent polymer substrate, characterised in that at least one photochromic compound, according to any one of claims 1 to 8, is incorporated in the substrate.

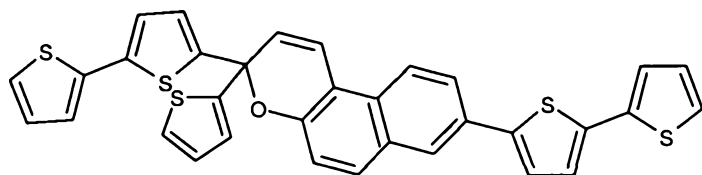
- 10 13. Transparent article comprising a transparent polymer substrate, characterised in that at least one face of the article is coated with a transparent polymer film incorporating at least one photochromic compound according to any one of claims 1 to 8.

14. Article according to claim 12 or 13, characterised in that the article is
15 glazing for buildings, a windscreen for a car or aircraft, a helmet visor or a spectacle glass.

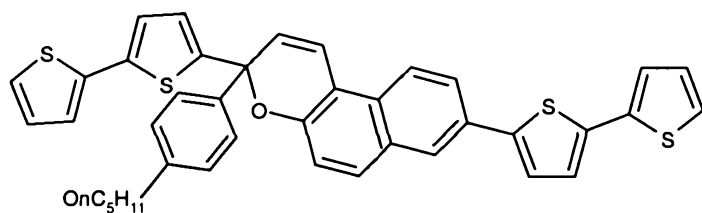
15. Photochromic compound 3,8-di(2,2'-bithien-5-yl)-3-(4-methoxyphenyl)-[3H]-naphtho[2,1-b]pyran.



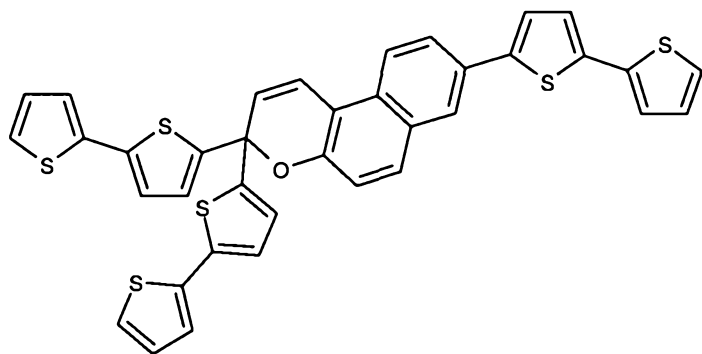
16. Photochromic compound 3,8-di(2,2'-bithien-5-yl)-3-(thien-2-yl)-[3H]-naphtho[2,1-b]pyran.



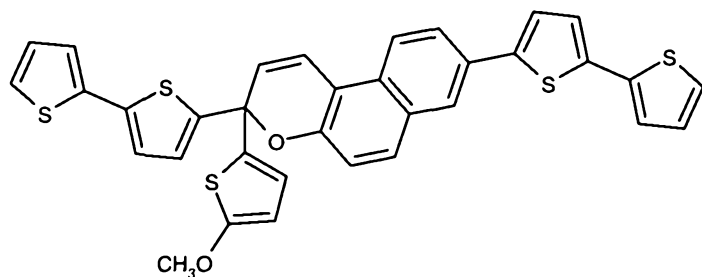
17. Photochromic compound 3,8-di(2,2'-bithien-5-yl)-3-(4-pentyloxyphenyl)-[3H]-naphtho[2,1-b]pyran.



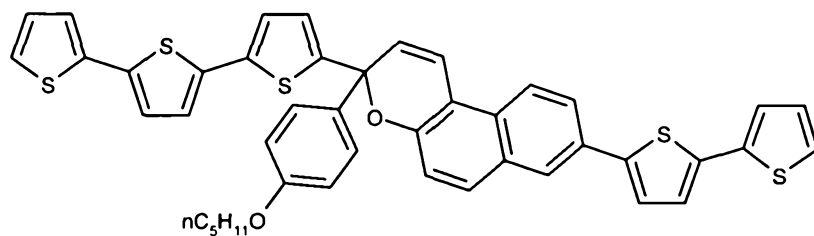
18. Photochromic compound 3,3,8-tri(2,2'-bithien-5-yl)-[3H]-naphtho[2,1-b]pyran.



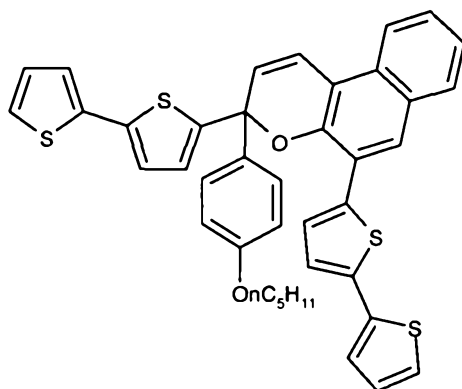
19. Photochromic compound 3,8-di(2,2'-bithien-5-yl)-3-(5-methoxythien-2-yl)-[3H]-naphtho[2,1-b]pyran.



20. Photochromic compound 8-(2,2'-bithien-5-yl)-3-(4-pentyloxyphenyl)-3-(2,2'-5',2''-terthien-5-yl)-[3H]-naphtho[2,1-b]pyran.



21. Photochromic compound 3,5-di(2,2'-bithien-5-yl)-3-(4-pentyloxyphenyl)-[3H]-naphtho[2,1-b]pyran.



22. Method of preparing a photochromic compound, which method is substantially as hereinbefore described with reference to any one of Examples 1 to 7.

23. A polyurethane film substantially as hereinbefore described with reference to Example 11.

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