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(54) Titre : POLYURETHANE PHOTOCHROME

(54) Title: PHOTOCHROMIC POLYURETHANES

(57) Abrégé/Abstract:

The present invention relates to a novel photochromic polyurethane comprising an isocyanate reactive mixture comprising: i) from about 20 to about 60% by weight of one or more polyols having a functionality of from 1.8 to 4 and molecular weights of from 500 to 6000 g/mole; ii) from about 5 to about 35% by weight of one or more diols or triols or mixtures thereof having a functionality of from 1.8 to 3 and molecular weights of from 62 to 499; b) an aliphatic polyisocyanate having a functionality ranging from about 2 to about 3; and c) a photochromic compound selected from a group consisting of spirooxazines, fulgides, fulgimides, and naphthopyrans, wherein the photochromic compound is present in an amount of 0.01 to 5 parts per hundred parts by weight of the isocyanate reactive mixture.

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PHOTOCHROMIC POLYURETHANES

ABSTRACT OF THE DISCLOSURE

The present invention relates to a novel photochromic polyurethane comprising an isocyanate reactive mixture comprising: i) from about 20 to about 60% by weight of one or more polyols having a functionality of from 1.8 to 4 and molecular weights of from 500 to 6000 g/mole; ii) from about 5 to about 35% by weight of one or more diols or triols or mixtures thereof having a functionality of from 1.8 to 3 and molecular weights of from 62 to 499; b) an aliphatic polyisocyanate having a functionality ranging from about 2 to about 3; and c) a photochromic compound selected from a group consisting of spirooxazines, fulgides, fulgimides, and naphthopyrans, wherein the photochromic compound is present in an amount of 0.01 to 5 parts per hundred parts by weight of the isocyanate reactive mixture.

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PHOTOCHROMIC POLYURETHANES

FIELD OF THE INVENTION

The present invention relates to polyurethanes with improved photochromic behavior.

BACKGROUND OF THE INVENTION

Articles which have organic photochromic material(s) applied to or incorporated therein are characterized in that upon exposure to electromagnetic radiation or to solar light they exhibit a reversible change in color and in light transmission. Once the exposure to the original
5 radiation has been discontinued, the composition returns to its original color, or colorless state. Recently, photochromic plastic materials, most notably, such compositions which may be suitable for the preparation of ophthalmic lenses, films and automotive head lamp lenses have been the focus of attention in the relevant arts. Plastic materials as the medium for
10 the preparation of such lenses allow for the preparation of lighter and thinner lenses than does the traditionally used glass. Also of interest are the applications of photochromic technology to automotive, aircraft transparencies and greenhouse architecture and other glazing applications. It is known that photochromic behavior may be imparted to
15 glass and to certain plastic materials by using inorganic and organic dyes respectively.

Photochromic articles prepared from synthetic organic resins such as homopolymers of a poly(allyl carbonate) monomer are known (U.S. Patent Nos. 4,994,208, 5,246,630, 5,221,721 and 5,200,483.)

20 U.S. Patent No. 5,244,602 describes a naphthopyran useful for photochromic polymers and also organic hosts such as polyurethanes for such materials. However, a detailed description of the polyurethane is not given.

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SUMMARY OF THE INVENTION

The present invention relates to a novel photochromic polyurethane comprising an isocyanate reactive mixture comprising: i) from about 20 to about 60% by weight of one or more polyols having a functionality of from 1.8 to 4 and molecular weights of from 500 to 6000 g/mole; ii) from about 5 to about 35% by weight of one or more diols or triols or mixtures thereof having a functionality of from 1.8 to 3 and molecular weights of from 62 to 499; b) an aliphatic polyisocyanate having a functionality ranging from about 2 to about 3; and c) a photochromic compound selected from a group consisting of spirooxazines, fulgides, fulgimides, and naphthopyrans, wherein the photochromic compound is present in an amount of 0.01 to 5 parts per hundred parts by weight of the isocyanate reactive mixture.

An object of the present invention is to produce a transparent polyurethane material in which the photochromic dyes fade back to the "uncolored state" rapidly, that is, the absorbance of this novel polyurethane returns to less than 50% of the "colored state" within two minutes after the light source is removed. This is accomplished by adding an appropriate amount of a high molecular weight component into a polyurethane.

DETAILED DESCRIPTION OF THE INVENTION

The photochromic polyurethane of the present invention comprises an isocyanate reactive mixture comprising from about 20 to about 60% by weight, preferably 30 to 50% by weight, of one or more polyols having a functionality of from 1.8 to 4 and molecular weights of from 500 to 6000 g/mole; ii) from about 5 to about 35% by weight, preferably 10 to 25% by weight, of one or more diols or triols or mixtures thereof having a functionality of from 1.8 to 3 and molecular weights of from 62 to 499 and b) an aliphatic polyisocyanate having a functionality of less than about 3, preferably 2.

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The polyols of the present invention are those conventionally employed in the art for the preparation of polyurethane cast elastomers. Preferably, the polyols have molecular weights (number average) within the range of 500 to 6,000, preferably 1000 to 3,000. The functionality of the polyol ranges from about 1.8 to 4, preferably from 1.8 to about 2.0. From about 20 to 60 percent by weight of these polyols are present in the isocyanate reactive mixture. Naturally, and often times advantageously, mixtures of such polyols are also possible. Examples of the suitable polyols include polyether polyols, polyester polyols, and polycarbonate polyols.

Suitable polyether polyols are known, for example, from German Offenlegungsschrift 2,905,975, for example, such as polypropylene glycol. Other suitable polyethers are also derived from propylene oxide and/or ethylene oxide with molecular weights of about 500 to 6000 (OH numbers of 225 to 19) based on difunctional starters such as water, ethylene glycol or propylene glycol are also preferred. These preferred compounds include copolymers of ethylene oxide and propylene oxide with about 0 to 20% by weight of the oxides being ethylene oxides. Poly(tetramethylene glycol) diols having molecular weights of about 500 to 600 (OH numbers of 187 to 37) are also preferred.

The suitable polyester polyols include the ones which are prepared by polymerizing ϵ -caprolactone using an initiator such as ethylene glycol, ethanolamine and the like. Further suitable examples are those prepared by esterification of polycarboxylic acids. Further suitable polyester polyols include reaction products of polyhydric, preferably dihydric alcohols to which trihydric alcohols may be added and polybasic, preferably dibasic carboxylic acids. Instead of these polycarboxylic acids, the corresponding carboxylic acid anhydrides or polycarboxylic acid esters of lower alcohols or mixtures thereof may be used for preparing the polyesters. The polycarboxylic acids may be aliphatic, cycloaliphatic,

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aromatic and/or heterocyclic and they may be substituted, e.g., by halogen atoms, and/or unsaturated. The following are mentioned as examples: succinic acid; adipic acid; suberic acid; azelaic acid; sebacic acid; phthalic acid; isophthalic acid; trimellitic acid; phthalic acid anhydride; tetrahydrophthalic acid anhydride; hexahydrophthalic acid anhydride; tetrachlorophthalic acid anhydride, endomethylene tetrahydrophthalic acid anhydride; glutaric acid anhydride; maleic acid; maleic acid anhydride; fumaric acid; dimeric and trimeric fatty acids such as oleic acid, which may be mixed with monomeric fatty acids; dimethyl terephthalates and bis-glycol terephthalate. Suitable polyhydric alcohols include, e.g., ethylene glycol; propylene glycol-(1,2) and -(1,3); butylene glycol-(1,4) and -(1,3); hexanediol-(1,6); octanediol-(1,8); neopentyl glycol; cyclohexanedimethanol-(1,4-bis-hydroxymethylcyclohexane); 2-methyl-1,3-propanediol; 2,2,4-trimethyl-1,3-pentanediol; triethylene glycol; tetraethylene glycol; polyethylene glycol; dipropylene glycol; polypropylene glycol; dibutylene glycol and polybutylene glycol, glycerine and trimethylolpropane. A preferred polyester polyol is butylene adipate.

Suitable diols and triols with molecular weights of 62 to 499 used in the present invention include the polyhydric alcohols listed to form polyester polyols. Triols such as trimethylolpropane (TMP), glycerine or low MW polypropylene oxide polyols prepared from these or similar trifunctional starters are preferred.

A suitable polycarbonate polyol includes polyhexamethylene carbonate. Polycarbonates based on diols listed above are prepared by the reaction of the diol and a dialkyl carbonate as described in U.S. Patent No. 4,160,853.

Suitable additives for use in the present invention include the tin catalysts.

In accordance with the present invention, the aliphatic polyisocyanate component, having a viscosity of less than about 20,000

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mPa.s at 25°C and having an average NCO functionality of 2 to 3, most preferably about 2, is generally in the form of an NCO prepolymer or a polyisocyanate adduct, more preferably a polyurethane prepolymer. Suitable polyisocyanate adducts for the present invention may be based, for example, on organic aliphatic diisocyanates including, for example, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylene diisocyanate, 1,12-dodecamethylene diisocyanate, cyclohexane-1,3- and -1,4-diisocyanate, 1-isocyanato-2-isocyanatomethyl cyclopentane, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl-cyclohexane (isophorone diisocyanate or IPDI), bis-(4-isocyanatocyclohexyl)-methane, 2,4'-dicyclohexylmethane diisocyanate, 1,3- and 1,4-bis-(isocyanatomethyl)-cyclohexane, bis-(4-isocyanato-3-methylcyclohexyl)-methane, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3- and/or -1,4-xylylene diisocyanate, 1-isocyanato-1-methyl-4(3)-isocyanatomethyl cyclohexane, 2,4- and/or ,6-hexahydrotoluylene diisocyanate, and mixtures thereof. It is preferred that the isocyanate be based on mixtures of the various stereoisomers of bis-(4-isocyanato-cyclohexyl)-methane or the trans, trans isomer alone.

The dyes suitable in the context of the invention are photochromic compounds selected from the group consisting of benzopyrans, naphthopyrans, spirobenzopyrans, spironaphthopyrans, spirobenzoxazines, spironaphthoxazines, fulgides and fulgimides. Such photochromic compounds have been reported in the literature including U.S. Patents 4,826,977; 4,931,221; 5,106,998; 5,552,090; 5,628,935 and 5,565,147.

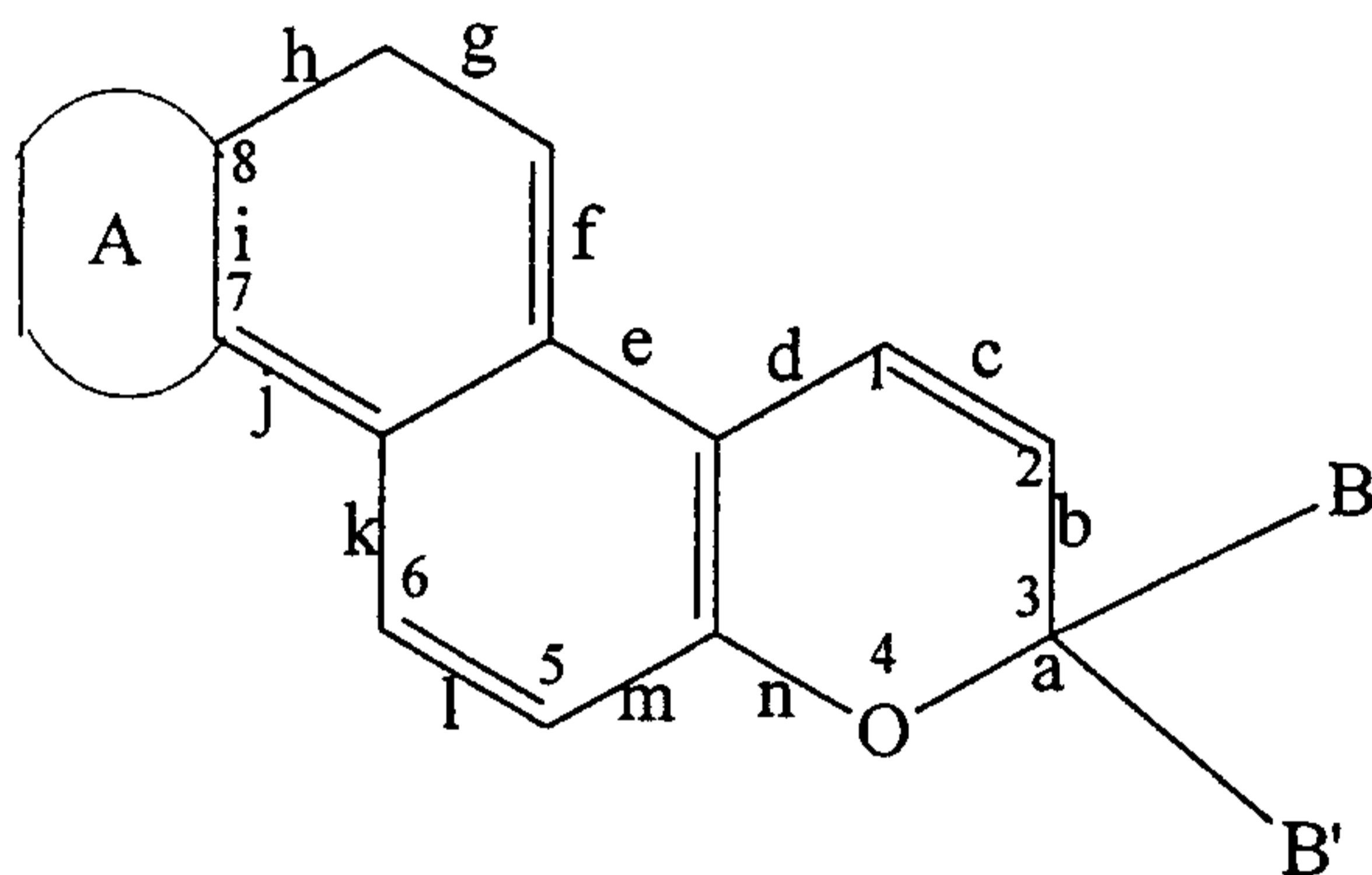
The color range of the naphthopyrans suitable in the present invention is 410 to 500 nm, thus they impart a yellow or orange coloration in their darkened state. In the faded, or bleached condition, the materials exhibit a colorless or pale yellow coloration. The present invention may be used in a mixture or combined with suitable organic photochromic

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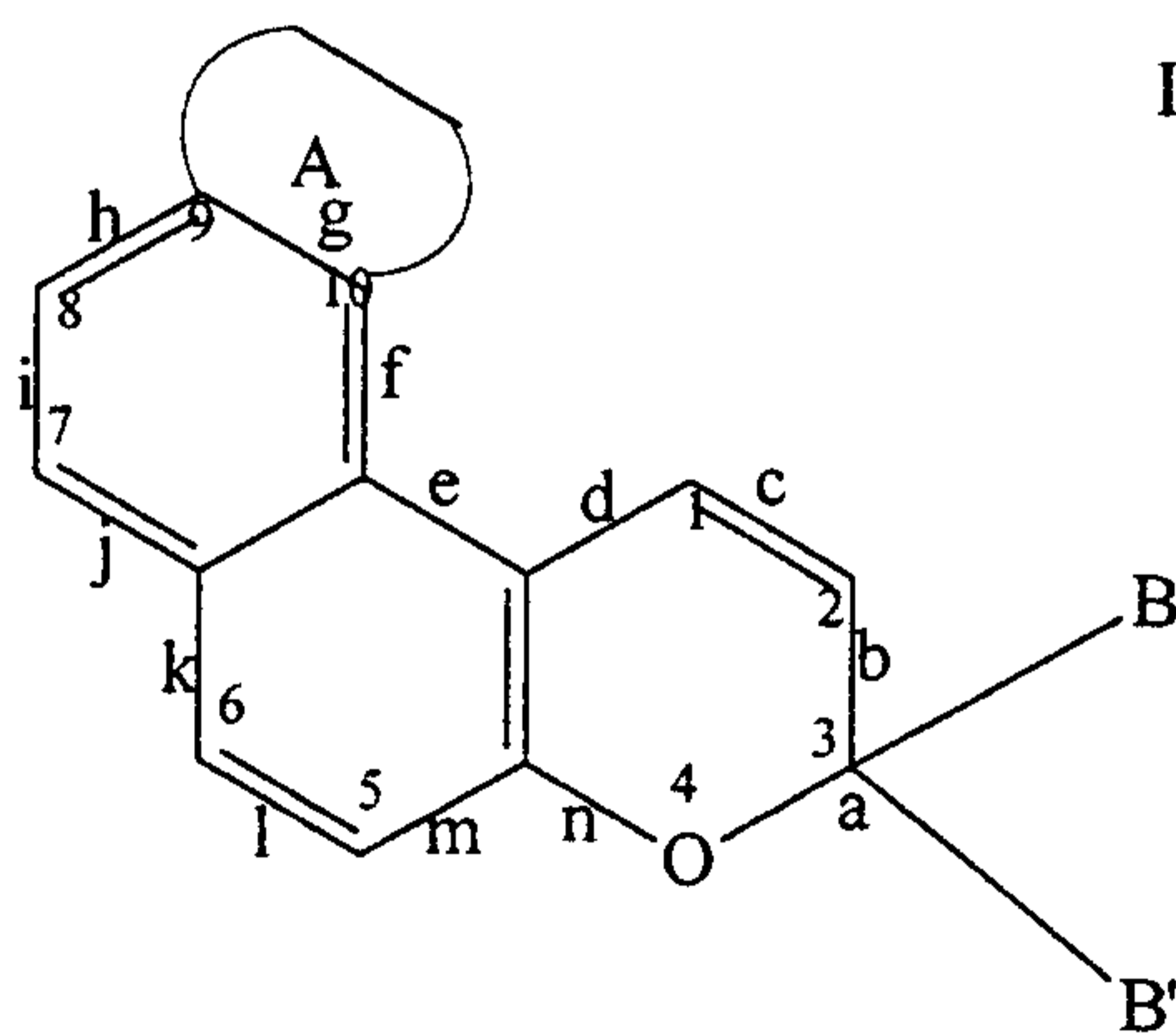
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compounds, to obtain, after activation, the formation of neutral coloring such as green, brown and grey. Particularly useful for the purpose are photochromic compounds belonging to the group of naphthopyrans, spiro-indolino-oxazines and spiro-indolino pyrans which are known and are available in commerce. These have a high quantum efficiency for coloring, a good sensitivity and saturated optical density, and an acceptable bleach or fade rate. These compounds may be represented by the following graphic formulae IA1, IA2, and IA3 in which the letters a through n represent the sides of the naphthopyran rings, and the numbers represent the numbering of the ring atoms of the naphthopyrans:

IA1



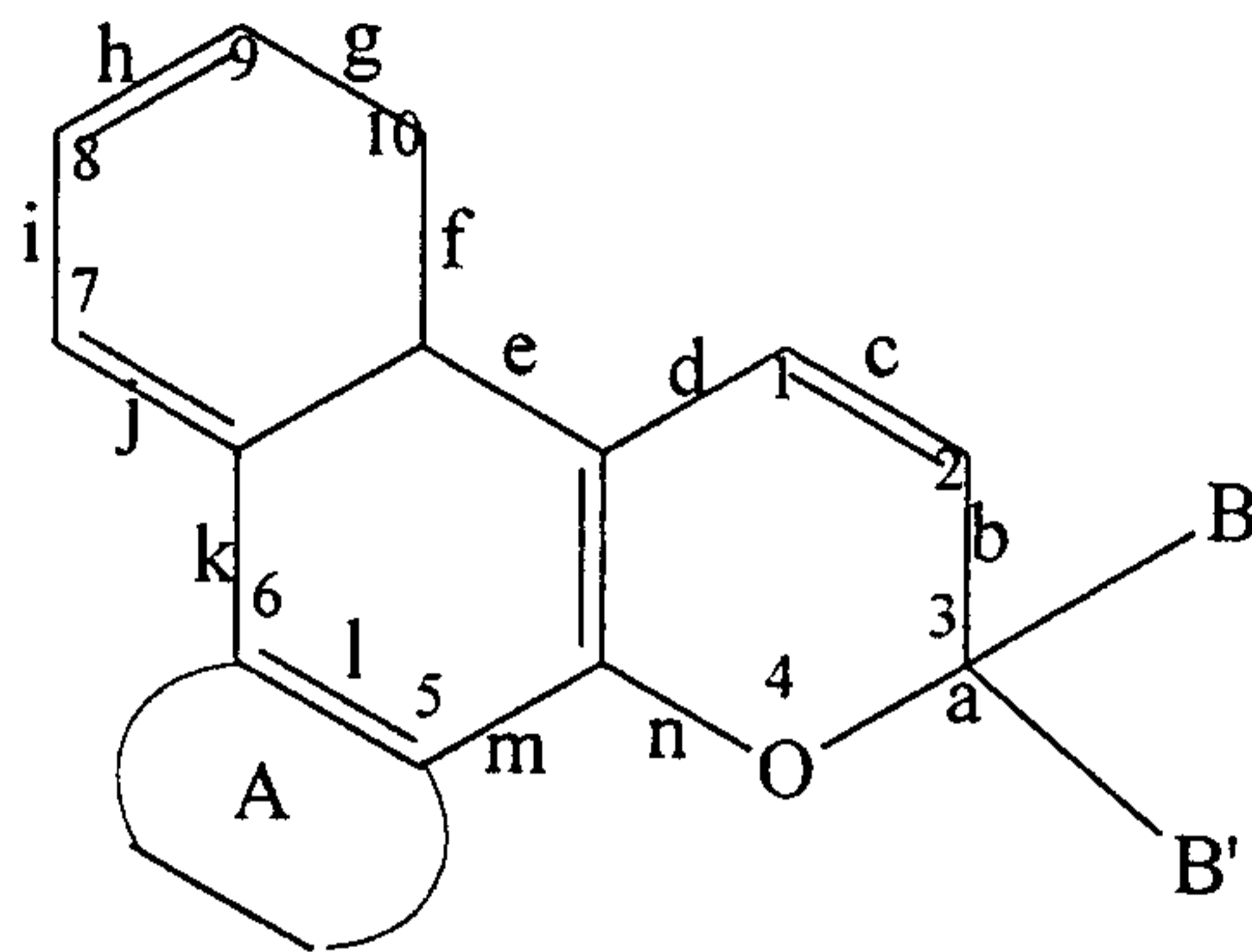
IA2



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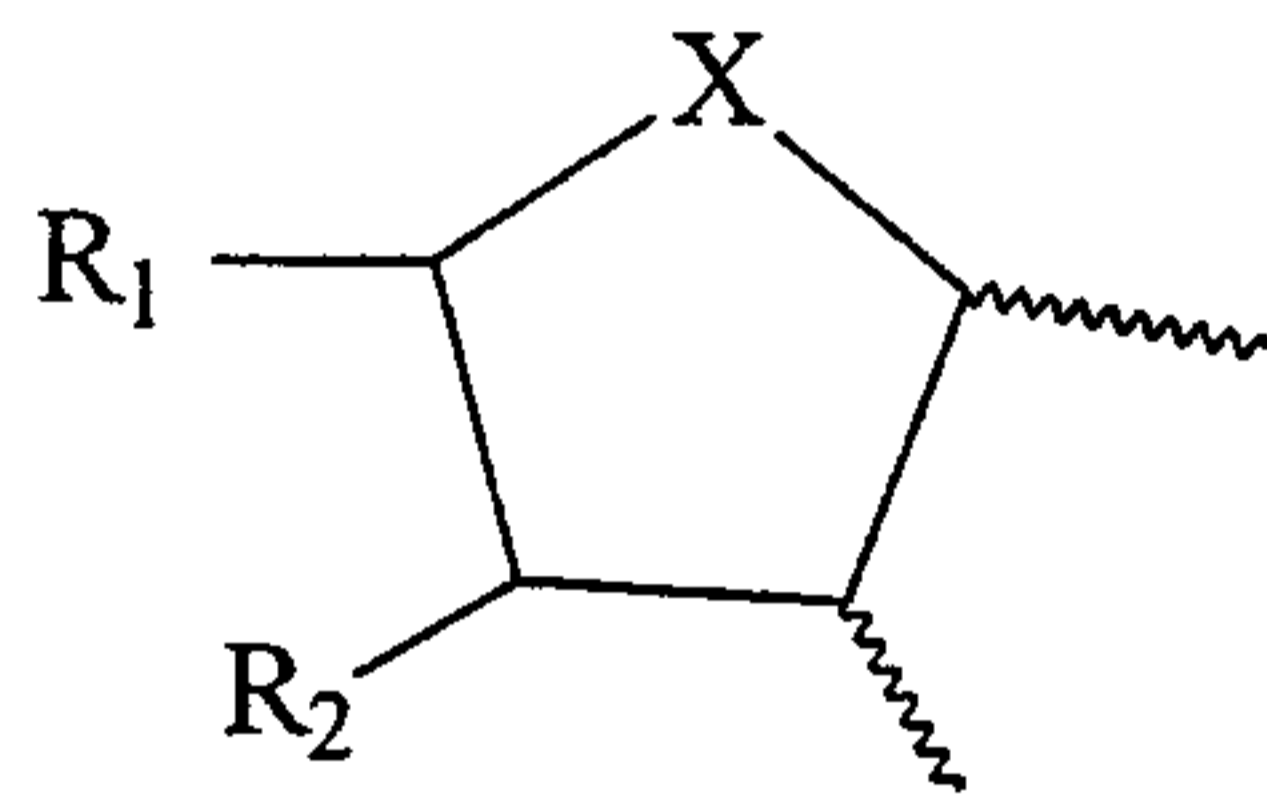
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IA3

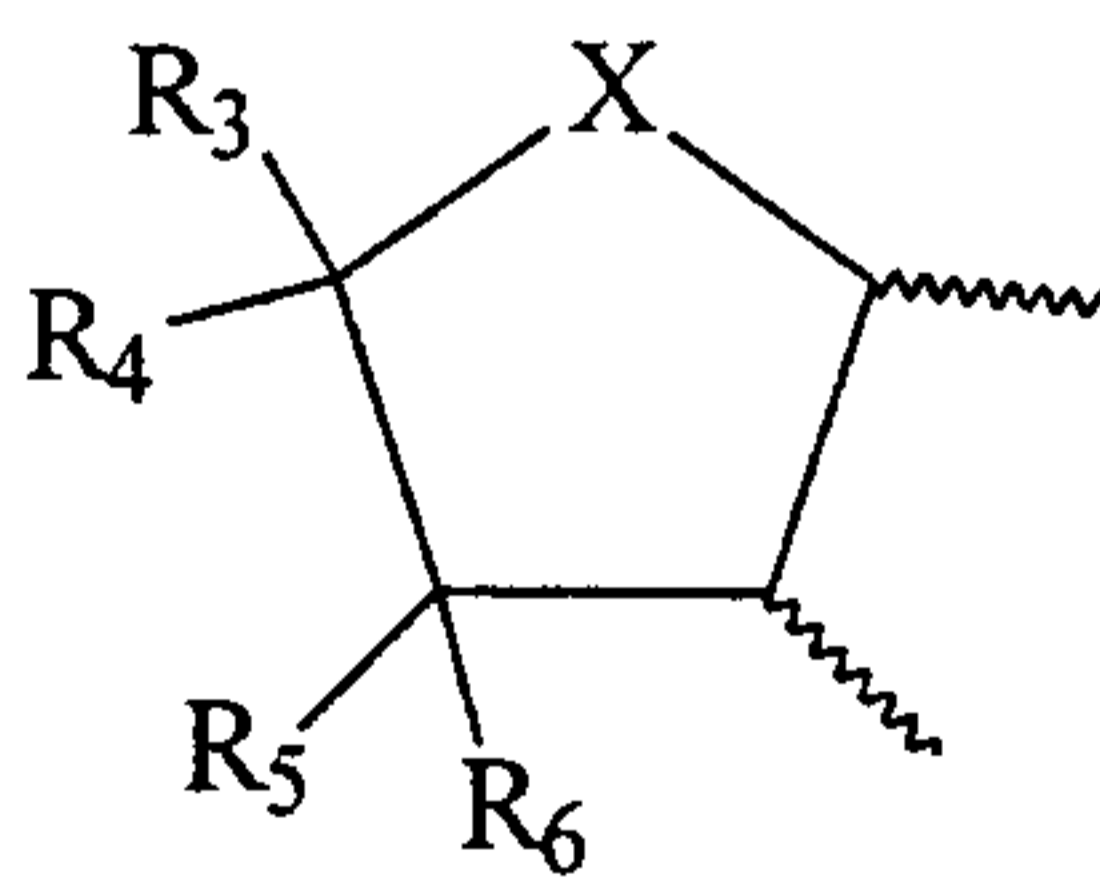


In graphic formulae IA1, IA2, and IA3, the group represented by A is a substituted or un-substituted, five or six member heterocyclic ring fused to the g, i, or l side of the naphthopyran and is represented by the following graphic formulae IIA through IIF:

IIA



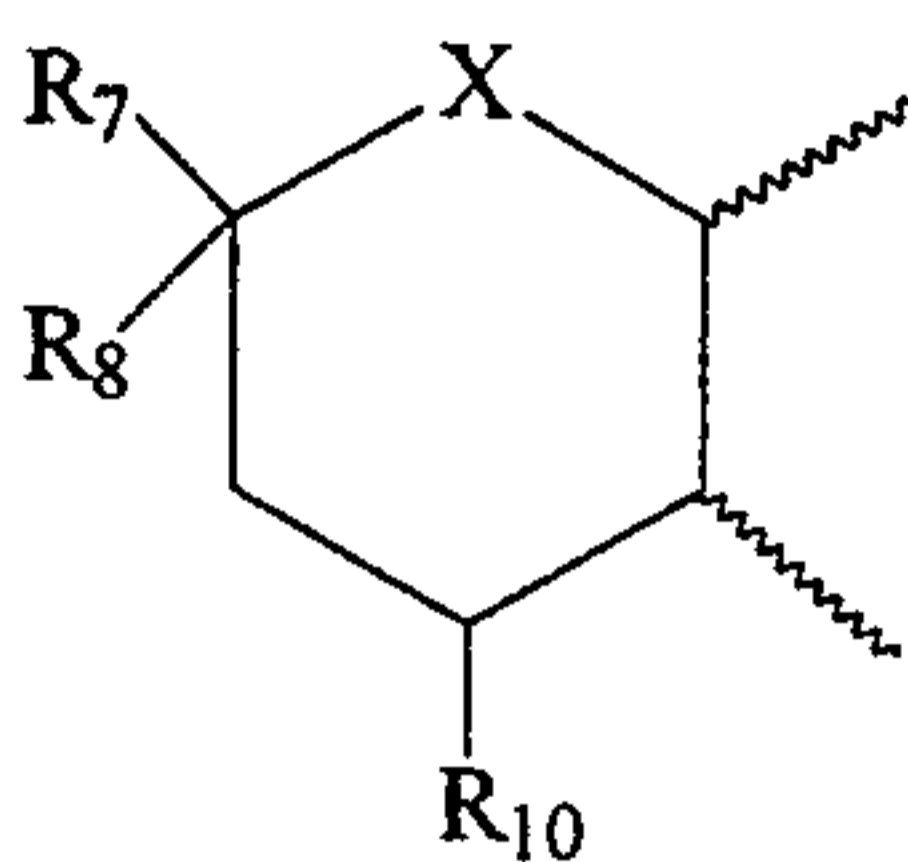
IIB



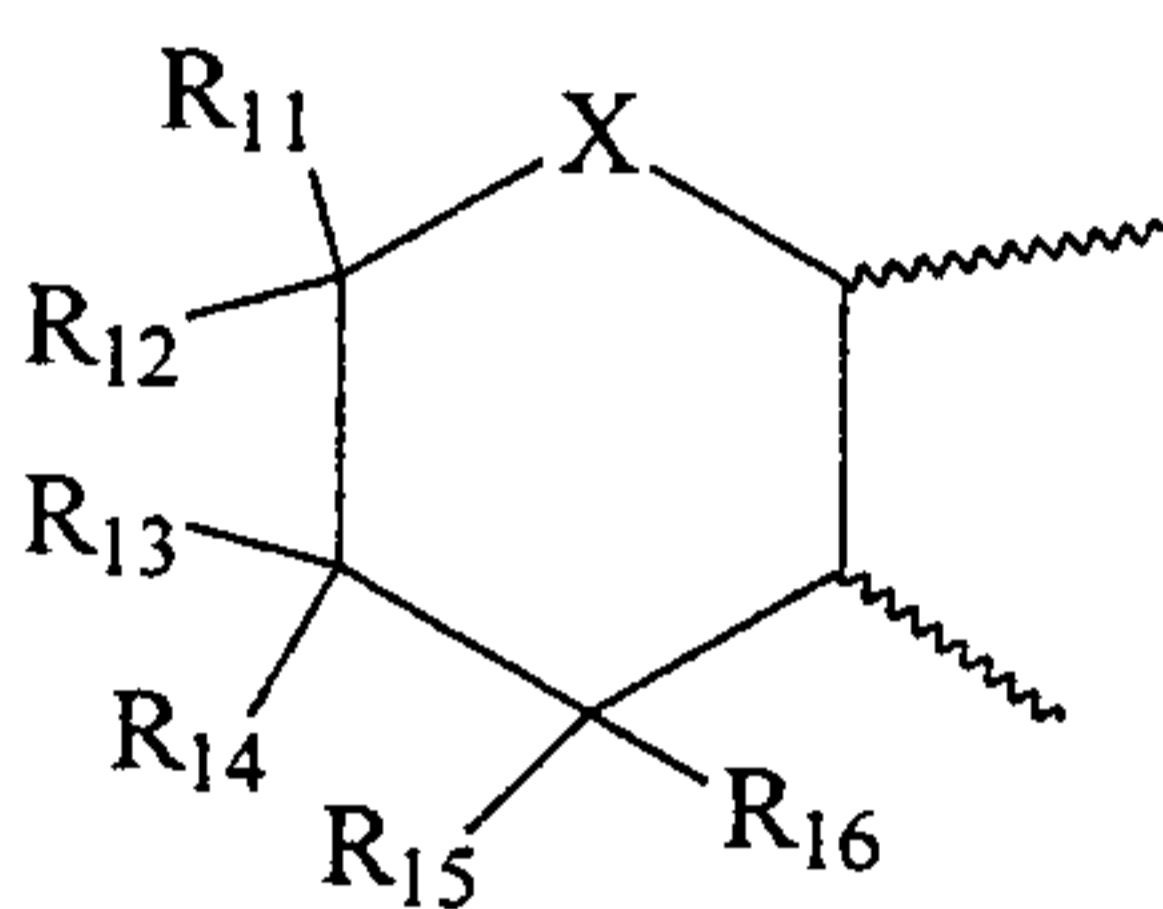
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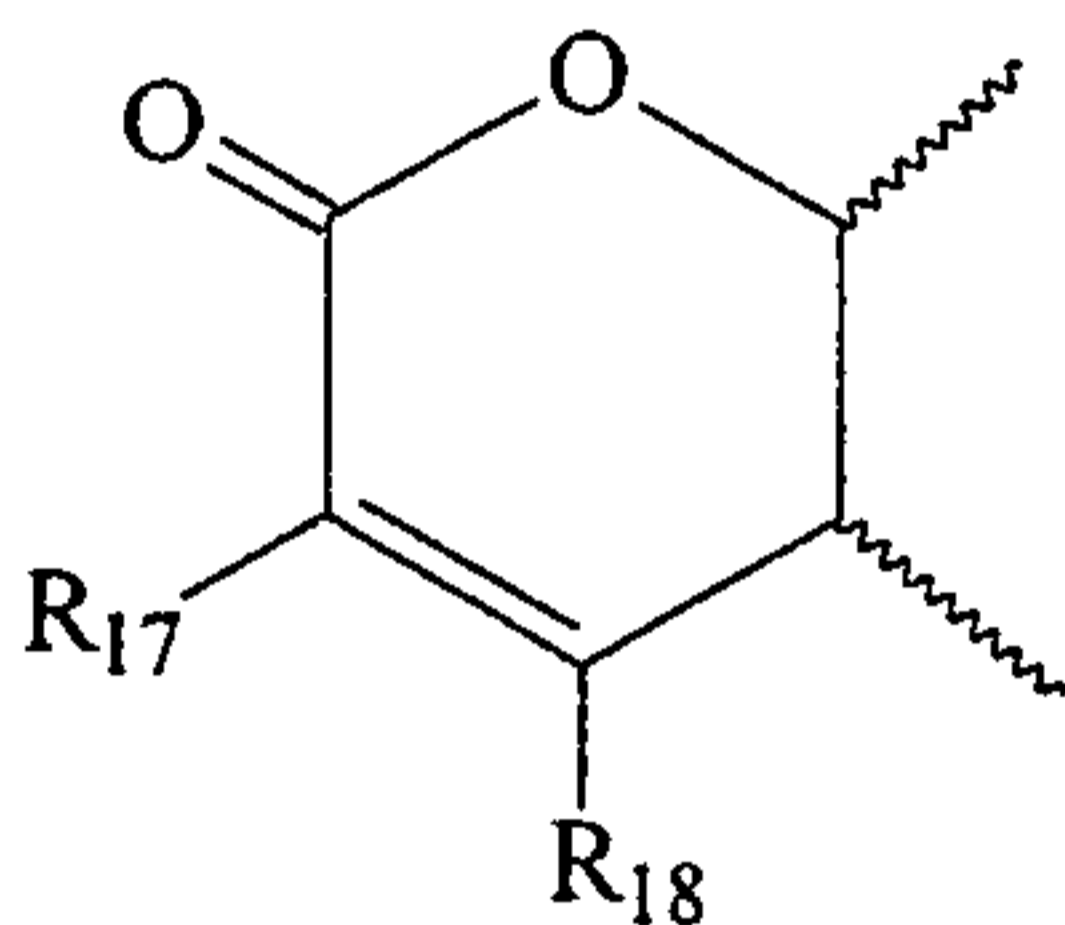
IIC



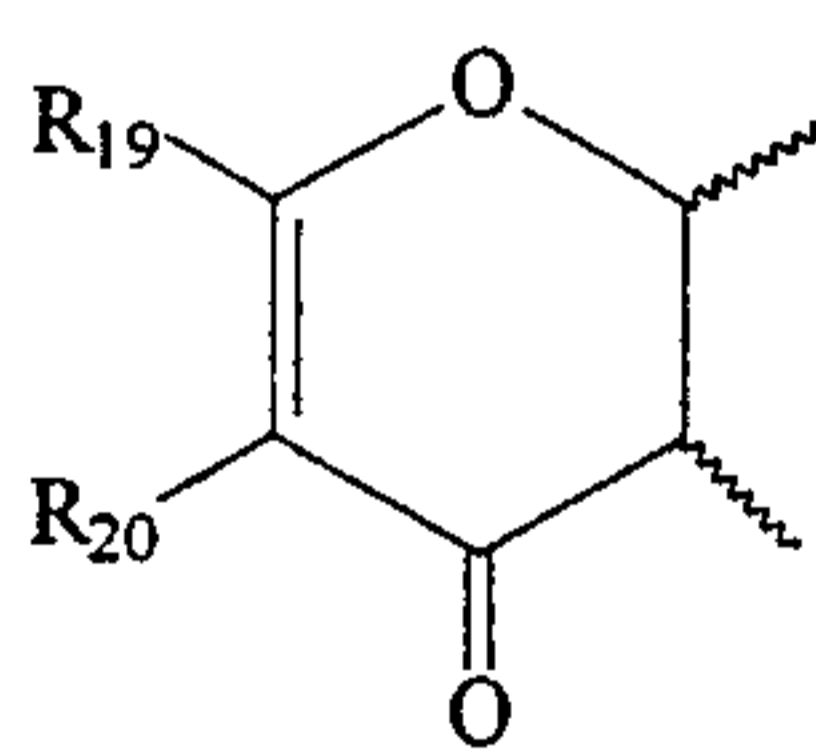
IID



IIE



IIF



In graphic formulae IIA through IID, X may be an oxygen or a nitrogen atom, the nitrogen atom being substituted with hydrogen or a C₁-C₄ alkyl. R₁ may be hydrogen, C₁-C₆ alkyl, substituted or unsubstituted phenyl, carboxy, or C₁-C₆ alkoxy carbonyl. Preferably, R₁ is

5 hydrogen, C₁-C₃ alkyl, substituted or unsubstituted phenyl, carboxy, or C₁-C₃ alkoxy carbonyl. R₂ may be hydrogen, C₁-C₆ alkyl, or substituted

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or unsubstituted phenyl. Preferably, R_2 is hydrogen, C_1-C_3 alkyl, or substituted or unsubstituted phenyl. R_3 and R_4 may each be hydrogen, C_1-C_6 alkyl or phenyl. Preferably, R_3 and R_4 are each hydrogen, C_1-C_3 alkyl, or phenyl, R_5 and R_6 may each be hydrogen, C_1-C_6 alkyl, phenyl, hydroxy, C_1-C_6 alkoxy, or acetoxy. Preferably, R_5 and R_6 are each hydrogen, C_1-C_3 alkyl, phenyl, hydroxy, C_1-C_3 alkoxy, or acetoxy, R_7 , R_8 , and R_{10} may each be hydrogen, C_1-C_6 alkyl, or phenyl, provided that when R_7 is phenyl, R_8 is hydrogen or C_1-C_6 alkyl and when R_8 is phenyl R_7 is hydrogen or C_1-C_6 alkyl. Preferably, R_7 , R_8 , and R_{10} are each hydrogen, C_1-C_3 alkyl, or phenyl. Most preferably, R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , and R_{10} are each hydrogen or methyl. R_{11} , R_{12} , R_{13} , R_{14} , R_{15} , and R_{16} may each be hydrogen, C_1-C_6 alkyl, C_1-C_6 alkoxy, or phenyl, Preferably, R_{11} , R_{12} , R_{13} , R_{14} , R_{15} , and R_{16} are each hydrogen, C_1-C_3 alkyl, C_1-C_3 alkoxy, or phenyl. Most preferably, R_{11} , R_{12} , R_{13} , R_{14} , R_{15} , and R_{16} are each hydrogen, methyl, or methoxy.

In graphic formulae IIE and IIF, R_{17} may be hydrogen, C_1-C_6 alkyl, substituted or unsubstituted phenyl, or halogen. Preferably, R_{17} is hydrogen, C_1-C_3 alkyl, substituted or unsubstituted phenyl, or halogen. Most preferably, R_{17} is hydrogen, methyl, or chloro. R_{18} may be hydrogen, C_1-C_6 alkyl, phenyl, carboxy, C_1-C_6 alkoxy-carbonyl, or C_1-C_6 haloalkoxycarbonyl. Preferably, R_{18} is hydrogen, C_1-C_3 alkyl, phenyl, carboxy, C_1-C_3 alkoxy-carbonyl, or C_1-C_3 haloalkoxycarbonyl. R_{19} and R_{20} may each be hydrogen, C_1-C_6 alkyl, or phenyl. Preferably, R_{19} and R_{20} are each hydrogen, C_1-C_3 alkyl, or phenyl. Most preferably, R_{18} , R_{19} , and R_{20} are each hydrogen or methyl. R_1-R_{20} the phenyl substituents may be C_1-C_3 alkyl and the halogen or (halo) groups may be chloro or bromo.

In graphic formulae IA1, IA2, and IA3, B and B' may each be selected from the group consisting of (i) the substituted or unsubstituted aryl groups phenyl and naphthyl; (ii) the substituted or unsubstituted

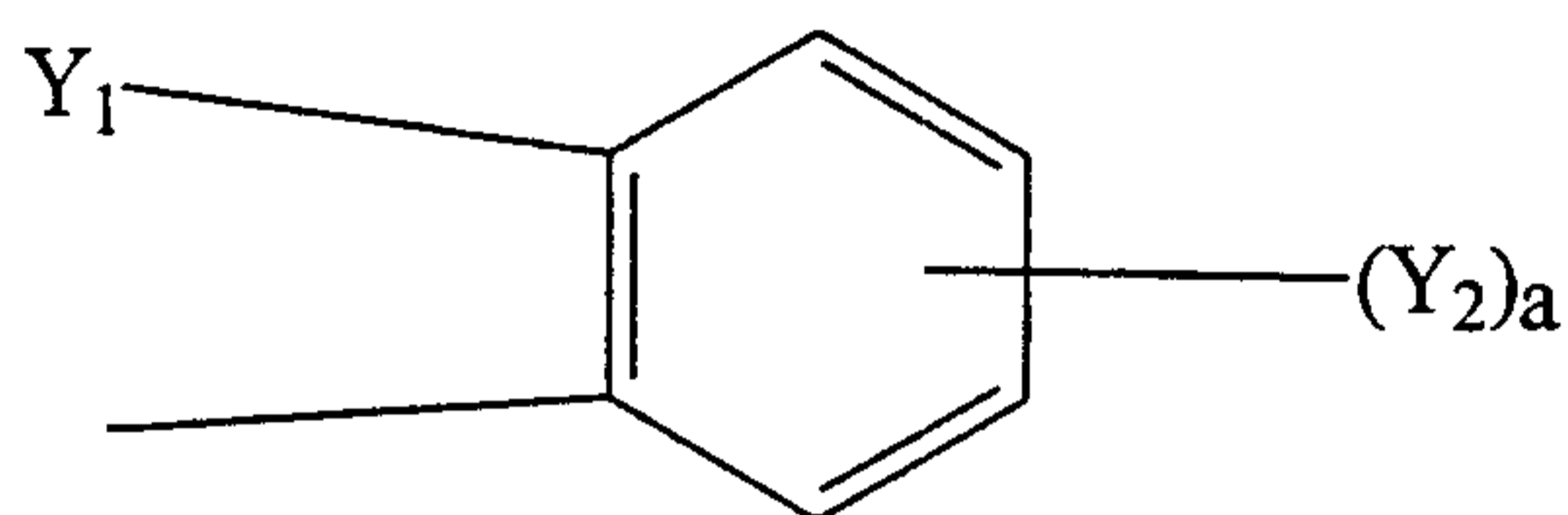
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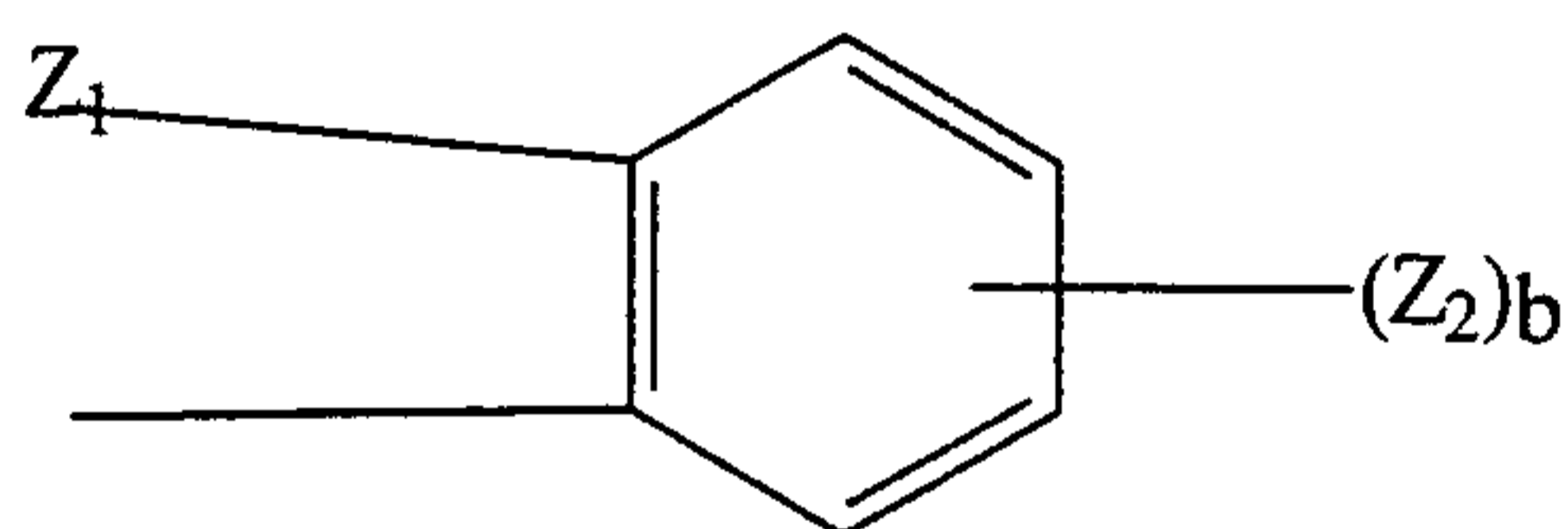
heterocyclic aromatic groups pyridyl, furyl, benzofuryl, thienyl, and benzothienyl; and (iii) B and B' taken together form the adamantyl group. The aryl and heterocyclic substituents of B and B' may each be selected from the group consisting of hydroxy, C₁-C₃ alkyl, C₁-C₅ haloalkyl, which includes mono-, di-, and trihalo substituents, C₁-C₅ alkoxy, C₁-C₅ alkoxy(C₁-C₄)alkyl, C₁-C₅ dialkylamino, acryloxy, methacryloxy, and halogen, said halogen or (halo) groups being fluoro, chloro, or bromo.

Preferably, B and B' are represented respectively by the following graphic formulae:

IIIA



IIIB



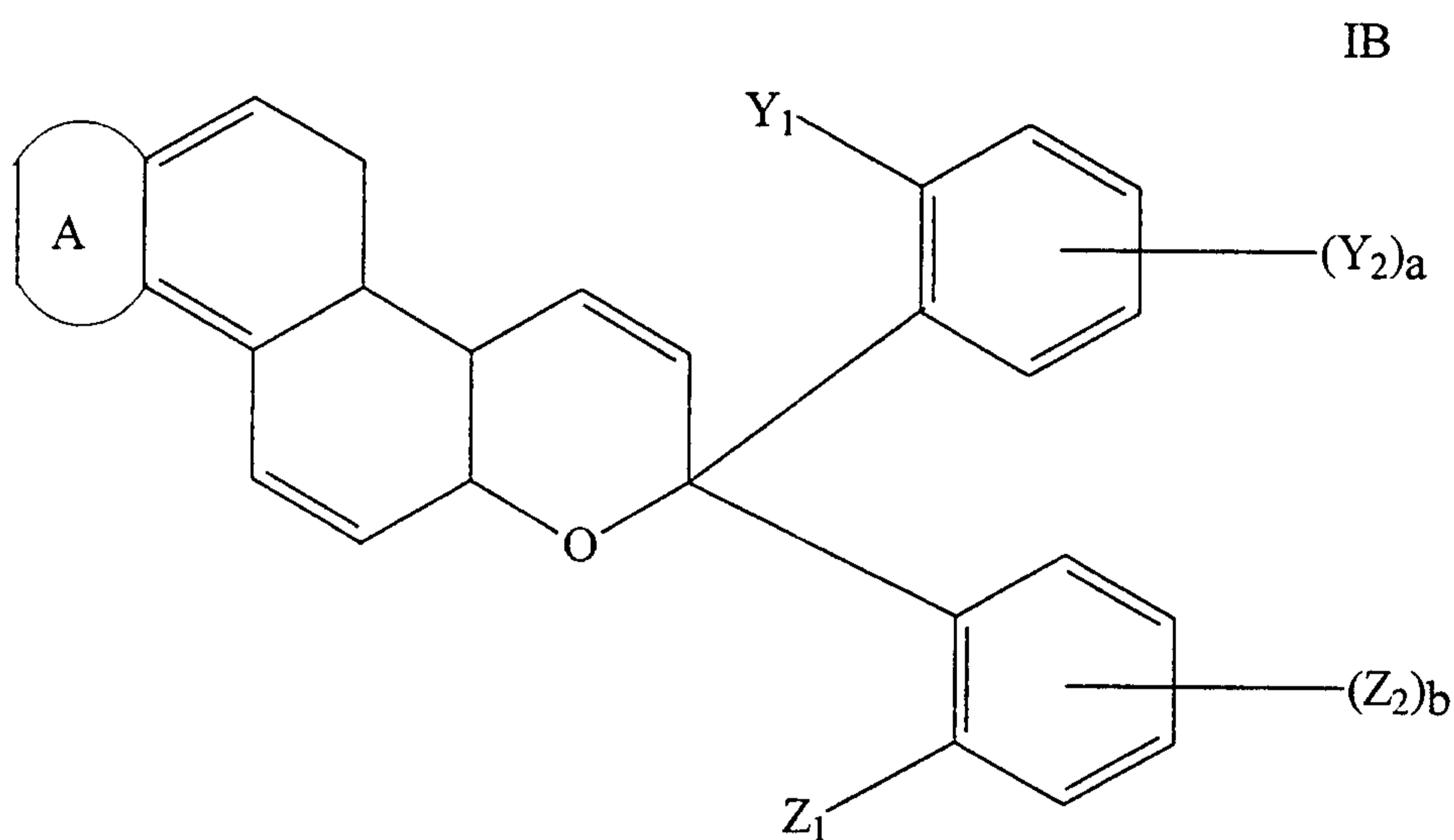
10 In graphic formulae IIIA and IIIB, Y₁ and Z₁ may each be selected from the group consisting of hydrogen, C₁-C₅ alkyl, C₁-C₅ alkoxy, fluoro, and chloro; Y₂ and Z₂ are each selected from the group consisting of C₁-C₅ alkyl, C₁-C₅ alkoxy, hydroxy, halogen, e.g., chloro, fluoro, and bromo, acryloxy, and methacryloxy, and a and b are each integers from 0
15 to 2. Most preferably, Y₁ and Z₁ are each hydrogen, C₁-C₃ alkyl, C₁-C₃

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alkoxy, or fluoro, Y_2 and Z_2 are each C_1 - C_3 alkyl or C_1 - C_3 alkoxy, a is the integer 0 or 1, and b is an integer from 0 to 2.

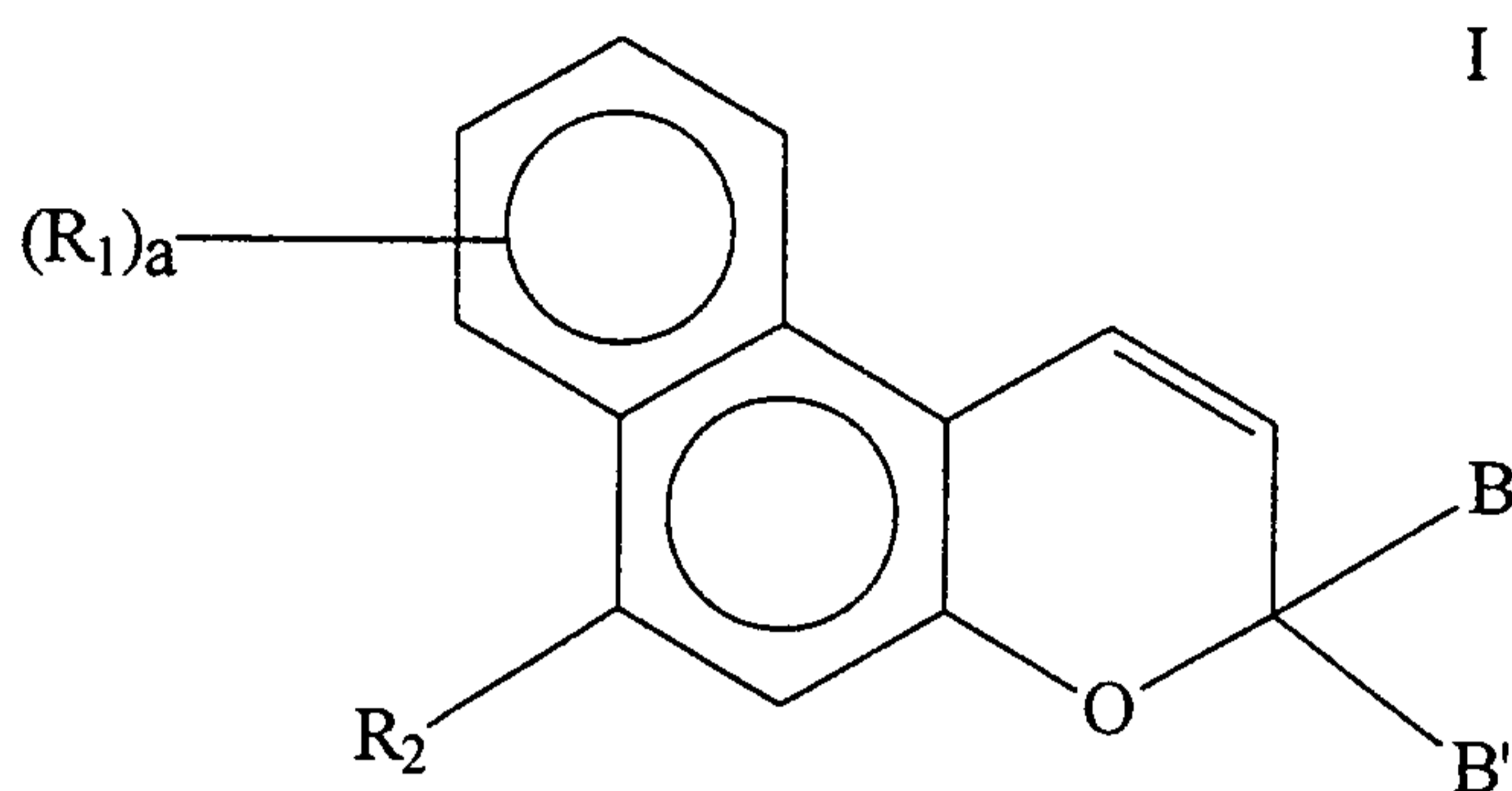
The preferred naphthopyrans of the present invention are represented in the following graphic formula IB. In graphic formula IB, the A group represents formulae IIA through IID with X being an oxygen atom, formulae IIE and IIF. The A group is fused so that the oxygen atom of formulae IIA through IIF is attached to the number 8 carbon atom of the naphtho portion of the naphthopyran.



A still preferred dye may be described as naphthopyrans substituted at the 3 position of the pyran ring with (i) an aryl substituent and (ii) a phenyl substituent having a 5- or 6-member oxygen and/or nitrogen containing heterocyclic ring fused at the number 3 and 4 carbon atoms of the phenyl substituent and with a nitrogen-containing heterocyclic ring at the 6 position of the naphthyl portion of the naphthopyran compound. These compounds may be represented by the following graphic formula:

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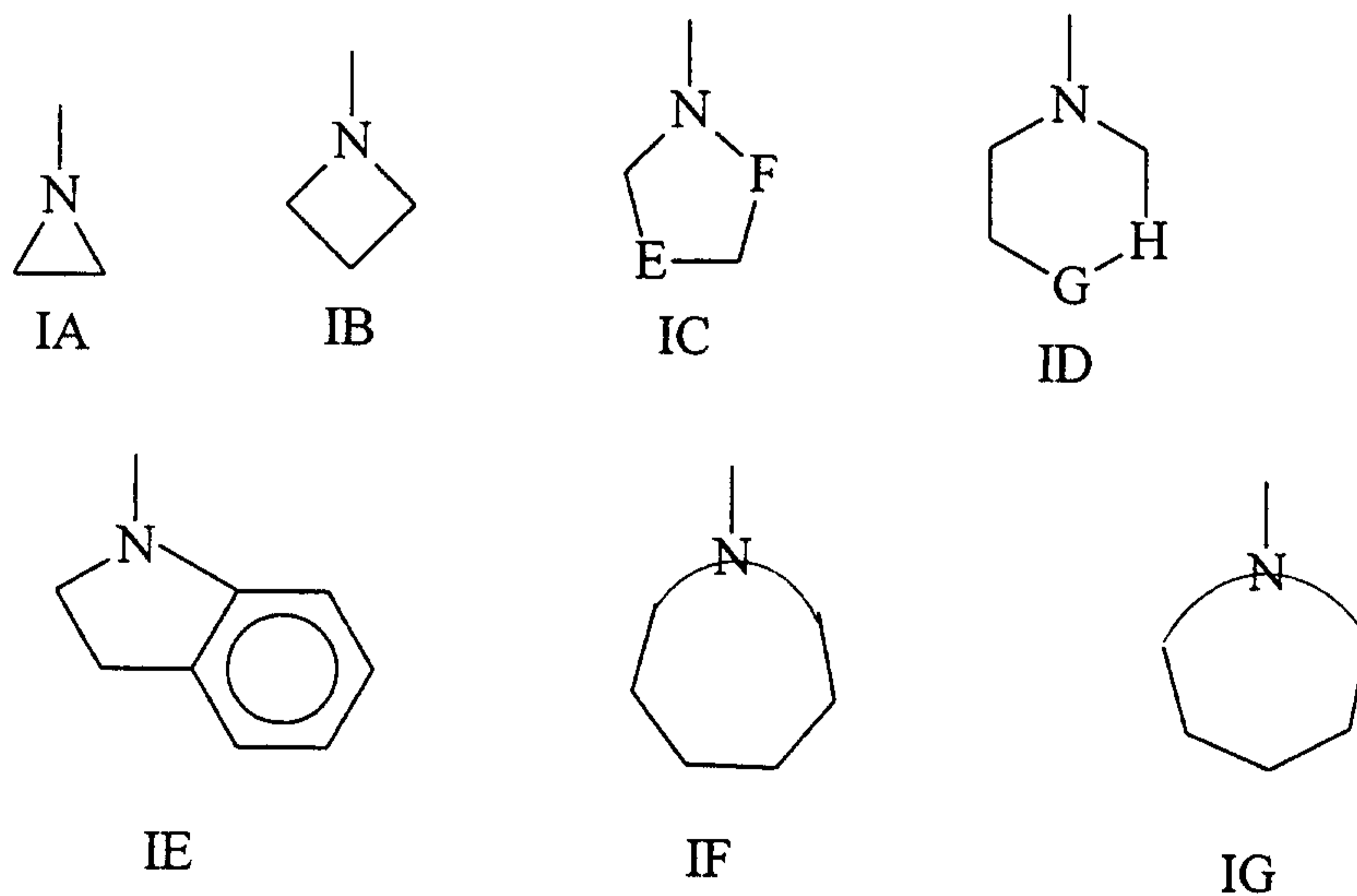
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In graphic formula I, R_1 may be C_1 - C_{10} alkyl, halogen, or the group, $-O-L$, wherein L is a C_1 - C_{12} alkyl, e.g., methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, and dodecyl, said halogen being chloro, fluoro, or bromo, and a is the integer 0, 1 or 2.

- 5 Preferably, R_1 is C_1 - C_5 alkyl, fluoro, bromo or the group, $-O-L$, wherein L is C_1 - C_4 alkyl and a is the integer 0 or 1. Most preferably, R_1 is C_1 - C_3 alkyl, fluorine or the group $-O-L$, wherein L is methyl, and a is the integer 0 or 1.

- 10 In graphic formula I, R_2 may be a saturated, unsubstituted or mono- or di-substituted nitrogen containing heterocyclic group selected from the following groups represented by graphic formulae IA through IG:



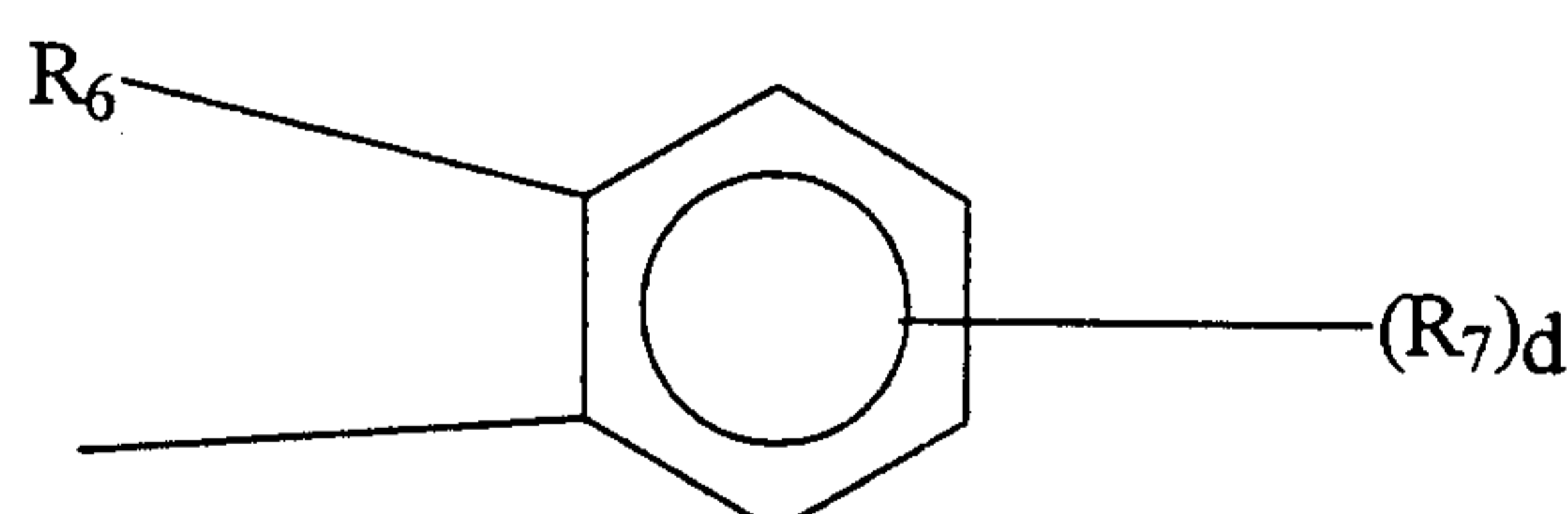
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wherein E and F in graphic formula IC, are each a nitrogen or carbon atom, provided that when E is nitrogen, F is carbon atom, and G in graphic formula ID, is a nitrogen, oxygen, or carbon atom and H is a nitrogen or carbon atom, provided that when H is nitrogen, G is a carbon atom. Examples of R_2 groups include aziridino, azetidino, 1-pyrrolidyl, 1-pyrrolinyl, 1-imidazolidyl, 2-imidazolin-1-yl, 2-pyrazolidyl, 3-pyrazolin-2-yl, morpholino, piperidino, piperazinyl, 4-methyl-1-piperazinyl, 1,4,5,6,-tetra-hydropyrimidinyl, 1-indolinyl, hexamethyleneimino, and heptamethyleneimino. The substituents for R_2 can be C_1 - C_6 alkyl and/or C_1 - C_6 alkoxy. Preferably, R_2 is an unsubstituted or mono-substituted member of the group consisting of indolinyl, morpholino, and piperidino. More preferably, R_2 is morpholino.

B may be the substituted or unsubstituted aryl group, naphthyl or phenyl, said aryl substituents being C_1 - C_5 alkyl, halo(C_1 - C_5)alkyl, hydroxy, C_1 - C_5 alkoxy, C_1 - C_4 alkoxy(C_1 - C_4)alkyl, halogen, morpholino, piperidino, or $R(R'')N$ -, wherein R and R'' are each hydrogen or C_1 - C_3 alkyl, said halogen (or halo) groups being fluoro or chloro. Preferably, B is represented by the following graphic formula II:

II



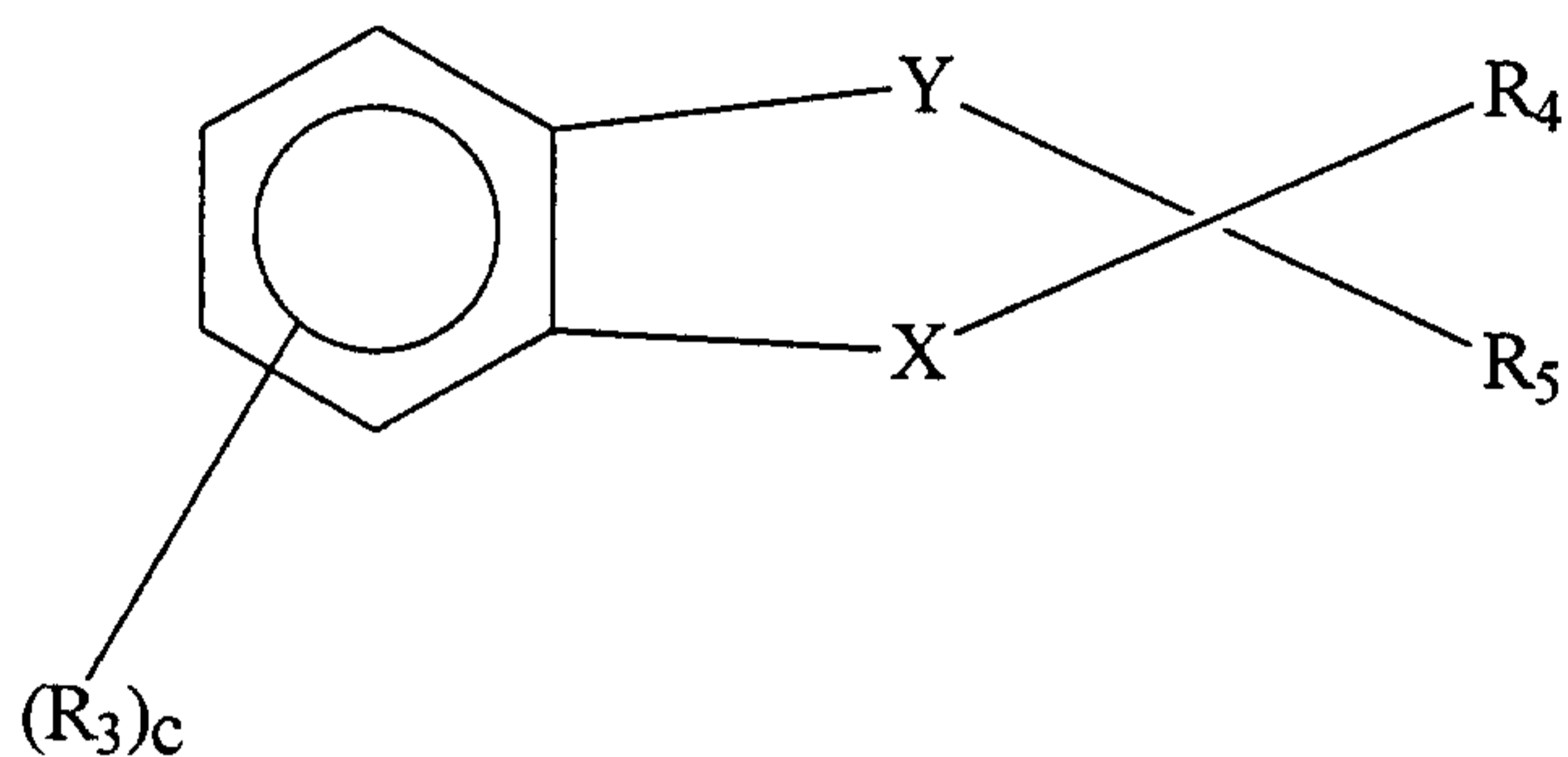
In graphic formula II, R_6 is hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, fluoro, or chloro and each R_7 is a C_1 - C_4 alkyl, C_1 - C_4 alkoxy, hydroxy, chloro, or fluoro and d is an integer from 0 to 2. Preferably, R_6 is hydrogen and R_7 is selected from the group consisting of fluoro, methyl and methoxy.

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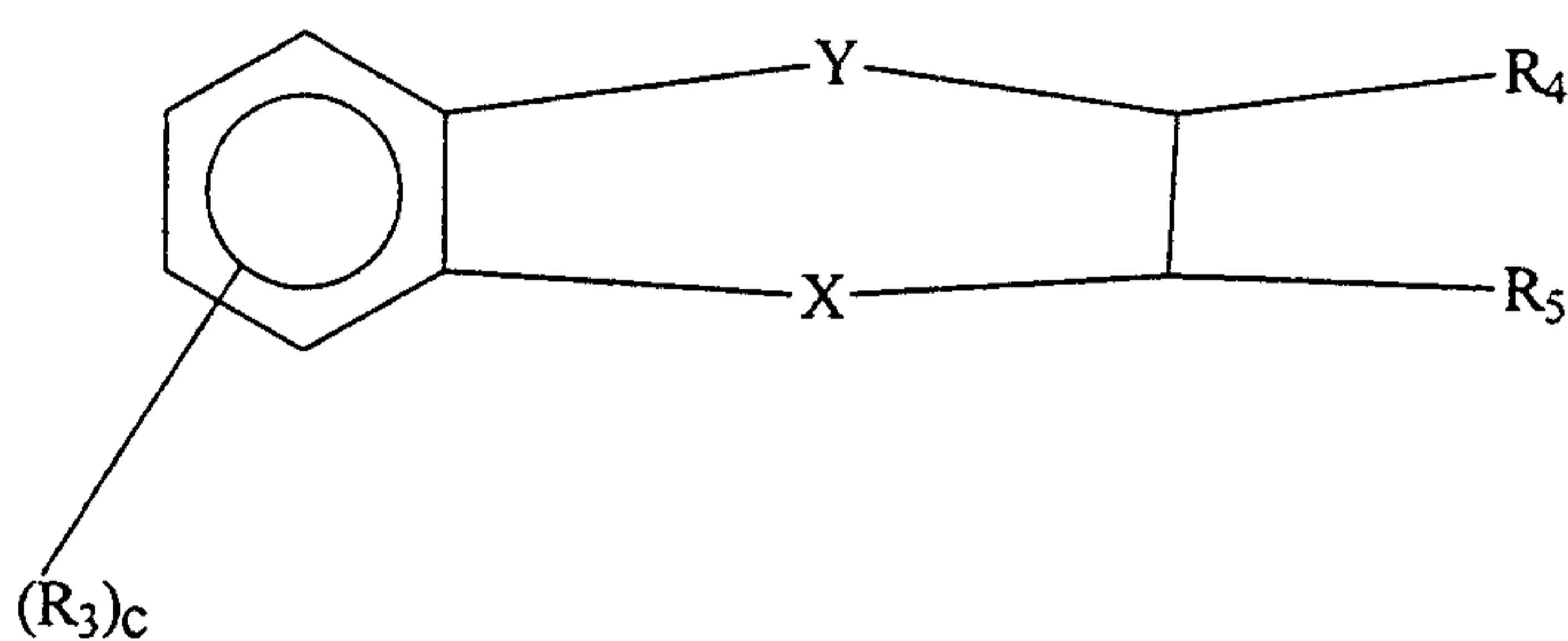
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B' may be represented by one of the following graphic formulae III or IV:

III



IV



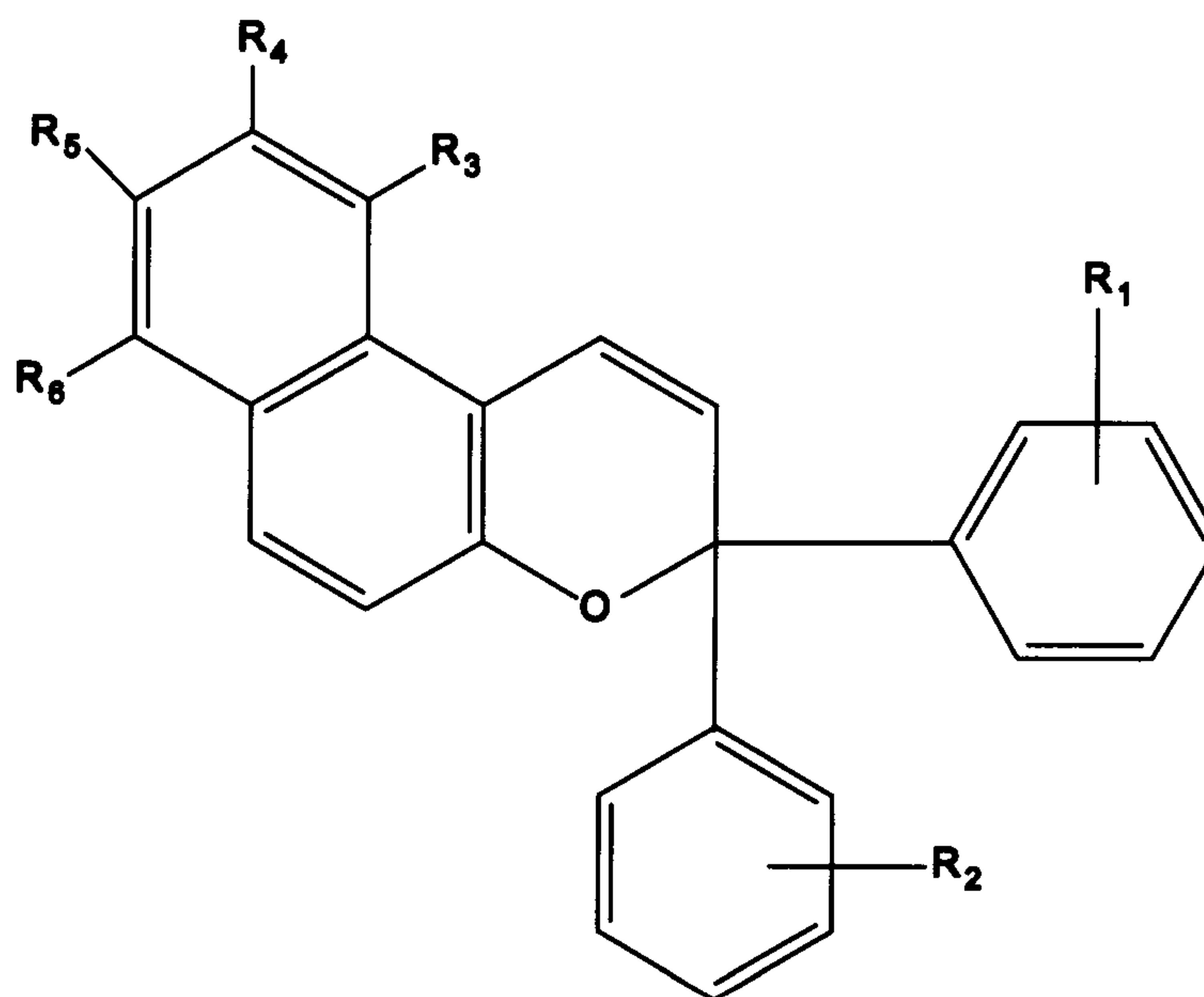
In graphic formula III and IV, X is oxygen or nitrogen and Y is carbon or oxygen, provided that when X is nitrogen, Y is carbon; R_4 and R_5 are each hydrogen or C_1 - C_5 alkyl; each R_3 is a C_1 - C_5 alkyl, C_1 - C_5 alkoxy, hydroxy, or halogen, said halogen substituent being chloro, fluoro, or bromo, and c is an integer from 0 to 3, e.g., 0, 1, 2, or 3. Preferably, B' is represented by graphic formula III or IV, wherein X is oxygen; Y is carbon or oxygen; R_4 and R_5 are each hydrogen or C_1 - C_4 alkyl; each R_3 is a C_1 - C_4 alkyl, C_1 - C_4 alkoxy, hydroxy, or fluoro; and c is the integer 0, 1 or 2. Most preferably, B' is 2,3-dihydroxybenzofuran-5-yl, 2-methyldihydroxybenzofuran-5-yl, indoline-5-yl, 1,2,3,4-tetrahydroquinoline-6-yl, chroman-6-yl or 1,3-benzodioxole-5-yl.

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In graphic formula III, when R₄ and R₅ are H and when X is oxygen and Y is carbon and c is zero, the group is a 2,3-dihydrobenzo-furan-5-yl; when X is carbon and c is zero, the group is a 2,3-dihydrobenzo-furan-5-yl; when X is oxygen and Y is oxygen and c is zero, the group is 1,3-benzodioxole-5-yl; and when X is nitrogen and Y is carbon and c is zero, the group is indoline-5-yl. In graphic formula IV, when X is oxygen and Y is carbon, the unsubstituted group is a chroman-6-yl; when X is oxygen and Y is oxygen, the unsubstituted group is a 1,4-benzodioxan-6-yl; and when X is nitrogen and Y is carbon, the unsubstituted group is 1,2,3,4-tetrahydroquinoline-6-yl. For brevity, these groups will be referred to herein as fused heterocyclicphenyl groups.

The preferred naphthopyran dye is 3,3-diphenyl-3-H-naphtho[2,1-b]pyran represented by the formula



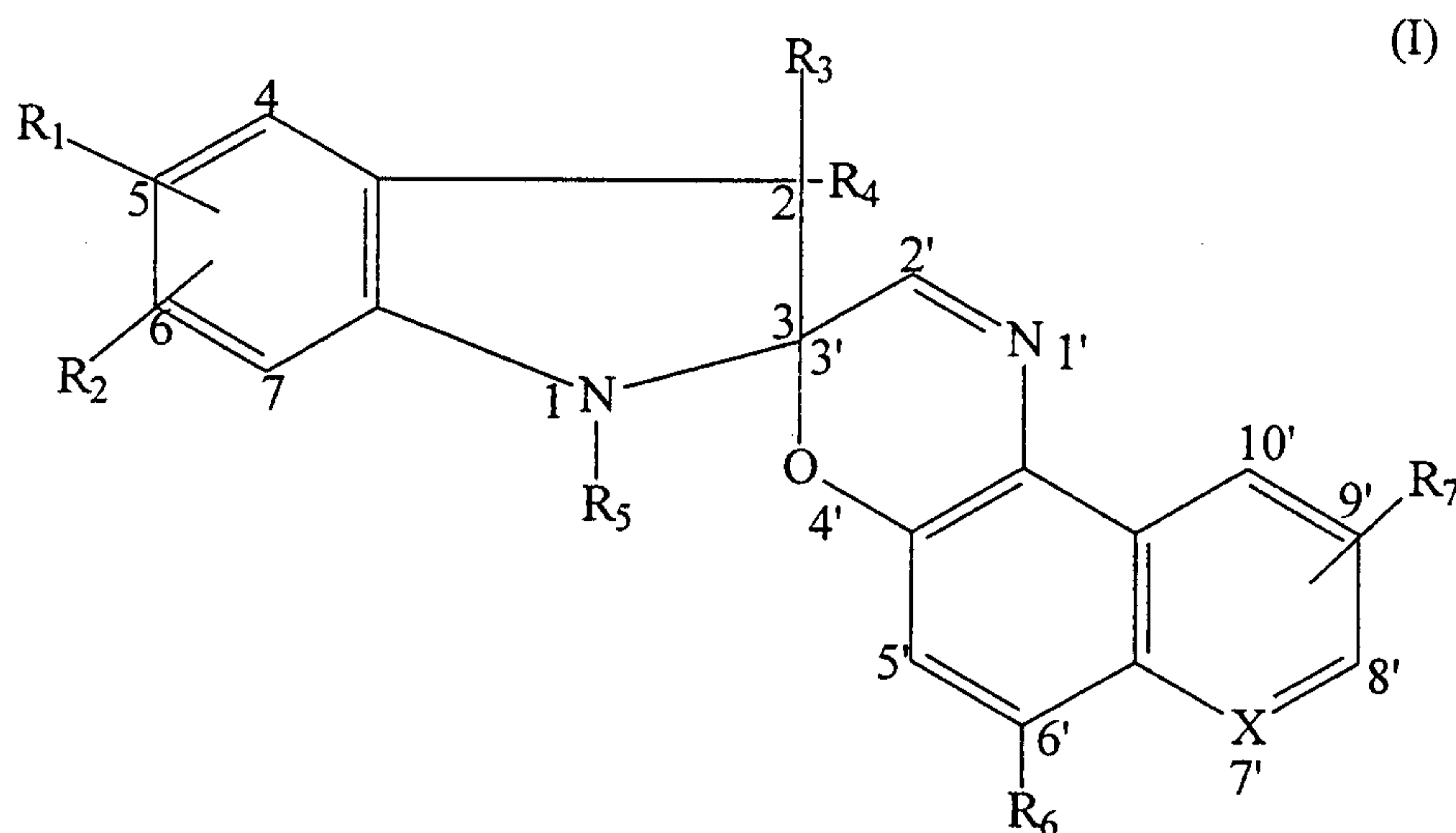
15 where R₁ to R₆ denote hydrogen.

The spiroxazines suitable in the present invention are known: see for instance U.S. Patents 3,562,172; 3,578,602; 4,215,010 and 4,342,668. Essentially,

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the spirooxazines suitable in the present invention may be described by the formula



where:

- R_1 and R_2 independently represent a hydrogen or halogen (fluorine, chlorine or bromine) atom or a group chosen from C_1 - C_5 linear or branched alkyl, C_1 - C_5 perfluoro-alkyl, C_1 - C_5 alkoxy, nitro or cyano;
- R_3 and R_4 independently represent C_1 - C_5 linear or branched alkyl, phenyl or benzyl groups; or R_3 and R_4 when considered jointly with the carbon atom to which they are linked form a C_5 - C_8 cycloalkyl group;
- R_5 represents a C_1 - C_5 linear or branched alkyl, phenyl, benzyl or allyl group;
- R_6 represents a hydrogen atom or a C_1 - C_5 linear or branched alkyl group or the group $-NR_8R_9$ where R_8 is a C_1 - C_5 linear or branched alkyl, phenyl or benzyl group, R_9 is hydrogen or has the same meaning as R_8 , or R_8 and R_9 when considered jointly with the nitrogen atom to which they are linked form a cyclic structure comprising 5-12 members and possibly containing a further heteroatom chosen from oxygen and nitrogen; and
- R_7 represents a hydrogen or halogen (fluorine, chlorine or bromine) atom or a group chosen from: C_1 - C_5 linear or branched alkyl, C_1 - C_5 alkoxy,

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cyano, thio-ether and carboxylated ester with 1-3 carbon atoms in the ester portion, or represents an aromatic or heterocyclic condensed ring; X represents CH or N-.

In particular, the groups R_1 and R_2 , when not hydrogen, can be
 5 linked in any of positions 4, 5, 6 and 7 of the indoline part of the molecule. In addition, the group R_7 , if not representing hydrogen or an aromatic or heterocyclic condensed ring, can be present in any of the positions 7', 8', 9' and 10' of the naphthalene part of the molecule.

In the preferred embodiment, photochromatic compounds
 10 corresponding to general formula (I) are used in which:

R_1 and R_2 independently represent a hydrogen atom or the methyl group;
 R_3 and R_4 each represent the methyl group or jointly represent the cyclohexyl group;

R_5 represents the methyl group;

15 R_6 represents a hydrogen atom or the $-NR_8R_9$ group where the groups R_8 and R_9 together with the nitrogen atom to which they are linked form a piperidyl, morpholyl, pyrrolidyl or hexamethyleneimino ring structure; and R_7 represents a hydrogen atom; and

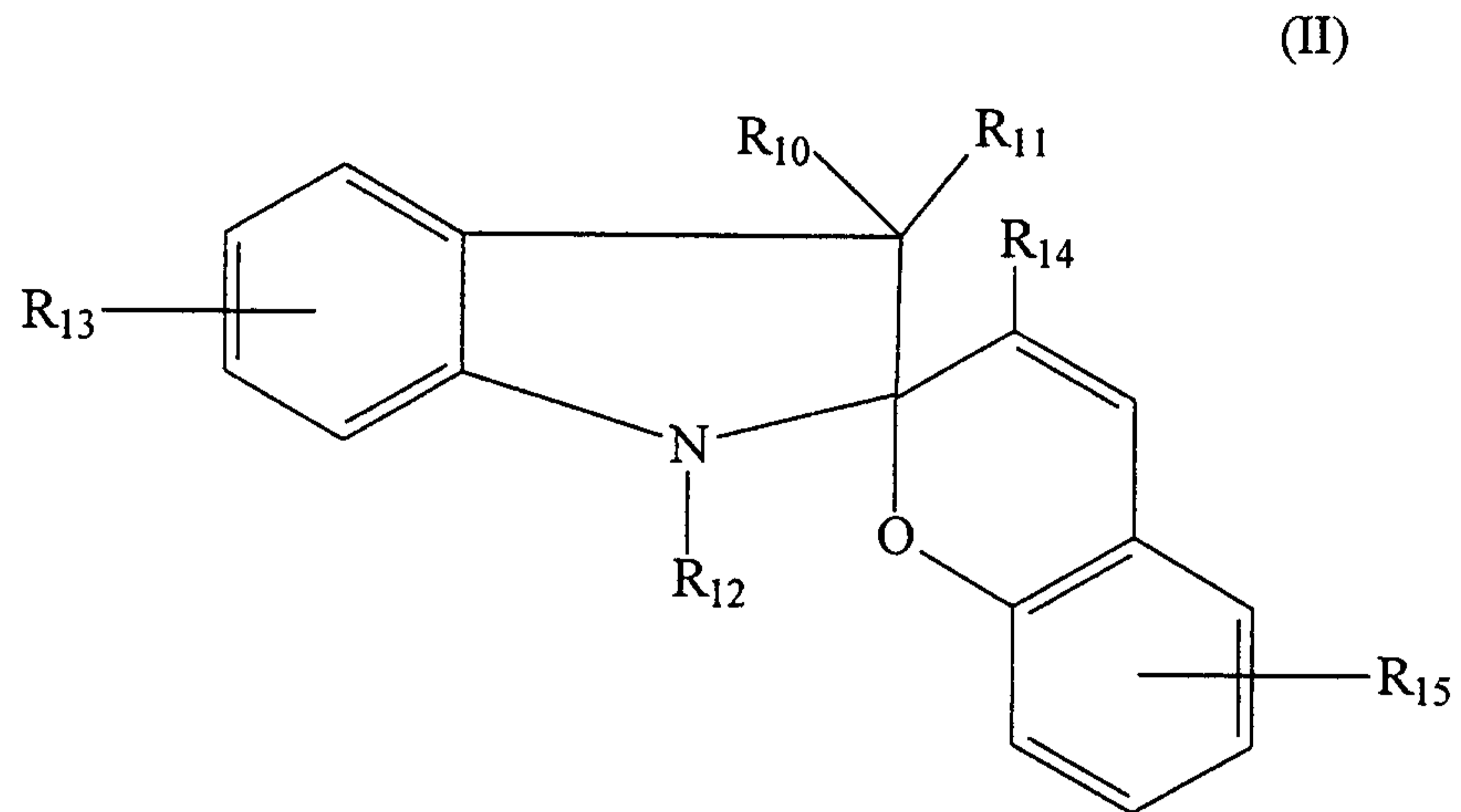
X represents CH.

20 Examples of preferred photochromatic compounds used according to the present invention are 1,3,3,4,5- or 1,3,3,5,6-pentamethyl spiro (indoline-2,3'-[3H]-naphtho-(2,1-b)-(1,4)-oxazine); 1,3,3-trimethyl spiro (indoline-2,3'-[3H]-naphtho-2,1-b)-(1,4)-oxazine); 1,3,3-trimethyl spiro (indoline-6-(1-piperidyl)-2,3'-[3H]-naphtho-2,1-b)-(1,4)-oxazine; 1,3,3-
 25 trimethyl spiro (indoline-6'-(1-morpholyl)-2,3'-[3H]-naphtho-(2,1-b)-(1,4)-oxazine); 1,3,3,4,5- or 1,3,3,5,6-pentamethyl spiro (indoline-6'-(1-piperidyl)-2,3'-[3H]-naphtho-(2,1-b)-(1,4)-oxazine); and 1,3,3-trimethyl spiro (indoline-6'-(1-piperidyl)-9'-(methoxy)-2,3'-[3H]-naphtho-(2,1-b)-(1,4)-oxazine).

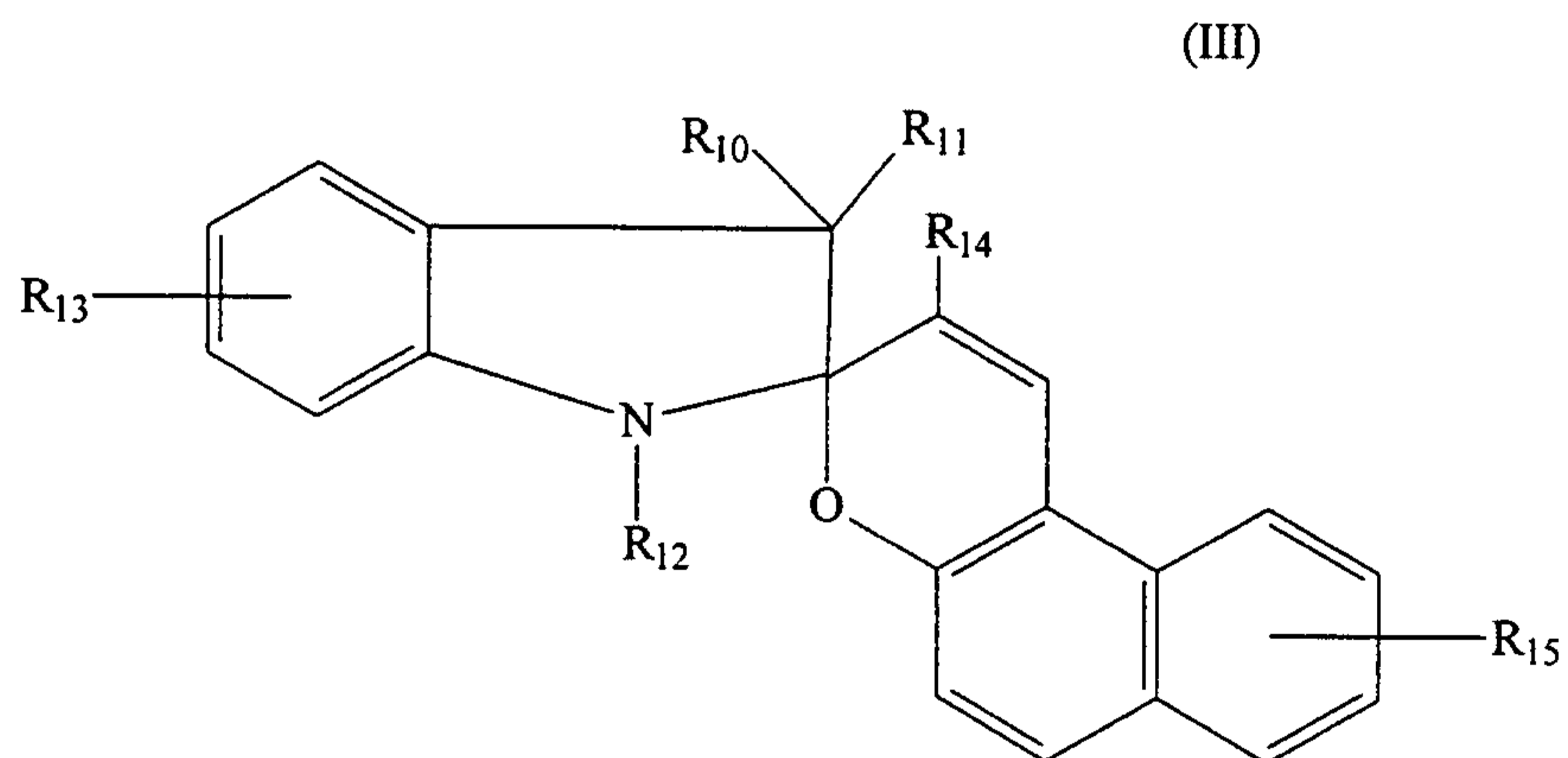
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The spiropyrans useful for the purposes of the present invention, are photochromatic organic compounds which can be defined by the following general formulae (II), (III), (IV) and (V):



indoline naphtho pyrans

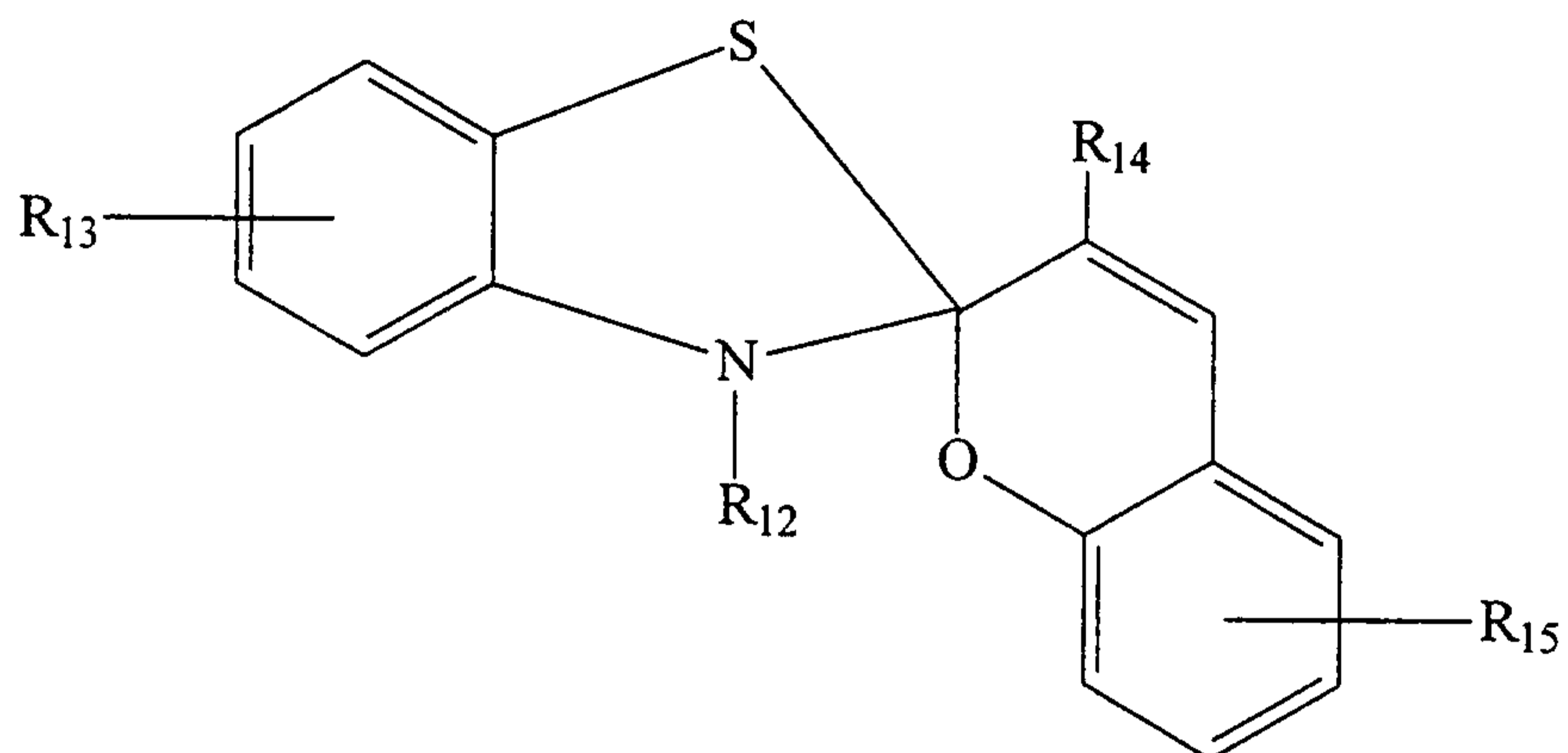


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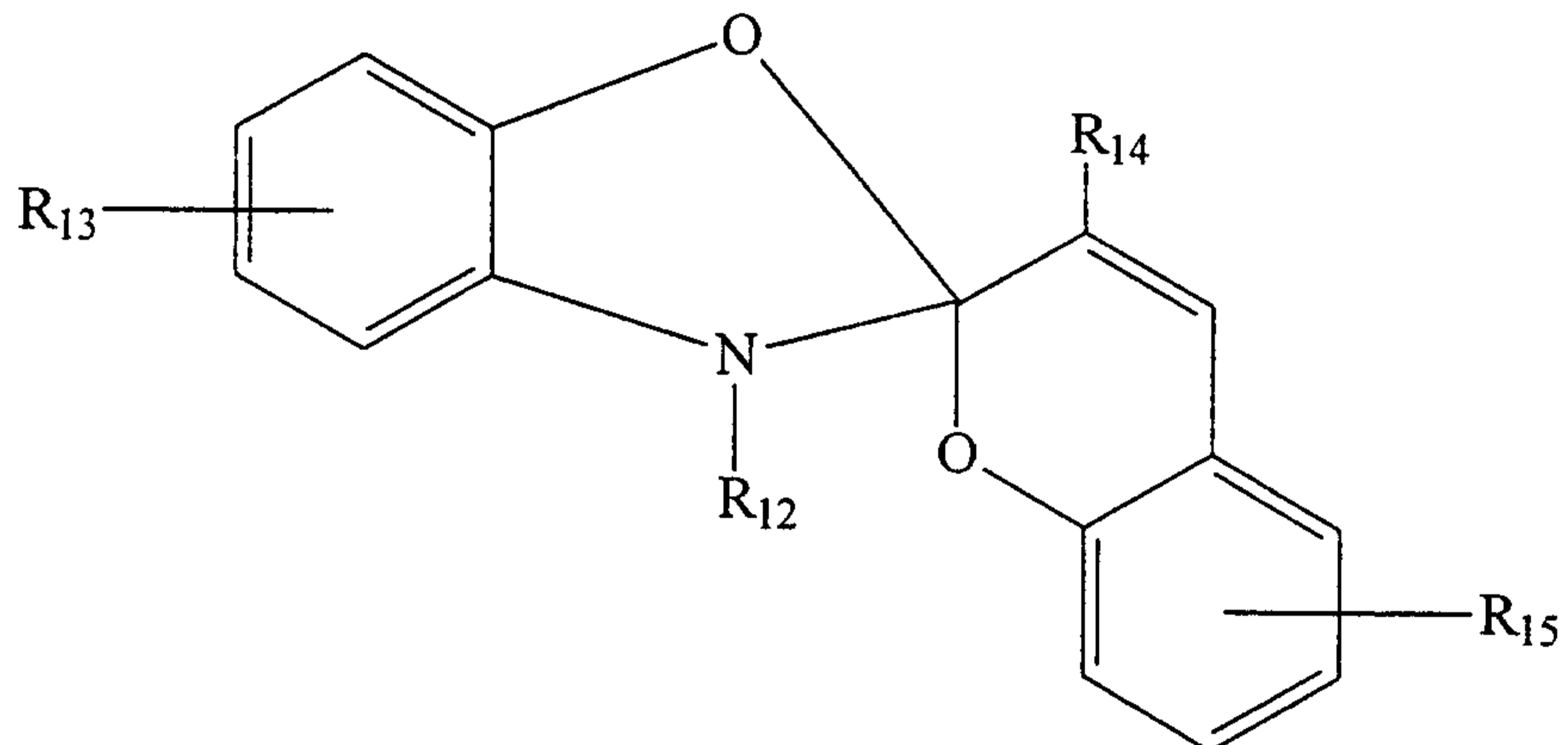
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benzothiazoline spiro pyrans

(IV)

**benzoxazoline spiro pyrans**

(V)



in the preceding general formulae:

R₁₀ and R₁₁ represent alkyl or aryl groups;

5 R₁₂ represents an alkyl, aryl group or alkyl substituted group (such as hydroxyalkyl, halogenalkyl, carbalcoxyalkyl, alkoxyalkyl and aminoalkyl);

R₁₄ represents hydrogen or an alkyl, aryl or alkoxy; and

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R₁₃ and R₁₅ represent hydrogen or mono- or poly-substitution groups, chosen among alkyl and substituted alkyl groups, or halogen, nitro or alkoxy.

Fulgides and fulgimides suitable in the context of the invention are known and have been described in the literature (see, for instance, Applied Photochromic Polymer Systems, Edited by C.B. McArdle, Blackie USA: Chapman & Hall, New York, 1992, pp. 80-120).

The inventive composition may be used in applications requiring photochromic materials which were referred to above. Included are photochromic lenses such as are described in U.S. Patent 5,531,940.

The invention is further illustrated but is not intended to be limited by the following examples in which all parts and percentages are by weight unless otherwise specified.

EXAMPLES

The following components were used to prepare the elastomers of this invention as illustrated in the examples:

Polyol A: A polytetramethylene glycol diol having an OH number of 112 mg KOH/g and a number average MW of ~ 1000 g/mole.

Polyol BA polypropylene glycol diol having an OH number of 112 mg KOH/g and a number average MW of ~ 1000 g/mole.

Polyol CA polyhexamethylene carbonate diol having an OH number of 56 mg KOH/g and a number average MW of ~ 2000 g/mole.

Polyol DA polybutylene adipate diol having an OH number of 56 mg KOH/g and a number average MW of ~ 2000 g/mole.

Polyol EA polypropylene glycol triol having an OH number of 550 mg KOH/g and a number average MW of ~ 306 g/mole.

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Polyol F A polypropylene glycol triol having an OH number of 370 mg KOH/g and a number average MW of ~ 455 g/mole.

Catalyst Solution: A solution of 1 g of dibutyltin dilaurate and 99 g of Polyol A.

- 5 **Isocyanate A**: The isocyanate was a mixture of isomers of 4,4'-dicyclohexylmethanediisocyanate having an isomer ratio of ~ 20% by weight trans, trans, 50% by weight cis, trans, and 30% by weight cis, cis isomer.

10 **Photochromic Dye A**: 3,3-diphenyl-3-H-naphtho[2,1-b]pyran, available commercially as Variacrol Yellow L from Great Lakes Chemical Company

Photochromic Dye B: 1,3-dihydro-1,3,3-trimethyl-spiro-2H-indole-2,3'-(3H)-naphtho(2,1-b)(1,4)oxazine available as Variacrol Blue A from the Great Lakes Chemical Company

- 15 Examples 1-10 illustrate the preparation of prepolymers that are used to prepare the photochromic materials of this invention.

Example 1:

In a 3-necked flask equipped with an overhead stirrer, thermocouple, and a vacuum adapter, Isocyanate A (690.6 g; 5.26 eq.)
20 was charged into the reactor and stirred at ambient temperature. Polyol A (809.4 g; 1.62 eq.) was preheated in an oven to 80°C and added to the reactor. The mixture was allowed to stir for ~ 15 minutes, before adding Catalyst Solution A. (3.75 g). The reaction flask was evacuated (< 0.1 mm HG) and held at 90°C for 3.5 hours. An aliquot of the prepolymer
25 was withdrawn and titrated for isocyanate content using standard n-butyl amine titration. The isocyanate content was found to be 9.92% (theory; 10.2%).

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Example 2:

In a 3-necked flask equipped with an overhead stirrer, thermocouple, and a vacuum adapter, Isocyanate A (1062.0 g; 8.09 eq.) was charged into the reactor and stirred at ambient temperature. Polyol
5 A (438.1 g; 0.876 eq.) was preheated in an oven to 80°C and added to the reactor. The mixture was allowed to stir for ~ 15 minutes, before adding catalyst solution A (3.75 g). The reaction flask was evacuated (< 0.1 mm HG) and held at 90°C for 3.0 hours. An aliquot of the prepolymer was withdrawn and titrated for isocyanate content using
10 standard n-butyl amine titration. The isocyanate content was found to be 19.80% (theory; 20.2%).

Example 3:

In a 3-necked flask equipped with an overhead stirrer, thermocouple, and a vacuum adapter, Isocyanate A (284.6 g; 2.17 eq.)
15 was charged into the reactor and stirred at ambient temperature. Polyol B (333.5 g; 0.667 eq.) was added to the reactor at ambient temperature. Catalyst A (1.55 g) was added and the reaction mixture was heated (90°C) under vacuum (< 0.1 mm Hg) for 4 hours. An aliquot of the prepolymer was withdrawn and titrated for isocyanate content using
20 standard n-butyl amine titration. The isocyanate content was found to be 9.92% (theory; 10.2%).

Example 4:

In a 3-necked flask equipped with an overhead stirrer, thermocouple, and a vacuum adapter, Isocyanate A (437.6 g; 3.34 eq.)
25 was charged into the reactor and stirred at ambient temperature. Polyol B (180.5 g; 0.361 eq.) was added to the reactor at ambient temperature. Catalyst A (1.55 g) was added and the reaction mixture was heated (90°C) under vacuum (< 0.1 mm Hg) for 4 hours. An aliquot of the prepolymer was withdrawn and titrated for isocyanate content using

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standard n-butyl amine titration. The isocyanate content was found to be 19.90% (theory; 20.2%).

Example 5:

In a 3-necked flask equipped with an overhead stirrer,
5 thermocouple, and a vacuum adapter, Isocyanate A (246.6 g; 1.88 eq.)
was charged into the reactor and stirred at ambient temperature.
Polyol C (372.8 g; 0.373 eq.) was added to the reactor at ca. 80°C.
Catalyst A (1.55 g) was added and the reaction mixture was heated
(90°C) under vacuum (< 0.1 mm Hg) for 4 hours. An aliquot of the
10 prepolymer was withdrawn and titrated for isocyanate content using
standard n-butyl amine titration. The isocyanate content was found to be
9.95% (theory; 10.2%).

Example 6:

In a 3-necked flask equipped with an overhead stirrer,
15 thermocouple, and a vacuum adapter, Isocyanate A (417.2 g; 3.18 eq.)
was charged into the reactor and stirred at ambient temperature.
Polyol C (201.8 g; 0.202 eq.) was added to the reactor at ca 80°C.
Catalyst A (1.55 g) was added and the reaction mixture was heated
(90°C) under vacuum (< 0.1 mm Hg) for 4 hours. An aliquot of the
20 prepolymer was withdrawn and titrated for isocyanate content using
standard n-butyl amine titration. The isocyanate content was found to be
19.93% (theory; 20.2%).

Example 7:

In a 3-necked flask equipped with an overhead stirrer,
25 thermocouple, and a vacuum adapter, Isocyanate A (246.2 g; 1.88 eq.)
was charged into the reactor and stirred at ambient temperature.
Polyol D (372.8 g; 0.373 eq.) was melted in an oven at ~ 80°C and added
to the reactor. Catalyst A (1.55 g) was added and the reaction mixture
was heated (90°C) under vacuum (< 0.1 mm Hg) for 4 hours. An aliquot
30 of the prepolymer was withdrawn and titrated for isocyanate content

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using standard n-butyl amine titration. The isocyanate content was found to be 9.90% (theory; 10.2%).

Example 8:

In a 3-necked flask equipped with an overhead stirrer,
5 thermocouple, and a vacuum adapter, Isocyanate A (417.2 g; 3.18 eq.)
was charged into the reactor and stirred at ambient temperature.
Polyol D (201.8 g; 0.202 eq.) was melted in an oven at ~ 80°C and added
to the reactor. Catalyst A (1.55 g) was added and the reaction mixture
was heated (90°C) under vacuum (< 0.1 mm Hg) for 4 hours. An aliquot
10 of the prepolymer was withdrawn and titrated for isocyanate content
using standard n-butyl amine titration. The isocyanate content was found
to be 19.90% (theory; 20.2%).

Example 9:

In a 3-necked flask equipped with an overhead stirrer,
15 thermocouple, and a vacuum adapter, Isocyanate A (559.0 g; 4.26 eq.)
was charged into the reactor and stirred at ambient temperature.
Polyol A (338.7 g; 0.677 eq.) was preheated in an oven to 80°C and
added to the reactor. The mixture was allowed to stir for ~ 15 minutes,
before adding catalyst solution A. (2.25 g). The reaction flask was
20 evacuated (< 0.1 mm HG) and held at 90°C for 3.0 hours. An aliquot of
the prepolymer was withdrawn and titrated for isocyanate content using
standard n-butyl amine titration. The isocyanate content was found to be
16.40% (theory; 16.7%).

Example 10 (comparative example):

25 Isocyanate A (554.9 g; 4.23 eq.), Polyol E (45.1 g; 0.442 eq.) and
catalyst solution A (1.5 g) were combined at room temperature in a 3-
necked flask equipped with an overhead stirrer, thermocouple, and a
vacuum adapter. The mixture was allowed to stir under vacuum (<0.1
mm HG) as the temperature was increased over ~ 30 minutes to 100°C.

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After 4 hours at 100°C, an aliquot was removed and titrated for isocyanate content (found 26.3% NCO; theory; 26.5%).

Examples 11-36:

General Procedure for Preparing the Photochromic Polyurethanes

5 The prepolymers from Examples 1-10 were cast to form photochromic polyurethanes according to the following general procedure. The prepolymer was heated in vacuo (< 0.1 mm HG) with stirring to 80°C and the photochromic dye was added at a level sufficient to give 0.1 wt.% in the cast polyurethane material. The amount of prepolymer
10 indicated in Table 1 was weighed into a disposable glass container. The desired chain extender was warmed in an oven to 60°C before combining with the prepolymer. The mixture was stirred for ~ 30 seconds and subsequently poured into an aluminum tray (~ 3" x 6" x 1") that had been pre-treated with a silicone based mold release (MR 515) available from
15 ChemTrend Inc. The tray containing the casting was cured in an oven (110°C) for 18 hours. The plaque was removed from the tray and analyzed for photochromic behavior as described below.

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Table 1. Description of Elastomers Example 11 through 22

Ex.	Prepolymer (Ex. #)	Prepolymer Amount (g:meq)	Chain Extender Type	Chain Extender (g:meq)	Photochromic Dye
11	1	90.8:214	1,4-butanediol	9.17:204	B
12	1	90.8:214	1,4-butanediol	9.17:204	A
13	2	83.2:392	1,4-butanediol	16.8:373	B
14	2	83.2:392	1,4-butanediol	16.8:373	A
15	1	81.3:192	Polyol E	19.8:194	B
16	1	81.3:192	Polyol E	19.8:194	A
17	2	68.7:324	Polyol E	31.4:308	B
18	2	68.7:324	Polyol E	31.4:308	B
19	3	90.9:215	1,4-butanediol	9.1:202	B
20	3	81.3:192	Polyol E	18.7:183	B
21	4	83.1:394	1,4-butanediol	16.9:376	B
22	4	68.5:324	Polyol E	31.5:309	B

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Table 1(Cont.). Description of Elastomers Example 23 through 36

Example	Prepolymer (Ex. #)	Prepolymer Amount (g:meq.)	Chain Extender Type	Chain Extender (g:meq.)	Photochromic Dye
23	5	90.8:215	1,4-butanediol	9.2:204	B
24	5	81.3:193	Polyol E	18.7:183	B
25	6	83.1:394	1,4-butanediol	16.9:376	B
26	6	68.5:325	Polyol E	31.6:310	B
27	7	90.8:214	1,4-butanediol	9.2:204	B
28	7	81.4:192	Polyol E	18.6:182	B
29	8	83.1:394	1,4-butanediol	16.9:375	B
30	8	68.5:324	Polyol E	31.5:309	B
31	9	79.1:309	1,4-butanediol	13.2:294	B
32	9	83.6:326	1,4-butanediol	14.0:311	A
33	9	57.8:226	Polyol E	22.2:218	A
34	9	57.8:226	Polyol E	22.2:218	B
35	10	89.6:561	Polyol F	80.2:529	A
36	10	89.6:561	Polyol F	80.2:529	B

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Determining Photochromic Behavior of the Polyurethanes

The initial absorbance value (A_0) for each plaque was recorded at the λ_{\max} of the photochromic dye (λ_{\max} of Dye A = 425 nm; λ_{\max} of Dye B = 610 nm). Absorbance is defined as the natural logarithm of the inverse of the ratio of transmitted over incident light intensity and is obtained from transmission spectroscopy. The plaque was then exposed to a hand-held light source (Spectroline Model EN-280 L; 365 nm output). After 1, 2, 4 and 10 minutes of exposure to the light, the optical absorption of the plaque (A) at the λ_{\max} of the photochromic dye was re-recorded. These values were used to calculate a ΔA value after each exposure, where ΔA is defined as $A - A_0$. The value of the ΔA after 2 minutes was divided by the ΔA after 10 minutes and multiplied by 100 to give a parameter that indicates the percentage of darkening that occurs within two minutes in the particular matrix. This value ($\Delta A @ 2$ minutes) for each of the polyurethanes is given in Table 2.

After 10 minutes of exposure to the light source, the sample was placed in the spectrometer and the absorption of the plaque at the λ_{\max} of the dye was monitored. The time at which the ΔA value decreased to 50% of its initial value (immediately after the 10 minute illumination) was recorded and is given in Table 2 as the T_{50} for fading of the dye in the particular matrix.

The photochromic performance (darkening and fading behavior) is summarized in Table 2 below. Examples 11-34 show acceptable performance, defined as a $\Delta A @ 2$ minutes of greater than 50% and a T_{50} of < 2 minutes. The comparative examples 35 and 36, where the polyurethanes were prepared without the requisite high MW component do not have acceptable photochromic performance by this definition.

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Table 2. Photochromic Behavior of Elastomers from Examples 11-36

Example	ΔA @ 2 minutes (% of max)	T_{50} Fade (sec.)
11	100	8
12	94	15
13	92	30
14	88	60
15	87	92
16	79	15
17	85	93
18	89	74
19	86	3
20	72	11
21	83	52
22	87	73
23	94	15
24	100	15
25	89	99
26	79	80
27	90	13
28	77	12
29	93	110
30	88	50
31	96	30
32	95	25
33	97	35
34	95	35
35	100	150
36	83	155

30 Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A photochromic polyurethane comprising:
 - a) an isocyanate reactive mixture comprising:
 - 5 i) from about 20 to about 60% by weight of one or more polyols having a functionality of from 1.8 to 4 and molecular weights of from 500 to 6000 g/mole;
 - ii) from about 5 to about 35% by weight of one or more diols or triols or mixtures thereof having a functionality of from 1.8 to 3 and molecular weights of
10 from 62 to 499.
 - b) an aliphatic polyisocyanate having a functionality ranging from about 2 to about 3;
 - c) a photochromic compound selected from a group consisting of spirooxazines, fulgides, fulgimides, and naphthopyrans,
15 wherein said compound is present in an amount of 0.01 to 5 parts per hundred parts by weight of said isocyanate reactive mixture.
2. A photochromic polyurethane according to Claim 1, wherein
20 said one or more polyols has a molecular weight of from 1,000 to 3,000 g/mole.
3. A photochromic polyurethane according to Claim 1, wherein said one or more polyols has a functionality ranging from 1.8 to about 2.
4. A photochromic polyurethane according to Claim 1, wherein
25 said one or more polyols is selected from a group consisting of polyether polyols, polyester polyols and polycarbonate polyols.
5. A photochromic polyurethane according to Claim 4, wherein said polyether polyol is selected from a group consisting of polypropylene glycol and poly(tetramethylene glycol).
6. A photochromic polyurethane according to Claim 4, wherein
30 said polyester polyol is butylene adipate.

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7. A photochromic polyurethane according to Claim 4, wherein said polycarbonate polyol is polyhexamethylene carbonate.
8. A photochromic polyurethane according to Claim 1, wherein said diol is 1,4-butanediol.
- 5 9. A photochromic polyurethane according to Claim 1, wherein said triol is polypropylene glycol.
- 10 10. A photochromic polyurethane according to Claim 1, wherein said aliphatic polyisocyanate has a functionality of about 2.
11. A photochromic polyurethane according to Claim 10,
10 wherein said aliphatic polyisocyanate comprises either the trans, trans isomer of bis-(4-isocyanatocyclohexyl) or mixtures of the stereoisomers of bis-(4-isocyanatocyclohexyl)-methane.
12. A photochromic polyurethane according to Claim 1, wherein said photochromic compound is 3,3-diphenyl-3-H-naphtho [2,1-b]pyran.
- 15 13. A photochromic polyurethane according to Claim 1, wherein said photochromic compound is 1,3-dihydro-1,3,3-trimethyl-spiro-2H-indole-2,3'-(3H)-naphtho(2,1-b)(1,4)oxazine.