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(72) Inventeurs/Inventors:
MELZIG, MANFRED, DE;
ROHLFING, YVEN, DE;
WEIGAND, UDO, DE

(73) Propriétaire/Owner:
RODENSTOCK GMBH, DE

(74) Agent: RIDOUT & MAYBEE LLP

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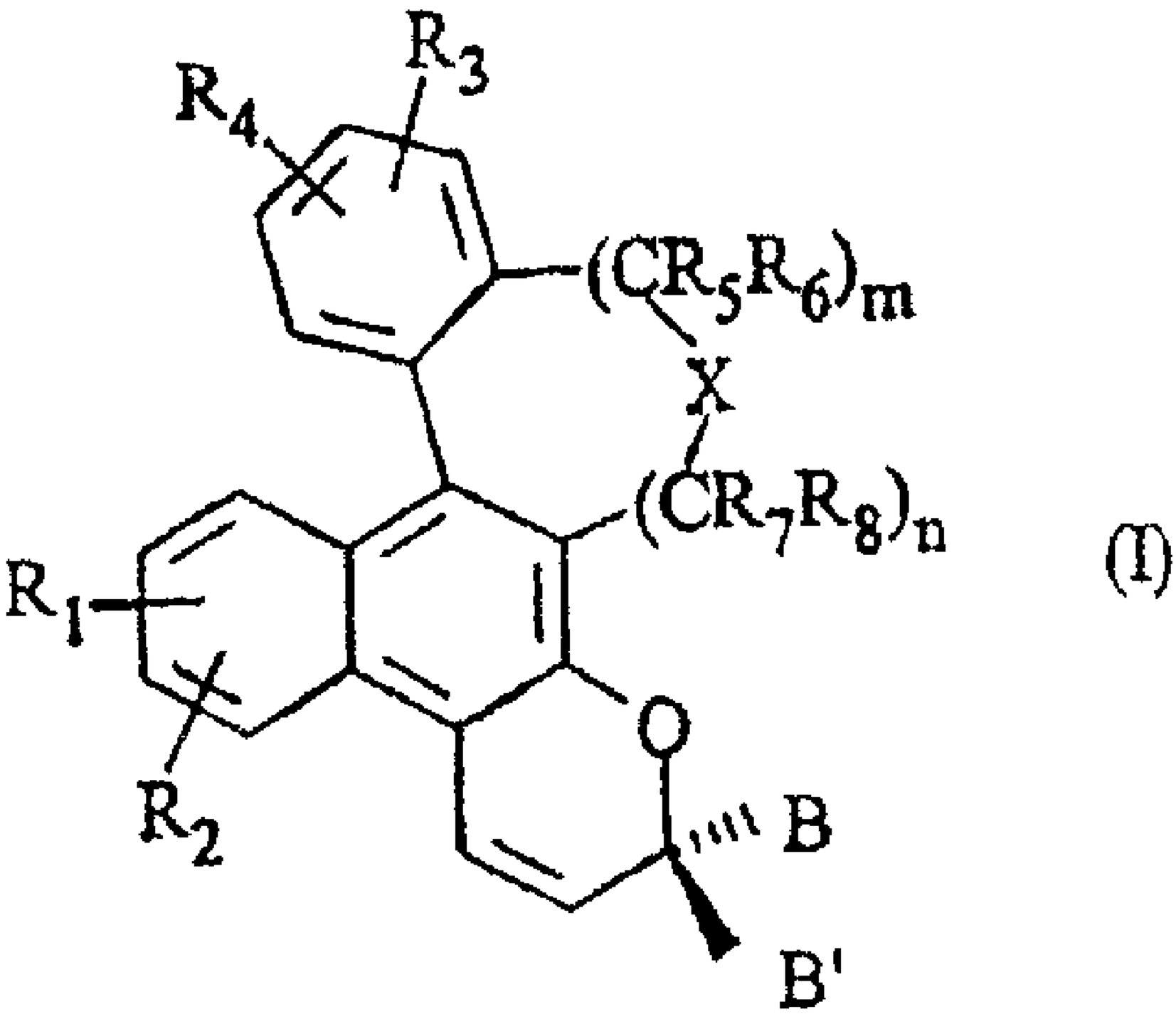
(54) Title: PHOTOCHROMIC H-FUSED BENZO[F]CHROMENE DERIVATIVES



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(57) Abrégé/Abstract:
The invention relates to specific photochromic h-fused benzo[f]chromene derivatives of the general formula (I), (see formula I) in addition to the use thereof in all types of plastic, in particular for ophthalmic purposes. The invention relates specifically to

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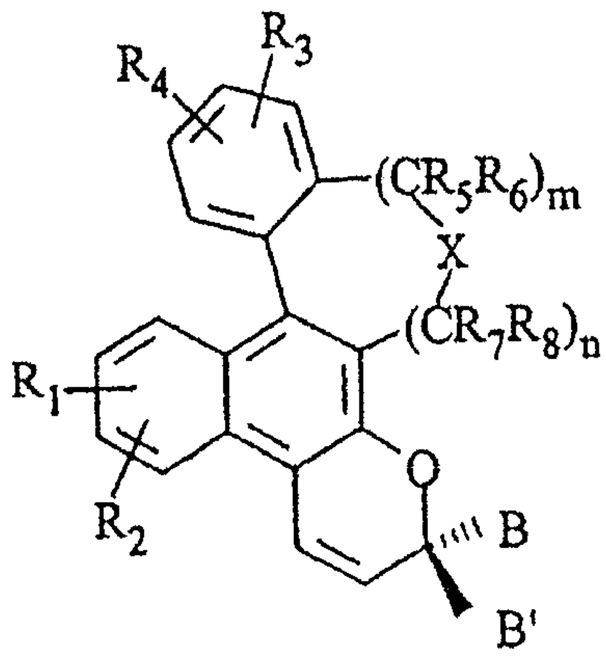
ABSTRACT

The invention relates to specific photochromic h-fused benzo[f]chromene derivatives of the general formula (I),



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in addition to the use thereof in all types of plastic, in particular for ophthalmic purposes. The invention relates specifically to photochromic compounds derived from benzo[f]chromenes, said compounds comprising in their closed form particular long wave length absorptions maxima and good performance in the open, coloured form, whereby good harmony is achieved with the indenonaphthopyranes which are diffused in said phototropic glass in applications of phototropic glass.

Photochromic h-Fused Benzo[f]chromene Derivatives

The present invention relates to specific photochromic h-fused benzo[f]chromene derivatives and their use in plastics of all types, in particular for ophthalmic purposes. The present invention relates in particular to photochromic compounds derived from benzo[f]chromenes which in their closed form have especially long wavelength absorption maxima with good efficiency in the open colored form at the same time, so that when used in phototropic lenses, they harmonize well with the indenonaphthopyrans widely used therein.

Various classes of dyes are known which undergo reversible changes in color when exposed to light of certain wavelengths, in particular sunlight. This is due to the fact that these dye molecules change to an excited colored state by energy input in the form of light, then leave this state again when the energy input is interrupted and return to their colorless or at least almost colorless normal state. These photochromic dyes include for example the naphthopyrans which have already been described with various substituents in the prior art.

Pyrans, specifically naphthopyrans and larger ring systems derived therefrom, are photochromic compounds which even today are the subject of intense investigations. Although a patent application was filed for these compounds for the first time back in 1966 (US 3,567,605), compounds that appeared to be suitable for use in eyeglass lenses were not developed until the 1990s.

The world market for photochromic eyeglasses made of silicate as well as plastic is dominated by the colors gray and brown. Colors such as green, blue, magenta, orange or yellow play a completely subordinate role.

In all photochromic plastic lenses currently on the market, these two colors are achieved by mixtures of at least two photochromic dyes. As explained in US 6,306,316 these may be divided into two groups, namely those whose longest wavelength absorption maximum is above 550 nm, i.e., those which in an excited state yield a violet blue

to green transmission color and those whose longest wavelength absorption maximum is below 550 nm. Their transmission color ranges from yellow to orange to red.

The first group includes 2H-naphthopyrans derived from 1-naphthols and their higher analogs derived therefrom by fusion. These are described in US 5,698,141, US 5,723,072, US 6,146,554, US 6,225,466, US 6,331,625 and US 6,340,765, for example. Although photochromic compounds belonging to other classes, as described in US 4,931,220 or EP 0 600 688, have absorption maxima above 550 nm, they are no longer in commercial use because of their short lifetime and/or short bandwidth of the long wavelength absorption. The long wavelength absorption of photochromic dyes of all gray or brown photochromic plastic lenses currently available on the market (e.g., Rodenstock Perfalit ColorMatic Extra® - since 1999, Transitions Next Generation® - since 2002, Hoya Solio® 1.55 - since 2004) belong to the compounds derived from 1-naphthols described above.

Dyes belonging to the second group include mostly 3H-benzopyrans and 3H-naphthopyrans which are derived from 2-naphthols and are mostly substituted with aryl or heteroaryl in position 2, as described in US 5,244,602, US 5,427,774, US 5,552,090, US 5,552,091, US 5,585,042 and WO 97/20239. The spiroadamantane-substituted compounds described in US 4,826,977 also belong to this group. It is possible to use 2H-naphtho[1,2-b]pyrans derived from 1-naphthols only if the open form is sterically hindered by substitution in position 5 of the system, as described in EP 1 248 778. Without this hindrance, the brightening effect is too slow for use in eyeglass lenses.

Commercially available photochromic compounds such as Reversacol Sunflower, Corn Yellow, Flame and Ruby (James Robinson) or CNN-4 and CNN-8 (Tokuyama Soda) are described in EP 0 691 965 and US 6,719,926. These compounds all have an amino group, usually piperidine or morpholine in position 6 of the naphthopyran system, yielding a very high molar extinction (IOD > 1.5) in the absorption maximum. Without this functional group, the value is approximately 1.5 lower. Unfortunately, this strongly polar substitution pattern results in

strong solvatochromism, so that a portion of the dye used is in the open form in the solid solution (plastic matrix). This is manifested even in the complete absence of exciting light in lightly colored lenses. In addition the transmission after V_λ is also reduced by 4 to 10%. Examples that can be mentioned here include mainly the brown variants of Rodenstock ColorMatic Extra® and Hoya Solio® 1.55.

Another disadvantage is the absorption of the closed form, which has a hipsochromic shift of 20 nm to 25 nm in comparison with the dyes of the first group. The composition is coordinated, i.e., the respective concentrations of the photochromic dyes used are coordinated to achieve a gray or brown color in such a way that the desired color is achieved in normal direct or indirect sunlight. If the very short wavelength portion of the visible sunlight (380-400 nm) is selectively filtered out or blocked, e.g., by window glass with a thermal insulation coating or laminated safety glass in motor vehicles, then the lenses assume a blue color in the case of a gray lens or a gray color in the case of a brown lens. This can be observed well in brightly lit rooms with the plastic photochromic lenses available on the market today and is a cosmetic disadvantage.

Compounds that have a longer wavelength absorption of the closed form due to their structure are described in WO 02/22594. However, the important aspect here is that powerful dyes which absorb in the long wavelength range, i.e., in the violet to blue range are provided, i.e., they have the longer wavelength absorption of the open form. This has been achieved by introducing amino substituents into the naphthopyran system. These compounds have the longest wavelength absorption maxima of the open form which are not below 540 nm. Here again, however, the precoloration when used in plastic eyeglass lens materials is a disadvantage.

US 5,869,658 describes compounds having a similar basic structure, whose open form absorbs in the desired spectral range. However, this publication discusses only indeno-fused naphtho[2,1-b]pyrans, which are also substituted by an alkoxy group in position 6. This is obligatory due to the synthesis because the ring closure does not take place

without an activating substituent that makes the linkage point in p-position nucleophilic. Fused ring systems larger than the five-membered ring are neither described nor possible by this route. Furthermore, the brightening rates are very high. For light exposure in equilibrium, this leads to only a small amount of open, i.e., colored, molecules. The darkening effect is minor ($\Delta OD < 0.5$). Likewise, the absorption of the closed form, usually with maxima below 370 nm, is at a much shorter wavelength than that of the compounds of the first group. However, this is not enough to utilize the long wavelength UV portion of sunlight. The dye molecules disclosed in US 5,869,658 are relatively planar because the repulsion of the H atoms (in positions 8 and 9 of the formula in column 21) is not very great. Example 3 is unusual because in this case the slow brightening and thus greater darkening ΔOD are achieved due to a fluorine substituent in position 2 on phenyl rings B and/or B'. This effect, which makes the ΔOD value approximately four times greater, was already described in US 5,066,818. However, this substitution which hinders the free rotation leads to an undesirably strong dependence of the brightening on the matrix surrounding the molecule, i.e., a very broad distribution of the brightening rate when the molecular ensemble in a matrix is considered and/or an extremely different brightening rate in different plastic materials.

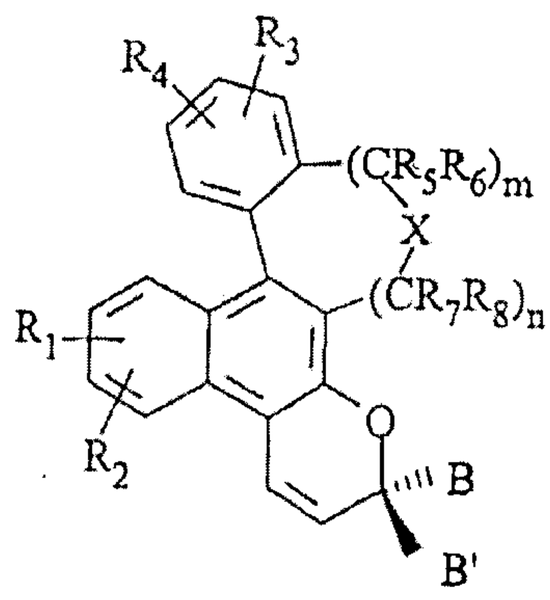
EP 1 230 234 also describes 2H-diarylnaphthopyrans substituted with condensed rings. Condensation within the indene ring in the structure shown here leads to compounds which usually brighten as quickly as the comparative compound C5 owing to the absence of steric hindrance between the CH_2 group of the five-membered ring and the H atom in position 8. As described in US 3,567,605, compounds having this structure have adequate photochromicity only at extremely low temperatures. With the six-membered ring, the hindrance is also very minor, the brightening is quick and thus the observed coloration is only minor. In addition, the choice of possible compounds is very small and the synthesis described allows only compounds substituted in positions 6 and 7 with activating groups. When using only one methoxy group or using less activating higher alkoxy groups, no ring closure reaction takes place. Larger alkane rings are possible through synthesis but the steric hindrance is always low in comparison with that of compounds of the

structure according to US 5,869,658 or WO 02/22594; likewise the darkening results are minor. The essential aspect of these compounds according to EP 1 230 234, however, was primarily providing intrinsically gray or brown compounds. In the open form, the (substituted) phenyl group is in meta-position to the ethylene bridge instead of being in para-position, which leads to completely different behavior which is even controversial in some cases.

Thus the object of the present invention is to provide novel photochromic dyes which have improved properties in comparison with the compounds available in the prior art. These photochromic compounds should be characterized, compared to comparable compounds of the prior art, particularly by a longer wavelength absorption in the unexcited state, i.e., in the range between approximately 380 nm and 400 nm while at the same time having a good efficiency in the open form, i.e., characterized by a higher molar extinction of the excited form after exposure to light and by good kinetic properties and lifetime properties, i.e., with a rapid brightening rate which is adapted to the compounds that absorb in the long wavelength range and are usually used at the same time in phototropic lenses and with good results in the lifetime test.

This object is achieved by the subjects characterized in the claims.

In particular, photochromic h-fused benzo[f]chromenes with general formula (I) are made available:



(I)

wherein

n and m independently of one another denote 0, 1 or 2,

the radicals R_1, R_2, R_3 and R_4 each independently of one another denote a substituent selected from

the group α, consisting of a hydrogen atom, a (C_1-C_6) alkyl radical, a (C_1-C_6) thioalkyl radical, a (C_3-C_7) cycloalkyl radical, which may have one or more heteroatoms such as O or S, for example, a (C_1-C_6) alkoxy radical, a hydroxyl group, a trifluoromethyl group, bromine, chlorine and fluorine;

the group β, consisting of an unsubstituted, a monosubstituted or disubstituted phenyl, phenoxy, benzyl, benzyloxy, naphthyl or naphthoxy radical, where the substituents may be selected from phenyl and the group α;

the group γ, wherein the radicals R_1 and R_2 and/or R_3 and R_4 each denote an $-A-(CH_2)_k-D-$ group or an $-A-(C(CH_3)_2)_k-D-$ group bound to the aromatic ring, where k = 1 or 2, where A and D independently of one another are selected from oxygen, sulfur, CH_2, $C(CH_3)_2$ or $C(C_6H_5)_2$ and again a benzo ring may be fused to this $-A-(CH_2)_k-D-$ group;

the radicals R_5, R_6, R_7 and R_8 each independently of one another are selected from phenyl and the group α or the radicals R_5 and R_6 together with the radical R_3 of the directly vicinal benzo ring form an unsubstituted, a monosubstituted or disubstituted benzo or pyrido ring fused thereto, its substituents being selected from phenyl and the group α or, if m and/or n denotes 2 the directly vicinal radicals R_5 and R_6 of two vicinal CR_5R_6 units and/or the directly vicinal radicals R_7 and R_8 of two vicinal CR_7R_8 units together form a fused, unsubstituted, monosubstituted or disubstituted benzo ring or pyrido ring, whose substituents may be selected from phenyl and the group α, or the radicals R_5 and R_6 and/or the radicals R_7 and R_8 together form a (C_3-C_7) cycloalkyl radical, which may have one or more heteroatoms, e.g., oxygen or sulfur, with a benzo ring optionally being fused to this cycloalkyl radical;

X is selected from O, S or CR_9R_{10}, where the radicals R_9 and R_{10} independently of one another are selected from phenyl and the group α or the radicals R_9 and R_{10} together form a (C_3-C_7) cycloalkyl radical which may have one or more heteroatoms such as oxygen or sulfur, or the radicals R_9 and R_{10} together with the radicals R_5 and R_6 and/or R_7 and R_8 of a directly vicinal CR_5R_6 unit and/or CR_7R_8 unit may stand for an unsubstituted, a monosubstituted or a disubstituted benzo or pyrido ring fused to the X-C(R_5R_6) and/or X-C(R_7R_8) bond, whose substituents may be selected from phenyl and the group α with the provision that X may not be CR_9R_{10} when both m and n are 0;

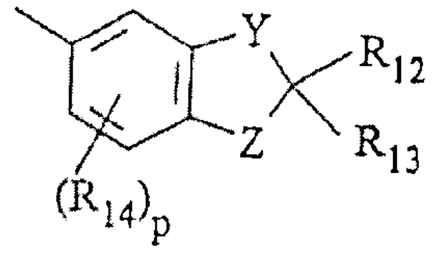
B and B' independently of one another are selected from one of the following groups a), b), c) or d), wherein [B and B']

a) are mono-, di- and trisubstituted aryl radicals, where the aryl radical is phenyl or naphthyl;

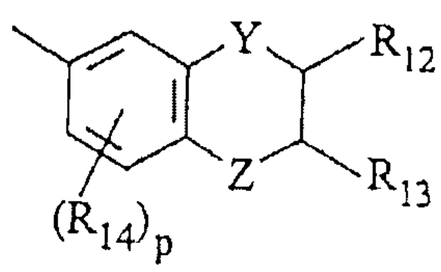
b) are unsubstituted, monosubstituted and disubstituted heteroaryl radicals where the heteroaryl radical is pyridyl, furanyl, benzofuran-2-yl, benzofuran-3-yl, dibenzofuranyl, thienyl, benzothien-2-yl, benzothien-3-yl or dibenzothienyl;

wherein the substituents of the aryl or heteroaryl radicals in a) and b) are those selected from the groups α, β or γ or an unsubstituted, monosubstituted or disubstituted amino group, where the amine substituents may be selected from a (C_1-C_6) alkyl radical, a (C_3-C_7) cycloalkyl radical, an unsubstituted phenyl or benzyl radical or a phenyl or benzyl radical substituted with one or more substituents from the group α, an N-morpholine group, an N-thiomorpholine group, an N-piperidine group, an N-azacycloheptane group, an N-piperazine group, an N-(N'-(C_1-C_6-alkyl)piperazine group, an N-pyrrolidine group, an N-imidazolidine group, an N-pyrazolidine group, an N-aziridine group, an N-azetidine group, an N-indoline group, an N-carbazole group, an N-phenothiazine group, an N-phenazine group, an N-phenoxazine group, an N-tetrahydroquinoline group or an N-tetrahydroisoquinoline group, wherein the substituents are preferably those from groups α and β;

c) are structural units having the following formulas (V) and (W)



(V)



(W)

wherein

Y and Z independently of one another stand for O, S, CH_2, CMe_2, NH, NPh or $N(C_1-C_6)$ alkyl, the radicals R_{12} and R_{13} independently of one another denote hydrogen or a (C_1-C_6) alkyl radical and the radical R_{14} denotes a substituent from the group α, where p is 1, 2 or 3

or

d) B and B' together form an unsubstituted, monosubstituted or disubstituted 9,10-dihydroanthracene radical, fluorine radical, thioxanthene radical or xanthen-9-ylidene radical, benzo[b]flouren-11--ylidene radical, 5H-dibenzo[a,c]cycloheptene, dibenzosuberone or 5H-dibenzo[a,c]cyclooctan-5-ylidene radical or a saturated hydrocarbon radical which is C_3-C_{12} spiromonocyclic, C_7-C_{12} spirobicyclic and/or C_7-C_{12} spirotricyclic, where the substituents on the unsaturated cyclic compounds are selected from the group α.

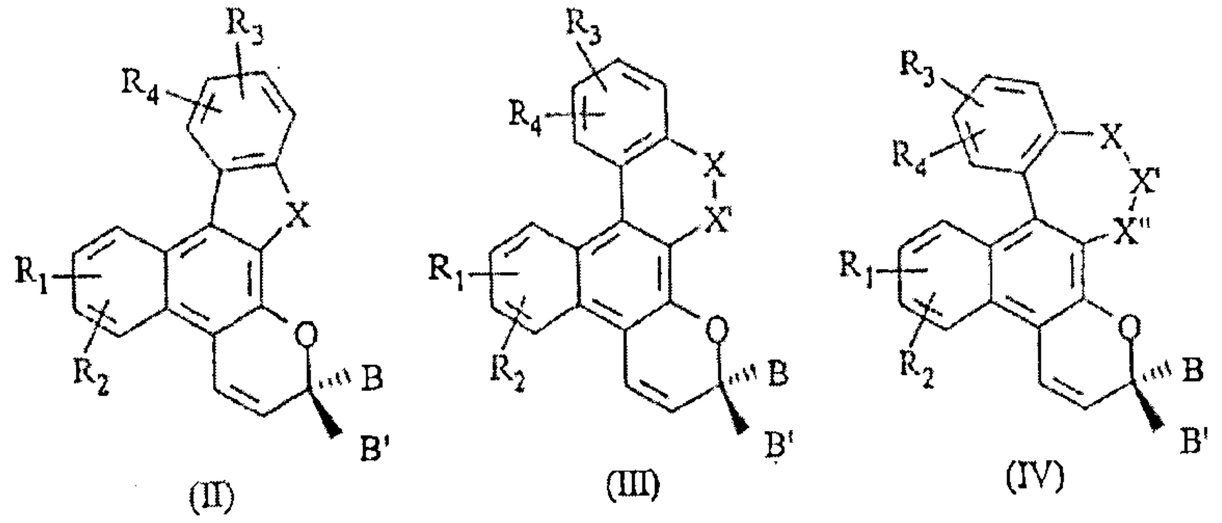
According to the present invention, compounds are made available by h-fusion of benzo[f]chromene systems such that their photochromic properties have important advantages in comparison with the compounds known in the art. In particular, the inventive compounds have long wavelength absorption maxima in the closed (colorless) form with at the same time a good efficiency in the open form, i.e., a higher molar extinction of the excited form on exposure to light as well as good kinetic properties and lifetime properties. Furthermore, the inventive photochromic H-fused benzo[f]chromene derivatives have good lifetime properties comparable to those of the corresponding compounds known in the art and/or better kinetic properties, i.e., a rapid rate of

brightening adapted to the photochromic dyes that today are usually used simultaneously in phototropic lenses and have a longer wavelength absorption as well as good behavior in the lifetime test.

The cyclic ring and/or heterocyclic ring fused in position h of the benzo[f]chromene system is preferably a five-membered ring (n = m = 0; see formula (II) below), a six-membered ring (n = 1, m = 0 and m = 1, n = 0; see formula (III) below) or a seven-membered ring (preferably with n = m = 1; see formula (IV) below).

The five-membered ring system having a CH_2 bridge is almost planar but is under a great deal of tension. With the standard molecular geometry program Hyperchem 7 (Monte Carlo, Mm+, 100 cycles), a value of -0.27° is obtained for the angle ε (rotation of the phenyl ring with respect to the plane of the naphthalene ring). The introduction of an oxygen atom relaxes the molecule by rotating the angle ε to -27.25°. Replacing the CH_2 bridge with a CH_2-CH_2 bridge to form a six-membered ring (ε = -25.39°) has the same effect. The seven-membered ring with a CH_2-CH_2-CH_2 bridge already yields a helicene-like structure (ε = -49.25°). The five-membered ring with O or S definitely has a stronger aromatic character than with a CH_2 or CR_2 group. This leads to a bathochromic shift of the absorption.

Preferred photochromic h-fused benzo[f]chromene derivatives according to the present invention have the following general formulas (II), (III) and/or (IV):



(II) (III) (IV)

wherein B, B', R_1, R_2, R_3 and R_4 are defined as given above and

in formula (II) X = O or S;

in formula (III) X and X' independently of one another are selected from O, S or CR_9R_{10}, with the provision that at least one of the two is CR_9R_{10}; and/or

in formula (IV) X, X' and X" independently of one another are selected from O, S or CR_9R_{10} with the provision that when X' = O or S, X and X" = CR_9R_{10}.

The radicals R_5, R_6, R_7 and R_8 are preferably selected from the group α independently of one another. If in formulas (III) and/or (IV), X, X' and/or X" stands for CR_9R_{10}, then the radicals R_9 and R_{10} together may stand for a (C_1-C_6) alkyl radical or a (C_3-C_7) cycloalkyl radical in particular which may have one or more heteroatoms.

The radicals R_1 and R_2 and/or R_3 and R_4 may each form an $-A-(CH_2)_k-D-$ group, where k = 1 or 2, bound to the aromatic ring, where A and D, independently of one another, are selected from oxygen, sulfur, CH_2, $C(CH_3)_2$ or $C(C_6H_5)_2$ and where a benzo ring may in turn be fused to this $-A-(CH_2)_k-D-$ group; in particular $-O-(CH_2)_2-O-$ may be listed as an $-A-(CH_2)_k-D-$ unit, with a benzocyclic ring optionally being fused to the ethylene group thereof. The $-A-(CH_2)_k-D-$ unit is bound to the respective benzo ring by A and D in ortho position to one another.

In an especially preferred embodiment, B and B', independently of one another, in the formulas (I), (II) (III) and/or (IV) given above are mono-, di- or trisubstituted aryl radicals, wherein the aryl radical is a phenyl radical or a naphthyl radical.

Especially preferred photochromic h-fused benzo[f]chromene derivatives according to the present invention include:

(1) 2-(4-methoxyphenyl)-2-phenyl-2H-benzofurano[1,2-h]benzo[f]-chromene,

(2) 2-(4-methoxyphenyl)-2-phenyl-2H-benzothiopheno[1,2-h]-benzo[f]chromene,

(3) 2-(4-methoxyphenyl)-2-phenyl-2H-13,14-dihydronaphtho[1,2-h]-benzo[f]chromene,

(4) 7-methoxy-2-(4-methoxyphenyl)-2-phenyl-2H-13,14-dihydro-naphtho[1,2-h]benzo[f]chromene,

(5) 11-methoxy-2-(4-methoxyphenyl)-2-phenyl-2H-13,14-dihydro-naphtho[1,2-h]benzo[f]chromene,

(6) 2-(4-methoxyphenyl)-2-phenyl-2H,13H-chromeno[1,2-h]benzo[f]-chromene,

(7) 2-(4-methoxyphenyl)-2-phenyl-2H,14H-chromeno[1,2-h]benzo[f]-chromene,

(8) 7-methoxy-2-(4-methoxyphenyl)-2-phenyl-2H-benzocycloheptano[1,2-h]benzo[f]chromene.

The longest wavelength absorption maxima λ_{max} of the closed (colorless) form and the open (colored) form of different compounds are shown in the following table (the numbers are based on the list of especially preferred compounds). Furthermore, the efficiency of the colored form of the inventive compounds is also shown. To do so, 500 ppm photochromic dye was incorporated into a phototropic matrix of ColorMatic Extra® and after polymerization, the transmission was measured in a defined procedure on a kinetic bench at 23°C (15 min exposure at 50 klux). The lower the transmission, the more intense is the power of the photochromic dye under exposure. However, it must also be pointed out that the transmission was measured as a factor weighted in relation to the optical sensitivity maximum V_λ so that yellow-orange dyes whose absorption maximum is farther away from the human sensitivity maximum will have a higher transmission than orange red dyes whose absorption maximum is closer to the human sensitivity maximum. The intensity of two photochromic dyes can thus be compared well only by way of the degree of transmission under illumination if their longest wavelength absorption maxima (open form) are not too far apart (otherwise yellower dyes would be classified at a seemingly lower level than redder dyes). A compound of the prior art according to US 5,869,658 is shown in the last row of the following table for comparison purposes.

The information given in the following table for m, n, X, R_1 and R_3 is based on the structure (I):

- B is 4-methoxyphenyl

- B' is phenyl
- $R_2 = R_4 = H$

No.	m $R_{5/6}$	n $R_{7/8}$	X	R_1	R_3	λ_{max} (closed)	λ_{max} (open)	Transmission darkened
(1)	0	0	O	H	H	380 nm	470nm	53%
(2)	0	0	S	H	H	385 nm	475 nm	49%
(3)	1 H/H	0 -	CH_2	H	H	385 nm	450 nm	58%
(4)	1 H/H	0 -	CH_2	7-OMe	H	400 nm	470 nm	40%
(5)	1 H/H	0 -	CH_2	H	11-OMe	390 nm	455 nm	55%
(6)	1 H/H	0 -	O	H	H	380 nm	455 nm	58%
(7)	0 -	1 H/H	O	H	H	395 nm	460 nm	57%
(8)	1 H/H	1 H/H	CH_2	7-OMe	H	380 nm	485 nm	40%
Prior art	0	0	CH_2	6-OMe	H	380 nm	465 nm	65%

It can be seen from this table that the inventive compounds have a higher efficiency in the darkened state in comparison with the exemplary compound of the prior art. Furthermore, the absorption maximum of the closed form has a bathochromic shift in most cases. This property is especially important when only a small amount of UV radiation is available for excitation owing to scattering effects in the atmosphere. Longer wavelength UV radiation is subject to less scattering than shorter wavelength radiation, so these dyes undergo good darkening even under unfavorable conditions in contrast with photochromic dyes that absorb at a shorter wavelength.

The inventive compounds may be used in plastic materials and/or plastic objects of all types and shapes for a plurality of applications for which photochromic behavior is important. A dye according to the present invention or a mixture of such dyes may be used. For example, the inventive photochromic benzo[f]chromene dyes may be used in lenses, in particular ophthalmic lenses, lenses of eyeglasses of all types such as ski goggles, sunglasses, motorcycle goggles, visors of safety helmets and the like. Furthermore, the inventive photochromic benzo[f]chromene dyes may also be used as solar protection in vehicles and residences in the form of windows, safety visors, covers, roofs or the like.

For producing such photochromic objects, the inventive photochromic benzo[f]chromene dyes may be applied to or embedded in a polymer material such as an organic plastic material by means of various methods described in the prior art such as those described in WO 99/15518.

A distinction is made between so-called bulk dyeing methods and superficial dyeing methods. A bulk dyeing method comprises, for example, dissolving or dispersing the photochromic compound or compounds according to the present invention in a plastic material, e.g., by adding the photochromic compound(s) to a monomoric material before polymerization takes place. Another possibility for producing a photochromic object is by impregnating the plastic material(s) with the photochromic compound(s) by immersing the plastic material in a hot solution of the photochromic dye(s) according to the present invention or by a thermal transfer method, for example. The photochromic compound(s) may also be provided in the form of a separate layer between adjacent layers of the plastic material, e.g., as part of a polymer film. Furthermore, applying the photochromic compound(s) as part of a coating on the surface of the plastic material is also possible. The term impregnation should be understood to refer to the migration of the photochromic compound(s) into the plastic material, e.g., through the solvent-supported transfer of the photochromic compound(s) into a polymer matrix, vapor phase transfer or other such surface diffusion processes. Such photochromic objects, e.g., eyeglass lenses, can advantageously be produced not only by means of the usual bulk dyeing but also in the same way by means of surface dyeing; a surprisingly lower migration tendency can be achieved with the latter variant. This is advantageous in particular in the case of subsequent finishing steps, e.g., when an antireflective coating is applied due to the lower backdiffusion *in vacuo*—drastically reducing layer separation and similar defects.

Thus on the whole, on the basis of the inventive photochromic h-fused benzo[f]chromene derivatives, any compatible dyeings (tolerated well from a chemical standpoint and with regard to the color), i.e., dyes may be applied to or embedded in the plastic material to comply

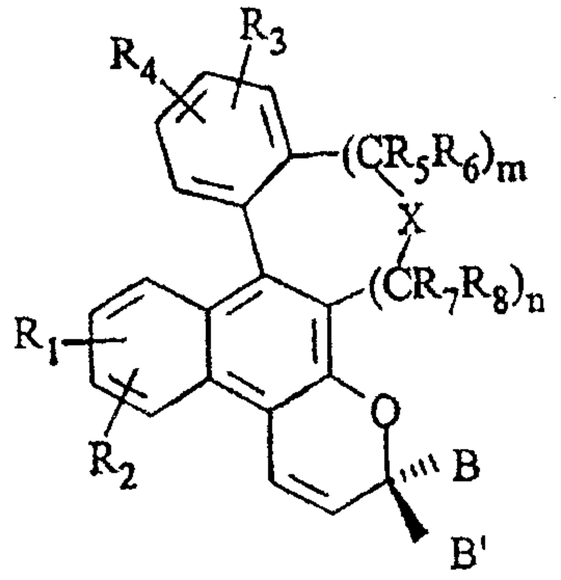
with aesthetic factors as well as medical or fashion aspects. The dye(s) selected specifically may consequently vary, depending on the intended effects and requirements.

The inventive photochromic h-fused benzo[f]chromene derivatives with the general formulas (I) and/or (II), (III) and (IV) can be synthesized by reaction of suitably substituted fused 2-naphthol derivatives with suitably substituted 2-propyn-1-ol derivatives in a known way (see WO 02/22594). Production of the inventive compounds is explained below on the basis of a general reaction scheme (see FIG 1).

Suitably substituted aromatic Grignard compounds having a protected acetic acid function in ortho position are added onto cyclic aromatic aliphatic ketones (step i). After splitting off water and removing the carboxylic acid protective group, substituted fused 2-naphthol derivatives (steps ii and iii) are formed via intramolecular cyclization. These 2-naphthol derivatives are then reacted with suitably substituted 2-propyn-1-ol derivatives according to step iv) to form the inventive compounds.

Claims

1. Photochromic h-fused benzo[f]chromenes of the general formula (I)



(I)

wherein

n and m independently of one another denote 0, 1 or 2,

the radicals R_1, R_2, R_3 and R_4 each independently of one another denote a substituent selected from

the group α consisting of a hydrogen atom, a (C_1-C_6) alkyl radical, a (C_1-C_6) thioalkyl radical, a (C_3-C_7) cycloalkyl radical which may have one or more heteroatoms, a (C_1-C_6) alkoxy radical, a hydroxyl group, a trifluoromethyl group, bromine, chlorine and fluorine;

the group β consisting of an unsubstituted, monosubstituted or disubstituted phenyl, phenoxy, benzyl, benzyloxy, naphthyl and naphthoxy radical, where the substituents may be phenyl or the group α;

the group γ wherein the radicals R_1 and R_2 and/or R_3 and R_4 each denote an $-A-(CH_2)_k-D-$ group or an $-A-(C(CH_3)_2)_k-D-$ group bound to the aromatic ring, where k = 1 or 2, where A and D independently of one another are oxygen, sulfur, CH_2, $C(CH_3)_2$ or $C(C_6H_5)_2$, and wherein a benzo ring may be fused to said $-A-(CH_2)_k-D-$ group;

the radicals R_5, R_6, R_7 and R_8 each independently of one another are selected from the group consisting of phenyl and the group α or the radicals R_5 and R_6 together with the radical R_3 of the directly vicinal benzo ring form an unsubstituted, monosubstituted or disubstituted benzo or pyrido ring fused thereto, its substituents being selected from the group consisting of phenyl and the group α or, if m and/or n denotes 2, the directly vicinal radicals R_5 and R_6 of two vicinal CR_5R_6 units and/or the directly vicinal radicals R_7 and R_8 of two vicinal CR_7R_8 units together form a fused, unsubstituted, monosubstituted or disubstituted benzo ring or pyrido ring whose substituents may be selected from the group consisting of phenyl and group α, or the radicals R_5 and R_6 and/or the radicals R_7 and R_8 together form a (C_3-C_7) cycloalkyl radical which may have one or more heteroatoms, with a benzo ring optionally being fused to this cycloalkyl radical;

X is O, S or CR_9R_{10}, where the radicals R_9 and R_{10} independently of one another are selected from the group consisting of phenyl and the group α or the radicals R_9 and R_{10} together form a (C_3-C_7) cycloalkyl radical, which may have one or more heteroatoms, or the radicals R_9 and R_{10} together with the radicals R_5 and R_6 and/or R_7 and R_8 of a directly vicinal CR_5R_6 unit and/or CR_7R_8 unit represent an unsubstituted, a

monosubstituted or a disubstituted benzo ring or pyrido ring fused to the X-C(R_5R_6) and/or X-C(R_7R_8) bond, whose substituents may be selected from the group consisting of phenyl and the group α, with the provision that X may not be CR_9R_{10} when both m and n are 0;

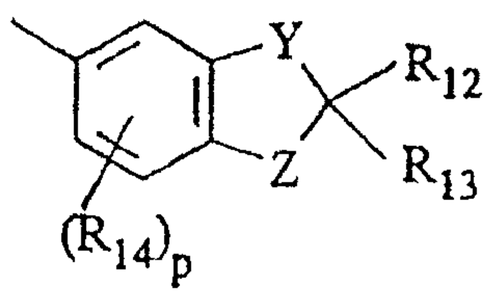
B and B' independently of one another are one of the following groups a), b), c) or d), wherein B and B'

a) are mono-, di- and trisubstituted aryl radicals, where the aryl radical is phenyl or naphthyl;

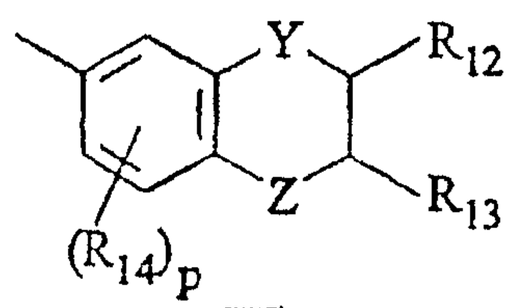
b) are unsubstituted, monosubstituted and disubstituted heteroaryl radicals, where the heteroaryl radical is pyridyl, furanyl, benzofuran-2-yl, benzofuran-3-yl, dibenzofuranyl, thienyl, benzothien-2-yl, benzothien-3-yl or dibenzothienyl;

wherein the substituents of the aryl or heteroaryl radicals in a) and b) are from group α, group β or group γ or an unsubstituted, monosubstituted or disubstituted amino group, where the amine substituents are a (C_1-C_6) alkyl radical, a (C_3-C_7) cycloalkyl radical, an unsubstituted phenyl or benzyl radical or a phenyl or benzyl radical substituted with one or more substituents from the group α, an N-morpholine group, an N-thiomorpholine group, an N-piperidine group, an N-azacycloheptane group, an N-piperazine group, an N-(N'-(C_1-C_6-alkyl)piperazine group, an N-pyrrolidine group, an N-imidazolidine group, an N-pyrazolidine group, an N-aziridine group, an N-azetidine group, an N-indoline group, an N-carbazole group, an N-phenothiazine group, an N-phenazine group, an N-phenoxazine group, an N-tetrahydroquinoline group or an N-tetrahydroisoquinoline group;

c) are structural units having the following formulas (V) and (W):



(V)



(W)

wherein

Y and Z independently of one another denote O, S, CH_2, CMe_2, NH, NPh or N(C_1-C_6) alkyl, the radicals R_{12} and R_{13} independently of one another denote hydrogen or a (C_1-C_6) alkyl radical and the radical R_{14} denotes a substituent from the group α, where p is 1, 2 or 3

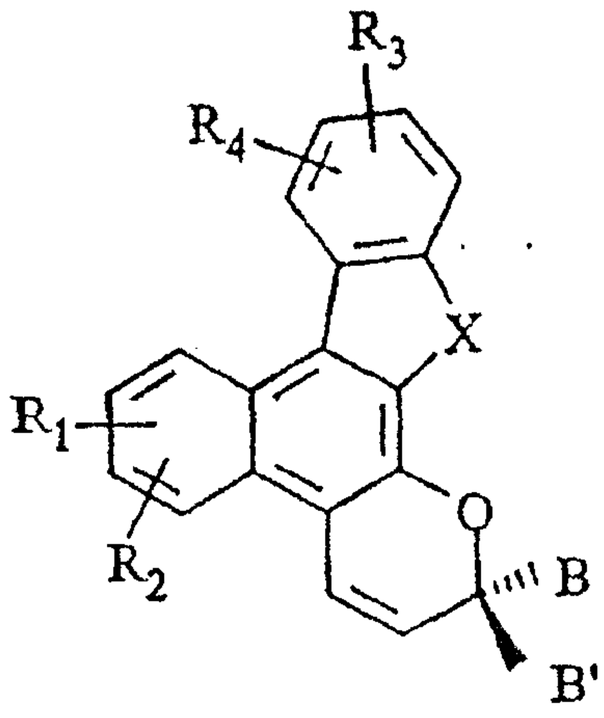
or

d) B and B' together form an unsubstituted, monosubstituted or disubstituted 9,10-dihydroanthracene radical, fluorine radical, thioxanthene radical or xanthen-9-ylidene radical, benzo[b]flouren-11ylidene radical, 5H-dibenzo[a,c]cycloheptene, dibenzosuberone or 5H-dibenzo[a,c]cyclooctan-5-ylidene radical or a saturated hydrocarbon radical which is C_3-C_{12} spiromonocyclic, C_7-C_{12} spirobicyclic and/or C_7-C_{12} spirotricyclic, where the substituents on the unsaturated cyclic compounds are from the group α.

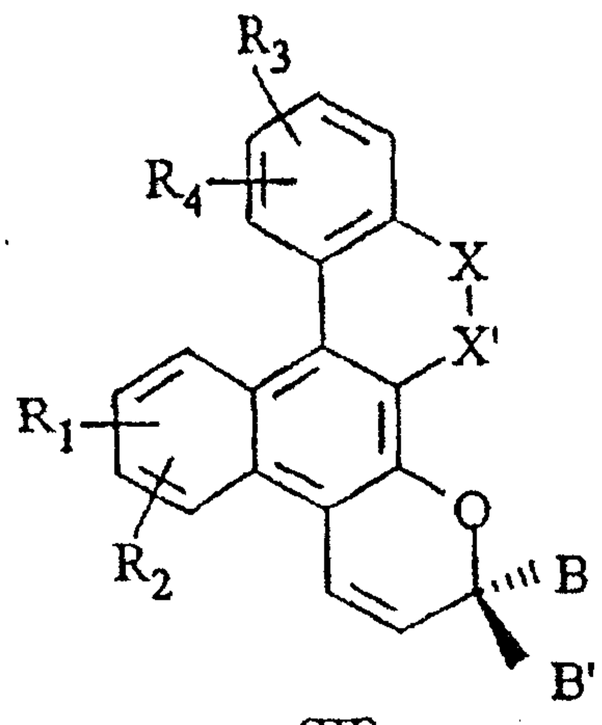
2. The photochromic h-fused benzo[f]chromenes of claim 1 wherein the radicals R_5 and R_6 and/or the radicals R_7 and R_8 together form a (C_3-C_7) cycloalkyl radical which may have one or more heteroatoms selected from the group consisting of oxygen and sulfur, with a benzo ring optionally being fused to this cycloalkyl radical.

3. Photochromic benzo[f]chromenes as claimed in any one of Claims 1 or 2, wherein the cyclic ring or the heterocyclic ring fused in the h-position of the benzo[f]chromene system according to formula (I) is a five-membered ring, a six-membered ring or a seven-membered ring.

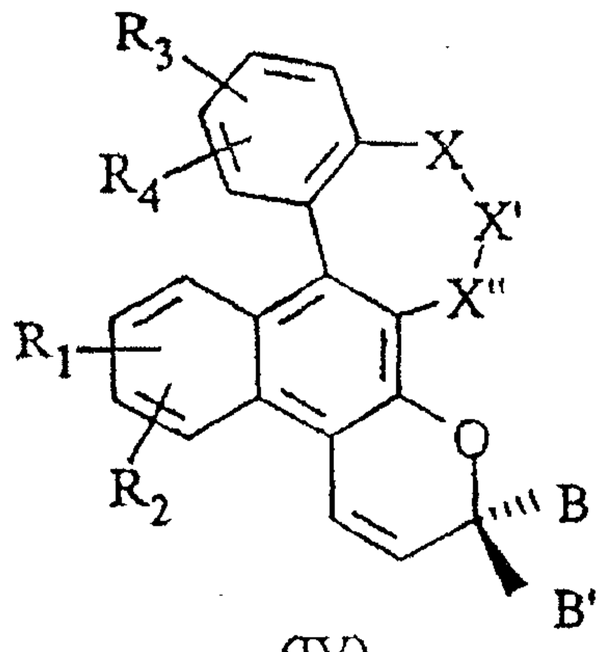
4. Photochromic benzo[f]chromenes as claimed in any one of Claims 1-3, having the following general formulas (II), (III) or (IV):



(II)



(III)



(IV)

wherein B, B', R_1, R_2, R_3 and R_4 are defined as in claim 1 and

in formula (II) X = O or S;

in formula (III) X and X' independently of one another are O, S or CR_9R_{10}, with the provision that at least one of the two is CR_9R_{10};

in formula (IV) X, X' and X" independently of one another are O, S or CR_9R_{10} with the provision that when X' = O or S, X and X" = CR_9R_{10};

wherein R_9 and R_{10} are defined as in claim 1.

5. Photochromic benzo[f]chromenes as claimed in any one of Claims 1 through 4, wherein the radicals R_1, R_2, R_3 and R_4 are radicals from group α or group β.

6. Photochromic benzo[f]chromenes as claimed in any one of Claims 1 through 5, wherein the radicals R_5, R_6, R_7 and R_8 are each selected independently of one another from the group α.

7. Photochromic benzo[f]chromenes as claimed in any one of Claims 1 through 6, wherein B and B' denote mono-, di- or trisubstituted aryl radicals, independently of one another, where the aryl radical is a phenyl radical or a naphthyl radical.

8. Photochromic benzo[f]chromenes as claimed in claim 1, selected from the group consisting of

2-(4-methoxyphenyl)-2-phenyl-2H-benzofurano[1,2-h]benzo[f]-chromene,

2-(4-methoxyphenyl)-2-phenyl-2H-benzothiopheno[1,2-h]benzo[f]-chromene,

2-(4-methoxyphenyl)-2-phenyl-2H-13,14-dihydronaphtho[1,2-h]-benzo[f]chromene,

7-methoxy-2-(4-methoxyphenyl)-2-phenyl-2H-13,14-dihydro-naphtho[1,2-h]benzo[f]chromene,
11-methoxy-2-(4-methoxyphenyl)-2-phenyl-2H-13,14-dihydro-naphtho[1,2-h]benzo[f]chromene,
2-(4-methoxyphenyl)-2-phenyl-2H,13H-chromeno[1,2-h]benzo[f]-chromene,
2-(4-methoxyphenyl)-2-phenyl-2H,14H-chromeno[1,2-h]benzo[f]-chromene and
7-methoxy-2-(4-methoxyphenyl)-2-phenyl-2H-benzocycloheptano[1,2-h]benzo[f]chromene.

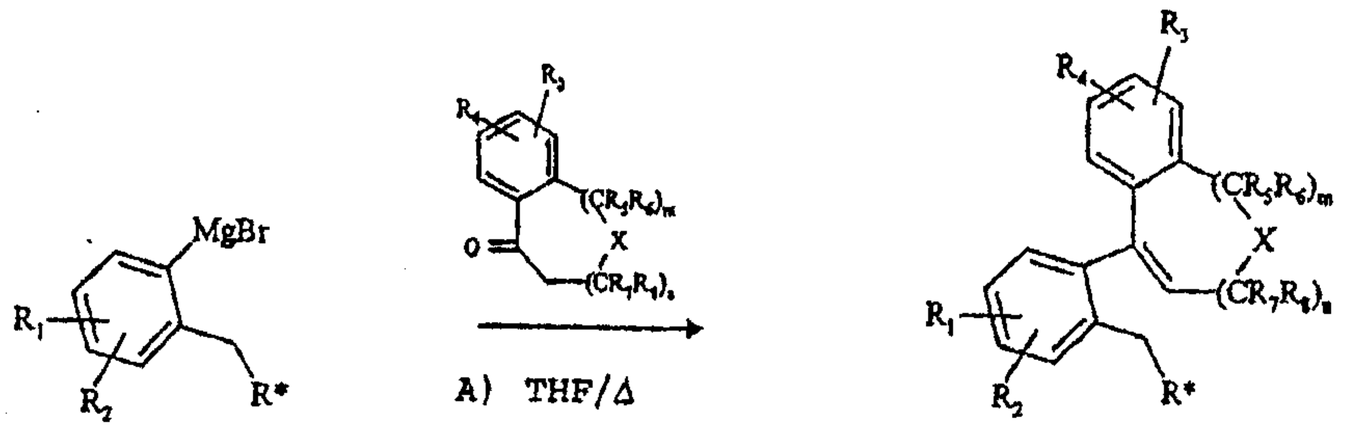
9. Use of the photochromic benzo[f]chromenes as claimed in any one of Claims 1 through 8 in plastic materials.

10. Use as claimed in Claim 9 wherein the plastic material is an ophthalmic lens.

Figure 1

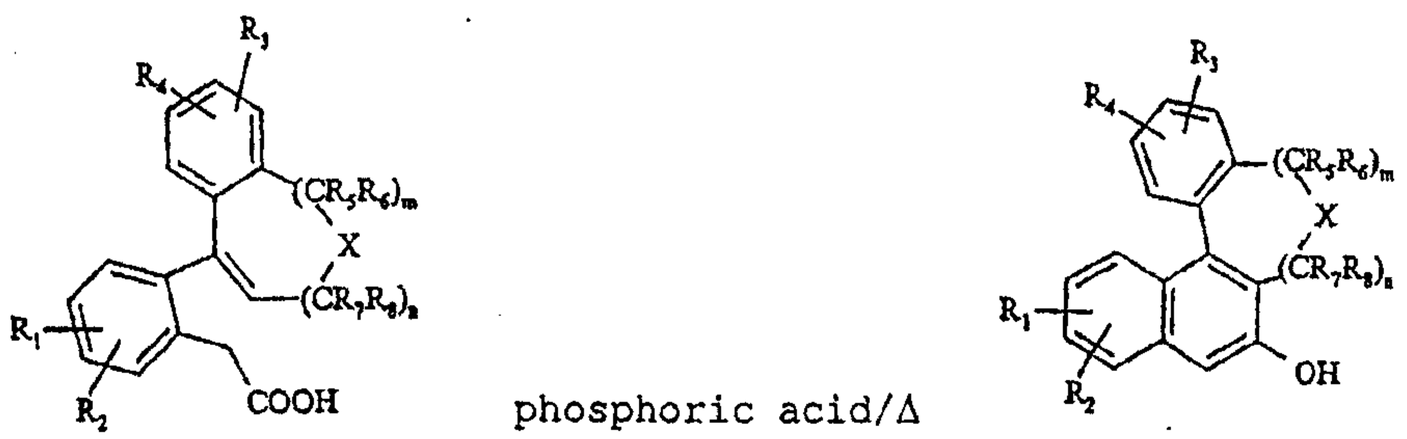
Reaction scheme

i) Addition/cleavage of water (R* = carboxylic acid protective group, e.g., ortho ester)

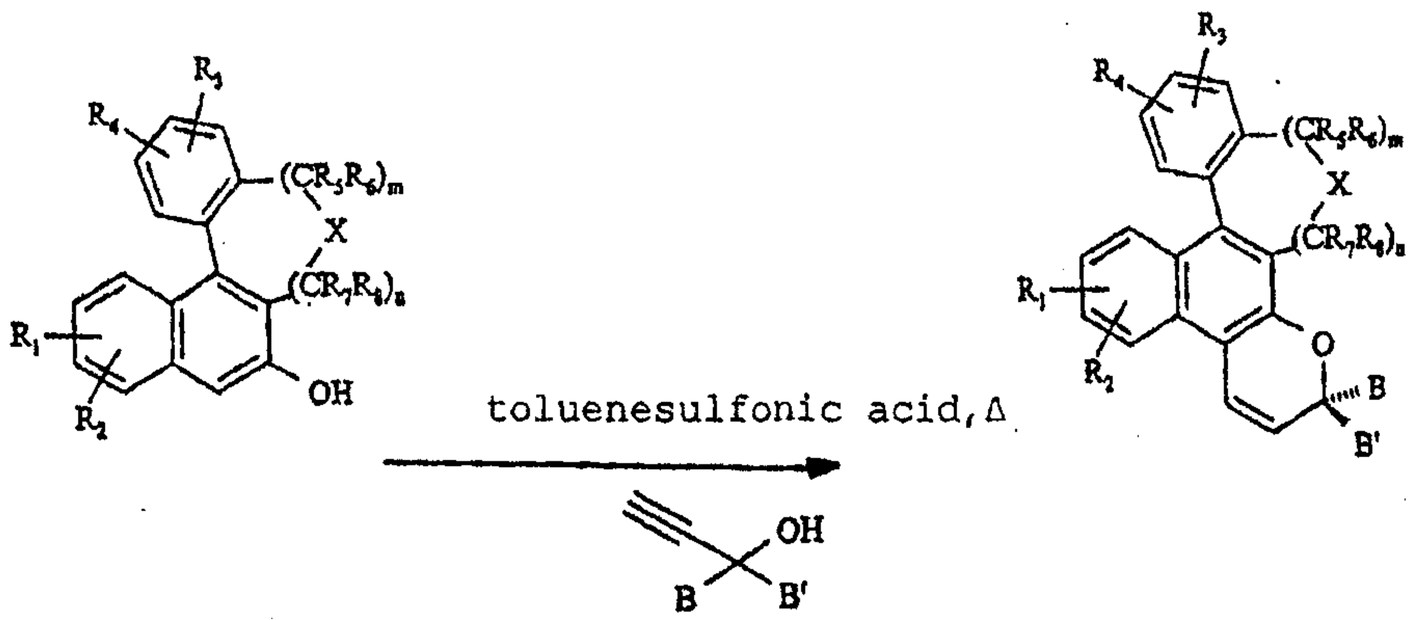


ii) Hydrolysis of carboxylic acid protective group R* to -COOH

iii) Intramolecular cyclization



iv) Naphthopyran condensation



(I)