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PATENT SPECIFICATION

NO DRAWINGS

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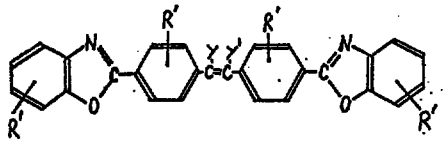
COMPLETE SPECIFICATION

Bisbenzoxazolyl Stilbenes and their use as Fluorescent Brightening Agents

We, KODAK LIMITED, a Company registered under the Laws of Great Britain, of Kodak House, Kingsway, London, W.C.2. do hereby declare the invention (which was communicated from Eastman Kodak Company of 343, State Street, Rochester 4, New York, United States of America), for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel chemical compounds and their methods of manufacture.

According to the present invention there is provided a compound having the formula:



in which R′ represents one or more substituents which may be present on the benzene rings and which may be halogen atoms, alkyl, aryl, alkaryl, arylalkyl, alkoxy, aryloxy, acyl, acyloxy, hydroxyl amino substituted amino quaternized ammonium sulpho, substituted sulphonyl, sulphamyl, substituted sulphamyl, cyano, thiocyano, thiol, carbamyl, substituted carbamyl, carbamyloxy or nitro groups and Y and Y′ each represent a hydrogen atom, alkyl, aryl or cyano group.

[*Price 4s. 6d.*]

The compounds of the invention thus comprise the novel class of stilbene derivatives having benzoxazolyl substituents in the 4,4′ positions of the stilbene radicals. Many of the compounds of this class have unexpectedly superior fluorescent properties when used as optical whitening or brightening agents and, in addition, have certain other properties; such as, heat stability, light stability, stability toward bleaches, stability in textile processing treatments, which make them especially useful as whitening or brightening agents for textile materials, particularly for synthetic linear polyester textile fibres as is hereinafter described.

Typical monovalent substituents Y and Y′ which are suitable include a hydrogen atom and alkyl, aryl and cyano radicals. When Y or Y′ is alkyl it is preferably alkyl of 1 to 18 carbon atoms such as methyl, ethyl, n-butyl, i-butyl, 2-ethylhexyl, n-pentyl, n-hexyl, n-decyl, dodecyl or cetyl, for example. When Y or Y′ is aryl it is preferably mononuclear aryl such as phenyl, methylphenyl, methoxyphenyl, ethylphenyl, chlorophenyl and bromophenyl for example.

Typical monovalent substituents R′ which are suitable include a hydrogen atom, a halogen atom and alkyl, aryl, substituted aryl, hydroxy, alkoxy, aryloxy, acyl, acyloxy, amino, substituted amino, quaternized ammonium, sulpho, substituted sulphonyl, sulphamyl, substituted sulphamyl, cyano, thiocyano, thiol, carbamyl, substituted carbamyl,

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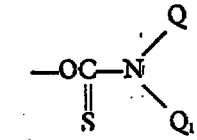
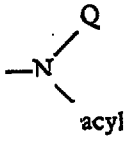
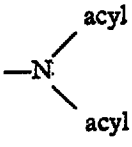
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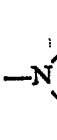
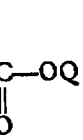
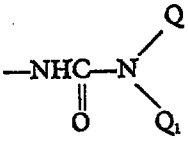
carbamoyloxy, and nitro groups, for example.

Chlorine, bromine, fluorine and iodine atoms are illustrative of the halogen atoms represented by R'. When R' is alkyl it preferably has 1 to 18 carbon atoms, such as methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, n-pentyl, n-hexyl, n-decyl, n-dodecyl, nhexadecyl, or n-octadecyl, for example. When R' is aryl or substituted aryl it is preferably mononuclear aryl such as phenyl, methylphenyl, ethylphenyl, chlorophenyl, bromophenyl, methoxyphenyl or ethoxyphenyl. However, R' can also be an aryl nucleus such as 1-naphthyl or 2-naphthyl and substituted derivatives thereof, or a heterocyclic nucleus such as furyl or thienyl, for example. Illustrative of the alkoxy groups represented by R' are alkoxy groups having from 1 to 18 carbon atoms, and preferably from 1 to 4 carbon atoms, such as methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy, n-amoxy, isoamoxy and hexoxy, for example. Phenoxy and naphthoxy are illustrative aryloxy groups represented by R'. Formyl, acetyl, propionyl, butyryl, isobutyryl, benzoyl and naphthoyl, for example are illustrative of the acyl groups represented by R'. Acetoxy, benzoxy, CH_3CH_2COO—, $CH_3CH_2CH_2COO$— and $CH_3CH_2CH_2CH_2CH_2COO$—, for example, are illustrative of the acyloxy groups represented by R'. Monoalkylamino, dialkylamino, wherein the alkyl groups are the same or different, arylamino, aralkylamino, cycloalkylamino, monohydroxyalkylamino, dihydroxyalkylamino, alkoxyalkylamino and other aliphatic amino groups, for example are illustrative of the substituted amino groups represented by R'. Normally the alkyl, hydroxy alkyl or alkoxyalkyl groups present in such amino groups contain no more than 4 carbon atoms although they can contain more.

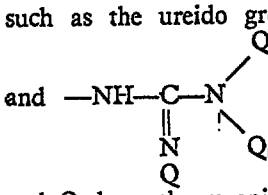
Illustrative of the substituted sulphonyl groups represented by R' are alkylsulphonyl groups having from 1 to 18 carbon atoms and preferably from 1 to 4 carbon atoms such as methylsulphonyl, ethylsulphonyl, propylsulphonyl, butylsulphonyl, etc, and arylsulphonyl, preferably mononuclear arylsulphonyl such as phenylsulphonyl, methylphenylsulphonyl, chlorophenylsulphonyl and ethoxyphenylsulphonyl. Illustrative of the substituted sulphamyl groups represented by R' are alkyl and dialkylsulphamyl such as N,N-dimethylsulphamyl, N,N - diethylsulphamyl, N,N - dipropylsulphamyl, N - ethylsulphamyl, N - methylsulphamyl, N - butylsulphamyl and N - ethyl - N - butylsulphamyl; aryl and diarylsulphamyl such as N-phenylsulphamyl, N,N - diphenylsulphamyl, N,N - diethylphenylsulphamyl, N - phenyl - N - ethylphenylsulphamyl, N,N - dibutylphenylsulphamyl and N - ethoxyphenylsulphamyl; N - alkyl - N - arylsulphamyl such as N - ethyl - N - phenylsulphamyl, N - methyl - N - (methoxyphenyl)sulphamyl and N - butyl - N - chlorophenylsulphamyl.

Illustrative of the substituted carbamyl groups represented by R' are alkylcarbamyl and dialkylcarbamyl groups wherein the alkyl radicals preferably contain from 1 to 4 carbon atoms, such as N - methylcarbamyl, N - ethylcarbamyl, N - propylcarbamyl, N - isopropylcarbamyl, N - butylcarbamyl, N,N - dimethylcarbamyl, N,N - diethylcarbamyl, N,N - dibutylcarbamyl and N - ethyl - N - methylcarbamyl; aryl and diarylcarbamyl such as N - phenylcarbamyl, N,N - diphenylcarbamyl, N,N - di(ethylphenyl) carbamyl and N,N - di(methoxy)carbamyl.

R' can also be a  ;—$NHSO_2Q$;  ;  ;

 ;  or a  group for example wherein

Q and Q_1 each are a hydrogen atom, an alkyl group (preferably having 1 to 4 carbon atoms), a substituted alkyl group (preferably having no more than 4 carbon atoms); an aryl group (such as phenyl, methylphenyl, ethylphenyl, methoxyphenyl, ethoxyphenyl, chlorophenyl or bromophenyl, for example) and a cycloalkyl group (such as cyclobutyl, cyclopentyl or cyclohexyl).

The term acyl, unless otherwise indicated, is used broadly and includes, in addition to the acyl groups noted hereinbefore, groups such as the ureido groups, $—SO_2Q$ groups and  groups, wherein Q and Q_1 have the meaning previously assigned to them.

R' can also be a fluorinated alkyl group having 1 to 18 carbon atoms. Difluoroalkyl groups having the formula $—(CH_2)_nCHF_2$ and

trifluoroalkyl groups having the formula $-(CH_2)_nCF_3$ wherein n is a whole number from 1 to 17 are illustrative. Higher fluorinated alkyl groups such as

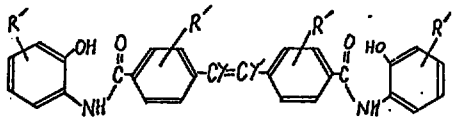
$$-(CH_2)_m1(CF_2)_m-CF_3$$

wherein m is 1 to 4, for example, and $_m1$ is 1 or 2, can also be present. 2,2 - Difluoroethyl, 3,3 - difluoro - n - propyl, 4,4 - difluoro - n - butyl, 5,5 - difluoro - n - amyl, 6,6 - difluoro - n - hexyl, 2,2,2 - trifluoroethyl, 3,3,3 - trifluoro - n - propyl, 4,4,4 - trifluoro - n - butyl, 5,5,5 - trifluoro - n - amyl 6,6,6 - trifluoro - n - hexyl, $-CH_2CH_2CF_3$; $-CH_2CH_2CF_2CF_3$; $CH_2CH_2CH_2CF_2CF_3$ and $-CH_2CH_2CF_2CF_2CF_3$ are illustrative of the fluorinated alkyl groups which R′ can be.

R′ can also be an unsaturated acylic hydrocarbon radical such as allyl, 1 butenyl, 2-butenyl, 3-butenyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, isobutenyl and 1-isopentenyl for example.

Normally no more than 1 of the R′ substituents present in each of the phenyl nuclei of the bivalent 4,4′-stilbene radical is other than a hydrogen atom. The simpler 4,4′-bis-(benzoxazol - 2 - yl)stilbene compounds are often preferred because they are cheaper, more easily prepared and, in some instances, are better fluorescent brightening agents than the more complex 4,4′ - bis(benzoxazol - 2 - yl)stilbene compounds.

The novel fluorescent compounds of the invention can be prepared by the method which comprises heating under a vacuum to a temperature of 200°C to 300°C a 4,4′ - bis(2 - hydroxyphenylcarbamoyl)stilbene compound having the formula



A preferred embodiment of the invention comprises preparing a fluorescent compound by heating a 4,4′ - bis(2 - hydroxyphenylcarbamoyl)stilbene compound to a temperature of 300°C to 350°C under a pressure less than 20″ Hg. The 4,4′ - bis(2 - hydroxyphenylcarbamoyl)stilbene compounds that are useful in the practice of the invention can be prepared by reacting a 4,4′ - stilbene dicarboxylic acid chloride with an o-aminophenol in the presence of a solvent such as dioxan. The 4,4′ - stilbene dicarboxylic acid chloride compounds that are useful in the practice of the invention can be prepared by reacting a 4,4 - stilbene dicarboxylic acid with thionyl chloride and phosphorus pentachloride according to the method of Hager et al, *J.A.C.S.*, *68*, 2167 (1946).

The desired 4,4′ - stilbene dicarboxylic acid can be prepared by a number of methods. One is the method disclosed in Toland et al, *J.A.C.S.*, *75*, 2263 (1953) which comprises reacting a p-toluic acid with sulphur. Another is the method of Harris, *J.C.S.* 1947, 690 which comprises condensing a 4 - bromophenylacetate with a 4 - bromobenzaldehyde to give a 4,4′ - dibromostilbene - α - carboxylic acid which is converted to the desired 4,4′ - stilbene dicarboxylic acid. Another method comprises condensing a p-cyanobenzaldehyde with a p-cyanobenzylcyanide according to the method of Bell et al, *J.C.S.*, 1948, 1024 to give a 4,4′ - α - tricyanostilbene which is converted to an α-cyanostilbene dicarboxylic acid.

Fibres, films and shaped articles made of normally translucent or transparent synthetic materials, and particularly of polymeric materials such as regenerated cellulose, rayon, cellulose esters, polyesters, polyamides, polyolefins, polyacrylics and modacrylics and polyurethanes, have an inherent yellowish colour which becomes more pronounced as the material ages. The yellowish colour is apparent in uncoloured or undyed articles made of these materials. In the case of dyed or coloured articles made from these materials, the inherent yellow colour causes a diminished brightness which becomes more pronounced as the material ages.

Compositions embodying the compounds of formula I above are unexpectedly superior to the prior art compositions containing a fluorescent brightening agent. Such compositions are described and claimed in application No. 9791/64 (Serial No. 1072917). Many prior art compositions containing a fluorescent brightening agent often exhibit undesirable colours because of the intrinsic colour of the brightening agent or because of fluorescence at undesirable wave-lengths. Other prior art compositions containing a fluorescent brightening agent are unstable to one or more of the following: heat, light, washing, dry cleaning, bleaches, textile processing, and discolour with use. However, the novel compositions of the invention exhibit a remarkable combination of properties in that they possess a superior brightness and/or whiteness of highly desirable hue which is unexpectedly stable to light, heat, sublimation, crocking and the processing and cleaning procedures referred to hereinbefore.

The novel compounds of the invention are also useful in photographic colour print materials comprising a white reflecting support carrying three silver halide emulsion layers, each sensitized to the red, green or blue ranges of the spectrum, wherein the top silver halide emulsion layer contains a dispersion of an organic solvent in which is dissolved or dispersed one or more of the novel compounds of the invention. For example, the top silver halide emulsion layer may contain an oily dispersed phase having dissolved there-

in a cyan forming colour coupler and one or more of the novel compounds of the invention. Alternatively, one or more of the novel compounds of the invention may be dissolved in a separate oily phase dispersed within the said layer.

Photographic colour prints made on the foregoing materials containing one or more of the novel fluorescent compounds of the invention show enhanced whiteness in the low density range of images formed in them due to the fluorescence of the novel compound. Further, the inherent ultraviolet absorption of the novel compounds in the photographic colour print material protects any magenta and yellow images developed in the layers below the cyan layer. The ultraviolet absorption of usual cyan dyes formed by colour development prevents the said compounds from fluorescing in the cyan image areas and thereby obviates the "bloom" which occurs when fluorescent brightening agents are coated on top of colour print materials or introduced therein by bathing.

The novel fluorescent 4,4′ - bis(benzoxazol - 2 - yl) stilbene compounds within the scope of the invention comprise those compounds absorbing ultraviolet light and having a peak ultraviolet absorption in the range of 350 millimicrons to 390 millimicrons. These novel compounds have ultraviolet light molar absorptivities ranging from 47,000 to 94,000 when measured at the point of strongest ultraviolet absorption (Lambda Max.). In solution or on a substrate the novel fluorescent compounds of the invention fluoresce visible light at a wavelength of FL maximum emission (λ max) of 420 to 450 millimicrons and thus appear green-blue to violet when viewed in daylight or ultraviolet light. The preferred fluorescent 4,4′ - bis(benzoxazol - 2 - yl)stilbene compounds of the invention impart little or no visible colour to a polyester substrate when present therein in an amount effective for whitening or brightening purposes and, accordingly, are free of substituents which would cause the fluorescent compound to impart a visible colour to the substrate when used in such an amount.

Further, the preferred fluorescent 4,4′ - bis(benzoxazol - 2 - yl)stilbene compounds of the invention have satisfactory stability. Thus, when incorporated in a polyester substrate in an amount effective for whitening or brightening purposes, the novel fluorescent compounds of the invention produce a composition of exceptional whiteness or brightness that is highly resistant to discolouration or loss of whiteness or brightness upon exposure to light, air, washing and bleaching agents such as sodium hypochlorite and calcium hypochlorite.

The terms brightness and whiteness are used in their usual sense in accordance with the "Comparative List of Color Terms", a report of the Inter-Society Council, January, 1949.

The hydrogen atoms or other substituents on the carbon atoms of the ethylene linkage of the stilbene moiety of the novel compounds of the invention may exist in either the cis or trans configuration or a mixture thereof.

The following examples illustrate the preparation of typical 4,4′ - bis(benzoxazol)-stilbene compounds of the invention.

Example 1

4,4′ - Bis(benzoxazol - 2 - yl)stilbene

4,4′ - Stilbenedicarboxylic acid was prepared from p-toluic acid by the method of *J.A.C.S.*, 1953 *75*, 2263. 4,4′ - Stilbenedicarboxylic acid chloride was prepared from the 4,4′ - stilbenedicarboxylic acid according to the method of *J.A.C.S.*, 1946, *68*, 2167.

4,4′ - Bis(2 - hydroxyphenylcarbamoyl)-stilbene was prepared by dissolving the 4,4′-stilbenedicarboxylic acid chloride (1.5 grams) in hot dioxan (50 ml.) and adding o-aminophenol (1.1 gram) dissolved in dioxan (5 ml.) to the solution. An immediate precipitate came down. The mixture was refluxed 2 hours to complete the reaction, cooled and 1.8 grams of a brown precipitate decomposing at 300—320°C was collected. The brown precipitate of 4,4′ - bis(2 - hydroxyphenylcarbamoyl)stilbene (1.8 grams) was heated under vacuum in an oil bath at 320—340° until the reaction subsided. The product was cooled under vacuum and Soxhlet extracted with benzene. From the benzene solution crystallized lustrous yellow flakes of 4,4′bis-(benzoxazol - 2 - yl)stilbene (0.93 gram) M.P. 365—8° Anal. found: C 81.3, H 4.60, N 6.65%, $C_{28}H_{18}N_2O_2$ requires C 81.2, H 4.35, N 6.77%.

Example 2

4,4′ - Di - (benzoxazol - 2 - yl) - 2 - methylstilbene

2 - Methyl - 4,4′ - stilbenedicarboxylic acid chloride was prepared from the corresponding acid according to the method of J.A.C.S., *68*, 2167, (1946). The acid was obtained by hydrolysis of the dinitrile [J.A.C.S., *68*, 2167 (1946)] which in turn was prepared according to the procedure of J.C.S., (1947), 690 (41 C.A. 6229a).

2 - Methyl - 4,4′ - stilbene dicarboxylic acid chloride (3.2 g.) (0.01 mole) was dissolved in hot dioxan (100 ml.) and o-aminophenol (2.2 g.) (0.02 mole) in dioxan (10 ml.) added. An immediate precipitate came down. The mixture was refluxed 2 hours to complete the reaction, cooled and the precipitate collected. There was obtained 3.7 g. of light brown solid product.

The above 3.7 g. (0.008 mole) of 4,4′ -

di - (2 - hydroxyphenylcarbamoyl) - 2 - methylstilbene was heated under vacuum in an oil bath at 320—340° until the reaction subsided. The product was cooled under vacuum and Soxhlet extracted with benzene. The benzene solution deposited 2.0 g. of 4,4′ - di - (benzoxazol 2 - yl) - 2 - methylstilbene as yellow flakes.

EXAMPLE 3

4,4′ - Di(benzoxazol - 2 - yl) - α - cyanostilbene

α-Cyanostilbene dicarboxylic acid chloride was prepared from the corresponding acid according to the method of J.A.C.S., *68*, 2167 (1946). The acid was obtained by the partial hydrolysis of 4,4′ - α - tricyanostilbene with sulphuric acid in acetic acid at 140° (J.C.S., 1948, 1024). The latter was obtained by condensing p-cyanobenzaldehyde with p-cyanobenzyl cyanide (J.C.S., 1948, 1024).

α-Cyanostilbene dicarboxylic acid chloride (3.3 g.) was dissolved in hot dioxan (100 ml.) and o-aminophenol (2.2 g) (0.02 mole) in dioxan (10 ml.) added. The addition caused an intermediate precipitate to form. The mixture was then refluxed 2 hours to complete the reaction, cooled and the final precipitate was collected. It consisted of 3.32 g. (70%) of a pale brown solid.

The above 3.32 g. of 4,4′ - di - (2 - hydroxyphenylcarbamoyl) - α - cyanostilbene was heated under vacuum in an oil bath at 320—340° until the reaction subsided. The product was cooled under vacuum and Soxhlet extracted with benzene. The benzene solution deposited 1.84 g. (60%) of 4,4′ - di(benzoxazol - 2 - yl) - α - cyanostilbene as yellow flakes.

EXAMPLE 4

4,4′ - Di(benzoxazol) - 2,2′ - dimethylstilbene

2,2′ - Dimethyl - 4,4 - stilbenedicarboxylic acid chloride was prepared by reacting the corresponding acid with thionyl chloride and phosphorus pentachloride. The acid was obtained by hydrolysis of the dinitrile with 10% KOH in propylene glycol [J.A.C.S., *68*, 2167, (1946)]. The dnitrile resulted from the reaction of cuprous cyanide with α - carboxy - 4,4′ - dibromo - 2,2′ - dimethylstilbene. The latter was obtained by condensing potassium 4 - bromo - 2 - methylphenyl acetate with 4 - bromo - 2 - methylbenzaldehyde and acetic anhydride in the presence of pyridine [J.C.S., (1947), 690].

2,2′ - Dimethyl - 4,4′ - stilbenedicarboxylic acid chloride (3.3 g.) (0.01 mole) was dissolved in hot dioxan (100 ml.) and o-aminophenol (2.2 g.) (0.02 mole) in dioxan (10 ml.) added. After an intermediate precipitate formed, the mixture was refluxed 2 hours to complete the reaction, cooled and the precipitate collected. There was obtained 3.1 g. (65%) of pale brown leaves of product. This 3.1 g. of 4,4′ - di(2″ - hydroxyphenylcarbamoyl) - 2,2′ - dimethylstilbene was heated under vacuum in an oil bath at 320—340° until the reaction subsided. The product was cooled under vacuum and Soxhlet extracted with benzene. The benzene solution yielded yellow leaves of 4,4′ - di(benzoxazol - 2 - yl) - 2,2′ - dimethylstilbene (2.75 g.).

EXAMPLE 5

4,4′ - Di - 6 - methoxybenzoxazol - 2 - yl)-stilbene

4,4 - Stilbenedicarboxylic acid chloride (3.0 g.) prepared as in Example 3 was dissolved in hot dioxan (100 ml.) and 2 - amino - 5 - methoxyphenol (2.78 g.) (Ber. 46, 3382) in dioxan (10 ml.) was added. After an intermediate precipitate came down the mixture was refluxed 2 hours to complete the reaction, cooled and the precipitate collected. There was obtained (3.7 g.) 75% of product.

The above 3.7 g. of 4,4′ - di(2 - hydroxy - 4 - methoxyphenylcarbamoyl) - stilbene was heated under vacuum in an oil bath at 320—340° until the reaction subsided. The product was cooled under vacuum and Soxhlet extracted with benzene. From the benzene solution there crystallized 2.28 g. of yellow flakes of 4,4′ - di(6 - methoxybenzoxazol - 2 - yl) - stilbene.

EXAMPLE 6

4,4′ - Di(benzoxazol - 2 - yl) - 2 - nitrostilbene

2 - Nitro - 4,4′ - stilbenedicarbonyl chloride was prepared from the corresponding acid and dinitrile according to the method of J.A.C.S., *68*, 2167 (1946). The dinitrile was obtained by condensing 4 - methyl - 3 - nitrobenzonitrile with 4 - cyanobenzaldehyde according to U.S. patent 2,510,047, C.A. *44*: p 9482b.

2 - Nitro - 4,4′ - stilbenedicarbonyl chloride (3,5 g.) was dissolved in hot dioxan (100 ml.) and o-aminophenol 2.2 g. in dioxan (10 ml.) was added. After refluxing 2 hours to complete the reaction, the mixture was cooled and the precipitate collected. There was obtained 3.0 g. of yellow 4,4′ - di(2 - hydroxyphenyl carbamoyl) - 2 - nitrostilbene which was heated under vacuum in an oil bath at 320—340° until the reaction subsided. The product was cooled under Vacuum and Soxhlet extracted with benzene. There crystallized from the benzene 2.1 g. of yellow leaves of 4,4′ - di(benzoxazol - 2 - yl) - 2 - nitrostilbene.

EXAMPLE 7

4,4′ - Di - (benzoxazol - 2 - yl) - 2 - aminostilbene

4,4′ - Di(benzoxazol - 2 - yl) - 2 - nitrostilbene (2.1 g.) prepared as in Example 21

was reduced by treating with stannous chloride in concentrated hydrochloric acid. Upon working up in the usual manner for stannous chloride reductions, there was obtained 1.2 g. of yellow plates of 4,4′ - di - (benzoxazol - 2 - yl) - 2 - aminostilbene.

EXAMPLE 8

4,4′ - di(benzoxazol - 2 - yl) - 2 - hydroxystilbene

The 4,4′ - di(benzoxazol - 2 - yl) - 2 - aminostilbene (1.2 g.) of Example 7 was dissolved in 17 ml. of acetic and 3 ml. of propionic acid and diazotised at 0—5° by adding dropwise with stirring an equivalent of nitrosyl sulphuric acid in 5 cc. sulphuric acid and 10 cc. of acetic-propionic acid. When diazotization was complete the reaction mixture was poured into 100 cc. of water and boiled. Cooling yielded 0.96 g. of a yellow precipitate of 4,4′ - Di(benzoxazol - 2 - yl) - 2 - hydroxystilbene.

EXAMPLE 9

4,4′ - Di(benzoxazol - 2 - yl) - 2 - chlorostilbene

A solution of diazotized 4,4′ - di(benzoxazol - 2 - yl) - 2 - aminostilbene (6.0 g.) prepared as described in Example 8 was poured into a solution of 3 g. freshly precipitated cuprous chloride dissolved in 10 ml. concentrated hydrochloric acid and 15 cc. water. The reaction mixture was boiled and then cooled to yield a yellow precipitate of 4,4′ - di(benzoxazol - 2 - yl) - 2 - chlorostilbene (4.4 g.).

EXAMPLE 10

4,4′ - Di(benzoxazol - 2 - yl) - 2 - cyanostilbene

A solution of diazotized 4,4′ - di(benzoxazol - 2 - yl) - 2 - aminostilbene (6.0 g.) prepared as described in Example 8 was carefully neutralized with sodium carbonate at 0—5°.

This neutralized diazonium solution was then added slowly with rapid stirring to a suspension of 5 g. of freshly precipitated cuprous cyanide in 20 ml. of water and 20 ml. of benzene. (See Organic Syntheses, Coll. Vol. 1, p. 514). Upon the evolution of nitrogen, the product precipitated is partially taken up in the benzene. The precipitate and benzene layer were combined and heated. Upon cooling the benzene solution yielded 3.8 g. of 4,4′ - di(benzoxazol - 2 - yl) - 2 - cyanostilbene as yellow leaflets.

EXAMPLE 11

4,4′ - Bis(6 - chlorobenzoxazol - 2 - yl)-stilbene

This compound was prepared by the method of Example 1 except that an equimolar amount of 2 - amino - 5 - chlorophenol was used in place of the o-aminophenol in the third stage of the synthesis.

EXAMPLE 12

4,4′ - Bis(6 - methylsulphonylbenzoxazol - 2 - yl)stilbene

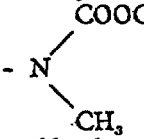
This compound was prepared by the method of Example 1 except that an equimolar amount of 2 - amino - 5 - methylsulphonylphenol was used in place of the o-aminophenol in the third stage of the synthesis.

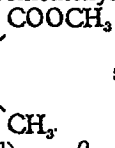
EXAMPLE 13

4,4′ - Bis(5 - cyanobenzoxazol - 2 - yl)-stilbene

This compound was prepared by the method of Example 1 except that an equimolar amount of 2 - amino - 4 - cyanophenol was used in place of o-aminophenol in the third stage of the synthesis.

The following tabulation sets forth additional novel 4,4′ - bis(benzoxazol - 2 - yl)-stilbene fluorescent brightening agents within the scope of the present invention. These compounds can be prepared in accordance with the procedure described hereinbefore. The compounds set forth below are illustrative of the 4,4′ - bis(benzoxazol - 2 - yl)-stilbene compounds within the scope of the invention.

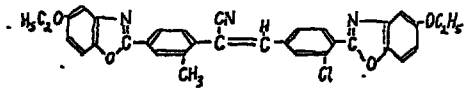
1. 4,4′ - bis(6 - acetylbenzoxazol - 2 - yl)stilbene
2. 4,4′ - bis(6 - trifluoromethylbenzoxazol - 2 - yl)stilbene
3. 4,4′ bis(6 - carbethoxybenzoxazol - 2 - yl)stilbene
4. 4,4′ - bis(6 - phenoxybenzoxazol - 2 - yl)stilbene
5. 4,4′ - bis(6 - dimethylsulphamylbenzoxazol - 2 - yl)stilbene
6. 4.4′ - bis(6 - dimethylcarbamylbenzoxazol - 2 - yl)stilbene
7. 4,4′ - bis(6 - thiocyanobenzoxazol - 2 - yl)stilbene
8. 4,4 - bis(6 -  benzoxazol - 2 - yl(stilbene
9. 4,4′ - bis(6 - chlorobenzoxazol - 2 - yl)stilbene
10. 4,4′ - bis(6 - bromobenzoxazol - 2 - yl)stilbene
11. 4,4′ - bis(benzoxazol 2 - yl) - 2 -methylsulphonylstilbene
12. 4,4′ - bis(benzoxazol 2 - yl) - 2 - dimethylsulphamylstilbene

13. 4,4′ - bis(benzoxazol - 2 - yl) - 2 - acetylstilbene
14. 4,4′ - bis(benzoxazol - 2 - yl) - 2 - thiocyanostilbene
15. 4,4′ - bis(benzoxazol - 2 - yl) - 2 - trifluoromethylstilbene
16. 4,4′ - bis(benzoxazol - 2 - yl) - 2 - carbomethoxystilbene
17. 4,4 - bis(benzoxazol - 2 - yl) - 2 -  stilbene
18. 4,4′ - bis(6 - methoxybenzoxazol - 2 - yl) - α,β - diethylstilbene
19. 4,4′ - bis(6 - chlorobenzoxazol - 2 - yl) - α,β - diethylstilbene
20. 4,4′ - bis(6 - ethylsulphonylbenzoxazol - 2 - yl) - α,β - diethylstilbene
21. 4,4′ - bis(6 - dimethylsulphamylbenzoxazol - 2 - yl) - α,β - diethylstilbene
22. 4,4′ - bis(6 - dimethylcarbamylbenzoxazol - 2 - yl) - α,β - diethylstilbene
23. 4,4′ - bis(6 - trifluoromethylbenzoxazol - 2 - yl) - α,β - diethylstilbene
24. 4,4′ - bis(6 - difluoromethylbenzoxazol - 2 - yl) - α,β - diethylstilbene
25. 4,4′ - bis(6 - bromobenzoxazol - 2 - yl) - α,β - diethylstilbene
26. 4,4′ - bis(5 - methoxybenzoxazol - 2 - yl) - α,β - diethylstilbene
27. 4,4′ - bis(5 - chlorobenzoxazol - 2 - yl) - α,β - diethylstilbene
28. 4,4′ - bis(5 - thiomethylbenzoxazol - 2 - yl) - α,β - diethylstilbene
29. 4,4′ - bis(5 - ethylsulphonylbenzoxazol - 2 - yl) - α,β - diethylstilbene
30. 4,4′ - bis(5 - dimethylsulphamylbenzoxazol - 2 - yl) - α,β - diethylstilbene
31. 4,4′ - bis(5 - dimethylcarbamylbenzoxazol - 2 - yl) - α,β - diethylstilbene
32. 4,4′ - bis(5 - carbethoxybenzoxazol - 2 - yl) - α,β - diethylstilbene
33. 4,4 - bis(5 - trifluoromethylbenzoxazol - 2 - yl) - α,β - diethylstilbene
34. 4,4′ - bis(5 - hydroxybenzoxazol - 2 - yl) - α,β - diethylstilbene
35. 4,4′ - bis (5 - acetamidobenzoxazol - 2 - yl) - α,β - diethylstilbene
36. 4,4′ - bis(6 - methoxybenzoxazol - 2 - yl) - 2 - chlorostilbene
37. 4,4′ - bis(6 - dimethylcarbamylbenzoxazol - 2 - yl) - 2 - chlorostilbene
38. 4,4′ - bis(6 - acetamidobenzoxazol - 2 - yl) - 2 - chlorostilbene
39. 4,4′ - bis(6 - phenoxybenzoxazol - 2 - yl) - 2 - chlorostilbene
40. 4,4′ - bis(6 - bromobenzoxazol - 2 - yl) - 2 - chlorostilbene
41. 4,4′ - bis(6 - cyanobanzoxazol - 2 - yl) - 2 - chlorostilbene
42. 4,4′ - bis(6 - acetylbenzoxazol - 2 - yl) - 2 - chlorostilbene
43. 4,4′ - bis(6 - methoxybenzoxazol - 2 yl) - 2 - acetamidostilbene
44. 4,4′ - bis(6 - acetamidobenzoxazol - 2 yl) - 2 - acetamidostilbene
45. 4,4′ - bis(6 - cyanobenzoxazol - 2 - yl) - 2 - acetamidostilbene
46. 4,4′ - bis(6 - thiocyanobenzoxazol - 2 - yl) - 2 - acetamidostilbene
47. 4,4′ - bis(6 - methylbenzoxazol - 2 - yl) - 2 - acetamidostilbene
48. 4,4′ - bis(6 - dimethylsulphamylbenzoxazol - 2 - yl) - 2 - acetamidostilbene
49. 4,4′ - bis(6 - methoxybenzoxazol - 2 - yl) - 2,2′ - dimethylstilbene
50. 4,4′ - bis(6 - ethoxybenzoxazol - 2 - yl) - 2,2′ - dimethylstilbene
51. 4,4′ - bis(6 - dimethylsulphamylbenzoxazol - 2 - yl) - 2,2′ - dimethylstilbene
52. 4,4′ - bis(6 - thiomethylbenzoxazol - 2 - yl) - 2,2′ - dimethylstilbene
53. 4,4′ - bis(6 - cyanobenzoxazol - 2 - yl) - 2,2′ - dimethylstilbene
54. 4,4′ - bis(6 - acetamidebenzoxazol - 2 - yl) - 2,2′ - dimethylstilbene
55. 4,4′ - bis(5 - chlorobenzoxazol - 2 - yl) - 2 - chlorostilbene
56. 4,4′ - bis(5 - methoxybenzoxazol - 2 - yl) - 2 - methylstilbene
57. 4,4′ - bis(5 - bromobenzoxazol - 2 - yl) - 2 - methylstilbene
58. 4,4′ - bis(5 - thiomethylbenzoxazol - 2 - yl) - 2 - methylstilbene
59. 4,4′ - bis(5 - dimethylsulphamylbenzoxazol - 2 - yl) - 2 - methylstilbene
60. 4,4′ - bis(5 - trifluoromethylbenzoxazol - 2 - yl) - 2 - methylstilbene
61. 4,4′ - bis(5 - iodobenzoxazol - 2 - yl) - 2 - methylstilbene
62. 4,4′ - bis(5 - methoxybenzoxazol - 2 - yl) - 2 - cyanostilbene
63. 4,4′ bis(5 - methylbenzoxazol - 2 - yl) - 2 - cyanostilbene
64. 4,4′ - bis(5 - p - methoxyphenylbenzoxazol - 2 - yl) - 2 cyanostilbene
65. 4,4′ - bis(5 - trifluoromethylbenzoxazol - 2 - yl) - 2 - cyanostilbene
66. 4,4′ - bis(5 - carbomethoxybenzoxazol - 2 - yl) - 2 - cyanostilbene
67. 4,4′ - bis(5 - acetamidobenzoxazol - 2 - yl) - 2 - cyanostilbene
68. 4,4′ - bis(5 - cyanobenzoxazol - 2 - yl) - 2 - cyanostilbene
69. 4,4′ - bis(6 - ethoxybenzoxazol - 2 - yl) - α - cyanostilbene
70. 4,4′ - bis(6 - phenoxybenoxazol - 2 - yl) - α - cyanostilbene
71. 4,4′ - bis(6 - [p - methoxyphenoxy]-benzoxazol - 2 - yl) - α - cyanostilbene
72. 4,4′ - bis(6 - carbomethoxybenzoxazol - 2 - yl) - α - cyanostilbene
73. 4,4′ - bis(6 - methoxybenzoxazol - 2 - yl) - α - cyanostilbene

74. 4,4′ - bis(5 - ethoxybenzoxazol - 2 - yl) - α - cyano - 2 - methyl - 3′ - chlorostilbene
75. 4,4′ - bis(6 - methoxybenzoxazol - 2 - yl - α - cyano - 2 - methyl - 3′ - chlorostilbene

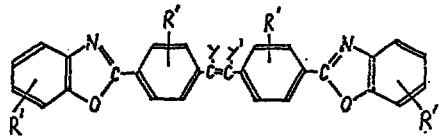
For the purposes of clarity it is here noted that by dimethylsulphamyl is meant the N,N dimethylsulphamyl group having the formula —$SO_2N(CH_3)_2$. Similarly, by dimethylcarbamyl is meant the N,N-dimethylcarbamyl group having the formula —$CON(CH_3)_2$. Sulphamyl and carbamyl as used herein, are synonymous with sulphamoyl and carbamoyl as recognised by "The Naming and Indexing of Chemical Compounds from Chemical Abstracts", Introduction to the subject Index of Chemical Abstracts, Vol. 56 (January—June 1962).

The numbering used herein for benzoxazole is that given in The Ring Index, Patterson, Capell and Walker, Second Edition (1960), American Chemical Society. To illustrate Compound 74, 4,4′ - bis(5 - ethoxybenzoxazol - 2 - yl) - α - cyano - 2 - methyl - 3′ - chlorostilbene has the formula:



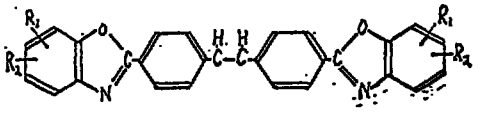
WHAT WE CLAIM IS:—

1. A compound having the formula:



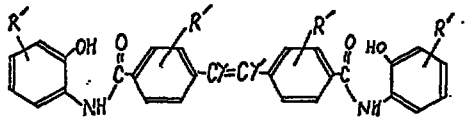
in which R′ represents one or more substituents which may be present on the benzene rings and which may be halogen atoms, alkyl, aryl, aralkyl, aryalkyl, alkoxy, aryloxy, acyl, acyloxy, hydroxyl, amino, substituted amino, quaternized ammonium, sulpho, substituted sulphonyl, sulphamyl, substituted sulphamyl, cyano, thiocyano, thiol, carbamyl, substituted carbamyl, carbamoyloxy or nitro groups and Y and Y′ each represent a hydrogen atom, alkyl, aryl or cyano group.

2. A compound as claimed in claim 1 having the formula:



in which R_1 and R_2, which may be the same or different; represent optional chlorine, bromine, methyl, ethyl, propyl, butyl, tolyl, methoxy or ethoxy substituents such that the two benzoxazole groups are substituted identically with regard to number, position, and kind of the R_1 and R_2 groups.

3. 4,4′ - Di -[benzoxazol - 2 - yl)stilbene.
4. 4,4′ - bis(6 - methoxybenzoxazol - 2 - yl)stilbene.
5. 4,4′ - bis(6 - methoxysulphonylbenzoxazol - 2 - yl)stilbene.
6. 4,4′ - bis(5 - chlorobenzoxazol - 2 - yl)stilbene.
7. 4,4′ - bis(5 - cyanobenzoxazol - 2 - yl)stilbene.
8. Fluorescent compounds as claimed in claim 1 as herein described or exemplified.
9. The method of preparing a fluorescent compound according to claim 1 wherein an intermediate compound having the formula:



is heated under a vacuum to a temperature between 200°C and 400°C.

10. Method according to claim 9 wherein the intermediate compound is heated under a vacuum of less than 20 inches of mercury to a temperature between 300°C and 350°C.

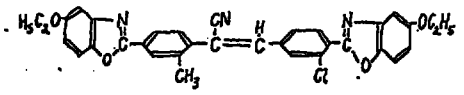
L. E. T. BRANCH, B.Sc., F.R.I.C.,
Patent Agent.

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74. 4,4′ - bis(5 - ethoxybenzoxazol - 2 - yl) - α - cyano - 2 - methyl - 3′ - chlorostilbene
75. 4,4′ - bis(6 - methoxybenzoxazol - 2 - yl - α - cyano - 2 - methyl - 3′ - chlorostilbene

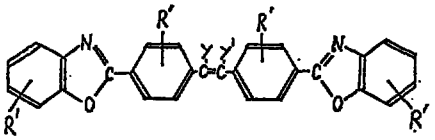
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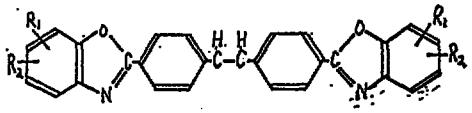
WHAT WE CLAIM IS:—

1. A compound having the formula:



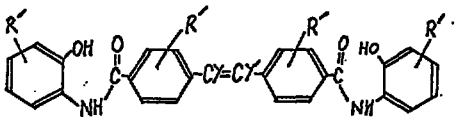
in which R′ represents one or more substituents which may be present on the benzene rings and which may be halogen atoms, alkyl, aryl, aralkyl, aryalkyl, alkoxy, aryloxy, acyl, acyloxy, hydroxyl, amino, substituted amino, quaternized ammonium, sulpho, substituted sulphonyl, sulphamyl, substituted sulphamyl, cyano, thiocyano, thiol, carbamyl, substituted carbamyl, carbamoyloxy or nitro groups and Y and Y′ each represent a hydrogen atom, alkyl, aryl or cyano group.

2. A compound as claimed in claim 1 having the formula:



in which R_1 and R_2, which may be the same or different, represent optional chlorine, bromine, methyl, ethyl, propyl, butyl, tolyl, methoxy or ethoxy substituents such that the two benzoxazole groups are substituted identically with regard to number, position, and kind of the R_1 and R_2 groups.

3. 4,4′ - Di -[benzoxazol - 2 - yl)stilbene.
4. 4,4′ - bis(6 - methoxybenzoxazol - 2 - yl)stilbene.
5. 4,4′ - bis(6 - methoxysulphonylbenzoxazol - 2 - yl)stilbene.
6. 4,4′ - bis(5 - chlorobenzoxazol - 2 - yl)stilbene.
7. 4,4′ - bis(5 - cyanobenzoxazol - 2 - yl)stilbene.
8. Fluorescent compounds as claimed in claim 1 as herein described or exemplified.
9. The method of preparing a fluorescent compound according to claim 1 wherein an intermediate compound having the formula:



is heated under a vacuum to a temperature between 200°C and 400°C.

10. Method according to claim 9 wherein the intermediate compound is heated under a vacuum of less than 20 inches of mercury to a temperature between 300°C and 350°C.

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