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PYRAZOLO-TRIAZOLE OPTICAL BRIGHTENERS

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8 Claims. (Cl. 260—240)

This invention is concerned with improvements in or relating to optical whitening agents and is more particularly concerned with certain new compounds for use as optical whitening agents.

Optical whitening agents have in recent years found extensive use in the treatment of textiles particularly during washing and are designed to counteract the yellow or off-white colour which white textiles, particularly cellulosic textiles, may possess, especially after repeated washing. Such optical whitening agents also tend to improve coloured textiles as they impart a general brightness to them. They are also widely used to impart whiteness to other cellulosic material, particularly paper.

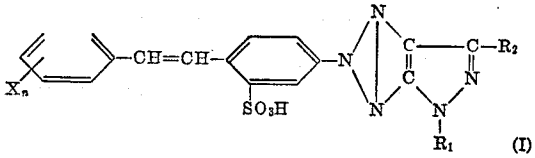
Optical whitening agents in general absorb light in the ultra-violet range of the spectrum and emit in the visible spectrum, usually in the bluish-green to bluish-violet. Thus, the fluorescence of such compounds in white material tends to counteract any yellowing as for example that resulting upon repeated washing of a white cotton or linen textile. The compounds used as optical whitening agents must be substantive to the material being treated, and must be substantially stable when "dyed" on the material being treated.

In general best results are obtained when optical whitening agents which give a shade of fluorescence which is complementary to that of the aged fibre, so that the colours will cancel out each other. Since, in general, the most common off-white shade of textiles resulting from ageing or repeated washing is yellow, the most desirable optical whitening agent is one that fluoresces blue.

It is also of importance that the optical whitening agent should not be destroyed or removed by bleaching agents; that is, it should be bleach-fast. Thus, fluorescent optical whitening agents are generally incorporated into soaps and synthetic detergents, which are marketed for household use and articles washed therewith are often subjected to bleaching with various bleaching agents, for example sodium hypochlorite. It is therefore desirable that the optical whitening agent already on the fibre or in the treating solution should be affected as little as possible by the action of any bleaching agent which may be present.

It is an object of the present invention to provide optical whitening agents having improved properties in these respects.

We have now found that certain new compounds represented by the general formula:



(I)

(in which X is hydrogen or a non-chromophoric or non-auxochromic group e.g. an alkyl, aryl or aralkyl group or halogen atom, *n* is a whole number from 1–5, R_1 is

hydrogen, or a hydrocarbon radical (such as alkyl, araikyl or aryl) or a hydroxyalkyl or polyethanoxy group and R_2 is hydrogen, or a hydrocarbon radical (such as alkyl, aralkyl or aryl) and salts thereof, in particular water-soluble, for example alkali-metal such as sodium salts, can be used with advantage as optical whitening agents in that they possess favourable properties from the point of view of the above-mentioned desiderata for the ideal optical whitening agent.

Accordingly the invention comprises such compounds, together with salts thereof, in particular water-soluble, for example alkali-metal, salts.

Preferred new compounds according to the invention are those in which R_1 and R_2, which may be the same or different, are hydrogen, lower alkyl groups or aryl or aralkyl groups. The lower alkyl group can for example be an ethyl or methyl group whilst the aryl group can for example be a phenyl group or a substituted phenyl group, such as a chloro-phenyl or sulpho-phenyl group. The group X is preferably hydrogen or a lower alkoxy group, for example methoxy or ethoxy, which is preferably in the ortho or para position to the side chain.

Particularly preferred compounds are those in which X is hydrogen or an ortho and/or para-halogen, particularly chloro, substituent, R_1 is phenyl, substituted phenyl or tolyl and R_2 is hydrogen or lower alkyl.

As specific preferred compounds may be mentioned the following:

2-(4''-styryl-3''-sulpho phenyl)(1'-phenyl-3'-methyl-pyrazolo-4':5'-4:5)-1:2:3-triazole.

2-(4''-(4'''-methoxy styryl)-3''-sulpho phenyl)(1'-phenyl-3'-methyl-pyrazolo-4':5'-4:5)-1:2:3-triazole.

2-(4''-(4'''-chlorostyryl)-3''-sulpho phenyl)(1'-phenyl-3'-methyl-pyrazolo-4':5'-4:5)-1:2:3-triazole.

2-(4''-(2'''-chlorostyryl)-3''-sulpho phenyl)(1'-phenyl-3'-methyl-pyrazolo-4':5'-4:5)-1:2:3-triazole.

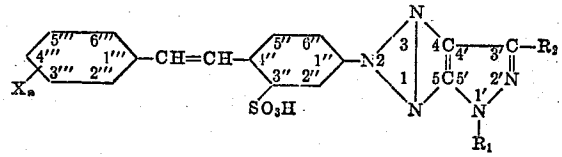
2-(4''-styryl-3''-sulpho phenyl)(1'-(p-chlorophenyl)-3'-methyl-pyrazolo-4':5'-4:5)-1:2:3-triazole.

2-(4''-styryl-3''-sulpho phenyl)(1'-(p-tolyl)-3'-methyl-pyrazolo-4':5'-4:5)-1:2:3-triazole.

2-(4''-styryl-3''-sulpho phenyl)(1'-(p-sulpho phenyl)-3'-methyl-pyrazolo-4':5'-4:5)-1:2:3-triazole.

Of these 2-(4''-styryl-3''-sulpho phenyl)(1'-phenyl-3'-methyl-pyrazolo-4':5'-4:5)-1:2:3-triazole is the most preferred.

The nomenclature adopted for the compounds mentioned above is based on the following numbering:

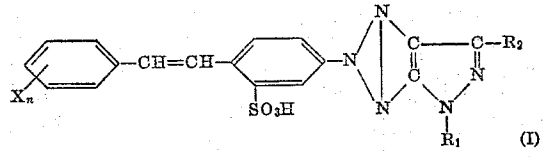


The compounds of the present invention are substantive to cellulosive materials and exhibit a blue fluorescence imparting a particularly pleasant hue to the material being treated. They are substantially bleach-fast and have good "build-up" qualities; that is—due to well-balanced substantivity—on repeated treatments with a bath of the same concentration, the whiteness of the fabric being treated continually increases up to a maximum, which maximum does not in general cause unpleasant visible colour or hue as is often the case.

The compounds according to the present invention can with advantage be incorporated in compositions normally used for the treatment of textiles, for example detergents and soaps in solid or liquid form. They may also be incorporated in baths for the treatment of cellulosic materials during their production or for treatment of the finished textile article. In addition, the new

compounds may also be incorporated in compositions for the treatment of paper and photographic paper where high whiteness is necessary.

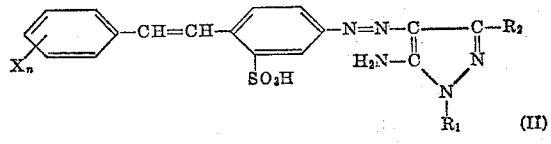
According to a feature of the invention therefore there is provided a composition adapted for the treatment of cellulosic materials comprising a compound of the formula:



(I)

(in which X, n, R_1 and R_2 have the above-stated meanings) and salts thereof, in particular water-soluble, for example, alkali-metal such as sodium, salts. The composition also includes cellulosic materials when treated with the above composition, in particular cotton or linen textiles.

The new compounds according to the invention can conveniently be prepared by oxidising an o-amino azo dye of Formula II given below, and according to a feature of the invention therefore we provide a process for the preparation of compounds of the general Formula I above which comprises oxidising an o-amino azo dye of the general formula

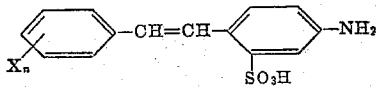


(II)

(in which X, n, R_1 and R_2 have the above-stated meanings).

It is preferred to use a mild oxidising agent; suitable oxidising agents for effecting the above reaction including alkali-metal hypochlorites, for example sodium hypochlorite; cuprammonium sulphate or copper sulphate in the form of a soluble complex with pyridine as well as thionyl chloride and sulphuryl chloride may also be used.

The compounds of general Formula II may be prepared in any convenient manner, such as, for example, by diazotising a compound of the formula:



(III)

(where X and n have the above-stated meaning) and coupling the diazotized compound with 5-amino pyrazole or a substituted derivative thereof for example 1-phenyl-3-methyl-5-aminopyrazole. If desired the intermediate diazo compound may be isolated before it is coupled.

In order that the invention may be more fully understood the following examples are given by way of illustration only:

EXAMPLE 1

2-(4''-styryl-3''-sulpho phenyl)(1'-phenyl-3'-methylpyrazolo-4':5'-4:5)-1:2:3-triazole

A solution of 16.32 parts of the sodium salt of 4-amino-stilbene-2-sulphonic acid (91% pure) and 3.45 parts of sodium nitrite in 150 parts of water is indirectly diazotised at 8–10° C. with 20 parts of concentrated HCl. The diazo compound is isolated, suspended in aqueous pyridine, and mixed with a solution of 8.65 parts of 1-phenyl-3-methyl-5-amino-pyrazole in aqueous acetic acid to effect coupling of the components. The acidity of the mixture is controlled by addition of sodium acetate during coupling. When the coupling is complete the o-amino-azo dyestuff obtained is salted out and filtered off at 25–30° C.

The o-amino-azo dyestuff is dissolved in aqueous alcohol and sodium hydroxide and is oxidised by addition of an excess of sodium hypochlorite solution added dropwise at 70–75° C. On completion of the oxidation which is shown by the change of colour from red to orange the 2-stilbyl-(1-phenyl-3-methyl)-pyrazolyl-triazole obtained is salted out. The compound is slurried with aqueous alcohol, made alkaline, and treated with sodium hydrosulphite for a few hours at 70° C. to remove the last trace of coloured impurities. Finally, the compound is recrystallised from aqueous alcohol.

The compound so obtained is a pale yellow powder which in dilute solution gives a vivid blue fluorescence and when a piece of cotton is washed in a detergent solution containing a small amount of this compound the material acquires a much whiter appearance than before treatment. The compound has a λ max. 344 mμ.

A piece of aged white poplin (slightly yellowish) is washed in a detergent solution containing 0.05 gm./litre of the compound. After rinsing and drying the material shows a brilliant white appearance.

EXAMPLE 2

2-(4''-(4'''-methoxy styryl)-3''-sulpho phenyl)(1'-phenyl-3'-methyl-pyrazolo-4':5'-4:5)-1:2:3-triazole

A solution of 18.17 parts of the sodium salt of 4'-methoxy-4-aminostilbene-2-sulphonic acid (90% pure) and 3.45 parts of sodium nitrite in 150 parts of water is indirectly diazotised at 8–10° C. with 20 parts of concentrated HCl. The diazo compound is isolated, suspended in water, and mixed with a solution of 8.65 parts of 1-phenyl-3-methyl-5-amino pyrazole in dilute hydrochloric acid to effect coupling of the components. The acidity of the mixture is controlled by the addition of sodium acetate during coupling. When coupling is completed the o-amino-azo dyestuff obtained is salted out and filtered off at 25–30° C. the o-amino-azo dyestuff is dissolved in pyridine and oxidised by refluxing for 3 hours with 30 parts of copper sulphate and 35 parts of ammonia, with 60 parts of water. On completion of the oxidation the mixture is acidified, and the crude product obtained is recrystallised from aqueous acetone. It has λ max. 360 mμ.

EXAMPLE 3

2-(4''-(4'''-chloro styryl)-3''-sulpho phenyl)(1'-phenyl-3'-methyl-pyrazolo-4':5'-4:5)-1:2:3-triazole

A solution of 18.62 parts of the sodium salt of 4'-chloro-4-aminostilbene-2-sulphonic acid (89% pure) and 3.45 parts of sodium nitrite in 150 parts of water is indirectly diazotised at 8–10° C. with 20 parts of concentrated HCl. The diazo compound is iso'ated, suspended in water and mixed with a solution of 8.65 parts of 1-phenyl-3-methyl-5-aminopyrazole in dilute hydrochloric acid to effect coupling of the components. The pH of the mixture is controlled at 7–8 by the addition of sodium acetate during coupling. When coupling is complete the o-amino-azo dyestuff obtained is salted out and filtered off at 25–30° C. The o-amino-azo dyestuff is dissolved in pyridine and oxidised by refluxing for 3 hours with 30 parts of copper sulphate and 35 parts of ammonia with 60 parts of water. After oxidation the mixture is acidified and the crude product filtered off. The triazole is recrystallised from aqueous alcohol by boiling with sodium hydrosulphite and activated charcoal, screening and allowing to cool. It has λ max. 346 mμ.

EXAMPLE 4

2-(4''-(2'''-chloro styryl)-3''-sulpho phenyl)(1'-phenyl-3'-methyl-pyrazolo-4':5'-4:5)-1:2:3-triazole

This is prepared as in Example 3, but replacing 4'-chloro-4-aminostilbene-2-sulphonic acid by 2'-chloro-4-aminostilbene-2-sulphonic acid.

EXAMPLE 5

2-(4''-styryl-3''-sulpho phenyl)(1'-(p-chlorophenyl)-3'-methyl-pyrazolo-4':5'-4:5)-1:2:3-triazole

A solution of 16.5 parts of the sodium salt of 4-amino-stilbene-2-sulphonic acid (90% pure) and 3.45 parts of sodium nitrite in 150 parts of water is indirectly diazotised at 8–10° C. with 20 parts of concentrated HCl. The diazo compound is isolated, slurried in water and mixed with a solution of 10.38 parts of 1-(p-chlorophenyl)-3-methyl 5-aminopyrazole in dilute hydrochloric acid to effect coupling of the components. The acidity of the reaction mixture is controlled by the addition of sodium acetate. When coupling is complete the o-amino-azo dyestuff obtained is salted out and filtered off at 25–30° C. The o-amino-azo dyestuff is dissolved in pyridiae and oxidised by refluxing for 3 hours with 30 parts copper sulphate and 35 parts of ammonia, with 60 parts of water. On completion of the oxidation the mixture is acidified, and the crude product obtained is recrystallised from aqueous acetone. It has λ max. 344 mμ.

EXAMPLE 6

2-(4''-styryl-3''-sulpho phenyl)(1'-(p-tolyl)-3'-methyl-pyrazolo-4':5'-4:5)-1:2:3-triazole

A solution of 16.5 parts of the sodium salt of 4-amino-stilbene-2-sulphonic acid (90% pure) and 3.45 parts of sodium nitrite in 150 parts of water is indirectly diazotised at 8–10° C. with 20 parts of concentrated HCl. The diazo compound is isolated, parts of 1-(p-tolyl)-3-methyl-5-aminopyrazole in dilute hydrochloric acid to effect coupling of the components. The acidity of the reaction is controlled by the addition of sodium acetate. When coupling is complete the o-amino-azo dyestuff obtained is salted out and filtered off at 25–30° C. The o-amino-azo dyestuff is dissolved in pyridine and oxidised by refluxing for 3 hours with 30 parts copper sulphate and 35 parts ammonia, with 60 parts of water. On completion of the oxidation the mixture is acidified, and the crude product obtained is recrystallised from aqueous acetone. It has λ max. 345 mμ.

EXAMPLE 7

2-(4''-styryl-3''-sulpho phenyl)(1'-(p-sulpho phenyl)-3'-methyl-pyrazolo-4':5'-4:5)-1:2:3-triazole

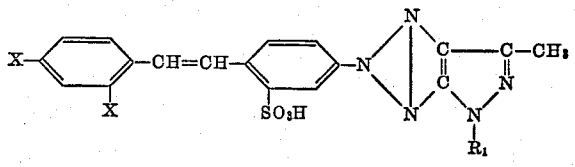
A solution of 16.5 parts of the sodium salt of 4-amino-stilbene-2-sulphonic acid (90% pure) and 3.45 parts sodium nitrite in 150 parts of water is indirectly diazotised at 8–10° C. with 20 parts concentrated hydrochloric acid. The diazo compound is isolated, slurried in water and mixed with a solution of 12.65 parts of 1-(phenyl-4'-sulphonic acid)-3-methyl-5-aminopyrazole and 5.3 parts of sodium carbonate in water to effect the coupling of the components. The pH of the mixture is controlled at 7–8 by the addition of sodium acetate during coupling. After coupling is complete the solution is saturated with salt and the o-amino-azo dyestuff filtered off at 25–30° C.

The o-amino-azo dyestuff is dissolved in water and oxidised by refluxing for 3 hours with 30 parts of copper sulphate and 35 parts of ammonia. On completion of the oxidation the mixture is acidified and the crude product obtained is recrystallized from aqueous alcohol in the presence of sodium hydrosulphite. It has λ max. 344 mμ.

It will be appreciated that although in the foregoing examples the groups X, R_1 and R_2 have been illustrated by certain specific embodiments that the invention is not in any way limited thereto and that these groups can be modified within the scope of the invention as set out in the appended claims. Thus X can be ethoxy, propoxy etc.; R_1 and R_2 can be ethyl, propyl, butyl, naphthyl etc. Other variations will be apparent to those skilled in the art.

We claim:

1. A compound selected from the group consisting of a compound having the formula



in which X is a member selected from the group consisting of a hydrogen atom, a halogen atom, and a lower alkoxy group and R_1 is a member selected from the group consisting of a hydrogen atom and phenyl, halophenyl, sulphophenyl and tolyl groups; and alkali metal salts thereof.

2. 2 - (4'' - styryl - 3'' - sulpho phenyl)(1' - phenyl-3' - methyl - pyrazolo - 4':5' - 4:5) - 1:2:3-triazole.

3. 2 - (4'' -(4''' - methoxy styryl) - 3'' - sulpho-phenyl) - (1' - phenyl - 3' - methyl - pyrazole - 4':5' - 4:5)-1:2:3 - triazole.

4. 2 - (4'' - (4''' - chloro styryl) - 3'' - sulpho phenyl)-(1' - phenyl - 3' - methyl - pyrazolo - 4':5' - 4:5) - 1:2:3-triazole.

5. 2 - (4'' - (2''' - chloro styryl) - 3'' - sulpho phenyl)-(1' - phenyl - 3' - methyl - pyrazolo - 4':5' -4:5) - 1:2:3-triazole.

6. 2 - (4'' - styryl - 3'' - sulpho phenyl)(1' - (p - chlorophenyl) - 3' - methyl - pyrazolo - 4':5' - 4:5) - 1:2:3-triazole.

7. 2 - (4'' - styryl - 3'' - sulpho phenyl)(1' - (p - tolyl)-3' - methyl - pyrazolo - 4':5' - 4:5) - 1:2:3 - triazole.

8. 2 - (4'' - styryl - 3'' - sulpho phenyl)(1' - (p - sulphophenyl) - 3' - methyl - pyrazolo - 4':5' - 4:5) - 1:2:3-triazole.

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