United States Patent Office **3,793,340**
Patented Feb. 19, 1974

3,793,340

NOVEL 1,2,4-OXADIAZOLE DERIVATIVES

Asim Kumar Sarkar, Vlaardigen, Netherlands, assignor to Hickson & Welch Limited, Castleford, Yorkshire, England

No Drawing. Filed Sept. 21, 1970, Ser. No. 74,175
Claims priority, application Great Britain, Sept. 23, 1969, 46,891/69
Int. Cl. C07d *85/48*
U.S. Cl. 260—307 D **8 Claims**

ABSTRACT OF THE DISCLOSURE

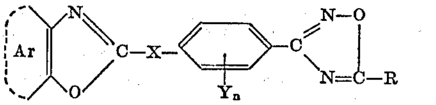
A novel series of 1,2,4-oxadiazole derivatives useful in the whitening, brightening and/or bleaching of various synthetic materials, such as textile fibers.

This invention is concerned with new chemical compounds of use in the whitening, brightening and/or bleaching of polyamide, polyester, polyolefin, acrylic and other synthetic materials in the form for example of textile yarns and fibres, synthetic resin sheets and the like.

Optical whitening agents have in recent years found extensive use in the treatment of textile yarns and fibres, both in their preparation and during washing, and are designed in general to counteract the yellow or off-white color which white textiles may develop. Such optical whitening agents also tend to improve colored textiles as they impart a general brightness to them.

The present invention is based upon the discovery of certain 1,2,4-oxadiazole derivatives which have particularly advantageous properties in the whitening, brightening and/or bleaching of textile fibres.

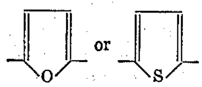
According to one feature of the present invention, there are provided compounds of the general formula:



(I)

wherein

Ar represents a substituted or unsubstituted benzene or naphthalene ring fused to the oxazole ring; Y represents an alkyl or alkoxy group or a halogen atom;
N represents 0, 1 or 2;
R represents a substituted or unsubstituted alkyl, cycloalkyl or aryl group; and
X represents a group of formula —CH=—,



Where X represents a group of formula —CH=CH— the compounds of Formula I may exist in either cis- or trans-forms.

According to a further feature of the present invention, there are provided compositions for use in the treatment of an at least in part synthetic textile material comprising at least one compound of Formula I as hereinbefore defined together with a solid or liquid carrier.

According to a still further feature of the present invention, there is provided textile material which is at least in part synthetic having at least one compound of Formula I as hereinbefore defined in association therewith.

The compounds according to the invention have especially advantageous properties in the whitening, brightening and/or bleaching of textile yarns and fibres, in particular, synthetic textile fibres (e.g. polyamide, polyolefin, acrylic and more especially polyester fibers).

The compounds according to the invention may also, if desired, be incorporated into synthetic melts e.g. of polyester resin which may subsequently be formed into textile yarns and fibres or other shaped articles such as for example synthetic resin sheets and fibres. Where for example textile yarns and fibres are to be formed, the compounds according to the invention may be incorporated into a synthetic resin melt e.g. a polyester resin melt, and the melt then extruded to form the yarns or fibres.

The compounds according to the invention in general have a desirable blue fluorescence, have good light fastness and have good stability to chlorine-containing and oxygen bleach baths. In addition, they in general show a high degree of thermal stability and may thus be used for example in polyester resin melts for the production of textile yarns and fibres and other shaped articles as described above. They are also of course suitable for use in a more conventional manner, for example in normal dyeing processes e.g. in a dye-bath at elevated temperatures and pressures, or in the pad-bake process. Solutions or dispersions of the compounds according to the invention are convenient in these processes.

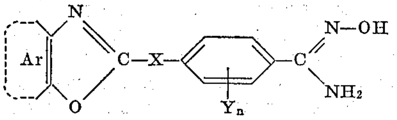
In the compounds of Formula I according to the present invention, Ar can for example preferably represent a benzene ring fused to the oxazole ring. The fused benzene or naphthalene ring can, if desired, be substituted by at least one alkyl or alkoxy group each advantageously containing 1 to 6 carbon atoms, e.g. a methyl or methoxy group. The substituent Ar may also, if desired, be substituted with a halogen atom, for example a chlorine atom. Particularly preferred compounds according to the invention by virtue of their interesting whitening, brightening and/or bleaching properties are those wherein Ar in conjunction with the oxazole ring forms a 5-methyl, 5-methoxy or 5,6-dimethylbenzoxazol-2-yl group. When Ar represents a naphthyl group it preferably is fused to the oxazole ring via the 1- and 2-positions of the naphthalene ring system.

The substituent Y where present in compounds of Formula I preferably represents an alkyl or alkoxy group which advantageously contains from 1 to 6 carbon atoms or a halogen atom advantageously a fluorine or chlorine atom. The substituent R may, if desired, carry, for example, a halogen substituent and it preferably represents an alkyl group containing from 1 to 6 carbon atoms, advantageously a methyl or chloromethyl group, a cycloalkyl group containing from 5 to 7 carbon atoms or when it represents an aryl group, a phenyl group.

For the purpose of treating previously-formed textile yarns and fibres in general, the compounds according to the invention may be incorporated into compositions comprising at least one compound of Formula I together with a solid or liquid carrier. Such compositions may for example be adapted for use in the washing of finished polyamide, polyolefin, polyester and acrylic fibres and can take the form of solutions, suspensions and dispersions of compounds of Formula I in appropriate liquid carriers such as water, sulpholane, dimethylformamide and dimethylsulphoxide. When dispersions are used they conveniently include dispersing agents such as for example alkyl naphthalene sulphonates. Aqueous compositions may, if desired, also contain, for example, synthetic detergents, soaps or surface active agents. Alternatively the compositions may be in solid form and comprise at least one compound according to the invention together with a solid synthetic detergent or soap as carrier. The compounds of Formula I may be employed in the manufacture of synthetic yarns and fibres, e.g. by addition to compositions from which the fibres are prepared by spinning or extrusion.

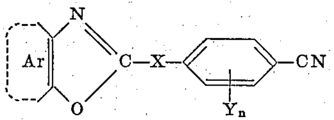
The 1,2,4-oxadiazole derivatives of Formula I may for example be prepared by any convenient method (e.g. of the kind described in "Review of Chemistry of 1,2,4-oxadiazoles" F. Eloy, Fortshr. Chem. Forsch., 1965, 4, 807–876) and are advantageously prepared by one of the following processes:

(a) Reaction of an amidoxime of formula



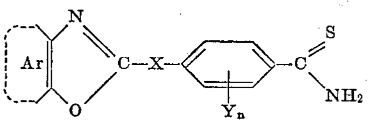
(II)

(wherein Ar, X, Y and *n* are as hereinbefore defined) with a functional derivative of a carboxylic acid of formula R.COOH (wherein R is as hereinbefore defined). The functional derivative of the carboxylic acid may, for example, be an acid halide, e.g. the acid chloride, anhydride or amide. Ortho esters of carboxylic esters may also be used to cyclize compounds of Formula II e.g. triethyl orthoacetate. The compounds of Formula II used as starting materials can for example be prepared by the reaction of a nitrile of formula



(III)

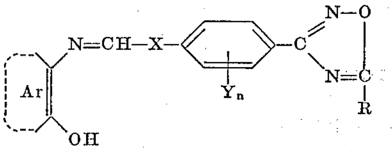
(wherein Ar, X, Y and *n* are as hereinbefore defined) with hydroxylamine. However, the amidoximes of Formula II may also be prepared by the intermediate formation of a thioamide of formula



(IV)

(wherein Ar, X, Y and *n* are as hereinbefore defined) which may be prepared, for example, by reacting the corresponding nitrile of Formula III with hydrogen sulphide. Methods which may be used for the preparation of amidoximes have been reviewed by F. Eloy in "Chemical Reviews."

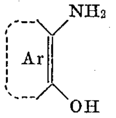
(b) The oxidative cyclization of a compound of formula



(V)

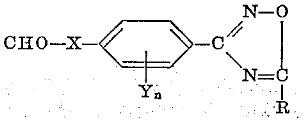
(wherein Ar, X, Y, *n* and R as hereinbefore defined). The cyclization may be effected under conventional conditions, for example using a mild oxidizing agent such as oxygen, manganese dioxide, copper acetate, chloranil and the like. The oxidation may conveniently be effected in a solvent which advantageously is inert to the oxidizing conditions. Suitable solvents include, for example halogenated hydrocarbons such as chlorobenzene.

The 1,2,4-oxadiazoles of Formula V may be prepared by a convenient method, for example, by conventional processes for the formation of amine and azomethine type compounds. A suitable method may, for example, be the reaction of an aromatic compound containing adjacent hydroxy and amino groups i.e. a compound of formula



(VI)

(wherein Ar is as hereinbefore defined) with a compound of formula



(VII)

(wherein X, Y, *n* and R are as hereinbefore defined). The 1,2,4-oxadiazoles of Formula VII used as starting materials for this process may, for example, be prepared by a method analogous to that used for the preparation of the compounds of Formula I according to process (a) above such as the reaction of an amidoxime with a functional derivative of a carboxylic acid. The various substituents required on the oxadiazole ring of the compound of Formula VII are advantageously introduced so as to prevent incompatibility of the reagent used to prepare the oxadiazole ring system and any particular group in the compound of Formula VII. Thus, it is advantageous to prepare compounds of Formula VII by the introduction of the substituent CHO—X— into a pre-formed 3-aryl-1,24-oxadiazole system, for example by diazotizing a 3-(4 - aminophenyl) - 1,2,4 - oxadiazole and coupling with a suitable reagent such as furfuraldehyde, since the aldehyde group may itself react with hydroxylamine during formation of the amidoxime.

In the preparation of amidoximes used for the preparation of 1,2,4-oxadiazoles of Formula I or VII, hydroxylamine is preferably used in its free form and may conveniently be liberated from a salt thereof which in general is more stable than hydroxylamine itself. Suitable salts include hydroxylamine hydrochloride and sulphate.

The following examples, in which all parts are by weight, are given by way of illustration only:

EXAMPLE 1

1-(5,6-dimethylbenzoxazol-2-yl)-2-[4-(5-methyl-1,2,4-oxadiazol-3-yl)-phenyl]-ethylene

2-(4-cyanostyryl)-5,6-dimethyl - benzoxazole (6 pts.) was dissolved in butanol (350 pts.) and hot ethanol (150 pts.) was added to this solution. Hydroxylamine hydrochloride (1.7 parts) and 1.3 pts. of sodium carbonate in water (25 pts.) were added to this solution and the mixture refluxed for 24 hrs. At the end of 24 hrs. the mixture was concentrated to remove most of the solvent and quenched in water (100 pts.). The resulting amidoxime (6.5 pts.) was filtered and dried. M.Pt. 270–275° C.

The amidoxime obtained above was dissolved in hot glacial acetic acid (75 pts.) and cooled to room temperature. To this solution, acetic anhydride (75 pts.) was added and the mixture slowly heated to reflux. The mixture was refluxed for ½ hr. and the mixture of acetic acid and acetic anhydride distilled over till only a small volume was left. This mixture was quenched in water (100 pts.) and the resulting oxadiazole filtered off and dried. The solid was recrystallized from toluene. M.Pt. 237–239° C.

$\lambda_{max.}$ 345–356. $E^{1\%}_{1\,cm.}$ 1320 and 1315

A dilute solution of the compound in alcohol gives blue violet fluorescence.

2-(4-cyanostyryl)-5,6-dimethylbenzoxazole may be prepared by the condensation of 2,5,6-trimethylbenzoxazole with 4-cyanobenzaldehyde or from 2-amino-4,5-dimethylphenol for example by a conventional reaction with 4-cyanocinnamic acid.

EXAMPLE 2

2-(5,6-dimethylbenzoxazol-2-yl)-5-[4-(5-methyl-1,2,4-oxadiazol-3-yl)-phenyl]-furan

5-[4(5-methyl-1,2,4-oxadiazol-3-yl) - phenyl] - furfuraldehyde (12.7 pts.) and 2-amino-4,5-dimethylphenol (6.9 pts.) are refluxed in monochlorobenzene for 1½ hours.

The water formed is removed by azeotropic distillation. At the end of the reaction, when the required amount of water is removed, 30 pts. of manganese dioxide (activated) is added portionwise over ½ hr. The mixture is refluxed for a further 15 mins. with good stirring, filtered hot, and the residue is washed with hot monochlorobenzene. The combined filtrate is concentrated and evaporated to dryness. The residue, a yellow solid, is slurried in acetone (cold) and filtered, to give 14.5 pts. of the desired compound in crude form. The product is crystallized from Cellosolve. M.Pt. 225–227° C. A dilute solution of the product in alcohol has blue violet fluorescence.

$\lambda_{max.}$ 360 mμ. $E^{1\%}_{1\,cm.}$ 1330

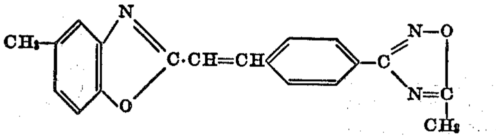
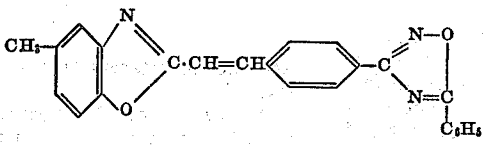
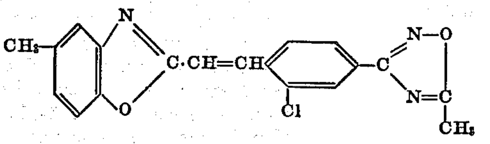
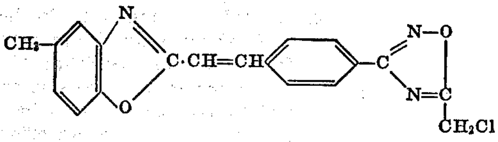
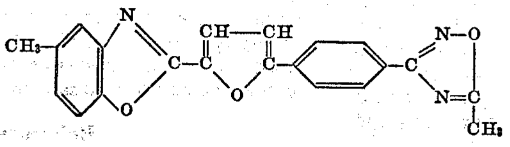
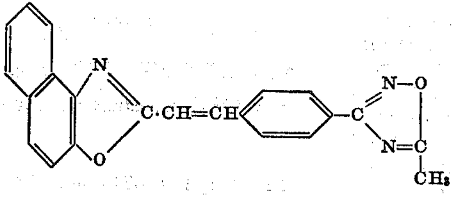
The starting material used for this example was prepared as follows. 13.9 pts. of hydroxylamine hydrochloride and 16.4 pts. of sodium acetate in 20 pts. of water were added to 14.8 pts. of 4-nitrobenzonitrile in 100 pts. of ethanol. The mixture was refluxed for 12 hrs. After 12 hrs. the mixture was poured into 300 pts. of water, cooled, filtered, washed and dried to give 14.4 pts. of amidoxime, M.Pt. 176–178 (lit. M.Pt. 179–181° C.).

14.4 pts. of 4-nitrobenzamidoxime was added to a mixture of 25 pts. of glacial acetic acid and 25 pts. of acetic anhydride, refluxed for 2 hrs. and poured into 200 pts. of water and boiled for ½ hr., then cooled and filtered to give 14.6 pts. of crude 3-(4-nitrophenyl)-5-methyl-1,2,4-oxadiazole. M.Pt. 136–138° C.

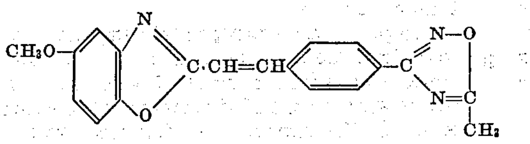
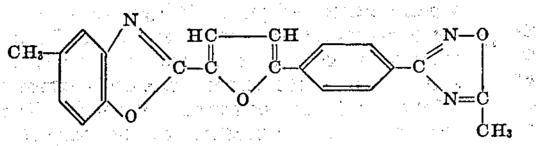
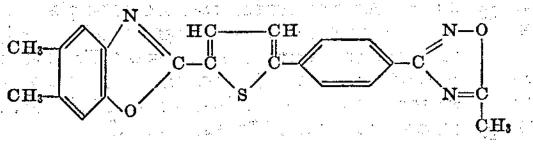
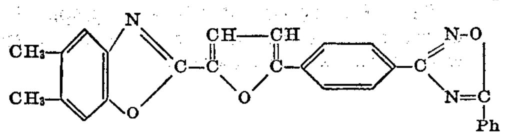
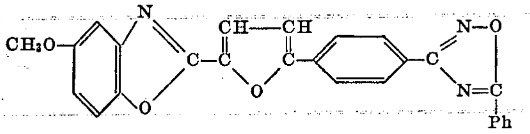
To a boiling mixture of 40 pts. of sodium sulphide ($Na_2S \cdot 9H_2O$), 10 pts. of sulphur, 100 pts. of water and 80 pts. of methanol, 26 pts. of 3-(4-nitrophenyl)-5-methyl-1,2,4-oxadiazole were added and the mixture boiled for ½ hr. The mixture was then poured into 1000 pts. of water, filtered, washed and dried. Yield 19.5 pts. (M.Pt. 113–114° C.) of 3-(4-aminophenyl)-5-methyl-1,2,4-oxadiazole.

116 pts. of the aminophenyl compound obtained above were dissolved in 300 pts. of acetic acid, cooled to room temperature with stirring and 204 pts. of conc. HCl in 500 pts. of water were added quickly to the solution and cooled to 0° C. The mixture was diazotized with a solution of sodium nitrite (46 pts. in 200 pts. of water) maintaining the temperature between 0° and 5° C. To the diazonium chloride, a solution of 80 pts. of furfural in 450 pts. of acetone was added and the mixture warmed to 15° C. A solution of 30 pts. of cupric chloride in 200 pts. of water were added to the mixture and the temperature raised to 20° C. An exothermic reaction took place and the temperature rose to 30° C. (slight cooling used). The mixture was left overnight at this stage. The mixture was then filtered and washed, and the solid recrystallized from ethanol to give 5-[4-(5-methyl-1,2,4-oxadiazol-3-yl)-phenyl]-furfural. M.Pt. 182–183° C.

The following compounds were prepared analogously to the methods described in the above examples, some physical data also being given:

Example		M.P., °C.	Color of fluorescence	U.V. absorption characteristic	
				$\lambda_{max.}$	$E^{1\%}_{1\,cm.}$
3		212–214	Blue violet	336 347	1,425 1,364
4		217–219	do	337 348	1,220 1,156
5		219–221	do	341	1,136
6		202–203	do	338 352	1,336 1,220
7		213–214	do	355	1,425
8		208–211	Violet-blue	359	1,050

TABLE—Continued

Example		M.P., ° C.	Color of fluorescence	U.V. absorption characteristic $\lambda_{max.}$	U.V. absorption characteristic $E^{1\%}_{1cm}$
9		206-208	Blue	347	1,072
10		247	Blue-violet	355	1,240
11		246-247	do	358	1,140
12		236	do	361	1,250
13		198-199	do	363	1,224

EXAMPLE 14

The compound obtained in Example 2, as such or in solution in a suitable solvent, is added to a hot melt of a polyester resin, which is extruded through a spinnerette to form filaments of polyester fibres by melt spinning. 0.1% of the compound (based on the weight of the resin) gives a very good brightening effect. Alternately, a solution obtained by dissolving the same compound in a suittable solvent may be sprayed on to the extruded filament during or after stretching.

The compound may also be incorporated in other colourless polymeric materials like polyamides, polyolefins and polyacrylics, and the resins may be in the forms of fibres, films or shaped articles.

EXAMPLE 15

0.5 part of the compound prepared as described in Example 2 and 1.5 pts. of a polyethylene glycol ether of aliphatic higher alcohols are milled together and made up to 100 pts. of liquid dispersion with distilled water. A polyester fabric is dipped into this dispersion liquid and squeezed out to 80% water content. This is dried at 50-60° C. and heat treated at 200° C. for 30 secs. to produce a fabric having a very bright and white appearance and very good light fastness.

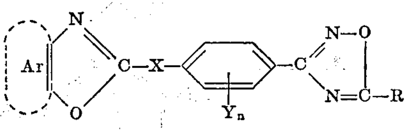
EXAMPLE 16

Polyester fibres are introduced into an aqueous liquor containing 1 g. sodium oleyl sulphate, 0.75 g. formic acid and 0.1 g. of the compound of Example 8 per litre at a goods to liquor ratio of 40:1. The treatment liquor is heated to boiling and maintained at the boiling temperature for 50 mins. The fibres are then rinsed and dried; they exhibit a very good brightening effect. The compound of Example 8 may be introduced into the dye bath as a dispersion as described in the previous example or as a solution in a suitable solvent like dimethyl formamide.

The above compounds may also be used with a shading blue or violet dyestuff. They may also be used for brightening polyester-cotton blends in conjunction with known cellulosic brighteners, for example, the triazinylstilbene or other types.

I claim:

1. A compound of the formula:



wherein:

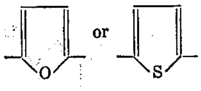
Ar is phenyl, naphthalene, or phenyl or naphthalene substituted by halogen or by an alkyl or alkoxy group containing from 1 to 6 carbon atoms, said phenyl or naphthalene being fuzed to the oxazole ring;

Y is a halogen atom or an alkyl or alkoxy group containing from 1 to 6 carbon atoms;

n is 0, 1, or 2;

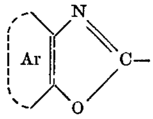
R is an alkyl group containing from 1 to 6 carbon atoms, a cycloalkyl group containing from 5 to 7 carbon atoms, a phenyl group, an alkyl group containing from 1 to 6 carbon atoms substituted by a halogen group, a cycloalkyl group containing from 5 to 7 carbon atoms substituted by a halogen atom, or a phenyl group substituted by a halogen atom; and

X is



2. A compound as claimed in claim 1 wherein R is selected from the group consisting of a methyl group, a chloromethyl group, and a phenyl group.

3. A compound as claimed in claim 1 wherein the group



is selected from the group consisting of a 5-methyl-, a 5-methoxy-, and a 5,6-dimethyl-benzoxazol-2-yl group.

4. A compound as claimed in claim 1 wherein Ar represents a naphthylene ring system fused at the 1- and 2-positions to the oxazole ring.

5. A compound as defined in claim 1 which is 2-(5,6-dimethylbenzoxazol-2-yl)-5-[4-(5-methyl - 1,2,4 - oxadiazol-3-yl)-phenyl]-furan.

6. The compound of claim 1 wherein Ar is phenyl or naphthalene substituted by chlorine.

7. The compound of claim 1 wherein Ar is phenyl or naphthalene substituted by a methyl or methoxy group.

8. The compound of claim 1 wherein Y is a chlorine or fluorine atom.

References Cited

UNITED STATES PATENTS

3,264,315	12/1963	Maeder et al. ----	260—307 D X
3,637,672	1/1972	Seino et al. -------	260—240.9

FOREIGN PATENTS

58,961	12/1967	East Germany --	260—240 CA

JOHN D. RANDOLPH, Primary Examiner

U.S. Cl. X.R.

117—33.5 R, 33.5 T; 252—117, 301.2 W, 543; 260—37 NP, 41 C, 75 N, 78 R, 93.7, 240 D, 307 G