PATENT SPECIFICATION

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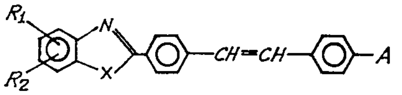
(54) STILBENE DERIVATIVES AND PROCESS FOR PREPARING THEM

(71) We, HOECHST AKTIENGESELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention, 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:—

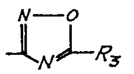
This invention relates to stilbene derivatives and to a process for preparing them.

The present invention provides compounds of the formula



(I)

in which X is O or S, each of R_1 and R_2 is a hydrogen, fluorine or chlorine atom, a phenyl group, an alkyl group having from 1 to 9, preferably from 1 to 4, carbon atoms, or a lower alkoxy, lower dialkylamino, lower trialkylammonium, acylamino, carboxy, sulfo or functionally modified carboxy or sulfo group or, when attached to adjacent carbon atoms, R_1 and R_2 together may form a fused benzene ring or a lower alkylene or 1,3-dioxapropylene group, and A is a group of the formula



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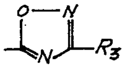


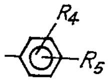
in which R_3 is

(a) a straight chain or branched alkyl group having from 1 to 18 carbon atoms, preferably from 1 to 6 carbon atoms, which may carry one or more substituents selected from halogen atoms, hydroxy, lower alkoxy, lower diakylamino, morpholino, piperidino, 1-piperazinyl, lower alkylmercapto, chloro-aryloxy, aryloxy, arylmercapto, and aryl groups,

(b) a group of the formula $—(CH_2CH_2O)_n—R$, in which n is 1, 2 or 3 and R is a hydrogen atom or a lower alkyl, dialkylaminoalkoxyalkyl, or alkylthioalkoxyalkyl group, the alkyl groups of the dialkylaminoalkoxyalkyl group optionally forming together with the nitrogen atom to which they are attached a piperidine, pyrrolidine, hexamethylene-imine, morpholine or piperazine ring,

(c) a group of the formula $—(CH_2)_m—CH=CH—R$, in which m is zero or an integer from 1 to 5, or

(d) a group of the formula



in which each of R_4 and R_5 is a hydrogen, fluorine or chlorine atom or a phenyl, lower alkyl, lower alkoxy, $(C_1{-}C_4)$-acylamino, carboxy, sulfo or functionally modified carboxy or sulfo group, or, when attached to adjacent carbon atoms, R_4 and R_5 together may form a lower alkylene group, a fused benzene ring or a 1,3-dioxapropylene group.

Compounds of special interest are those in which X, A, R_1 and R_2 have the meanings given above and R_3 is a $(C_1{-}C_6)$ - alkyl, $(C_1{-}C_6)$ - chloroalkyl, dimethyl- or diethyl - amino - $(C_1{-}C_4)$ - alkyl, morpholino - ethyl, β - piperidino - ethyl, β - (4 - methylpiperazinyl - 1) - ethyl, benzyl, phenoxy - $(C_1{-}C_4)$alkyl, chlorophenoxy - $(C_1{-}C_4)$ - alkyl, $(C_1{-}C_4)$ - alkylmercapto - $(C_1{-}C_4)$ - alkyl, phenylmercapto - $(C_1{-}C_4)$ - alkyl, phenyl, $(C_1{-}C_6)$ - alkylphenyl, di - $(C_1{-}C_6)$-alkylphenyl, chlorophenyl, dichlorophenyl, $(C_1{-}C_6)$ - alkoxyphenyl, or α- or β-naphthyl group, or a group of the formula $-(CH_2CH_2O)_n-R$ in which n is 1, 2 or 3 and R is a hydrogen atom or a $(C_1{-}C_7)$ - alkyl, $(C_1{-}C_4)$ - alkylmercapto-$(C_1{-}C_4)$ - alkyl, dimethyl- or diethyl - amino - $(C_1{-}C_4)$ - alkyl, or morpholino-$(C_1{-}C_4)$ - alkyl group.

One group of preferred compounds of the formula I are those in which X is O or S, R_1 and R_2 are in the 5- and 7-positions and each is a hydrogen or chlorine atom or a $(C_1{-}C_4)$ - alkyl or phenyl group or together form a fused phenyl ring, and R_3 is a $C_1{-}C_6)$ - alkyl, $(C_1{-}C_6)$ - chloroalkyl, $(C_1{-}C_4)$ - alkoxy - $(C_1{-}C_4)$-alkyl or hydroxy - $(C_1{-}C_4)$ - alkyl group or a group of the formula $-(CH_2CH_2O)_n-R$ in which n is 2 or 3 and R is a hydrogen atom or a $(C_1{-}C_4)$-alkyl group.

Another group of preferred compounds of the formula I are those in which X is oxygen, R_1 is in the 5-position and is a hydrogen or chlorine atom or a methyl or phenyl group, R_2 is a hydrogen atom or R_1 and R_2 are both methyl groups either in the 5,6-positions or in the 5,7-positions, and R_3 is a methyl, ethyl, n- or i-propyl, n- or i-butyl, pentyl, chloromethyl, β-chloroethyl, β-hydroxyethyl, β-methoxyethyl, β-ethoxyethyl, benzyl, phenyl, *o*-tolyl, *p*-tolyl, 2,4-dimethylphenyl, *o*-chlorophenyl, *p*-chlorophenyl, 2,4-dichlorophenyl, or *p*-methoxyphenyl group.

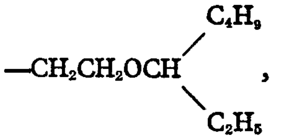
The term "lower" is used herein to designate that the group which it qualifies has from 1 to 4 carbon atoms.

The term "functionally modified carboxy or sulfo groups" includes, for example cyano, carboxylic acid ester, carboxylic acid amide, mono- and di-alkylcarbamide, sulfonic acid ester, and mono- and di-alkyl-sulfonamide groups.

The substituents R_1 and R_2 may be for example, methyl, ethyl, n- or i-propyl, n- or i-butyl, pentyl, hexyl, methoxy, ethoxy, propoxy, butoxy, pentyloxy, hexyloxy, dimethylamino, diethylamino, trimethylammonium, triethylammonium, acetylamino, cyano, sulfo, carboxy, methoxy-, ethoxy-, propoxy- and butoxycarbonyl, and the corresponding alkoxysulfonyl groups methyl-, ethyl-, propyl- and butyl-carbonamide and the corresponding alkylsulfonamide groups and the corresponding dialkylcarbonamide and -sulfonamide groups. In addition, two adjacent substituents R_1 and R_2 may together form a fused benzene or cyclohexyl ring. Those compounds containing a benzoxazolyl group (X=O) are preferred.

The substiuents R_3 may be, for example a methyl, ethyl, n- or i-propyl, n- or i-butyl, pentyl or hexyl group, or a chloroalkyl, hydroxyalkyl, dimethylaminoalkyl, diethylaminoalkyl, methoxyalkyl, ethoxyalkyl, propoxyalkyl, butoxyalkyl, methylmercaptoalkyl, ethylmercaptoalkyl, chlorophenoxyalkyl, phenoxyalkyl, phenylmercaptoalkyl, phenylalkyl or naphthylalkyl group derived therefrom; a group of the formula $-(CH_2CH_2O)_n$ in which n is 1, 2 or 3 and R is a hydrogen atom or a methyl, ethyl, propyl, or butyl group, a dimethyl- or diethylaminoalkoxyalkyl group in which the alkyl and alkoxy groups each have from 1 to 4 carbon atoms, or an alkylthioalkoxyalkyl group in which the alkyl and alkoxy group have from 1 to 4 carbon atoms, for example a group of the formula

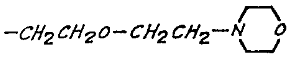
$$-CH_2CH_2OCH_3,\quad -CH_2CH_2OC_2H_5,\quad -CH_2CH_2OC_3H_7,\quad -CH_2CH_2OC_4H_9,$$



$$-CH_2CH_2OCH(C_4H_9)(C_2H_5)\ ,\quad -CH_2CH_2OC_6H_{11},$$

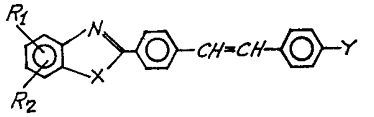
$—(CH_2CH_2O)_2CH_3$, $—(CH_2CH_2O)_2C_2H_5$, $—(CH_2CH_2O)_2C_4H_9$

$—(CH_2CH_2O)_3C_2H_5$, $—CH_2CH_2OCH_2CH_2SC_2H_5$, $—CH_2CH_2OCH_2CH_2—N(CH_2)_2$,

$—CH_2CH_2OCH_2CH_2—N(C_2H_5)_2$ or 

R_3 can also be an unsubstituted or a mono- or di-substituted phenyl group in which the alkyl, alkoxy, acyl, alkoxycarbonyl, alkylcarbamoyl, alkylsulfoyl and alkoxysulfonyl substituent groups may contain from 1 to 4 carbon atoms. Two adjacent substituents R_4 and R_5 together may also form a fused phenyl or cyclohexyl ring.

The present invention also provides a process for preparing compounds of the formula I, which comprises reacting a compound of the formula

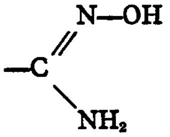


(II)

in which R_1, R_2 and X have the meanings given above, with a compound of the formula

$$R_3—Z \qquad (III)$$

in which R_3 has the meaning given above and one of Y and Z is a group of the formula



$$—C\begin{matrix}\nearrow\!\!\!\!\!=N—OH \\ \searrow NH_2\end{matrix} \qquad (IV)$$

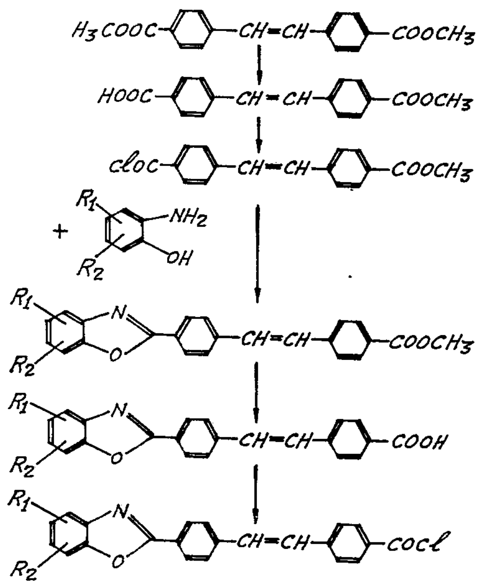
and the other is a group of the formula

$$—COCl \qquad (V)$$

When Y is a group of the formula IV, the resulting compounds of the formula I contain a 1,2,4-oxadiazolyl-3 group and when Y is a group of the formula V, the resulting compounds of the formula I contain the 1,2,4-oxadiazolyl-5 group.

The reaction is preferably carried out in the presence of an acid-binding agent in an inert solvent at a temperature of from 20 to 200°C. Suitable solvents for the reaction are, for example, chlorobenzene, di- and trichlorobenzene and especially dimethylformamide, N-methylpyrrolidone, dimethylsulfoxide and nitrobenzene. As the acid-binding agent, sodium carbonate, calcium carbonate, potassium carbonate, triethylamine or ethyldiisopropylamine may be used.

The compounds of the formula II in which Y is a group of the formula IV can be obtained by reacting the corresponding nitriles with hydroxylamine, preferably in an alcohol or N-methylpyrrolidone. The corresponding nitriles are described in the literature and can be prepared by known processes (cf. Japanese Patent -42-21013, United States Patent 3,577,411, German Offenlegungsschrift 2,00,027). Benzoxazolylstilbene-carboxylic acid carrying appropriate substituents can be transformed, for example, in known manner, via the acid chloride into the amide, which is then reacted with an agent splitting off water to obtain the nitrile. The starting compounds of the formula II in which Y is a group of the formula IV can be prepared for example, by the process described in Chem. Rev. 62 (1962), pages 155 et seq.. The starting compounds of the formula III in which Z is a group of the formula IV can be prepared in an analogous manner by the same process. The starting compounds of the formula II in which Y represents a group of the formula V can be obtained by the following reaction steps;



The reaction products of the formula I obtained by the above processes can be further transformed in known manner, for example the sulfo- or carboxy-containing molecules can be transformed into functionally modified sulfo- or carboxy groups, or groups of this type can be transformed into other corresponding groups or into the free acids. In known manner chloromethyl groups can be introduced or methyl groups can be oxidized. Halogenation is also possible as well as further reactions with introduced halogen atoms, for example the exchange of chlorine or bromine for an amine group.

The compounds of the formula I are almost colourless, fluorescent substances which can be used as optical brighteners.

Materials which can be brightened with the compounds of the present invention are, for example: lacquers, natural and synthetic fibers, for example those of natural or regenerated cellulose, acetyl cellulose, natural and synthetic polyamides, such as wool, polyamide-6 and -6,6, polyesters, polyolefins, polyvinyl chloride, polyvinylidene chloride, polystyrene, and polyacrylonitrile, as well as sheets, films, ribbons or other shaped articles of these materials.

The compounds of the present invention, which are insoluble in water, can be used in the form of solutions in organic solvents or in aqueous dispersion, preferably with the addition of a dispersant, for example soaps, polyglycol ethers derived from fatty alcohols, fatty amines, or alkyl phenols, sulfite cellulose liquor, and condensation products of optionally alkylated naphthalene-sulfonic acids with formaldehyde.

Compounds of the formula I can also be added to detergents which may contain the usual fillers and auxiliaries such as alkali metal silicates, alkali metal phosphates and polymetaphosphates, alkali metal borates, alkali metal salts of carboxymethyl cellulose; foam stabilizers such as alkanolamides of higher fatty acids, or complex forming agents, such as soluble salts of ethylenediamine tetraacetic acid or diethylenetriamine pentaacetic acid, as well as chemical bleaching agents, such as perborates or percarbonates.

In order to brighten fiber materials with such aqueous or possibly organic brightening compositions there is used either the exhaustion process, which is carried out at a temperature preferably of from 20°C to 150°C, or the thermosol process in which the textile material is impregnated or sprayed with the solution or dispersion of the brightener, squeezed between rolls to a residual moisture content of 50 to 120% and then subjected to a thermal treatment for 10 to 300 seconds, preferably with dry heat of 120 to 240°C. This thermosol process can also be combined with other finishing operations, for example finishing with artificial resins to obtain easy-care properties.

Alternatively, the compounds of the invention can be added to high molecular weight organic substances prior to or during shaping, for example in the manufacture of films, sheets, ribbons, or other shaped structures, to the masses to be moulded, or prior to spinning they can be dissolved in the spinning mass. Suitable compounds can be added prior to polycondensation or polymerization, to the low molecular weight compounds, for example in the case of polyamide-6, polyamide-6,6, or linear polyesters of the polyethylene terephthalate type.

Compounds of the present invention substituted by one or preferably two carboxy or alkoxycarbonyl groups can be bound to linear polyester molecules and synthetic polyamides by an ester or amide linkage by adding them to these materials or preferably to the starting compounds under suitable conditions. In this case, the brighteners are anchored by a chemical bond in the substrate and are then characterized by a much higher stability to sublimation and to solvents.

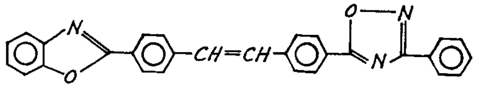
The amount of compounds of the present invention to be added to the material to be brightened can vary within wide limits depending on the intended application and the desired effect. It can be easily determined by preliminary tests and, in general, it is in the range of from 0.01 and 2%, calculated on the material.

The following examples illustrate the invention, the parts and percentages being by weight unless otherwise stated.

EXAMPLE 1.

18 parts of 4' - (benzoxazolyl - 2) - stilbene - 4 - carboxylic acid chloride and 6.8 parts of benzamidoxime in 300 parts of o-di-chlorobenzene were refluxed while stirring for 7 hours.

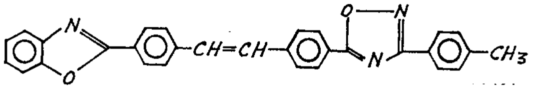
The ice cold reaction mixture was filtered off with suction and the residue washed with o-dichlorobenzene and methanol. After drying, 15.1 parts (68.4% of the theory) of 3 - phenyl - 5 - [4' - (benzoxazolyl - 2) - stilbenyl - 4''] - 1,2,4 - oxadiazole



were obtained which melted at 250 to 252°C after recrystallization from dioxane
Absorption: $\lambda_{max}=367$ nm
(in DMF) $\epsilon=77\ 700$

EXAMPLE 2.

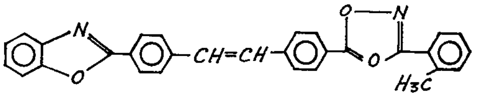
Under the conditions specified in Example 1, 16.5 parts (72.3%) of the compound of the formula



were obtained using 7.5 parts of p-tolyamidoxime.

EXAMPLE 3.

18 parts of 4' - (benzoxazolyl - 2) - stilbene - 4 - carboxylic acid chloride and 5 parts of triethyl-amine were added to 7.5 parts of o-tolylamidoxime in 150 parts of N-methylpyrrolidone and the whole was stirred for 1 hour at room temperature. The mixture was then heated to 160 to 170°C, stirring was continued for 15 minutes, cooled and the ice cold mixture was filtered off with suction and washed with methanol. 16.2 parts (71%) of the theory) of the compound of the formula

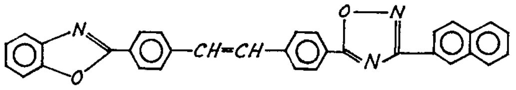


were obtained, which after recrystallization from o-dichlorobenzene/bleaching earth had the following melting properties: it sintered at 222°C, showed a liquid-crystalline transition at 229 to 232°C and melted at 293°C
Absorption: $\lambda_{max}=367$ nm
(in DMF) $\epsilon=70\ 200$

EXAMPLE 4.

Using 9.3 parts of 2-naphthylamidoxime under the conditions specified in

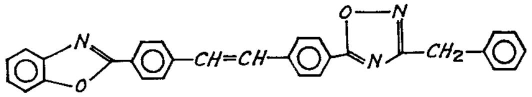
Example 3 there were obtained 20.2 parts (82% of the theory) of the compound of the formula



which, after recrystallization from dimethylformamide/animal charcoal, had the following melting properties: it sintered at 242°C, showed a liquid-crystalline transition at 243 to 268°C and melted above 300°C.
Absorption: $\lambda_{max}=366$ nm
(in DMF) $\epsilon=75\ 500$

EXAMPLE 5.

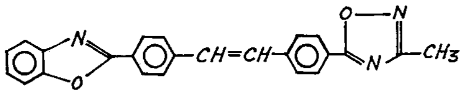
Using 7.5 parts of benzylamidoxime under the conditions of Example 3 there were obtained 16.8 parts (74% of the theory) of the compound of the formula



which, after recrystallization from dimethylformamide/animal charcoal ,had the following melting properties: it sintered at 225°C, showed a liquid-crystalline transition at 237 to 242°C and melted at 249°C.
Absorption: $\lambda_{max}=366$ nm
(in DMF) $\epsilon=64\ 700$

EXAMPLE 6.

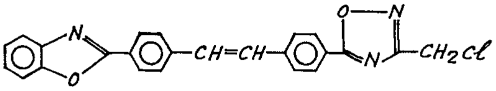
Using 3.7 parts of acetamidoxime under the conditions of Example 3 there were obtained 13.8 parts (73% of the theory) of the compound of the formula



which, after recrystallization from dimethylformamide/animal charcoal, had the following melting properties: it sintered at 195°C, showed a liquid-crystalline transition at 217 to 225°C and melted at 264°C.
Absorption: $\lambda_{max}=363$ nm
(in DMF) $\epsilon=65\ 400$

EXAMPLE 7.

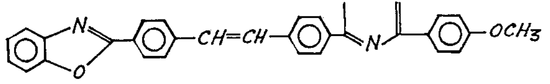
Using 5.5 parts of chloroacetamidoxime under the conditions of Example 3 there were obtained 9.9 parts (48% of the theory) of the compound of the formula



which, after recrystallization from methyl glycol/animal charcoal, had the following melting properties: is sintered at 205°C, it showed a liquid-crystalline transition at 240 to 244°C and had a decomposition point of about 300°C.

EXAMPLE 8.

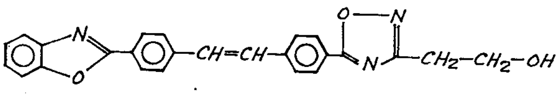
Using 8.3 parts of 4-methoxybenzamidoxime under the conditions of Example 3 there were obtained 14.3 parts (61% of the theory) of the compound of the formula



which, after recrystallization from dimethylformamide/animal charcoal, had the following melting properties: it sintered at 229°C, showed a liquid-crystalline transition at 270 to 280°C and melted above 300°C.
Adsorption: $\lambda_{max}=368$ nm
(in DMF) $\epsilon=76\ 700$

EXAMPLE 9.

Using 8.3 parts of 3-oxypropionic amidoxime under the conditions of Example 3 there were obtained 13.0 parts (55% of the theory) of the compound of the formula

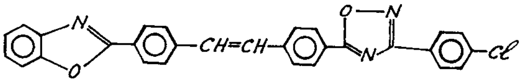


which, after recrystallization from dimethylformamide/animal charcoal, had the following melting properties: it sintered at 211°C, showed a liquid-crystalline transition at 215 to 221°C and melting at 280°C with decomposition.

Absorption: $\lambda_{max}=368$ nm
(in DMF) $\epsilon=76\ 700$

EXAMPLE 10.

Using 8.5 parts of 4-chlorobenzamidoxime under the conditions of Example 3 there were obtained 16.2 parts (68% of the theory) of the compound of the formula

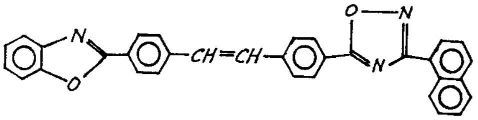


which, after recrystallization from dimethylformamide/animal charcoal, had the following melting properties: it sintered at 225°C, showed a liquid-crystalline transition at 230 to 234°C and it melted above 300°C.

Absorption: $\lambda_{max}=367$ nm
(in DMF) $\epsilon=67\ 100$

EXAMPLE 11.

Using 9.3 parts of 1-naphthylamidoxime under the conditions of Example 3 there were obtained 16.0 parts (65% of the theory) of the compound of the formula



which, after recrystallization from dimethylformamide/animal charcoal, had the following melting properties: it sintered at 233°C, showed a liquid-crystalline transition at 260 to 261°C and melted above 300°C.

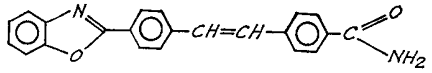
Absorption: $\lambda_{max}=368$ nm
(in DMF) $\epsilon=69\ 700$

EXAMPLE 12.

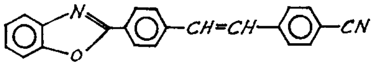
Step (a)

171 g of 4' - (benzoxazolyl - 2) - stilbene - 4 - carboxylic acid in 1,500 ml of toluene, 428 g of thionyl chloride and 1 g of dimethylformamide were refluxed for 5 hours, the excess thionyl chloride was distilled off with the toluene, the contents of the reaction flask were cooled to 30°C and ammonia was introduced until saturation. Introduction of ammonia was continued while refluxing for a further 2 hours, the reaction mixture was cooled, washed and dried.

146 g (86% of the theory) of 4' - (benzoxazolyl - 2) - stilbene - 4 - carboxamide of the formula



were obtained which, without purification, was refluxed while stirring in a mixture of 1,400 g of thionyl chloride and 5 g of DMF. The thionyl chloride was distilled off until the residue was dry, the residue was stirred with water, filtered off with suction, washed until neutral dried. 131 g (95% of the theory) of 4' - (benzoxazolyl - 2)-stilbene - carboxylic acid nitrile of the formula



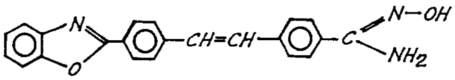
were obtained which, after recrystallization from methyl glycol and animal charcoal, melted at 240 to 242°C.

IR: $\nu C{\equiv}N$ 2222 cm^{-1}

UV: $\lambda_{max}=358$ nm $\epsilon=7.1\times10^4$

Step (b)

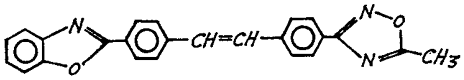
7.4 g of hydroxylamine hydrochloride and 50 ml of n-butanol were mixed while stirring at 70°C. A little phenolphthalein was added and a solution of 5.0 g of sodium methylate in 50 ml of n-butanol was added at a rate such that the red color of the phenolphthalein disappeared at once. The mixture was allowed to cool, filtered to separate the sodium chloride and washed with 20 ml of n-butanol. 14.6 g of 4'-(benzoxazolyl - 2) - stilbene - carboxylic acid nitrile were added to the filtrate and the mixture was stirred for 48 hours at 80°C. The cold reaction mixture was filtered off with suction, washed with n-butanol and dried. 15.2 g (94.6% of the theory) of 4' - (benzoxazolyl - 2) - stilbene - 4 - amidoxime of the formula



were obtained in the form of a light yellow powder. The crude product melted at 270 to 271°C with decomposition. It could be further used without purification.

Step (c)

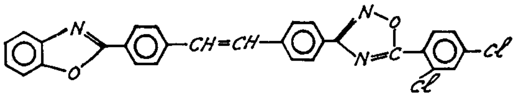
3.6 g of 4' - (benzoxazolyl - 2) - stilbene - 4 - amidoxime are mixed while stirring with 40 ml of dimethylformamide and 0.9 g of acetyl chloride and 1.3 g of triethylamine were added. The mixture was stirred for 1 hour at room temperature, rapidly cooled and then refluxed for 30 minutes and cooled again. After cooling, the mixture was filtered with suction and washed with a little dimethylformamide and methanol. After drying, 2.4 g (63.3 g of the theory) of 3 - [4' - (benzoxazolyl - 2)-stilbenyl - 4] - 5 - methyl - 1,2,4 - oxadiazole of the formula



were obtained which, after recrystallization from dimethylformamide while clarifying with animal charcoal, showed a crystalline-liquid transition at 259°C to 263°C and melted at 333°C.

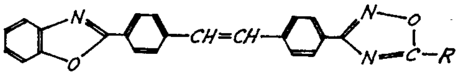
EXAMPLE 13.

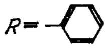
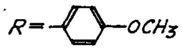
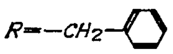
Instead of acetyl chloride as in Example 12 Step (c), 2.1 g of 2,4-dichlorobenzoyl chloride were used and 3.6 g (71% of the theory) of 3 - [4' - benzoxazolyl-2) - stilbenyl - 4] - 5 - (2,4 - dichlorophenyl) - 1,2,4 - oxadiazole of the formula

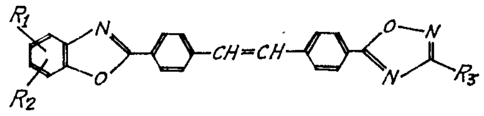


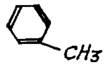
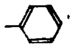
were obtained, which after recrystallization from dimethylformamide while clarifying with animal charcoal, had a crystalline-liquid transition at 210—214°C and melted at 245°C.

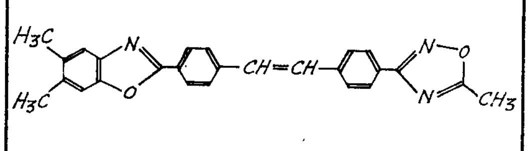
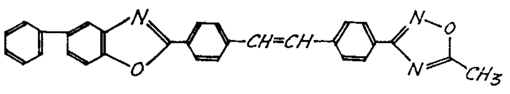
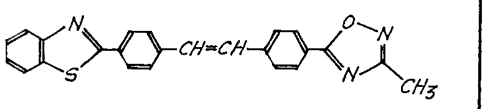
The compounds listed in the following tables were prepared in analogous manner.



		Melting properties
	sintered at	235 – 239°C
	liquid crystalline transition	241 – 247°C
	melting point	325°C
	sintered at	214°C
	liquid crystalline transition	255 – 275°C
	melting point	323°C
	sintered at	229°C
	liquid crystalline transition	230 – 231°C
	melting point	256 – 258°C
	sintered at	212°C
	liquid crystalline transition	265 – 276°C
R = $-CH_2-CH_3$	melting point	317°C
	sintered at	213°C
	liquid crystalline transition	249 – 258°C
R = $-CH=CH-CH_3$	melting point	263°C
	sintered at	225°C
R = $-CH_2Cl$	crystalline transition	230 – 235°C
	melting point	237°C

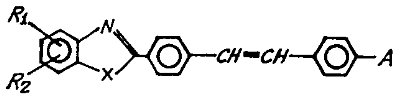


Example	R₁	R₂	R₃	Yield (% of theory)	Melting properties (°C)			Absorption (in DMF)	
					Sintered	Liquid/crystal-line transition	Melting point	λ max (nm)	ε
14	H	H	$-CH_2-N(CH_3)_2$	76	212	228–229	261	–	–
15	H	H		73	222	242–254	300	367	74 000
16	H	H	$-CH_2CH_2OCH_3$	75	–	218	220–221	366	67 200
17	H	H	$-CH_2CH_3$	79	223	258–275	300	366	72 000
18	5-Cl	H	$-CH_3$	65	294	313–320	325	367	69 200
19	5-CH_3	H	$-CH_3$	72	212	226–241	272	366	69 300
20	5 	H	$-CH_3$	75	–	260–264	300	368	76 200
21	5-CH_3	7-CH_3	$-CH_3$	68	230	232–234	296–300	–	–
22	5-CH_3	H	$-CH_2CH_2OCH_3$	65	–	205–210	215	–	–
23	5-CH_3	6-CH_3	$-CH_3$	67	–	265–267	300	366	75 300

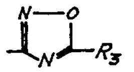
Example No.	Compound	Yield (% of theory)	Melting properties (°C)			Absorption (in DMF)	
			Sintered	Liquid crystal-line transition	Melting point	λ max (nm)	ε
24		82	–	268–271	320	367	69 500
25		82.5	–	275–276	330	364	65 200
26		–	225	246–250	300	–	–

WHAT WE CLAIM IS:—

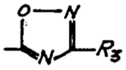
1. A compound of the formula



in which X is O or S, each of R_1 and R_2 is a hydrogen, fluorine or chlorine atom, a phenyl group, an alkyl group having from 1 to 9 carbon atoms or a lower alkoxy, lower dialkylamino, lower trialkylammonium, acylamino, carboxy, sulfo or functionally modified carboxy or sulfo group or, when attached to adjacent carbon atoms, R_1 and R_2 together may form a fused benzene ring or a lower alkylene or 1,3-dioxapropylene group, and A is a group of the formula



or



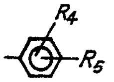
in which R_3 is

(a) a straight chain or branched alkyl group having from 1 to 18 carbon atoms, which may carry one or more substituents elected from halogen atoms, hydroxy, lower alkoxy, lower dialkylamino, morpholino, piperidino, 1-piperazinyl, lower alkylmercapto, chloroaryloxy, aryloxy, arylmercapto and aryl groups,

(b) a group of the formula $—(CH_2CH_2O)_n—R$, in which n is 1, 2, or 3 and R is a hydrogen atom or a lower alkyl, dialkylaminoalkoxyalkyl or alkylthioalkoxyalkyl group, the alkyl groups of the dialkylaminoalkoxyalkyl group optionally forming together with the nitrogen atom to which they are attached a piperidine, hexamethylene-imine, pyrrolidine, morpholine or piperazine ring,

c) a group of the formula $—(CH_2)_m—CH=CH—R$ in which m is zero or an integer from 1 to 5, or

(d) a group of the formula



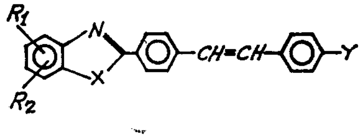
in which each of R_4 and R_5 is a hydrogen, fluorine or chlorine atom or a phenyl, lower alkyl, lower alkoxy, $(C_1—C_4)$-acylamino, carboxy, sulfo or functionally modified carboxy or sulfo group, or, when attached to adjacent carbon atoms, R_4 and R_5 together may form a lower alkylene group, a fused benzene ring or a 1,3-dioxapropylene group.

2. A compound as claimed in claim 1 in which X, A, R_1 and R_2 have the meanings specified therein and R_3 is a $(C_1—C_6)$alkyl, $(C_1—C_6)$ - chloroalkyl, dimethyl- or diethylamino - $(C_1—C_4)$ - alkyl, morpholino - ethyl, β - piperidino - ethyl, β-(4 - methylpiperazinyl - 1) - ethyl, benzyl, phenoxy - $(C_1—C_4)$alkyl, chlorophenoxy-$(C_1—C_4)$ - alkyl, $(C_1—C_4)$ - alkylmercapto - $(C_1—C_4)$alkyl, phenylmercapto-$(C_1—C_4)$ - alkyl, phenyl, $(C_1—C_6)$ - alkylphenyl, di - $(C_1—C_6)$ - alkylphenyl, chlorophenyl, dichlorophenyl, $(C_1—C_6)$ - alkoxyphenyl, or α- or β-naphthyl group, or a group of the formula $—(CH_2CH_2O)_n—R$ in which n is 1, 2 or 3 and R is a hydrogen atom or a $(C_1—C_7)$ - alkyl, $(C_1—C_4)$ - alkylmercapto - $(C_1—C_4)$ - alkyl, di-methyl- or diethylamino - $(C_1—C_4)$ - alkyl or morpholino - $(C_1—C_4)$ - alkyl group.

3. A compound as claimed in claim 1, in which X is O or S, R_1 and R_2 are in the 5- and 7-positions and each is a hydrogen or chlorine atom or a $(C_1—C_4)$ - alkyl or phenyl group or together form a fused phenyl ring, and R_3 is a $(C_1—C_6)$ - alkyl, $(C_1—C_6)$ - chloroalkyl, $(C_1—C_4)$ - alkoxy - $(C_1—C_4)$ - alkyl or hydroxy - $(C_1—C_4)$-alkyl group or a group of the formula $—(CH_2CH_2O)_n—R$ in which n is 2 or 3 and R is a hydrogen atom or a $(C_1—C_4)$ - alkyl group.

4. A compound as claimed in claim 1 in which X is oxygen, R_1 is in the 5-position and is a hydrogen or chlorine atom or a methyl or phenyl group, R_2 is a hydrogen atom, or R_1 and R_2 are both methyl groups in the 5,6-positions or in the 5,7-positions, and R_3 is a methyl, ethyl, n- or i-propyl, n- or i-butyl, pentyl, chloromethyl, β-chloroethyl, β-hydroxyethyl, β-methoxyethyl, β-ethoxyethyl, benzyl, phenyl, *o*-tolyl, *p*-tolyl, 2,4-dimethylphenyl, *o*-chlorophenyl, *p*-chlorophenyl, 2,4-dichlorophenyl, or *p*-methoxyphenyl group.

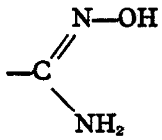
5. A process for preparing a compound as claimed in claim 1, which comprises reacting a compound of the formula



in which R_1, R_2 and X have the meanings specified in claim 1, with a compound of the formula

$$R_3—Z$$

in which R_3 has the meaning specified in claim 1, and one of Y and Z is a group of the formula



$$-C\begin{matrix}\diagup\!\!\!\diagup N{-}OH\\ \diagdown NH_2\end{matrix}$$

and the other is a group of the formula

—COCl

6. A process as claimed in claim 5, wherein the reaction is carried out in the presence of an acid-binding agent in an inert solvent at a temperature of from 20 to 200°C.

7. A process as claimed in claim 5 carried out substantially as described in any one of Examples 1 to 26 herein.

8. A compound as claimed in claim 1 whenever prepared by a process as claimed in any one of claims 5 to 7.

9. A process for optically brightening a material, which comprises incorporating in the material a compound as claimed in claim 1.

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