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3,623,882

BENZIMIDAZOLE DERIVATIVES AND THEIR USE IN PHOTOGRAPHY

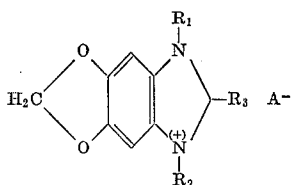
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Int. Cl. G03c 1/14; C09b 23/02; C07d 49/38
U.S. Cl. 96-137 2 Claims

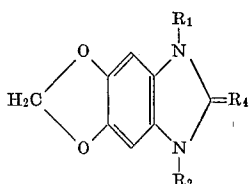
ABSTRACT OF THE DISCLOSURE

A substituted benzimidazole compound for photographic silver halide emulsions is provided in a compound according to the following general formulae:

I



II



in which

R₁ is an alkyl group;

R₂ is a saturated or unsaturated aliphatic group;

R₃ is a methyl or methylthio group or a methine chain;

R₄ is one of the usual cyclic ketomethylene radicals of cyanine chemistry;

A⁻ is any anion, A being absent if R₂ contains an acid group in which case a betaine structure is present.

The invention relates to benzimidazole compounds in which the benzene ring is substituted by a methylene dioxy group and to the use of such compounds as spectral sensitizers for photographic silver halide emulsions.

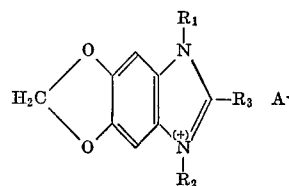
Benzimidazole compounds are known in many different forms. As carbocyanine and merocyanine dyes, benzimidazole compounds are of considerable importance for sensitizing photographic silver halide emulsions. As photographic techniques have developed, spectral sensitizers have had to meet increasingly stringent requirements with regards to their intensity of sensitization. There is therefore a constant demand for new sensitizers which have great intensity of sensitization in many different regions of the spectrum.

It is an object of the invention to produce substituted benzimidazole compounds. Another object of the invention is to improve photographic silver halide emulsions by spectral sensitization.

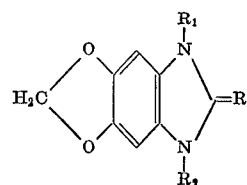
Benzimidazole compounds have now been found which are substituted with a methylene dioxy group in the 5,6-position in the benzene ring and which can be prepared

2

by a simple method. The compounds according to the invention are of the following formulae:



II



in which

R₁ is an alkyl group preferably containing up to 5 carbon atoms, for example a methyl, ethyl or butyl group;

R₂ is a saturated or unsaturated aliphatic group preferably containing up to 5 carbon atoms, in which the alkyl groups may be substituted, for example with sulfonic acid, sulfonamide, carboxyl, or carbamyl groups or with halogen atoms, e.g. chlorine, or with hydroxyl groups;

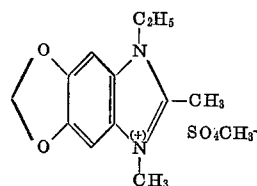
R₃ is a methyl or methylthio group or a methine chain having 1, 3, 5 or 7 carbon atoms which carries in the terminal position a 5- or 6-membered heterocyclic ring containing nitrogen as ring member and, if desired, condensed benzene rings, e.g. an oxazole, benzoxazole, naphthoxazole, thiazoline, thiazole, diphenylthiazole, benzothiazole, naphthothiazole, selenazole, benzoselenazole, naphthoselenazole, thiadiazole, imidazole or benzimidazole ring, which rings may, if desired, be further substituted; or

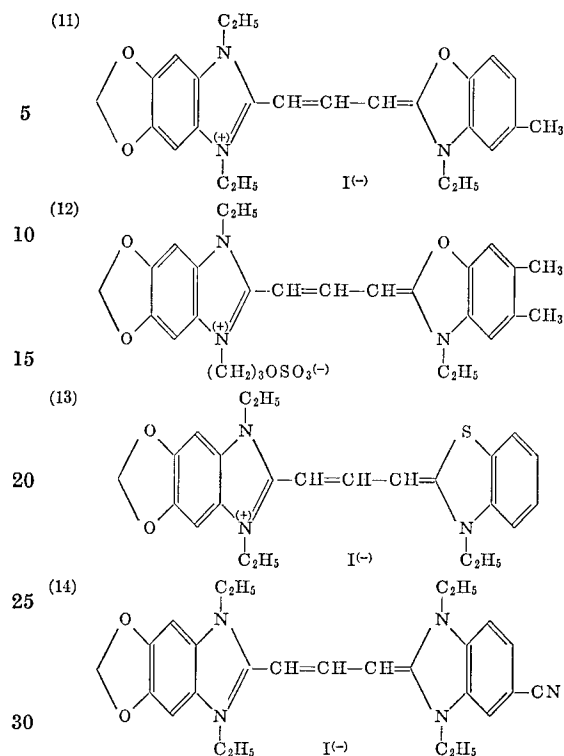
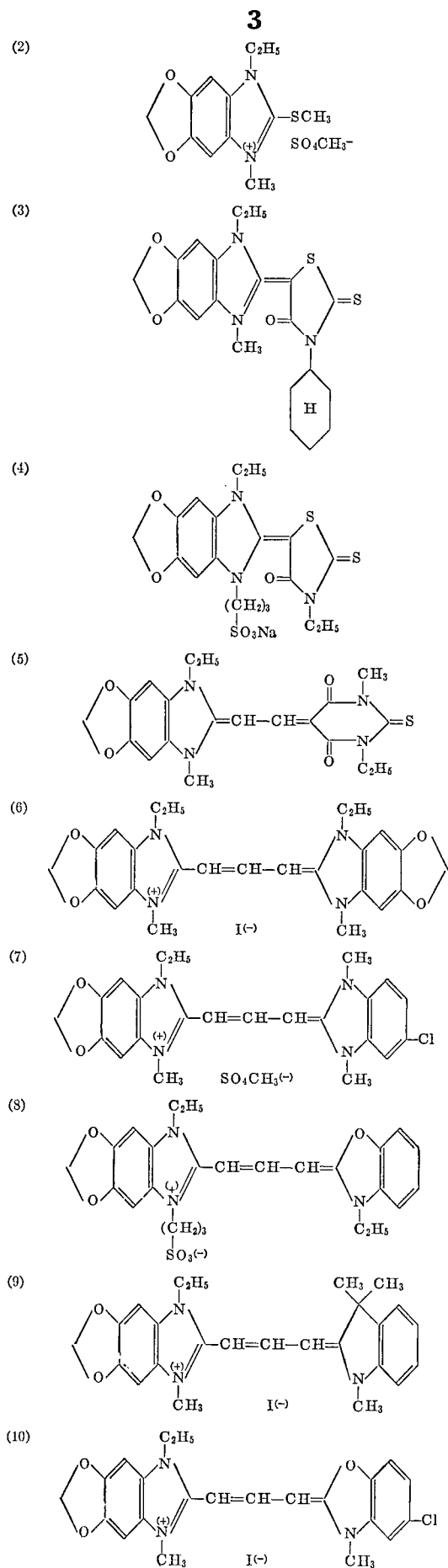
R₄ is one of the usual cyclic ketomethylene radicals of cyanine chemistry, preferably a rhodanine, thiohydantoin, thiobarbituric acid or pyrazolone radical which is attached to the benzimidazole ring either directly or via a methine chain having 2 or 4 carbon atoms; and A⁻ is any anion, A being absent if R₂ contains an acid group in which case a betaine structure is present.

The methine chains may be substituted in the chain, preferably with aliphatic side chains containing up to 5 carbon atoms, especially methyl or alkyl groups or, in the case where the methine chain contains 2 or 4 carbon atoms, also by alkoxy or phenyl groups.

The following specific compounds are given as examples:

(1)





The compounds are prepared as follows:

COMPOUNDS 1 AND 2

35 4,5-methylenedioxybenzaldehyde is nitrated with nitric acid in two stages to form the 1,2-dinitro compound and then reacted with ethylamine to form 1-ethylamino-2-nitro-4,5-methylenedioxybenzene. The nitroamino compound may then be reduced to the corresponding diamine, for example with tin and hydrochloric acid.

COMPOUND 1

1-ethylamino - 2 - nitro - 4,5-methylenedioxybenzene has already been described in the literature (Rec. Trav. Chim. Pays Bas, 49 (1930) pages 17-32 and pages 45-56). To convert this compound into the corresponding diamine it is dissolved, for example, 20 g. in methanol, and treated in portions with 120 g. of $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$ in 200 cc. of HCl. After $\frac{1}{2}$ hours, the reaction mixture is made alkaline and then extracted at once with ether. The ether extract contains 1-ethylamino-2-amino-4,5-methylenedioxybenzene which is not isolated. The ethereal solution is treated with 200 cc. of acetic anhydride, and then ether, acetic acid and acetic anhydride are distilled off one after the other at normal pressure. 50 cc. of acetic anhydrides are thereupon added to the residue which is then mainly distilled off, then heated for $\frac{1}{2}$ hour at 140 to 150° C. and distilled under vacuum at 10 mm. Hg, B.P. 205 to 210° C. The distillate can be recrystallized from acetone/ether.

10 g. of the base from which compound 1 is derived, having a melting point of 160° C., are obtained.

Quaternisation to give compound 1 is carried out in the usual manner, for example with dimethylsulfate.

COMPOUND 2

1-ethylamino-2-amino - 4,5 - methylenedioxybenzene described above is in this case isolated from the ethereal solution by evaporating off the ether. 21 g. of the diamine compound are dissolved in a solution of 3.5 g. of sodium in 140 cc. of alcohol, and 22 g. of CS_2 are slowly added dropwise. The starting temperature of 22° C. rises in the course of this operation to 42° C. The reaction mixture is then heated for one hour on a steam bath, poured into water and adjusted to pH=5 with acetic acid. The base

5

of compound 2 crystallizes out and this has a melting point of 273 to 275° C. To methylate the product, 20.5 g. are dissolved in 4.5 g. of NaOH in 150 cc. of water. The filtered solution is then treated with 14 g. of dimethylsulfate, shaken for ½ hour and extracted with chloroform. The chloroform residue is distilled under vacuum. 17 g. of compound 2, which has a boiling point at 1.2 mm. Hg of 200 to 203° C. and a melting point of 76 to 80° C. are obtained.

COMPOUND 3

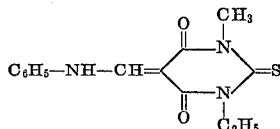
1.8 g. of compound 2 are dissolved in 10 cc. of pyridine, 1 g. of cyclohexyl rhodanine and 1 cc. of triethylamine are added and the reaction mixture is heated on a steam bath for 15 minutes. Compound 3 crystallizes out. It is recrystallized from methanol/chloroform.

COMPOUND 4

The method of preparation is similar to that used for compound 3 but quaternization is carried out with propanesultone.

COMPOUND 5

2 g. of compound 1, 1.9 g. of compound



30 cc. of acetic anhydride and 2 cc. of triethylamine are boiled under a reflux condenser for 15 minutes. The dye precipitates while the reaction mixture is still being heated, and when cold, it is separated by suction filtration and recrystallized from 90 cc. of dimethylformamide.

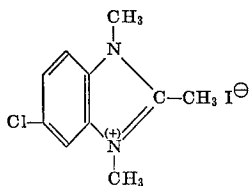
M.P. above 360° C.

COMPOUND 6

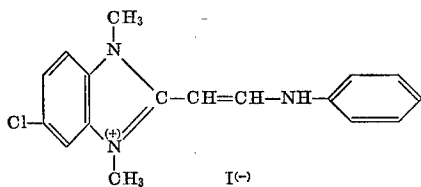
6.6 g. of compound 2, 4.4 g. of iodoform and 100 cc. of ethanol are mixed, treated with a solution of 1.4 g. of sodium in 30 cc. of ethanol and then heated at 65° C. for 3 hours. The precipitate is filtered using suction while still hot and the filtered residue is recrystallized from 50 cc. of CH₃OH and 15 cc. of chloroform. M.P. 294° C.

COMPOUND 7

35 g. of the quaternary salt

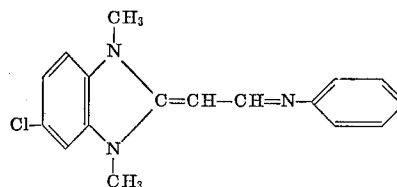


are melted at 170° C. under vacuum with 30 g. of dimethylformamide. 9 g. of aniline are distilled off and the residue is worked up with acetone and ether. The following substance is obtained:

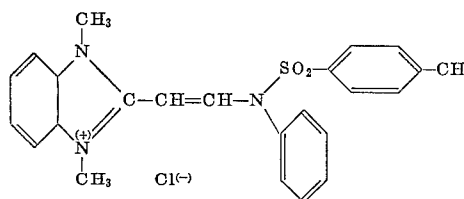


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This is suspended in acetone and shaken with dilute sodium hydroxide solution. The following base



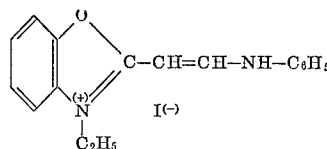
is taken up in the acetone and reprecipitated from it with water. When this compound is reacted with p-toluene sulfonyl chloride, the following compound is obtained:



This compound has a melting point of 230 to 232° C. 2.2 g. of this substance and 1.6 g. of compound 1 are dissolved in 30 cc. of ethanol. Sodium methylate solution is added, and the reaction mixture is heated on a steam bath for 30 minutes. The required dye crystallises overnight and is recrystallized from alcohol. M.P. 231° C. The iodide of the same dye is obtained by heating the above-mentioned components to boiling in nitrobenzene with triethylamine. After cooling, the product is poured into ether and a smeary substance is obtained. This is dissolved in hot methanol and poured into dilute KI solution, the dye then precipitating. It may be recrystallized from alcohol/methanol.

COMPOUND 8

(a) 3.9 g. of the following compound



are boiled with 35 cc. of acetic anhydride, the N-acetyl compound being formed.

(b) 3.3 g. of compound 1 and propanesultone are dissolved in 15 cc. of acetic anhydride and 8 cc. of cresol. The two solutions are mixed, treated with 6 cc. of triethylamine and then boiled for 15 minutes. After cooling, ethanol is added and as much ether as is necessary just to start crystallisation. The reaction mixture is cooled and the dye is removed by suction filtration. Recrystallization from ethanol, M.P. 303° C.

COMPOUND 9

The dye is obtained by condensation of 1,3,3-trimethyl-2-formylmethylene-indoline with compound 1 in pyridine/piperidine. The reaction mixture is left to cool, by-

products which have precipitated are removed by suction filtration, and the filtrate is precipitated with KI solution. The precipitate is washed with water, isopropanol, benzene and ether and then recrystallized from methanol/ethanol.

COMPOUND 10

12.7 g. of the base of compound 1 are quaternized with 12 g. of methyl iodide by boiling for 5 hours in 20 cc. of nitromethane on an oil bath. 1.32 g. of the quaternary salt and 1.8 g. of 2-phenyliminoethylidene-3-ethyl-5-chloro-2,3-dihydro-benzoxazole in 20 cc. of pyridine are treated with 0.6 cc. of acetic anhydride and 0.7 cc. of triethylamine. The reaction mixture is stirred at room temperature for 20 minutes and 1 hour at 60° C. The dye precipitates on cooling and is isolated by suction filtration, washed with water, isopropanol and ether and recrystallized from ethylene glycol monomethyl ether/isopropanol.

COMPOUND 11

1.8 g. of the quaternary salt just described, 1.3 g. of phenyliminoethylidene - 3 - ethyl - 5 - methyl - 2,3-dihydrobenzoxazole, 20 cc. of pyridine, 0.6 cc. of acetic anhydride and 0.7 cc. of triethylamine are stirred at room temperature for one hour. The dye can be purified as described in Example 8.

COMPOUND 12

6.1 g. of the base of compound 1 are reacted with 5 g. of ethylene sulphate by melting at 130° C. (reaction time 45 minutes) to form the corresponding quaternary salt. 1 cc. of acetic anhydride, 1.4 cc. of triethylamine and a solution of 2.4 g. of 2-phenyliminoethylidene-3-ethyl-5,6-dimethyl-2,3-dihydrobenzoxazole in 20 cc. of pyridine are added successively to 2.7 g. of this salt dissolved in 15 cc. of sulpholan (tetrahydrothiophene dioxide). After the reaction mixture has been heated to boiling, it is carefully diluted with water until crystallization starts. The dye is removed by suction filtration and washed with isopropanol and ether.

COMPOUND 13

7.2 g. of the quaternary salt described in the case of compound 10, 5 g. of 2-phenyliminoethylidene-3-ethyl-2,3-dihydrobenzothiazole, 100 cc. of pyridine, 2 cc. of acetic anhydride and 4.2 cc. of triethylamine are mixed, kept at room temperature for 15 minutes and heated on a boiling water bath for one hour. The dye precipitates on cooling and is recrystallized from phenol/ethanol.

COMPOUND 14

1.8 g. of the above quaternary salt, 1.58 g. of 2-phenyliminoethylidene-3-ethyl-5-cyano - 2,3 - dihydrobenzimidazole, 25 cc. of pyridine and 1 cc. of acetic anhydride are boiled for 20 minutes. Water is added until crystallization sets in and the product is recrystallized from water/pyridine.

The carbocyanines or merocyanines according to the invention are very suitable for spectral sensitization of photographic silver halide emulsions. They have an exceptionally high intensity of sensitization.

The preparation of photographic silver halide emulsions comprises substantially three stages:

- (1) Precipitation of the silver halide in the presence of a protective colloid and physical ripening;
- (2) Removal from the emulsion of excess water-soluble salts derived from the precipitation, generally by washing; and
- (3) Chemical ripening or after-ripening which serves to impart the required sensitivity to the emulsion.

The sensitising dyes according to the invention may be used in any silver halide emulsions. Suitable silver halides are silver chloride, silver bromide or mixtures thereof, if desired, with a small silver iodide content of up to 10

mols percent, the silver halides may be dispersed in the usual hydrophilic compounds such as carboxymethyl cellulose, polyvinyl alcohol, polyvinyl pyrrolidone, alginic acid and its salts, esters or amides, or preferably, in gelatin.

The sensitising dyes for use according to the present invention are preferably added to the photographic emulsion after chemical ripening and before casting. The methods used for this are generally known to the expert. Sensitising dyes are generally incorporated into the emulsion in the form of solutions. The solvents must, of course, be compatible with gelatine and must not have any undesirable influence on the photographic properties of the emulsion. The quantity of sensitising dye added may vary within wide limits, e.g. between 2 and 200 mg., preferably between 10 and 60 mg., per kg. of silver halide emulsion. The concentration of dye may be adapted to the particular requirements depending on the type of emulsion, the desired sensitization effect, etc. The most suitable concentration for any given emulsion can be easily determined by the usual test employed in photographic practice.

The emulsions may also contain chemical sensitizers, e.g. reducing agents such as stannous salts, polyamines such as diethylene triamine, and sulfur compounds such as described in U.S. patent specification 1,574,944. The above-mentioned emulsions may also contain salts of noble metals such as of ruthenium, rhodium, palladium, iridium, platinum or gold for chemical sensitisation, as described in the article by R. Koslowsky, Z. Wiss. Phot., 46, 65-72 (1951).

The emulsions may also contain polyalkylene oxides, especially polyethylene oxide and derivatives thereof, as chemical sensitizers.

The emulsions according to the invention may contain the usual stabilizers, e.g. homopolar or salt-type compounds of mercury with aromatic or heterocyclic rings, such as mercaptotriazoles, simple mercury salts, sulphonium mercury double salts and other mercury compounds. Azaindenes, especially tetra- and penta-azaindenes and in particular those which are substituted with hydroxyl or amino groups are also suitable as stabilizers. Such compounds are described in the article by Birr, Z. Wiss. Pot., 47, 2-58 (1952). Other suitable stabilizers are, inter alia, heterocyclic mercapto compounds, e.g. phenylmercaptotetrazole, quaternary benzothiazole derivatives, benzotriazole and the like.

The emulsions may be hardened in the usual manner, for example with formaldehyde or halogen-substituted aldehydes which contain a carboxyl group, such as mucobromic acid, diketones, methanesulfonic acid esters, dialdehydes and the like.

Example 1

A highly sensitive silver bromide gelatin emulsion containing 3 mols percent of silver iodide and the usual additives, such as 0.35 g. of saponin as wetting agent, 3 ml. of an aqueous/methanolic solution of N,N',N''-tris-acryloylhexahydro-1,3,5-triazine (5% concentration) as hardener and 300 mg. of 1,3,7-triaza-4-hydroxyl-6-methylindolizine as stabilizer is divided into several parts. The quantities of sensitizing dyes which are added to the individual parts are indicated in the following table in mg. per kg. emulsion. The emulsions are then poured onto a layer support and dried in the usual manner. The resulting layers are exposed in a conventional sensitometer behind step wedges which have a rate of density increase of $\sqrt{2}$. They are then developed and fixed in the usual manner.

The exceptionally high increase in sensitivity to light from the yellow region of the spectrum can be seen from the following table.

The relative sensitivities are given by the number of measurable steps of the test wedge.

The table also contains examples of other types of emulsions.

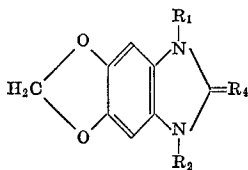
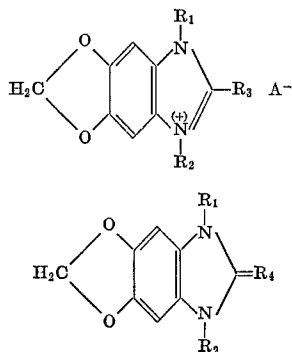
TABLE

Dye No.	Absorption maximum, m μ	Quantity, mg./kg. of emulsion	Sensitization maximum, m μ	Blue	Yellow
Emulsion A... (Highly sensitive silver iodobromide emulsion)					
No. 7.....	502	30	570	16	22
No. 8.....	4-2	30	530	19	23
No. 9.....	435	30	535	18	22
No. 10.....	440	30	535	18	43.5
Emulsion B... (Silver iodobromide emulsion of medium sensitivity)					
No. 11.....	436	60	555	8.5	12.5
No. 13.....	482	30	570	5.5	13.5
Emulsion C... (Pure silver chloride emulsion)					
No. 11.....	436	60	525	2.5	20
No. 12.....	460	60	530	2.5	20
No. 14.....	515	30	560	0.5	20.5

We claim:

1. Spectrally sensitized photographic silver halide emulsion, characterised by containing a sensitizer of the following formulae:

I



in which

R₁ is an alkyl group;

R₂ is a saturated or unsaturated aliphatic group;

R₃ is a methine chain having 1, 3, 5 or 7 carbon atoms which carries in the terminal position a 5- or 6-membered heterocyclic ring with nitrogen as ring member and optionally condensed benzene rings;

R₄ is a usual cyclic ketomethylene radical of cyanine chemistry which is attached either directly, or via an optionally substituted, methine chain with 2 or 4 carbon atoms;

A⁻ is any anion, A being absent in cases where R₂ contains an acid group so that a betaine structure is present.

2. Emulsion according to claim 1, in which R₁ denotes an alkyl group with up to 5 carbon atoms and R₂ denotes saturated or unsaturated aliphatic group with up to 5 carbon atoms.

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