HETEROCYCLIC COMPOUNDS AS ORGANIC LUMINOPHORES (REVIEW)

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A review of heterocyclic compounds having luminescence properties is given. Methods for the preparation of some of them, the relationship between structure and luminescence, and their areas of application are examined.

Most of the organic luminophores currently in use are heterocyclic compounds. Having fluorescence properties similar to the fluorescence properties of aromatic compounds, they are at the same time more accessible in a synthetic respect.

In the present review we deal only with the most important classes of heterocyclic compounds that, owing to their luminescence properties, have found wide application in the national economy, science, and technology.

Organic Luminophores with Five-Membered Heterorings

Luminescent aryl-substituted furans, pyrroles, and thiophenes, as well as compounds in which these heterocycles are condensed with aromatic rings have been investigated [1-6]. Compounds with sulfur-containing heterorings have less intense luminescence than their oxygen and nitrogen analogs [4]. However, the exclusion from conjugation of the unshared electrons of the sulfur atoms by conversion of the thiophene derivatives to the corresponding sulfones leads to a sharp increase in the luminescence intensity [5-7]. These compounds have not found great practical application.

Aryl-substituted oxazoles and 1,3,4-oxadiazoles have assumed greater significance. Interest in them increased considerably after 2,5-diaryloxazoles and 2,5-diaryl-1,3,4-oxadiazoles, which emit light in the violet and blue regions of the spectrum, had found application as activating additives in liquid and plastic scintillators [8, 9].

The most well-known and frequently used methods for the synthesis of 2,5-diaryloxazoles are condensation of ω-aminomethyl aryl ketones with aromatic acid chlorides and α-halo-substituted carbonyl compounds with acid amides. The ω-acylaminomethyl aryl ketones formed in both cases undergo cyclodehydration, most often in the presence of concentrated sulfuric acid [10, 11].

A recently proposed method [12], which consists in intramolecular condensation of N-(1-oxo-1-aryl-2-alkyl)nitrones, obtained by the reaction of α-halo ketones with anti-benzaldoxime, is interesting.

Aromatic carboxylic acid chlorides usually serve as the starting materials for the synthesis of 2,5-diaryl-1,3,4-oxadiazoles. The N,N'-diaroylhydrazines formed from them on reaction with hydrazine hydrate are cyclized by heating with phosphorus oxychloride [13] or with other reagents. Unsymmetrical 2,5-diaryl-1,3,4-oxadiazoles can also be obtained from aromatic carboxylic acid chlorides by using monoaroyl derivatives of hydrazine in place of hydrazine itself [14].

Data on the absorption and luminescence spectra and scintillation properties of 2,5-diaryloxazoles and 2,5-diaryl-1,3,4-oxadiazoles are available in [15-24] and in a number of other papers.

All-Union Scientific-Research Institute of Single Crystals, Kharkov. All-Union Scientific-Research Institute of Chemical Reagents, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1443-1460, November, 1974. Original article submitted November 26, 1973.

The similarities in the character of the UV absorption spectra and the luminescence spectra of diaryl-substituted ethylenes, oxazoles, and 1,3,4-oxadiazoles measured in aliphatic hydrocarbons at room temperature and 77°K led Nurmukhametov and co-workers [24, 25] to conclude that there are identical forms of conjugation in these systems. Bearing in mind that the contribution of the ethylene group to π conjugation of molecules of similar types is equivalent to the contribution of the phenylene radical [26], they feel that polyphenyls, diaryloxazoles, and diaryloxadiazoles have much in common with respect to their spectral properties, despite the fact that they differ from one another with respect to the position of the absorption and luminescence maxima.

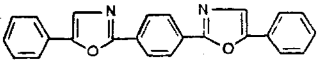
The introduction of initially a first and then a second nitrogen atom into the furan ring of 2,5-diphenylfuran in place of methylidyne groups is accompanied by a gradual short-wave shift of the absorption and luminescence spectra [3, 17]. The hypothesis that this effect is associated with weakening of the conjugation in nitrogen-containing heterocycles is confirmed by the results of measurements of the intensity of the line of the benzene ring in the Raman spectra, which decreases from 2,5-diphenylfuran to the corresponding substituted oxazoles and oxadiazoles [17].

Lengthening of the conjugation chain in the aryl groups of diaryloxazoles and diaryloxadiazoles leads to a substantial shift in the absorption and luminescence spectra to the long-wave region, and the fluorescence quantum yield increases [22]. Thus replacement of the phenyl groups in 2,5-diphenyloxazole by diphenylyl or naphthyl groups shifts the absorption maxima of heptane solutions by 25-30 nm, whereas the luminescence maxima of solutions in heptane and polystyrene are shifted by 30-40 nm. Diaryloxazoles and diaryloxadiazoles having diphenyl groups have the most intense luminescence [21].

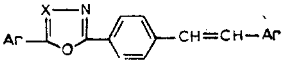
Electron-donor substituents in the para positions of phenyl groups also induce a bathochromic effect; this effect is more pronounced, the stronger the electron-donor effect of the substituent. A dimethylamino group in the 2-phenyl group of 2,5-diphenyloxazole shifts the absorption and luminescence maxima in toluene by 42 and 37 nm, respectively [27]. The introduction of a dimethylamino group into diaryloxadiazoles considerably increases their luminescence intensities [28]. The fluorescene quantum yield for 2,5-diaryloxazoles is higher than the yield for their oxadiazole analogs [22].

1,4-Di(5-phenyl-2-oxazolyl)benzene (I), which is obtained from terephthalic acid dichloride and ω-aminoacetophenone [29], is widely used as a shift reagent for spectra in liquid and plastic scintillators.

Effective scintillation activators are found among β-arylethylene derivatives of 2,5-diaryloxazoles (II, X = CH) [30].



I



II

These compounds, like the corresponding oxadiazole derivatives (X = N), can be obtained by using the Wittig reaction [31, 32] or, in higher yields, by the anil synthesis [33].

When an arylethylene grouping is introduced, the absorption intensity increases significantly in most cases, and the quantum yield increases sharply [31, 34].

In the preparation of plastic scintillators the formation of polymeric chains that include groupings responsible for scintillation seems of interest. With this in mind, p-vinyl-substituted 2,5-diphenyloxazoles and 2,5-diphenyl-1,3,4-oxadiazoles were synthesized [35]. Plastic scintillators prepared from styrene – vinyl-substituted diphenyloxazole copolymers – are more effective than polystyrene solutions of diphenyloxazole [36].

Aryl-substituted oxazoles and oxadiazoles of various structures have been proposed as optical bleaches [37, 38]. Their application in lasers and light transformers that convert the short-wave emission of pulse lamps to the emission of the necessary spectral composition in order to increase the efficiency of solid and liquid lasers [39, 40] is well known.

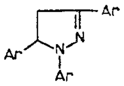
2,5-Diaryl-1,3,4-thiadiazoles are less effective as luminophores than the corresponding oxazole and oxadiazole derivatives. However, there are indications that they have been used for optical bleaching of various materials [41].

The relationship between the structure and luminescence of compounds containing a pyrazole ring was investigated in [42]. It was established that a benzoyl group in the 4-position increases the luminescence intensity considerably more than one in the 1 position. Carboxyl and β-cyanoethyl groups intensify fluorescence, whereas nitro and nitroso groups quench it. Bright luminescence was noted for 3-(p-aminophenyl)-5-aminopyrazole.

Substituents in the 5 position of the pyrazole ring of 1-phenylpyrazole [43] create steric hindrance, as a consequence of which there is a loss of luminescence properties: 1-phenyl-5-amino- and 1-phenyl-5-hydroxypyrazoles do not fluoresce, while the corresponding 3- and 4-substituted 1-phenylpyrazoles have strong fluorescence.

Pyrazole derivatives are not of great practical interest as luminophores, although some of them are known to be optical bleaches [44].

Aryl-substituted Δ^2-pyrazolines are of considerable interest as photo- and radioluminophores. The presence of aromatic groups in the 1 and 3 positions of the pyrazoline ring is sufficient for the appearance of luminescence [45]. However, 1,3,5-triaryl-Δ^2-pyrazolines (III), among which effective luminophores with blue and green luminescence are found, have had wider application.



III

The most widely used method for their preparation is the reaction of α,β-unsaturated ketones with aromatic hydrazines [46-48]. The intermediates of this reaction – arylhydrazones – are unstable and readily rearrange to triarylpyrazolines. A one-step method that makes it possible to synthesize triarylpyrazolines in good yields by heating a mixture of aromatic aldehydes with methyl ketones and phenylhydrazine in alcoholic alkaline media [49] was recently described.

The long-wave portion of the UV absorption spectra of Δ^2-pyrazolines is due mainly to the hydrazone fragment of the molecules and is similar in character to the spectra of the corresponding arylhydrazones [50]. Ring closing of the hydrazone grouping imparts to the molecules the rigidity necessary for the appearance of the luminescence properties that arylhydrazones lack.

The results of spectral [51-53] and polarographic [54] investigations and studies of the dipole moments in the ground and excited states [55, 56] provide evidence for conjugation of the π electrons of the aromatic groupings in the 1 and 3 positions of the pyrazoline ring with the p,π system of the heteroring.

The long-wave band in the UV spectrum of triphenylpyrazoline is a band due to intramolecular charge transfer in the 1,3-conjugated system [57]. The structures of the 1- and 3-aryl groups and the electronic nature of the substituents introduced into them therefore have a great effect on the optical properties of triarylpyrazolines. Lengthening of the chain of the conjugated bonds in these groups induces a bathochromic effect [58, 59]. The same result can be achieved by introduction of electron-donor substituents into the 1-phenyl group or electron-acceptor substituents into the 3-phenyl group [60]. This sort of effect of the electronic nature of the substituents is a consequence of strong polarization of the $C_6H_5-N-N=C-C_6H_5$ chromophore system in the ground state, inasmuch as the nitrogen atom in the 2 position, for which sp^2 hybridization is characteristic, is more electronegative than the nitrogen atom in the 1 position, which is in the sp^3 state. The introduction of electron-acceptor substituents into the 3-phenyl group or electron-donor substituents into the 1-phenyl group, by intensifying polarization in the $N_1 \rightarrow N_2$ direction, induces the indicated effects [61].

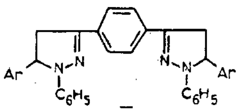
The character of the substituent in the 5 position of the pyrazoline ring has practically no effect on the optical properties of triarylpyrazolines [60, 62]. Compounds in which a bulky 5 substituent removes the 1-aryl group from the same planes as the heteroring constitute an exception to this; the luminescence of these compounds is markedly weakened [62].

Replacement of a phenyl group in the 3 position of pyrazoline by 2-furyl, 2-thienyl-, or 2-selenienyl groups leads to a long-wave shift of the spectra that increases in the same order. The observed shift in the luminescence intensity is explained by the increase in the weight of the groups and the associated additional loss of energy to intramolecular vibrations [63].

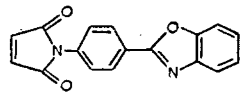
Luminophores that contain p-phenylene groups common to two pyrazoline rings in the 1, 3, or 5 positions, for example, IV [64], most of which have yellow-green luminescence in the crystalline state and green luminescence in solutions [65], are of interest.

Lengthening of the conjugation chain in IV, as well as their isomers containing phenylene residues in the 1 positions of the pyrazoline rings, as compared with triphenylpyrazoline is accompanied by a large bathochromic effect. It is interesting that the absorption spectra of di(1-pyrazolinyl)benzenes are shifted hypsochromically, whereas the luminescence spectra are shifted bathofluorically as compared with the spectra of di(3-pyrazolinyl)benzenes. The large Stokesian shift of the 1-isomers is associated with the absence in them of a rigid coplanar structure; as a consequence of this, the losses of electron excitation energy to emissionless transitions increase [66]. Di(5-pyrazolinyl)benzenes, in which there is no conjugation between the chromophores, are similar to the corresponding monopyrazolines with respect to their absorption and luminescence spectra, but they have additively increased molar absorption coefficients [66].

Compounds analogous to IV in which diphenyl and p-terphenyl residues are included in the conjugation chain in place of a phenyl group have been synthesized [67]. The accumulation of aromatic rings between the heterorings causes a gradually increasing hypsochromic effect, apparently due to weakening of the interaction between the chromophore systems and localization of the π-electron clouds in each of them [58]. Luminophores with CH_2, CH_2CH_2, and O bridges, which interrupt conjugation between the benzene rings of the diphenyl grouping that links the pyrazoline rings, differ little from monopyrazolines with respect to their optical properties [58].



IV



V

A considerable red shift of the luminescence (~ 80 nm) is observed when the phenylene residue of IV is replaced by a thiophene ring; the quantum yield also decreases [68].

Luminophores of the pyrazoline series are used as activators of liquid and plastic scintallators [52, 64, 69] and are used as luminescence dyes for plastics [70, 71], components of daylight-fluorescent pigments and dyes [72], and fluorescent indicators [73]. The use of triarylpyrazolines in lasers is well known [74]. The use of aryl-substituted pyrazolines as optical bleaches has been proposed. Not only 1,3,5-triarylpyrazolines [75] but also 1,3-diarylpyrazolines [76, 77] are suitable for this purpose.

Many compounds containing benzoxazole, benzimidazole, or benzothiazole groupings are used as organic luminophores and scintillation activators [78-91]. Some esters of imido acids with benzazole groupings are recommended for fluorescent labeling of proteins and amino acids [92], while N-substituted maleinimides that contain benzoxazole or benzimidazole groupings, for example, N-[p-(2-benzoxazolyl)-phenyl]maleinimide (V), have proved to be good reagents for the mercapto group, with which they form fluorescent complexes [93, 94].

The most widely spread methods for the preparation of benzoxazoles are cyclodehydration of salicylic acid anilides [95] and condensation of aromatic aldehydes with o-aminophenol with subsequent oxidation of the resulting azomethines [96-99].

The results of the first investigations of the fluorescence properties of benzoxazoles made it possible to consider the benzoxazole grouping to be a fluorophore [100]. A large number of substituted benzoxazoles were studied in [101, 102], and the relationship between their structure and luminescence properties was established. The introduction of p-dialkylamino groups into the phenyl group of 2-phenylbenzoxazole and lengthening of the chain of conjugated bonds by replacement of the phenyl group by a 4-diphenylyl group caused the most intense fluorescence and a large bathofluoric shift. Methoxy and methyl groups also promote an increase in the luminescence intensity but to a lesser extent than a dialkylamino group.

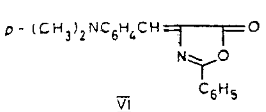
In bisbenzoxazoles that contain pyridine, vinylpyridine, α,β-dipyridylethylene, and divinylpyridylbenzene groupings as a linking bridge (103], a bathofluoric shift and an increase in the luminescence intensity are observed as the conjugation chain is lengthened, and the absorption and fluorescence bands are shifted to the longer-wave region as compared with bisbenzoxazoles in which the benzene ring serves as a bridge.

In a more detailed study of the nature of the fluorescence of benzoxazoles and the π-isoelectronic stilbenes, Nurmukhametov and co-workers [104] arrived at the conclusion that the long-wave band in the UV spectrum due to a π,π^* transition is responsible for the fluorescence. Nyilas and Pinter [105] have expressed the opinion that the bisbenzoxazole molecule on passing into the excited state acquires a quinoid structure and is reconverted to the benzoid form after emission of a fluorescence quantum.

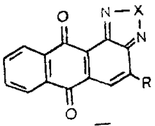
A similar relationship between the fluorescence and scintillation properties and the structure is observed in the 2-arylbenzimidazole series [102, 103, 106]. The substituent in the 2 position of the heteroring has the principal effect on the absorption and fluorescence spectra, whereas the influence of a substituent in the 1 position of the imidazole ring reduces primarily to an inductive effect [106].

Research involving a study of the fluorescence properties of more complexly constructed azoles – 2,6-bis(benzoxazolyl)naphthalenes [107], naphthoxazoles [102, 103, 108], phenanthro[9,10-d]oxazoles [109], etc. – is known.

Compounds of the azlactone class obtained by condensation of various aromatic aldehydes with hippuric acid have intense luminescence. The color of their luminescence depends on the starting aldehyde [110]. 4-(4-Dimethylaminobenzylidene)-2-phenyl-5-oxazolone (VI) – a luminophore with orange-red luminescence [111] – is of practical interest.



VI



VII

Compounds with a triazole ring [112-118], for which the relationship between the spectral (including fluorescence) properties and the character and position of the substituents has been investigated [119-121], are widely used for optical bleaching. Thus electron-acceptor substituents in the 4' position of 2-phenylnaphtho[1,2]triazole-6-sulfonic acid intensify the luminescence, whereas electron-donor substituents in the same position shift the absorption and luminescence to the long-wave region. Electron-donor groups in the 3' position quench luminescence, while electron-acceptor groups do not have a quenching effect [122].

Indole derivatives are not used as luminophores, but the ability of some of them to luminescence has been used to determine them in biological objects [123]. The relationship between the fluorescence properties of indoles and their structure was examined in [124-129].

Luminescence properties are also peculiar to indigo and thioinidgo [130]; only the trans isomers luminesce. The absorption and luminescence spectra of indigo are shifted to the long-wave region relative to the spectra of thioindigo. The introduction of halogens has practically no effect on the spectrum of indigo [131, 132]. A strong bathofluoric shift is observed for N, N'-dimethylindigo.

Anthraquinonediazoles with alkylamino, dialkylamino, or cycloalkylamino groups (R) in the 4 position (VII, X = O, S, Se) have deep color and long-wave and intense luminescence [133]. These compounds are used for the preparation of purple and violet daylight-fluorescent pigments and dyes of various shades [134].

Organic Luminophores with Six-Membered Heterorings

Six-membered heterocyclic systems contain a heteroatom with an unshared pair of electrons that is responsible for the appearance of an n,π* band in the absorption spectrum. In conformity with one of the discussed luminescence mechanisms [135, 136], these electrons are transferred from the $S_{n,\pi*}$ level to the triplet $T_{\pi,\pi*}$ level, the longer lifetime of which promotes emissionless loss of energy. It is for precisely this reason that many heterocycles do not fluoresce, in contrast to the corresponding aromatic hydrocarbons. Thus luminescence is absent in pyridine [130], whereas in the case of quinoline luminescence appears only in polar solvents [130, 137]. The introduction of electron-donor substituents or an increase in the length of the chain of conjugated bonds is manifested in a bathochromic shift of the π,π* band and overlapping of the n,π* band with it. This leads to blocking of the n,π* quenching mechanism and, consequently, to an increase in the fluorescence intensity [138]. For example, 2- and 3-aminopyridines have very intense fluorescence [139]. 2-(4-Dimethylaminophenyl)quinoline [138], acridine [140], 5,6-benzoquinoline [141], 3,4-benzazaphenanthrene, and 3,4-benzacridine [142] luminesce brightly.

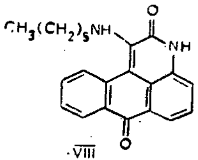
In speaking of the practical use of six-membered N-heterocyclic compounds, one should note the possibility of the use of 3,8-dimethyl-2-azanthracene and 3-methyl-8-ethyl-2-azanthracene in lasers [143]. Using the capacity of azaheterocyclic compounds to fluoresce, one can monitor the completeness of their separation from a polynuclear aromatic substance, inasmuch as they fluoresce in a longer-wave region than their hydrocarbon analogs [144]. Acridine and its substituted derivatives, which have green and yellow-green luminescence [145], have found the most significant application. Research involving a study of the luminescence properties of acridines [146-148] and acridones [149, 150] is known.

1-Amino-substituted 1,9-anthrapyridones, which luminesce in the yellow-green region of the spectrum, and 6-amino-substituted 1,9-anthrapyridones [151] (for example, VIII), which are used for the preparation of daylight-fluorescent pigments and dyes [152], are interesting as luminophores.

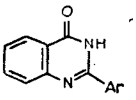
The luminescence properties of diazaphenanthrenes depend substantially on the position of the nitrogen atoms in their molecules and can be explained on the basis of an analysis of the relative spacing of the n,π* and π,π* levels [153].

The probability of n,π* quenching can be reduced by formation of a hydrogen bond with the participation of the unshared electrons of the heteroatom. For example, the fluorescence intensity of quinoline and acridine increases in the presence of proton-donor compounds. The higher the proton-donor capacity of the compound added, the more intense the luminescence [154]. Blue fluorescence appears in acidic media in the case of 2-methyl-3-aminoquinoline, which does not fluoresce in neutral media and in the crystalline state [155].

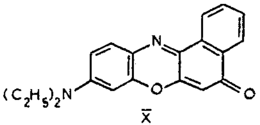
Six-membered heterocycles with two nitrogen atoms, for example, pyrimidines, have rather high fluorescence quantum yields and display scintillation properties, but they are less effective as scintillation activators than 2,5-diphenyloxazole and p-terphenyl [156].



VIII



IX



X

Benzopyrimidines – 2-substituted 4(3H)-quinazolones (IX) – are recommended as effective organic luminophores [157].

The greatest increase in the fluorescence intensity in the 2-aryl-4(3H)-quinazolone series is observed in the case of 6,7-annelation of the benzene ring or when an amino group is introduced into the 6 position of a benzene ring condensed with a heteroring [158].

In contrast to the unsubstituted compound, chloro- and methoxyphenazines fluoresce in the crystalline state and in solutions. Mataga and Ezumi [159] link this with a lowering of the π,π* level. However, it is interesting that in contrast to most other heterocycles, phenazines lose their capacity for fluorescence when they are protonated. This is explained by the vibrational interaction of the ground level with the lower excited level, which, owing to protonation, has a very low value.

Phenoxazine dyes luminesce in alcohol solutions. The presence of a quinoid structure leads to a long-wave shift of the luminescence. Some of them luminesce in the orange and orange-red regions of the spectrum. The introduction of a dialkylamino group into the para position relative to the heteroring nitrogen (X) promotes a bathofluoric effect. Substitution in the other positions is accompanied by a decrease in the fluorescence intensity or by complete quenching [160].

There is no information available regarding the practical utilization of the fluorescence of phenoxazines. At the same time, a fluorescence method for the qualitative and quantitative determination of sulfur analogs of phenoxazines – phenothiazines – is known [161].

Fluoresceins and rhodamines have long served as classical objects for the investigation of the luminescence properties of organic substances. Daylight-fluorescent pigments and dyes have been created from them [162, 163], and they are used for labeling aerosols [164] and for many other purposes. Replacement of the primary amino groups in rhodamine molecules by diethylamino groups causes a bathofluoric effect and a small increase in the fluorescence quantum yield. The introduction of two arylalkyl groups into the amino groups results in a more significant long-wave shift of the fluorescence maxima, the longer the alkyl chain; the quantum yield remains almost unchanged in this case. Replacement of the hydrogen atoms of the amino groups by aryl groups markedly reduces the luminescence intensity and induces an even greater bathofluoric effect [165, 166].

Coumarin derivatives are of interest as optical bleaches [167-169]. A study of their luminescence properties in the case of 4-methylcoumarin showed that electron-donor substituents in the 7 position increase the brightness of the luminescence, and the most significant effect is observed when a diethylamino group is introduced; hydroxy and methoxy gruoups have a lesser effect [170-174].

Of the other classes of heterocyclic compounds used as luminophores, one should note pyrylium salts (based on 4-aryl- and 4-styrylpyrylium perchlorates [175]).

Effective luminophores are found among barbituric acid derivatives. Specifically, 5-(p-dimethylaminobenzylidene)barbituric acid – a luminophore with red luminescence – is one such luminophore [176, 177].

Organic Luminophores – Phthalic and Naphthalic Acid Derivatives

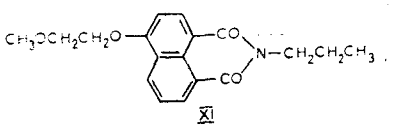
A number of studies involving the investigation of luminophores that are 3- and 4-aminophthalimide derivatives have been published; the effect of various structural factors and the environment on their luminescence has been studied [178-181]. These luminophores have not received substantial practical application.

Luminophores based on naphthalic acid, substituted naphthalic acid, and its derivatives have recently assumed great importance. Many of them contain groupings of atoms characteristic for the luminescent substances already noted above. However, the combination of these groupings with naphthalic anhydride, naphthalimide, and naphthoylenebenzimidazole groupings has made it possible to obtain effective luminophores with interesting new properties.

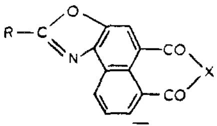
One should first of all note luminophores with blue luminescence – naphthalimide derivatives – which are used as optical bleaches. The overwhelming majority of them contain an alkoxy group in the naphthalimide grouping, most frequently in the 4 position [182-185]. Hydroxy [186], acylamino [187], phenoxy, alkyl or cycloalkyl [188], halo [189], alkyl- or arylmercapto [190, 191], and sulfamide [192] groups are sometimes introduced in place of them. The hydrogen of the imino group is unsubstituted only in rare instances [186]. Alkyl [193] or alkoxy [194] and alicyclic [195] groups are usually introduced in place of it, and sometimes alkyl groups containing a dialkylamino group [196] or an ester grouping [197], hydroxy or alkoxy groups, heterocyclic groupings [198, 199] are introduced in place of it.

Luminophore XI may serve as an example of compounds recommended for bleaching polyester and polyacrylic fibers [200].

Naphthalimide derivatives with heterocyclic substituents in the naphthalene ring and compounds in which this ring is condensed with a heteroring are of interest as bleaches. Thus, according to [201], 4-pyrazolyl-substituted naphthalimides can be used for bleaching synthetic materials. Compounds XI (X = O, NH), which are synthesized by condensation of 3-halo-4-aminonaphthalic acids or their imides with carboxylic acid derivatives and subsequent cyclization of the reaction products [202, 203], are used for bleaching natural and synthetic fibers, resins, paper, and leather.



XI



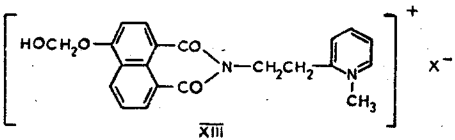
XII

Cationic bleaches that are naphthalimide derivatives have been described. A quaternary nitrogen atom, which may be included in the heteroring, enters into the substituent attached to the imide nitrogen in these compounds. Thus, for example, luminophore XIII is recommended for bleaching synthetic fibers [204].

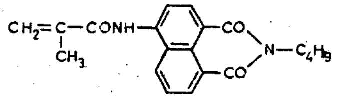
Bleaches with unsaturated acyl groupings are known. Copolymers of acrylonitrile with small amounts of luminophore XIV are more photostable than polyacrylonitrile bleached with 4-acetamidonaphthalic acid N-butylimide [205].

In addition to naphthalimide derivatives used for the optical bleaching of various materials, luminophores with yellow and orange luminescence that also contain a naphthalimide grouping have been described.

In contrast to N-substituted 4-acetamidonaphthalic acid imides – luminophores with blue luminescence – the corresponding 4-aminonaphthalic acid derivatives are yellow dyes that absorb light and luminesce in a longer-wave region than the analogous phthalimide derivatives [206, 207].



XIII

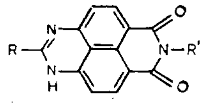


XIV

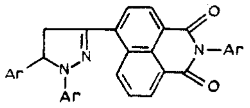
N-Substituted 4-aminonaphthalic acid imides serve as the luminescent components of daylight-fluorescent pigments and dyes [208, 209].

Compounds with a perimidine ring that are formed in the reaction of N-substituted 4,5-diaminonaphthalic acid imides with aliphatic or aromatic acid chlorides (XV, R, R' = Alk, Ar) [210, 211] are classified as greenish-yellow and yellow luminescent dyes.

Orange luminescent dyes XVI were obtained by introduction of a pyrazoline grouping into the 4 position of the naphthalimide grouping; they are used for dyeing polystyrene and poly(methyl methacrylate) [212, 213].



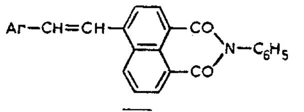
XV



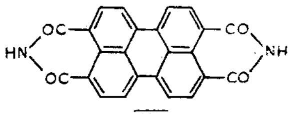
XVI

Luminophores with luminescence of a different color are found among azomethine derivatives of 4-amino-N-phenylnaphthalimide [214]. Their range of luminescence (λ_{max} in dimethylformamide 465-525 nm, 512-605 nm in the solid state) can be varied over considerable limits by changing the structure of the aldehyde residues.

Luminophores with azomethine groups are unsatable in acid media. Their arylethylene analogs (XVII), obtained from 4-chloromethylnaphthalic acid [215], do not have this disadvantage.



XVII



XVIII

Perilene-3,4,9,10-tetracarboxylic acid (XVIII), which has luminescence properties, was synthesized by alkaline fusion of naphthalimide [216]. Perilenetetracarboxylic acid N,N'-dialkyl(or cyclohexyl)imides dye polystyrene in bulk from reddish-yellow to orange (depending on the luminophore concentration). In addition to high photostability, fluorescing dyes have great brightness and resistance to chemical action [217, 218]. Photostable luminescent pigments that dye various polymers from red to claret can be obtained by condensation of perilenetetracarboxylic acid dianhydride with 4-aminonaphthalic acid N-substituted imides [219].

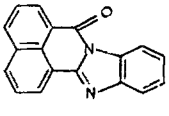
1,8-Naphthoylene-1',2'-benzimidazole (XIX) [220], which is readily formed in the reaction of naphthalic anhydride with o-phenylenediamine [221], is an effective luminophore with yellow-green luminescence. This luminophore, which luminesces intensely in hydrocarbon solvents and in the solid state, has received wide application in luminescence defectoscopy [222, 223] and has been used to impart luminescing colors to polystyrene and other polymers [224, 225], in γ-radiation dosimetry [226], and for other purposes.

Various substituted naphthoylenebenzimidazoles, primarily those containing chloro and methoxy groups in the benzene ring, have also been used to dye polymers [224, 227, 228].

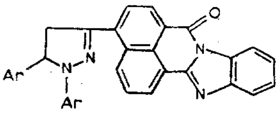
The product of the condensation of 3-sulfonaphthalic anhydride with o-phenylenediamine is a water-soluble luminophore with yellow-green luminescence [229].

Compounds that luminesce intensely in the solid state were obtained by condensation of amino-substituted naphthoylenebenzimidazoles (amino group in the peri position of the naphthalene ring) [203].

Luminophores with orange-red and red luminescence that contain interconjugated naphthoylenebenzimidazole and diphenylpyrazoline structural groupings (XX) are of interest [231].



XIX

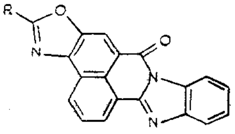


XX

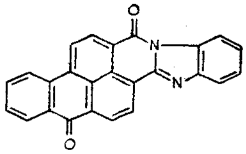
These compounds, which are soluble in organic media, dye polystyrene and poly(methyl methacrylate), and they give intensely fluorescing photostable colors even in low concentrations [232]. They are sometimes used for the same purpose in mixtures with thioindigo dyes [233].

Yellow luminescent dyes of the XXI type, which are suitable for dyeing polyester fibers, were recently described [234].

4- and 5-Benzoyl-substituted naphthoylenebenzimidazoles are used in the synthesis of compounds that contain a benzanthrone grouping, for example, XXII.



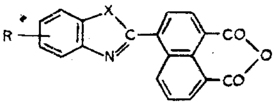
XXI



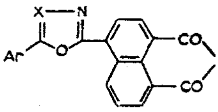
XXII

For this, they are heated with anhydrous aluminum chloride. Compound XXII is a luminophore with orange luminescence [235].

4-Carboxynaphthalic anhydride (the anhydride of naphthalene-1,4,5-tricarboxylic acid) assumes great importance in the synthesis of luminophores. Condensation of its acid chloride [236] with o-phenylenediamine, o-aminophenol, o-aminothiophenol, and their substituted derivatives gave benzazolylnaphthalic anhydrides XXIII (X = O, S, NH), which have intense luminescence in hydrocarbon solvents but luminesce less intensely in the solid state [237-240]. The anhydrides of aryloxazolyl- and aryloxadiazolylnaphthalic acids (XXIV, X = CH, N) were described almost simultaneously [241-243]. The corresponding naphthalimide and naphthoylenebenzimidazole derivatives were synthesized by condensation of these anhydrides with aniline or o-phenylenediamine [238, 240, 243-245].



XXIII



XXIV

The luminescence maxima of luminophores obtained from 4-carboxynaphthalic anhydride lie over a wide range of wave lengths: 425-628 nm in toluene, and 480-635 nm in the solid state. The absolute quantum yields of toluene solutions range from 0.14 to 0.95.

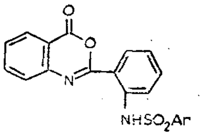
The anhydrides and phenylimides have been used for the preparation of daylight-fluorescent pigments [246, 247], and naphthoylenebenzimidazole derivatives can be used to dye polystyrene [240, 243].

Luminescent Heterocyclic Compounds with an Intramolecular Hydrogen Bond

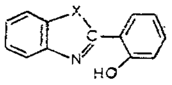
Luminophores based on heterocyclic compounds with an intramolecular hydrogen bond constitute a special group. It was noted above that bonding of the unshared pair of electrons of the heteroatom leads to a change in the relative spacing of the n,π^* and π,π^* levels and frequently entails the development of luminescence. This effect can also be achieved by means of an intramolecular hydrogen bond. In this case, an anomalously large Stokesian shift is observed simultaneously with the development of luminescence: substances that are colorless in daylight fluoresce in the blue [248], green [249], yellow [250], and even in the near-IR region of the spectrum [251].

The reason for the anomalously large Stokesian shift lives in the emissionless loss of a portion of the absorbed energy to transfer of a proton along the coordinate of the hydrogen bond. The decrease in the luminescence maximum depends on the strength of the hydrogen bond, which can be changed by introducing substituents of different nature. The weaker the hydrogen bond, the larger the bathofluoric effect [252].

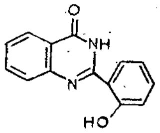
Luminophores with an intramolecular hydrogen bond are known in different classes of heterocyclic compounds. These include 2-(2-arylsulfonylaminophenyl)-4H-3,1-benzoxazin-4-ones (XXV) [250], 2-(2-hydroxyphenyl)-substituted benzoxazoles [249], benzothiazoles [253], benzimidazoles [254] (XXVI, X = O, S, NH), and 2-(2-hydroxyphenyl)-4(3H)-quinazolones (XXVII) [255].



XXV



XXVI



XXVII

The use of luminophores with a large Stokesian shift makes it possible to realize luminescent labeling of articles without changing their natural colors, for example, in the preparation of luminescent postage stamps for automatic sorting of letters [256] or luminescent coded cards [257-259].

LITERATURE CITED

1. National Distillers and Chemical Corp., US Patent No. 3222290 (1962); J. Soc. Dyers Col., 83, 126 (1967).
2. M. Tibu, I. Viserian, B. Arvertiev, H. Offenberg, and T. Nicolaescu, Analete Stiint. Univ. A. I. Cuza, Iasi Sect. I, 9, 261 (1963); Chem. Abstr., 60, 2434 (1964).
3. Yu. N. Panov, N. A. Adrova, and M. M. Koton, Opt. i Spektrosk., 7, 29 (1959).
4. D. G. Ott, F. N. Hayes, E. Hansbury, and V. N. Kerr, J. Amer. Chem. Soc., 79, 5448 (1957).
5. O. Dann and P. Nickel, Ann., 667, 101 (1963).
6. Yu. M. Vinetskaya, M. G. Voronkov, B. M. Krasovitskii, and V. É. Udre, Khim. Geterotsikl. Soedin., 180 (1968).
7. Procter and Gamble Co., French Patent No. 1453213 (1966); Chem. Abstr., 66, 20,244 (1967).
8. J. Birks, The Theory and Practice of Scintillation Counting, Pergamon Press, New York–London (1967), pp. 295, 355.
9. F. N. Hayes, D. G. Ott, V. N. Kerr, and B. S. Rogers, Nucleonics, 13, No. 12, 38 (1955).
10. R. Robinson, J. Chem. Soc., 95, 2167 (1909).
11. E. Fischer, Ber., 29, 205 (1896).
12. T. K. Sevast'yanova and L. B. Volodarskii, Zh. Organ. Khim., 7, 1974 (1972).
13. F. N. Hayes, B. S. Rogers, and D. G. Ott, J. Amer. Chem. Soc., 77, 1850 (1955).
14. A. P. Grekov and M. S. Marakhova, Zh. Obshch. Khim., 32, 542 (1962).
15. A. P. Grekov and O. P. Shvaika, in: Scintillators and Scintillation Materials [in Russian], Kharkov, No. 3 (1963), p. 5.
16. L. J. Basile, J. Chem. Phys., 27, 801 (1957).
17. L. M. Kutsyna and É. G. Verkhovtseva, Opt. i Spektrosk., 12, 785 (1962).
18. N. P. Shimanskaya, A. P. Kilimov, A. P. Grekov, L. M. Egupova, and R. S. Azen, Opt. i Spektrosk., 7, 366 (1959).
19. D. G. Ott, V. N. Kerr, F. N. Hayes, and E. Hansbury, J. Org. Chem., 25, 872 (1960).
20. L. L. Nagornaya, V. D. Bezuglyi, and A. P. Grekov, Opt. i Spektrosk., 10, 55 (1961).
21. L. L. Nagornaya, V. D. Bezuglyi, and N. P. Demchenko, Opt. i Spektrosk., 13, 518 (1962).
22. L. M. Kutsyna, R. P. Sidorova, L. V. Voevoda, I. K. Ishchenko, and N. P. Demchenko, Izv. Akad. Nauk SSSR, Ser. Fiz., 26, 1304 (1962).
23. L. L. Nagornaya and V. D. Bezuglyi, in: Scintillators and Scintillation Materials [in Russian], Kharkov, No. 3 (1963), p. 91.
24. R. N. Nurmukhametov and L. L. Nagornaya, Opt. i Spektrosk., 18, 109 (1965).
25. R. N. Nurmukhametov, O. S. Chepigo, and O. P. Shvaika, Zh. Fiz. Khim., 37, 2951 (1965).
26. T. N. Bolotnikova and G. V. Gobov, Izv. Akad. Nauk SSSR, Ser. Fiz., 27, 683 (1963).
27. N. P. Demchenko, E. I. Zorina, L. P. Snagoshchenko, V. F. Poduzhailo, and L. M. Kutsyna, in: Single Crystals, Scintillators, and Organic Luminophores [in Russian], Kharkov, No. 2 (1967), p. 108.
28. L. L. Nagornaya, T. R. Mnatsakanova, A. P. Grekov, and O. P. Shvaika, Opt. i Spektrosk., 18, 103 (1965).
29. D. Ott, F. Hayes, J. Hammel, and J. Rephart, Nucleonics, 13, No. 5, 62 (1955).
30. V. I. Grigor'eva, V. F. Poduzhailo, and B. M. Krasovitskii, in: Single Crystals, Scintillators, and Organic Luminophores [in Russian], Kharkov, No. 5, Part 1 (1969), p. 99.
31. V. I. Grigor'eva and B. M. Krasovitskii, Khim. Geterotsikl. Soedin., 761 (1967).

32. B. M. Krasovitskii and V. I. Grigor'eva, Khim. Geterotsikl. Soedin., 1127 (1968).
33. A. E. Siegrist, Helv. Chim. Acta, 50, 906 (1967).
34. V. I. Grigor'eva, R. S. Mil'ner, and B. M. Krasovitskii, in: Single Crystals, Scintillators, and Organic Luminophores [in Russian], Kharkov, No. 4 (1968), p. 98.
35. B. M. Krasovitskii, V. I. Grigor'eva, and R. S. Mil'ner, USSR Author's Certificate No. 182162; Byul. Izobr., No. 11 (1966).
36. V. I. Grigor'eva, O. A. Gunder, B. M. Krasovitskii, and I. B. Petrova, Zh. Prirodn. Soedin., 8, 884 (1968).
37. CIBA A.-G., Swiss Patent No. 484174 (1969); Ref. Zh. Khim., 24N203 (1970).
38. Nisso Kako Kabushiki Kaisha, Japanese Patent No. 36230 (1970).
39. Yu. V. Naboikin, L. A. Ogurtsova, A. P. Podgornyi, F. S. Pokrovskaya, V. I. Grigor'eva, B. M. Krasovitskii, and L. M. Kutsyna, Zh. Prirodn. Soedin., 13, 1065 (1970).
40. V. I. Grigor'eva, B. M. Krasovitskii, Yu. V. Naboikin, L. A. Ogurtsova, A. P. Podgornyi, F. S. Pokrovskaya, and V. G. Tishchenko, in: Scintillators and Organic Luminophores [in Russian], Kharkov (1972), p. 169.
41. CIBA A.-G, Swiss Patent No. 426848 (1967); Chem. Abstr., 68, 69,002 (1968).
42. I. I. Grandberg, S. V. Tabak, and A. N. Kost, Zh. Obshch. Khim., 33, 525 (1963).
43. I. I. Grandberg, S. V. Tabak, and A. N. Kost, Khim. Geterotsikl. Soedin., 901 (1965).
44. Hickson and Welch Ltd., British Patent No. 1052179 (1964); J. Soc. Dyers Col., 83, 161 (1967).
45. O. Neunhoeffer and H. Ulrich, Ber., 88, 1123 (1955).
46. K. Auwers and A. Kreuder, Ber., 58, 1974 (1925).
47. H. Vorländer, Ber., 58, 127 (1925).
48. L. Raiford and R. Manley, J. Org. Chem., 5, 590 (1940).
49. B. M. Krasovitskii and G. F. Slezko, USSR Author's Certificate No. 239344; Byul. Izobr., No. 11 (1969).
50. R. N. Nurmukhametov and V. G. Tishchenko, Opt. i Spektrosk., 23, 83 (1967).
51. S. R. Sandler and K. C. Tsou, J. Chem. Phys., 39, 1062 (1963).
52. O. Neunhoeffer and D. Rosahl, Ber., 86, 226 (1953).
53. N. A. Lodygin, Author's Abstract of Master's Dissertation, Moscow (1968).
54. G. G. Belous and V. D. Bezuglyi, Zh. Analiticheskoi Khim., 18, 1250 (1963).
55. A. E. Lutskii, A. V. Shepel', and E. M. Obuhova, Khim. Geterotsikl. Soedin., 948 (1967).
56. L. M. Kutsyna, L. V. Voevoda, and L. D. Kornilovskaya, Opt. i Spektrosk., 18, 520 (1965).
57. L. M. Kutsyna, L. V. Voevoda, V. G. Tishchenko, and A. V. Shepel', Opt. i Spektrosk., 26, 168 (1969).
58. D. G. Pereyaslova, V. E. Bondarenko, and B. M. Krasovitskii, Khim. Geterotsikl. Soedin., 114 (1968).
59. V. E. Bondarenko, D. G. Pereyaslova, and B. M. Krasovitskii, Zh. Prirodn. Soedin., 13, 552 (1970).
60. V. G. Tishchenko, Author's Abstract of Master's Dissertation, Kharkov (1968).
61. S. V. Tsukerman, E. G. Buryakovskaya, and V. F. Lavrushin, Opt. i Spektrosk., 26, 541 (1969).
62. N. A. Lodygin, and S. A. Il'ina, in: Single Crystals, Scintillators, and Organic Luminophores [in Russian], Kharkov (1967), p. 140.
63. V. F. Lavrushin, S. V. Tsukerman, E. G. Buryakovskaya, and Yu. M. Vinetskaya, Prom. Khim. Reaktivov i Osobo Chistykh Veshchestv, 8, 77 (1967).
64. V. F. Poduzhailo and V. G. Tishchenko, USSR Author's Certificate No. 161827; Byul. Izobr., No. 8 (1964).
65. V. E. Bondarenko, D. G. Pereyaslova, and B. M. Krasovitskii, in: Single Crystals, Scintillators, and Organic Luminophores [in Russian], Kharkov, No. 4 (1968), p. 26.
66. S. V. Tsukerman, V. P. Maslennikova, V. E. Bondarenko, and V. F. Lavrushin, Opt. i Spektrosk., 28, 914 (1970).
67. E. E. Baroni and K. A. Kovyrzina, Zh. Obshch. Khim., 33, 583 (1963).
68. S. V. Tsukerman, V. P. Maslennikova, Lam Ngok Thiem, V. M. Nikitchenko, and V. F. Lavrushin, in: Single Crystals, Scintillators, and Organic Luminophores [in Russian], Kharkov, No. 4 (1968), p. 36.
69. R. H. Wiley, C. H. Jarboe, F. N. Hayes, E. Hansbury, J. T. Nielsen, P. X. Collahan, and M. C. Sellers, J. Org. Chem., 23, 732 (1958).
70. V. E. Bondarenko, B. M. Krasovitskii, D. G. Pereyaslova, and V. M. Solomonov, USSR Author's Certificate No. 244607; Byul. Izobr., No. 18 (1968).
71. N. F. Levchenko, V. M. Solomonov, É. A. Shevchenko, and B. M. Krasovitskii, in: Single Crystals, Scintillators, and Organic Luminophores [in Russian], Kharkov, No. 4 (1968), p. 186.
72. G. F. Slezko, Author's Abstract of Master's Dissertation, Kharkov (1971).

73. S. V. Tsukerman, E. G. Buryakovskaya, V. P. Maslennikova, A. I. Bugai, and V. F. Lavrushin, USSR Author's Certificate No. 272461, Byul. Izobr., No. 19 (1970).
74. I. I. Kalosha, V. P. Maslennikova, and S. V. Tsukerman, Zh. Prirodn. Soedin., 15, 960 (1971).
75. Societa per Azione Ferrania, West German Patent No. 1008569 (1957); Chem. Abstr., 54, 1142 (1960).
76. Hickson and Welch Ltd., US Patent No. 3133080 (1964); Ref. Zh. Khim., 19N130 (1965).
77. Sandoz A.-G., British Patent No. 1301310 (1969); J. Soc. Dyers Col., 89, 192 (1973).
78. Nicco Chemical Ind. Ltd., Japanese Patent No. 2777 (1965); Chem. Abstr., 63, 4433 (1965).
79. Japan Chemical Works Co., Japanese Patent No. 6100 (1965); Chem. Abstr., 63, 18317 (1965).
80. Japan Chemical Ind. Co., Japanese Patent No. 21628 (1965); Chem. Abstr., 64, 3742 (1965).
81. Mitsui Chemical Ind. Co., Japanese Patent No. 21991 (1966); Chem. Abstr., 66, 10589 (1967).
82. Japan Chemical Works Co., Japanese Patent No. 20226 (1966); Chem. Abstr., 66, 105897 (1967).
83. Farbwerke Hoechst A.-G., Dutch Patent No. 6405251 (1964); Chem. Abstr., 62, 13287 (1965).
84. CIBA, French Patent No. 1384000 (1965); Chem. Abstr., 62, 13287 (1965).
85. Eastman Kodak Co., Belgian Patent No. 641426 (1964); Chem. Abstr., 63, 712 (1965).
86. CIBA, Dutch Patent No. 6511891 (1966); Chem. Abstr., 66, 116706 (1967).
87. B. G. Buell, US Patent No. 3167565 (1965); Chem. Abstr., 62, 13286 (1965).
88. Mitsui Kagaku Koguo K. K., British Patent No. 967483 (1962); J. Appl. Chem., 16, i-52 (1966).
89. Daito Chemical Ind. Co., British Patent No. 967360 (1961); J. Appl. Chem., 16, i-52 (1966).
90. Farbenfabriken Bayer A.-G., British Patent No. 1059256 (1965); J. Appl. Chem., 17, ii-418 (1967).
91. Farbwerke Hoechst A.-G., British Patent No. 1055183 (1963); J. Appl. Chem., 17, ii-188 (1967).
92. W. Ried, D. Piechaczek, and E. Vollberg, Ann., 734, 13 (1970).
93. Y. Kanaoka, M. Machida, H. Kokubun, and T. Sekine, Chem. Pharm. Bull. (Tokyo), 16, 1747 (1968); Chem. Zentralflatt, 140, 56-014 (1969).
94. Y. Kanaoka, T. Sekine, M. Machida, Y. Soma, K. Tanizawa, and Y. Ban, Chem. Pharm. Bull. (Tokyo), 12, 127 (1964); Chem. Abstr., 60, 15,856 (1964).
95. H. Hübner, Ann., 210, 385 (1881).
96. R. D. Desai, R. F. Hinter, and A. R. K. Knalidi, J. Chem. Soc., 1190 (1934).
97. F. F. Stephens and J. D. Bower, J. Chem. Soc., 2971 (1949).
98. F. F. Stephens and J. D. Bower, J. Chem. Soc., 1722 (1950).
99. V. V. Somayajulu and N. V. Subba Rao, Curr. Sci., 25, 86 (1956).
100. F. Heinrich and G. Opfermann, Ber., 37, 3108 (1904).
101. L. N. Pushkina and V. V. Tkachev, Zh. Prirodn. Soedin., 1, 275 (1964).
102. L. N. Pushkina, V. V. Tkachev, and I. Ya. Postovskii, Dokl. Akad. Nauk SSSR, 149, 135 (1963).
103. T. Marujama, N. Kuroki, and K. Konishi, Kogyo Kagaku Zasshi, 68, 2428 (1965).
104. R. N. Nurmukhametov, G. V. Gobov, and L. N. Pushkina, Zh. Fiz. Khim., 41, 1553 (1967).
105. E. Nyilas and J. L. Pinter, J. Amer. Chem. Soc., 82, 609 (1960).
106. V. V. Tkachev and L. N. Pushkina, Zh. Prirodn. Soedin., 2, 63 (1965).
107. M. Matsuoka, S. Fukushima, T. Kitao, and K. Konishi, Kogyo Kagaku Zasshi, 74, 724 (1971).
108. Yu Ling-Chung and Chang Kuei-Pao, Hua Hsuch Hsuch Pao, 31, 346 (1965); Chem. Abstr., 64, 2740 (1966).
109. G. Pfundt and W. M. Hardham, Tetrahedron Lett., 2411 (1965).
110. J. Eisenbrand, Arch. Pharm., 286, 441 (1953).
111. V. K. Matveev, Author's Certificate No. 112670 (1957); Chem. Abstr., 53, 4302 (1959).
112. Procter and Gamble Co., British Patent No. 1045977 (1966); Chem. Abstr., 66, 20244 (1967).
113. Farbenfabriken Bayer A.-G., Dutch Patent No. 6607767 (1966); Chem. Abstr., 66, 116705 (1967).
114. Farbenfabriken Bayer A.-G., Belgian Patent No. 672896 (1966); Chem. Abstr., 66, 96225 (1967).
115. CIBA, Belgian Patent No. 672957 (1966); Chem. Abstr., 66, 96226 (1967).
116. E. Compe, K. Obayashi, and I. Yamakawa, Japanese Patent No. 3134 (1964); Ref. Zh. Khim., 20N231 (1966).
117. Farbenfabriken Bayer A.-G., US Patent No. 2901477 (1959); Chem. Abstr., 54, 2767 (1960).
118. J. Dobač and J. Pirkl, Chem. Listy, 51, 2330 (1957).
119. J. Dobač, J. Pirkl, and V. Hanousek, Chem. Listy, 51, 1101 (1957).
120. J. Dobač, J. Pirkl, and V. Hanousek, Coll. Czech. Chem. Commun., 23, 926 (1958).
121. J. Dobač and J. Pirkl, Chem. Listy, 52, 1310 (1958).
122. J. Dobač and J. Pirkl, Coll. Czech. Chem. Commun., 25, 912 (1960).
123. A. Bertler, B. Falck, and C. Owman, Kgl. Fysiograf. Sallskap. Lund, Forh., 33, 13 (1963).
124. M. G. M. Balemans and F. C. G. van de Veerdonk, Experientia, 23, 906 (1967); Chem. Abstr., 68, 64258 (1968).

125. R. F. Chen, Proc. Nat. Acad. Sci. USA, 60, 598 (1968); Chem. Abstr., 69, 64670 (1968).
126. Pill-Soon Song and W. E. A. Kurtin, J. Amer. Chem. Soc., 91, 4892 (1969).
127. M. Piattelli, L. Minale, and G. Prota, Ann. Chim. (Roma), 54, 955 (1964); Ref. Zh. Khim., 20Zh434 (1965).
128. R. A. Heacock and O. Hutzinger, Can. J. Biochem., 43, 1771 (1965).
129. M. Matsuoka, M. Matsuhata, T. Kitao, and K. Konishi, Kogyo Kagaku Zasshi, 74, 440 (1971).
130. R. N. Nurmukhametov, Absorption and Luminescence of Aromatic Compounds [in Russian], Khimiya, Moscow (1971).
131. D. N. Shirogin, R. N. Nurmukhametov, and Yu. I. Kozlov, Optika i Spektroskopiya, 12, 659 (1962).
132. R. N. Nurmukhametov, D. N. Shigorin, and Yu. I. Kozlov, Izv. Akad. Nauk SSSR, Ser. Fiz., 27, 686 (1963).
133. M. V. Gorelik and Yu. M. Vinetskaya, in: Single Crystals, Scintillators, and Organic Luminophores [in Russian], No. 4, Kharkov (1968), p. 60.
134. D. G. Pereyaslova, Yu. M. Vinetskaya, M. V. Gorelik, and G. V. Tatsii, Zh. Vsesoyuzn. Khim. Obshchestva, 13, 472 (1968).
135. M. Kasha, Discussions of the Faraday Soc., 9, 14 (1950).
136. R. Müller and F. Dörr, Z. Elektrochem., 63, 1150 (1959); Chem. Abstr., 54, 5243 (1960).
137. N. Mataga, Bull. Chem. Soc., Japan, 29, 373 (1956).
138. M. Wilk and J. Rochlitz, Ann., 701, 6 (1967).
139. A. Weisstuch and A. C. Testa, J. Phys. Chem., 72, 1982 (1968).
140. E. J. Bowen and J. Sahu, J. Chem. Soc., 3716 (1958).
141. M. Nakamizo, Spectrochim. Acta, 22, 2039 (1966).
142. G. M. Badger, R. S. Pearse, and R. Pettit, J. Chem. Soc., 3199 (1951).
143. N. F. Itchenko, V. V. Dorogov, and N. I. Nizhegorodov, in: Postgraduate Scientific Research, Patrice Lumumba International Friendship University, Department of Physical Mathematics and Natural Sciences [in Russian], No. 11, Moscow (1972), p. 163).
144. E. Sawicki, T. W. Stanley, J. D. Pfaff, and W. C. Elbert, Anal. Chim. Acta, 31, 359 (1964).
145. A. Albert, J. Chem. Soc., 244 (1947).
146. W. Seiffert, V. Zanker, and H. Mantsch, Tetrahedron Lett., 4303 (1968).
147. B. Ya. Silant'ev, G. S. Vedernikov, B. S. Tanaseichuk, and S. G. Bogomolov, Material from the Ural Conference on Spectroscopy [in Russian], Vol. 4, Sverdlovsk (1963), p. 171.
148. B. L. van Duurem, B. M. Goldschmidt, and H. H. Seltman, J. Chem. Soc., B, 814 (1967).
149. A. I. Abramova, L. I. Gribova, A. N. Mezentsev, and M. K. Berestenko, Zh. Prirodn. Soedin., 15, 163 (1971).
150. R. N. Nurmukhametov, I. L. Belaits, D. N. Shigorin, and V. F. Shner, Zh. Fiz. Khim., 41, 3017 (1967).
151. M. V. Kazankov and Yu. M. Vinetskii, Prom. Khim. Reaktivov i Osobo Chistykh Veshchestv, 8, 32 (1967).
152. B. M. Krasovitskii, D. G. Pereyaslova, M. V. Kazankov, Yu. M. Vinetskaya, and G. V. Tatsii, USSR Author's Certificate No. 187193; Byul. Izobr., No. 20 (1966).
153. T. Bluhm, H. H. Perkampus, and J. V. Knop, Ber. Bunsenges. Phys. Chem., 76, 1251 (1972).
154. N. Mataga and S. Tsuno, Bull. Chem. Soc. Japan, 30, 368 (1957).
155. E. C. Lim and J. M. H. Yu, J. Chem. Phys., 47, 3270 (1967).
156. S. B. Visotskaite, É. A. Zhurauskene, R. I. Paeda, L. L. Yasinkas, and A. A. Kundra, Liet Fiz. Rinkinys, Lit. Fiz. Sbornik, 11, 871 (1971); Ref. Zh. Khim., 7B280 (1972).
157. American Cyanamid Co., French Patent No. 1416418 (1965); Ref. Zh. Khim., 14N682 (1967).
158. M. Matsuoka, H. Tani, and T. Kitao, and K. Konishi, Kogyo Kagaku Zasshi, 73, 2195 (1970).
159. N. Mataga and K. Ezumi, Bull. Chem. Soc. Japan, 40, 1350 (1967).
160. V. Struzhka, A. P. Golovina, I. P. Alimarin, and N. B. Zorov, Vestnik MGU, Ser. Khim., 11, 74 (1970).
161. J. B. Ragland and V. J. Kinross-Wright, Anal. Chem., 36, 1356 (1964).
162. Dai-Nippon Toryo Kabushiki Kaisha, Japanese Patent No. 2897 (1962); Ref. Zh. Khim., 18T295 (1963).
163. Switzen Brothers, Inc., US Patent No. 2851423 (1958); Chem. Abstr., 53, 737 (1959).
164. A. N. Miroshkina and G. M. Petrova, Proceedings of the Institute of Applied Geophysics [in Russian], No. 4, Moscow (1967), p. 3.
165. I. S. Ioffe and I. A. Gofman, Zh. Obshch. Khim., 34, 2039 (1964).
166. I. S. Ioffe and M. Z. Zel'manovich, Zh. Obshch. Khim., 32, 1480 (1962).
167. Farbenfabriken Bayer A.-G., British Patent No. 1054144 (1965); J. Appl. Chem., 17, i-187 (1967).
168. T. Maruyama, S. Roshimoto, N. Kuroki, and K. Konishi, Kogyo Kagaku Zasshi, 68, 1919 (1965).
169. T. Sakane, I. Tuda, E. Mihare, and M. Uchida, Kogyo Kagaku Zasshi, 73, 348 (1970).

170. S. Rangaswami and T. R. Seshadri, Proc. Ind. Acad. Sci., 12A, 375 (1940).
171. S. Rangaswami, T. R. Seshadri, and V. Venkateswarlu, Proc. Ind. Acad. Sci., 13A, 316 (1941).
172. V. Balaiah, T. R. Seshadri, and V. Venkateswarlu, Proc. Ind. Acad. Sci., 14A, 68 (1942).
173. C. E. Wheelock, J. Amer. Chem. Soc., 81, 1348 (1959).
174. H. Umemoto, T. Kitao, and K. Konishi, Kogyo Kagaku Zasshi, 73, 1146 (1970).
175. V. G. Tishchenko, USSR Author's Certificate No. 167866 (1965); Ref. Zh. Khim., 11L160 (1960).
176. D. A. Drapkina, V. G. Brudz', B. M. Bolotin, Ya. A. Terskoi, N. I. Doroshina, and O. N. Timoshevskaya, USSR Author's Certificate No. 166703 (1964); Byul. Izobr., No. 23 (1964).
177. V. G. Brudz', B. M. Bolotin, Ya. A. Terskoi, D. A. Drapkina, I. P. Plitina, and O. N. Korol'kova, USSR Author's Certificate No. 167881 (1965); Byull. Izobr., No. 3 (1965).
178. N. A. Borisevich, V. V. Gruzinskii, and V. A. Tolkachev, Optika i Spektroskopiya, 16, 171 (1964).
179. E. N. Viktorova, V. V. Zelinskii, and N. F. Neznaiko, Zh. Fiz. Khim., 40, 94 (1966).
180. A. Kawski and W. Kolakowski, Acta Phys. Pol., 29, 177 (1966); Chem. Abstr., 66, 70435 (1967).
181. D. G. Pereyaslova, É. G. Yushko, and B. M. Krasovitskii, Prom. Khim. Reaktivov i Osobo Chistykh Veshchestv, 8, 68 (1967).
182. Mitsubishi Chemical Industries Co., Ltd. Japanese Patent No. 42506 (1971); Chem. Abstr., 76, 142412 (1972).
183. Mitsubishi Kasei Kogyo Kabushiki Kaisha, Japanese Patent No. 38418 (1971); Ref. Zh. Khim., 12N196 (1972).
184. K. Toshiyasu, Japanese Patent No. 5595 (1971); Ref. Zh. Khim., 20N317 (1971).
185. K. Toshiyasu, Kogyo Kagaku Zasshi, 73, 2667 (1970).
186. Mitsubishi Kasei Kogyo Kabushiki Kaisha, Japanese Patent No. 2666 (1970); Ref. Zh. Khim., 5N286 (1972).
187. General Aniline and Film Corp., Canadian Patent No. 495719 (1954); Ref. Zh. Khim., 35701 (1955).
188. K. Toshiyasu, West German Patent No. 1419350 (1969); Chem. Abstr., 76, 26404 (1972).
189. Mitsubishi Kasei Kogyo Kabushiki Kaisha, Japanese Patent No. 7393 (1971); Ref. Zh. Khim., 12N264 (1971).
190. Mitsubishi Kasei Kogyo Kabushiki Kaisha, Japanese Patent No. 25837 (1963); Ref. Zh. Khim., 12N237 (1966).
191. Mitsubishi Chemical Industries Co., Ltd. US Patent No. 3330834 (1967); Chem. Abstr., 67, 91686 (1967).
192. T. Koyama, Japanese Patent No. 7499 (1965); Ref. Zh. Khim., 6N367 (1968).
193. H. Chiaki and M. Yamashita, Japanese Patent No. 11770 (1964); Chem. Abstr., 62, 6606 (1965).
194. Mitsubishi Kasei Kogyo Kabushiki Kaisha, Japanese Patent No. 3671 (1970); Ref. Zh. Khim., 5N254 (1971).
195. H. Tiaki and M. Yamashita, Japanese Patent No. 5532 (1969); Ref. Zh. Khim., 7S1323 (1970).
196. Research Institute for Production Development, Japanese Patent No. 27127 (1964); Chem. Abstr., 62, 11950 (1965).
197. Nippon Kayaku Co., Ltd., Japanese Patent No. 2672 (1970); Chem. Abstr., 72, 134167 (1970).
198. Nippon Kayaku Kabushiki Kaisha, Japanese Patent No. 7385 (1971); Ref. Zh. Khim., 22N263 (1971).
199. Nippon Kayaku Co., Ltd., Japanese Patent No. 18827 (1971); Chem. Abstr., 77, 7306 (1972).
200. Nippon Kayaku Co., Ltd., Japanese Patent No. 3247 (1969); Chem. Abstr., 72, 33190 (1970).
201. Farbenfabriken Bayer A.-G., Dutch Patent No. 6510292 (1966); Chem. Abstr., 65, 5572 (1966).
202. Dainiti Seika Kogyo Kabushiki Kaisha, Japanese Patent No. 3672 (1970); Ref. Zh. Khim., 4N304 (1971).
203. Dainicheiseika Color and Chemicals Manuf. Co., Ltd., Japanese Patent No. 3669 (1970); Chem. Abstr., 73, 16311 (1970).
204. Nippon Kayaku Kabushiki Kaisha, Japanese Patent No. 18957 (1969); Ref. Zh. Khim., 15S1474 (1970).
205. E. Osawa, O. Kurihara, and T. Nosawa, J. Soc. Dyers Col., 80, 205 (1964).
206. É. G. Yushko, Author's Abstract of Master's Dissertation [in Russian], Moscow (1973).
207. E. N. Viktorova, D. G. Pereyaslova, and É. G. Yushko, Zh. Fiz. Khim., 40, 1783 (1966).
208. Industrial Colors Ltd., British Patent No. 980583 (1965); Chem. Abstr., 62, 8010 (1965).
209. G. V. Tatsii, D. G. Pereyaslova, L. A. Chirva, and É. G. Yushko, in: Scintillators and Organic Luminophores [in Russian], No. 2, Kharkov (1973), p. 75.
210. Badische Anilin und Soda Fabrik A.-G., Belgian Patent No. 654604 (1965); Chem. Abstr., 65, 5570 (1966).
211. B. M. Krasovitskii and É. A. Shevchenko, Zh. Organ. Khim., 1, 2157 (1965).
212. B. M. Krasovitskii, É. G. Yushko, and D. G. Pereyaslova, USSR Author's Certificate No. 196873; Byul. Izobr., No. 12 (1967).

213. É. G. Yushko, D. G. Pereyaslova, and B. M. Krasovitskii, in: Single Crystals, Scintillators, and Organic Luminophores [in Russian], Kharkov, No. 4 (1968), p. 105.
214. D. G. Pereyaslova, É. G. Yushko, and B. M. Krasovitskii, Zh. Organ. Khim., 2, 134 (1966).
215. É. G. Yushko, D. G. Pereyaslova, and V. V. Reznichenko, in: Scintillators and Organic Luminophores [in Russian], Kharkov (1972), p. 47.
216. A. E. Porai-Koshits and I. S. Pavlushenko, Zh. Obshch. Khim., 17, 1739 (1947).
217. Farbwerke Hoechst A.-G., West German Patent No. 1130099 (1962); Ref. Zh. Khim., 3N197 (1964).
218. Farbwerke Hoechst A.-G., West German Patent No. 1138876 (1963); Ref. Zh. Khim., 2N153 (1965).
219. G. Siegle and Co.G. m. b. H., West German Patent No. 1569842 (1971); Ref. Zh. Khim., 8S561 (1972).
220. B. M. Krasovitskii, N. F. Levchenko, and Yu. I. Makarenko, USSR Author's Certificate No. 178821; Byul. Izobr., No. 4 (1966).
221. A. Bistrzycki and J. Risi, Helv. Chim. Acta, 8, 810 (1925).
222. B. M. Krasovitskii, L. Ya. Malkes, A. S. Borovikov, A. V. Karyakin, R. L. Globis, and E. D. Anorova, USSR Author's Certificate No. 196423; Byul. Izobr., No. 11 (1967).
223. L. Ya. Malkes, I. I. Kifer, B. M. Krasovitskii, A. M. Kuznetsov, and A. I. Nazarenko, USSR Author's Certificate No. 327225; Byul. Izobr., No. 5 (1972).
224. N. F. Levchenko, V. M. Solomonov, É. A. Shevchenko, and B. M. Krasovitskii, in: Single Crystals, Scintillators, and Organic Luminophores [in Russian], Kharkov, No. 4 (1968), p. 186.
225. T. I. Khoroshilova, Author's Abstract of Master's Dissertation [in Russian], Kharkov (1971).
226. B. A. Vainshtok, V. V. Generalova, and N. F. Levchenko, in: Radiation Dosimetry and Spectrometry of Ionizing Radiations [in Russian], FAN, Tashkent (1970), p. 178.
227. B. M. Krasovitskii, É. A. Shevchenko, and D. G. Pereyaslova, USSR Author's Certificate No. 176299; Byul. Izobr., No. 22 (1965).
228. B. M. Krasovitskii, É. F. Kravchenko, Yu. E. Gerasimenko, V. V. Reznichenko, and É. A. Shevchenko, USSR Author's Certificate No. 182327; Byul. Izobr., No. 11 (1966).
229. G. F. Slezko, USSR Author's Certificate No. 259892; Byul. Izobr., No. 3 (1970).
230. É. A. Shevchenko and B. M. Krasovitskii, USSR Author's Certificate No. 195008; Byull. Izobr., No. 9 (1967).
231. B. M. Krasovitskii and É. A. Shevchenko, USSR Author's Certificate No. 5 (1966).
232. B. M. Krasovitskii, O. A. Gunder, É. A. Shevchenko, and V. M. Solomonov, USSR Author's Certificate No. 191789; Byull. Izobr., No. 4 (1967).
233. I. D. Belkin, L. I. Voronai, Z. S. Gubareva, B. M. Krasovitskii, A. M. Kuznetsov, D. G. Pereyaslova, V. F. Poduzhailo, V. M. Popov, and G. F. Slezko, USSR Author's Certificate No. 346313; Byull. Izobr., No. 23 (1972).
234. V. L. Plakidin, T. N. Podrezova, S. I. Didenko, and N. A. Pacheva, USSR Author's Certificate No. 287218; Byul. Izobr., No. 35 (1970).
235. L. Sh. Afanasiadi and N. F. Levchenko, Zh. Prirodn. Soedin., 11, 358 (1969).
236. B. M. Krasovitskii, A. M. Kuznetsov, D. G. Pereyaslova, É. A. Shevchenko, V. V. Korshak, G. F. Slezko, V. V. Mikulenko, A. N. Izyneev, and M. M. Seleznev, USSR Author's Certificate No. 292953; Byul. Izobr., No. 5 (1971).
237. A. M. Kuznetsov, B. M. Krasovitskii, É. A. Shevchenko, and G. F. Slezko, USSR Author's Certificate No. 309306; Byul. Izobr., No. 22 (1971).
238. A. M. Kuznetsov, S. A. Petrova, and B. M. Krasovitskii, in: Scintillators and Organic Luminophores [in Russian], Kharkov (1972), p. 74.
239. A. M. Kuznetsov, S. A. Petrova, and L. I. Bogdanova, in: Scintillators and Organic Luminophores [in Russian], Kharkov (1972), p. 86.
240. A. M. Kuznetsov, Author's Abstract of Master's Dissertation [in Russian], Kharkov (1972).
241. S. E. Kovalev, B. M. Krasovitskii, and É. A. Shevchenko, USSR Author's Certificate No. 327226; Byul. Izobr., No. 5 (1972).
242. B. M. Krasovitskii and S. E. Kovalev, in: Scintillators and Organic Luminophores [in Russian], Kharkov (1972), p. 63.
243. S. E. Kovalev, Author's Abstract of Master's Dissertation, Kharkov (1973).
244. A. M. Kuznetsov, B. M. Krasovitskii, G. F. Slezko, and É. A. Shevchenko, USSR Author's Certificate No. 309035; Byul Izobr., No. 22 (1971).
245. S. E. Kovalev and V. M. Shershukov, in: Scintillators and Organic Luminophores [in Russian], Kharkov (1972), p. 69.
246. D. G. Pereyaslova, A. M. Kuznetsov, G. V. Tatsii, and L. A. Chirva, in: Scintillators and Organic Luminophores [in Russian], Kharkov (1973), p. 71.

247. D. G. Pereyaslova, S. E. Kovalev, and D. A. Avyagintseva, in: Scintillators and Organic Luminophores [in Russian], Kharkov (1972), p. 131.
248. General Electric Co., US Patent No. 3658817 (1972); Ref. Zh. Khim., 2N220 (1973).
249. V. K. Matveev and M. I. Skryabinskaya, USSR Author's Certificate No. 118043; Chem. Zentralblatt, 15771 (1962).
250. B. M. Bolotin, D. A. Drapkina, V. G. Brudz', Ya. A. Terskoi, L. S. Kurnosova, and O. N. Timoshevskaya, British Patent No. 1070326 (1967); Chem. Abstr., 68, 59592 (1968).
251. C. M. Orlando, J. G. Wirth, and D. R. Heath, Chem. Commun., 1551 (1971).
252. M. V. Loseva, B. M. Bolotin, G. A. Ivanova, and R. N. Nurmukhametov, Zh. Fiz. Khim., 46, 2195 (1972).
253. R. F. Smith, US Patent No. 3647812 (1972).
254. The National Marking Machine Co., US Patent No. 3162642 (1964); Ref. Zh. Khim., 12S361 (1966).
255. American Cyanamid Co., Dutch Patent No. 6409642 (1966); Chem. Abstr., 65, 2393 (1966).
256. D. V. Shiryaev, T. M. Kosykh, D. A. Drapkina, and B. M. Bolotin, USSR Author's Certificate No. 279333; Byul. Izobr., No. 26 (1970).
257. E. E. Shiryaev, USSR Author's Certificate No. 254695; Byul. Izobr., No. 32 (1969).
258. E. E. Shiryaev, USSR Author's Certificate No. 269170; Byul. Izobr., No. 15 (1970).
259. E. E. Shiryaev, I. D. Maslakov, and V. V. Komissarov, USSR Author's Certificate No. 279070; Byul. Izobr., No. 26 (1970).