

Various types of bifluorophoric heterocyclic compounds are described and a classification of them based on chemical structure is given; the connection between the structure of the bifluorophors and their luminescent properties is discussed.

In 1964, the first publication from our laboratory on the study of the link between the structure and luminescence of organic substances appeared [1]. These investigations were subsequently considerably expanded in the direction of the synthesis of compounds with two structural groupings each of which can, if it contains certain substituents and a sufficiently extensive π -system, lead to the manifestation of luminescent properties.

We call such groupings fluorophors. In the case of an arylethylene the fluorophor is the vinylene group included in the system of conjugated bonds of the aromatic nucleus; for an azomethine it is the $\text{CH}=\text{N}$ group linked with two aromatic radicals, one of which, the "aldehyde" radical, most frequently contains a substituent forming an intramolecular hydrogen bond with the nitrogen of the azomethine group; this may be an azole ring included in an extended π -electronic system together with the vinylene group, aryl or hetaryl substituents, etc.

Today the accumulated experimental material permits the results of the investigations performed to be systematized.

Depending on the nature of the structural fragment connecting the individual fluorophors, bifluorophoric compounds (bifluorophors) can be divided into several groups. Examples of luminophors belonging to each of them that have been obtained in our laboratory are given below. The overwhelming majority of the compounds considered in this review contain a heterocycle in at least one of the fluorophors. In some cases, for comparison, information is given on luminophors of simpler structure that we have also studied or that are known from other literature sources.*

Luminophors Containing Fluorophoric Groupings

In spite of the fact that it is possible to speak only nominally of the individuality of a fluorophor after its inclusion in a conjugated bifluorophoric system, in a number of cases it is possible to trace the influence of each fluorophoric grouping on the spectral-luminescent characteristics of a bifluorophoric molecule and some specific properties that it imparts to the molecule, such as solubility in organic solvents, or, when salt-forming groups are present in the fluorophor, in water, reactivity, etc. We can consider various conjugated bifluorophors in light of these observations.

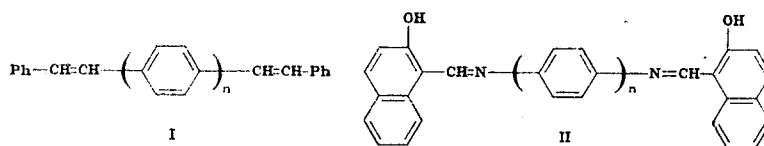
Symmetrical Bifluorophors. In this series of compounds, through the conjugation of two similar structural fluorophoric groupings a considerable longwave shift in absorption and luminescence is observed. The quantum yields of solutions of bifluorophoric compounds are higher than or close to the quantum yields of the individual fluorophors.

Arylethylenes and azomethines may be regarded as model compounds for the investigation of the spectral-luminescent properties of symmetrical bifluorophors. Doubling the trans-

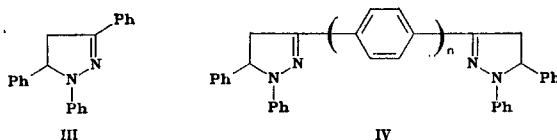
*Methods of synthesizing the bifluorophors are not considered in this review. It is possible to become acquainted with them by making use of the literature cited. In the majority of publications mentioned, the synthesis and spectral-luminescent properties of the luminophors obtained are described.

stilbene molecule leads to trans,trans-4,4'-distyrylbiphenyl (I, n = 2). In organic solvents, the first of these luminophors fluoresces in the violet region with a low quantum yield ($\eta < 0.1$) while the second is a luminophor with an intense blue luminescence (η in toluene 0.6) [2], the difference in the positions of their luminescent maxima in the same solvent amounting to ~70 nm [3].

The passage from 2-hydroxy-1-naphthylmethylenylaniline, having a yellow-green fluorescence (λ_{\max} 435, 505 nm) in dimethylformamide at 77°K, to bis(2-hydroxy-1-naphthylmethylen)benzidine (II, n = 2), fluorescing in the yellow region (520, 550 nm) under the same conditions, is also accompanied by a sharp rise in the intensity of fluorescence [4].



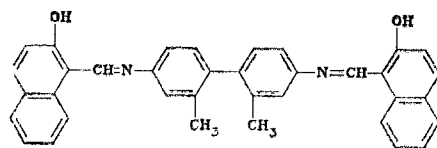
The same change in the position of the electronic spectra on the doubling of a molecule with one fluorophoric group can be well seen from a comparison of the spectral-luminescent properties of 1,3,5-triphenyl-2-pyrazoline (III) and of 4,4'-bis(1,5-diphenyl-2-pyrazolin-3-yl)biphenyl (IV, n = 2). In toluene, the fluorescence maxima of these compounds are at 445 and 465 nm, respectively*; the quantum yields of their solution are close (0.45 and 0.5) [5; 6, pp. 99, 325].



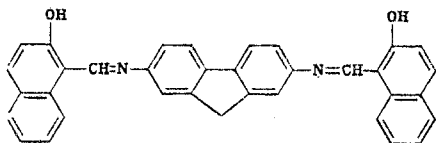
The examples given show the existence of conjugation between the fluorophors. The steric hindrance arising on the introduction into the ortho positions to the biphenyl bond of compound (II, n = 2) of methyl groups (V), weakening this conjugation, causes a substantial short-wave shift in absorption and in fluorescence, and lowers their intensity [7]. At the same time, bisazomethines from 2,7-diaminofluorene — for example (VI) — in which the central part of the molecule is fixed in one plane by a third, five-membered ring, absorb and emit light in the longer-wave region and more intensely than the corresponding benzidine derivatives [8].

The longest-wave coloration and luminescence in the compounds of series (II) and (IV) are possessed by bifluorophors with a common aromatic nucleus (n = 1) in each case. An increase in the number of phenylene groups from one to three leads to a short-wave shift of the electronic spectra. It is known, however, that in the unsubstituted para-polyphenyls each new phenylene group causes bathochromic and bathofluoric effects. In a long chain of conjugation including two fluorophors the polyphenyl chain loses its individuality and its extreme members become component parts of the individual fluorophors, retaining in this case a considerable autonomy in the distribution of electron density. The interaction of the fluorophors must therefore be strongest when there is present between them an aromatic nucleus included in the chains of conjugation of both fluorophors. In more extended aromatic systems (n = 2, 3) the rigidity of the structure of the molecule decreases with an elongation of the chain of the phenylene group and the noncoplanarity of the polyphenyl chain rises. Because of this, the degree of localization of the π -electron clouds in each of the chromophoric systems increases. This leads to a hypsochromic shift of the long-wave band in the absorption that is responsible for luminescence and to a hypsofluoric shift in the luminescence spectrum. Together with an increase in the number of phenylene groups the intensity of absorption approximates more and more to the additive value composed of the intensities of the absorption of the individual chromophoric groups, and it rises with an intensification of the autonomy of each of them [6, p. 98].

*The fluorescence spectrum of compound (IV) contains, together with the main maximum, an inflection on the curve at 485 nm.



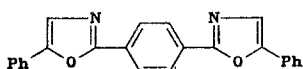
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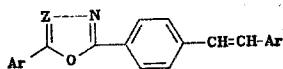
VI

The luminophors of this group also include the widely used scintillation activator (spectrum-mixing agent) 1,4-bis(5-phenyloxazol-2-yl)benzene (VII; POPOP). Its molecule can be considered as consisting of two 2,5-diphenyloxazole (PPO) residues with a common phenylene group. PPO fluoresces in the violet and POPOP in the blue region of the spectrum ($\Delta\lambda_{\max}$ in toluene, 55 nm) [6, p. 324; 9].

Unsymmetrical Bifluorophors. Unsymmetrical bifluorophors possess a great diversity of structures, and among them are found many compounds of practical interest. A feature of this group of luminescing substances is the wide range of colors and shades of fluorescence that can be obtained by different combinations of fluorophoric groupings in the molecules of the bifluorophors.



VII



VIII

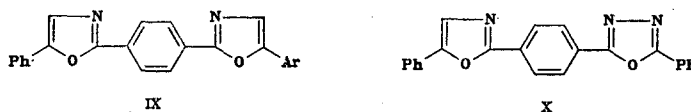
Examples of unsymmetrical bifluorophors are the compounds (VIII, Z = CH or N), which include the fluorophoric groupings of the 2,5-diaryloxazoles or of the 2,5-diaryl-1,3,4-oxadiazoles and those of the 1,2-diarylethylenes with an aromatic nucleus common to both fluorophors [10-12].

The introduction of an aryethylene grouping into the molecule of a diaryl-substituted azole is accompanied in the majority of cases by considerable bathochromic and hyperchromic effects, and the luminescence spectra acquire a well-defined vibrational structure, while the quantum yield increases sharply. Thus, the absorption and luminescence maxima of the simplest compound of type (VIII) containing an oxazole ring — 5-phenyl-2-(4-stilbenyl)oxazole (Ar and Ar' = C₆H₅; Z = CH) — in toluene are shifted by approximately 50 nm in comparison with 2,5-diphenyloxazole, the molar extinct coefficient has doubled, and the absolute quantum yield has risen from 0.51 to 0.88. A further lengthening of the chain of conjugation with an increase in the complication of the structure of the aromatic radicals in the aryethylene part of the molecule does not, in the majority of cases, change the nature of the spectrum but causes a long-wave displacement of the absorption and luminescence maxima by 10-20 nm.

It is interesting that in the series of aryethylene-substituted 2,5-diaryloxazoles, unlike the unsubstituted compounds, the quantum yield depends substantially on the positions of the radicals Ar and Ar' in the molecule. In all cases when the aryethylene moiety of the molecule contains biphenyl or naphthyl radicals and the aryloxazole moiety a phenyl radical the quantum yield is higher than when their positions are reversed. For example, for the compounds in which Ar is 1-naphthyl and Ar' is a phenyl radical it is 0.53 in toluene, while if these radicals change places it rises to 0.73 [11]. This effect is the result of changes in the electron density distribution in diaryloxazole molecules under the influence of aryethylene groupings. According to quantum-chemical calculations, the long-wave band in the absorption spectrum of 5-phenyl-2-(4-stilbenyl)oxazole is the band of the transfer of charge from the phenyloxazole fragments to the stilbene fragment. With a lengthening of the chain of conjugation in the aryethylene grouping the electronic displacements in this direction must be intensified.

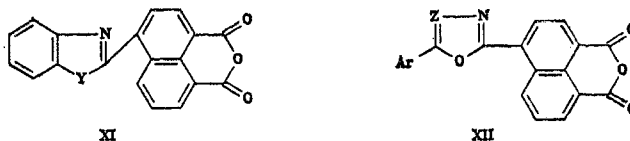
This also explains the different effects of functional substituents according to their positions in the molecules of compounds (VIII). When a p-dimethylamino group is present in the stilbene fragment, the long-wave absorption band can no longer be considered as the result of the transfer of charge through the whole conjugated system, since an oppositely directed electronic displacement from the phenyl radical containing the dimethylamino group to the second aromatic nucleus of the stilbene residue appears. The conjugation in the system decreases and the quantum yield of a toluene solution falls sharply in the case of the oxazole derivative (Z = CH) from 0.88 to 0.14 and for the same compound with an oxadiazole ring (Z = N) from 0.43 to 0.07 [13]. At the same time, if the strongly electron-accepting group SO₂CHF₂ is introduced into the stilbene fragment of the oxazole derivative in place of a dimethylamino group, the quantum yield remains high (0.8), as for the unsubstituted compound [14]. It is interesting that electron-donating substituents in the para position of the aryl radical (Ar) of the phenylazole grouping do not merely not decrease but, in the case of oxadiazole derivatives, even increase the quantum yield.

A disturbance of the symmetry of the POPOP molecule on the introduction of electron-donating substituents into one of the extreme phenyl nuclei — a para-methoxy or a para-dimethylamino group (IX) — leading to a more uniform distribution of the electron density over the whole chain of conjugation, causes a bathofluoric effect ($\Delta\lambda_{\max} = 15-30$ nm) and, in the case of the methoxy-substituted compound, an increase in the quantum yield of a solution in toluene from 0.41 to 0.52. The same effect on the introduction of a methoxy group is observed when the π -system of the aryl radical is lengthened by one phenyl unit. The replacement of one of the oxazole nuclei of POPOP by a 1,3,4-oxadiazole group (X), conversely, is accompanied by a small short-wave shift (~ 10 nm) in the luminescence spectrum with a simultaneous rise in the quantum yield to 0.57 [15].



Compounds in which one of the fluorophors is an arylazole or benzazole grouping and the other a naphthalic anhydride, naphthalimide, or 7H-benzimidazo[1,2-b]benz[de]isoquinolin-7-one residue are used as luminescent dyes for plastics. Without dwelling on a description of a large number of such compounds, we may mention the most characteristic of them.

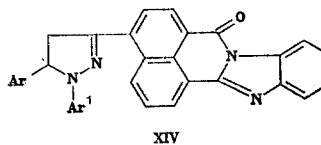
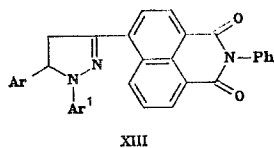
A large group of benzazolyl- and arylazolynaphthalic anhydrides of types (XI) and (XII) containing various substituents in the azole fragments has been synthesized [16-21].



We have already spoken of 2,5-diaryloxazoles as fluorophors. The 2-arylbenzazoles (Y = O, NH, or S) also possess intensive luminescence, but in the shorter-wave region [22]. Effective luminophors containing electron-donating groups in position 4 of the naphthalic anhydride residue that interact through the chain of conjugation with the carbonyl group of the anhydride grouping are also known [23, 24]. If the group concerned is a secondary amino group, the luminophors have a yellow-green luminescence. In the cases that we are considering, the naphthalic anhydride group in, for example, a compound of type (XII) becomes a fluorophor as a consequence of the appearance of an extended π -system — an arylazole grouping — in position 4 of the naphthalic anhydride molecule. Being linked by the chain of conjugation to the CO group, it causes the lowering of the energy of the π , π^* level in the molecule to a value lower than that of the $n\pi^*$ level[†] that is necessary for the appearance

[†]Naphthalic anhydride derivatives contain a reactive grouping which permits luminophors of more complex structure to be obtained from them. Aryloxazylphthalic anhydrides fluorescing with the same intensity but in the shorter-wave region possess an even greater reactivity [25]. When the anhydride ring opens, they change the color of their fluorescence; this property is used for revealing proteins in cytochemical investigations [26].

of fluorescence. These considerations are also applicable to the corresponding naphthalimide derivatives such as, for example, the compounds of type (XIII). The simplest of them (Ar and Ar' = C₆H₅) is known under the name of "lyuminor oranzhevyi 575RT" [27].



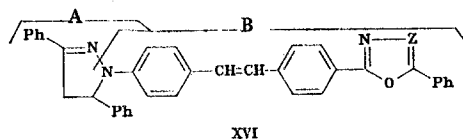
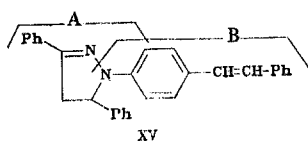
In these compounds, one of the fluorophors is a 1,3,5-triphenyl-2-pyrazoline residue. Thanks to the presence of 2p_z electrons on the N(1) atom of the pyrazoline ring, on the excitation of the molecule the electron density is readily displaced either in the direction of the aryl radical attached to this nitrogen atom or in the direction of the azomethine group and, further, to the aryl radical present in position 3 of the heterocycle. The direction of this displacement depends mainly on the nature of the substituents in the aromatic radicals and, primarily on electron-accepting groups effectively interacting with the unshared electrons of the nitrogen atom [28].

In the molecule of a compound of type (XIII), there is a naphthalimide residue in position 3 of the pyrazoline ring. An imide grouping exhibiting a strong electron-accepting influence has been introduced into its naphthalene nucleus, in which, according to quantum-calculations, the long-wave transition responsible for the fluorophoric properties of the whole structural fragment is largely localized [29]. It interacts through the chain of conjugation with the 2p_z electrons of the nitrogen of the pyrazoline ring, and the electron density is displaced in its direction.

The same electron displacements are characteristic for compounds of types (XIV), but the 7H-benzimidazo[1,2-b]benz[de]isoquinolin-7-one residue in them, which is a stronger electron acceptor than the naphthalimide residue, leads to a deeper coloration and to long-wave fluorescence [30, 31]. One of such luminophors (Ar = p-CH₃OC₆H₄, Ar' = C₆H₅), under the name of "lyuminor krasnyi 2Zh 600RT," like "lyuminor oranzhevyi 575RT," has found use as a luminescent dye for polystyrene and poly(methyl methacrylate) [32]; it is used in the dosimetry of radioactive radiations [33] and for other purposes. The high quantum yield of this compound (~0.9), considerably exceeding the quantum yield of each of the fluorophors present in it, must be mentioned.

In the bifluorophoric molecule (XV), one of the fluorophoric groupings is again a triphenylpyrazoline residue but this is substituted in the phenyl radical directly attached to the nitrogen atom of the heterocycle. When an aryethylene grouping, which possesses an electron-accepting action, is present in the para position to this atom the unshared electrons of the nitrogen atom are displaced in its direction [34, 35]. Compound (XV) fluoresces in the blue-green region (λ_{\max} in toluene 470 nm) with a quantum yield of 0.45. It follows from a comparison of the spectral characteristics with its long-wave absorption band and the same bands of model substances — trans-stilbene and triphenylpyrazoline — that this band is due to a S₀ → S₁^{*} electronic transition in the chromophoric system including both the arylazomethine grouping of the pyrazoline moiety of the molecule (A) and also the stilbene fragment (B). The small influence that increased complication of the structure of the 3-aryl radical in the pyrazoline moiety exerts on the position of the absorption and luminescence maxima shows that it is electronic interaction within fragment B that has decisive value for the spectral-luminescence properties of the compounds.

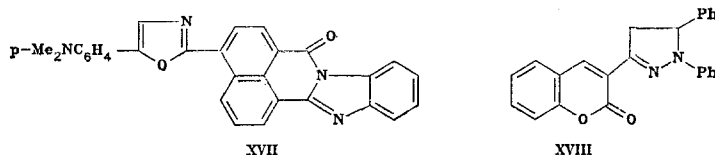
An attempt has been made by modifying the structure of the luminophor (XV) to combine two fluorophoric groupings in the B fragment. With this aim, compounds of type (XVI, Z = CH, N) have been synthesized and investigated [36-38]. An arylazole grouping has been introduced in fragment B in addition to the stilbene grouping.



The fluorescence spectra of toluene solutions of compounds of type (XVI) possess a well-defined vibrational structure and, just like the long-wave bands in their absorption spectra, are shifted bathochromically relative to compound (XV) because of the increase in the

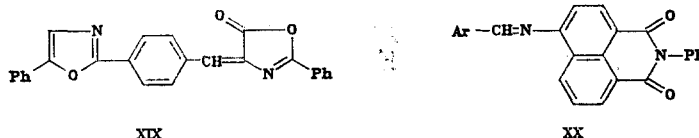
size of the π -electronic system of fragment B with the introduction of the phenylazole grouping. The electronic transition responsible for the fluorescence is localized predominantly in fragment B, although the arylazomethine grouping of the pyrazoline fragment exerts a substantial influence on it because of some displacement in this direction of the unshared pair of electrons of the nitrogen in fragment A. The quantum yield of the compound with the oxazole ring (0.57) is higher than that with the oxadiazole ring (0.47) and that of the luminophor (XV) (0.45).

The combination in a conjugated system of the fluorophoric groupings of 7H-benzimidazo[1,2-b]benz[de]isoquinolin-7-one and of a 2,5-diaryloxazole substituted in the 5-phenyl radical by a para-dimethylamino group enabled luminophor (XVII) with a red fluorescence (λ_{\max} 628 nm) and a quantum yield in toluene close to unity to be obtained [39].



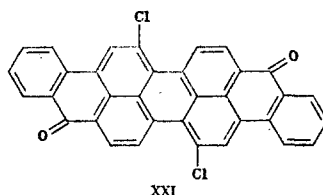
In the molecule of the luminophor (XVIII) the structural groupings of 1,5-diphenyl-2-pyrazoline and of coumarin are combined. The coumarin residue, which possesses an electron-accepting nature, intensifies the polarization of the pyrazoline fragment. A consequence of this is a bathofluoric effect ($\Delta\lambda_{\max} = 130$ nm) as compared with 1,3,5-triphenyl-2-pyrazoline [40].

The majority of luminophors consisting of azlactone derivatives luminesce only in the solid state and in frozen solutions. They include, for example, a luminophor emitting orange-red light - 4-(4-dimethylaminobenzylidene)-2-phenyloxazol-5-one [41, 42]. By replacing the dimethylamino group by a phenyloxazole grouping it is possible to obtain compound (XIX), which emits light in organic solvents at room temperature. In the solid state, this compound has a longer-wave luminescence, apparently reflecting the intensifying action of the two fluorophors [43].

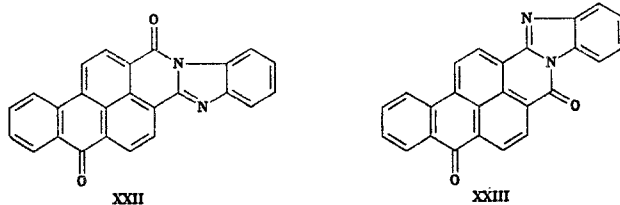


Finally, we must mention the azomethine derivatives of N-phenylnaphthalimide (XX). These compounds, regardless of the structure of the aldehyde component, luminesce not only in the solid state and in frozen solutions, like azomethines of simpler structure, but they also exhibit luminescent properties in solutions at room temperature. This has permitted the conclusion that their luminescence is due to the 4-aminonaphthalic acid phenylimide grouping substituted in the amino group [44]. Nevertheless, by changing the structure of the aldehyde residues it is possible to change the region of luminescence of the luminophors within fairly wide limits (λ_{\max} in dimethylformamide 465-525, and in the solid state 512-605 nm).

Polycondensed bifluorophors are compounds in which both fluorophors participate in the formation of a polycyclic system possessing longer-wave luminescence than each of the fluorophors. As an example of a symmetrical compound of this type we can give the well-known vat dye dichloroisoviolanthrone (XXI), which has been proposed as a luminescent dye for polystyrene [45]. Its molecule includes two 1-chlorobenzanthrone groupings, each of which is substituted in positions 3 and 4 (which are conjugated with the CO group) by a structural grouping with a developed π -electronic system that is responsible for a decrease in the energy of the π , π^* -level that is necessary for the luminescence of carbonyl-containing compounds.



The products of the cyclization of 4- and 5-benzoyl-7H-benzimidazo[1,2-b]benz[de]-isoquinolin-7-one under the conditions of the Friedel-Crafts reaction - (XXII) and (XXIII) - have unsymmetrical structures [46].



Each compound - of which the first is an orange luminophor and the second a yellow-orange one - contains substituted benzanthrone and 7H-benzimidazo[1,2-b]benz[de]isoquinolin-7-one groupings, while the naphthalene fragment may belong to both fluorophoric groupings. In compound (XXII), the benzanthrone fragment is conjugated with the benzimidazole residue in position 4, and in (XXIII) with that in position 3. This determines the dissimilar colors of their fluorescence. Both compounds may also be considered as peri-substituted 7H-benzimidazo[1,2-b]benz[de]isoquinolin-7-ones.

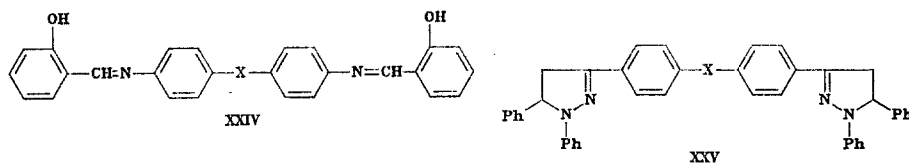
Luminophors with Unconjugated Fluorophoric Groupings

Fluorophors with unconjugated bifluorophoric systems behave completely differently from conjugated bifluorophors. In the majority of cases they retain their individual properties, which are shown in the spectral-luminescent characteristics of the bifluorophors.

Unconjugated bifluorophors have been studied less than the conjugated ones. In spite of this, they are of great scientific and practical interest, since many of them permit an intermolecular transfer of energy to be effected from a structural fragment of the molecule playing the role of donor fluorophor to another structural grouping, not conjugated with the first one, acting as an acceptor of energy and thereby increasing the intensity of its luminescence.

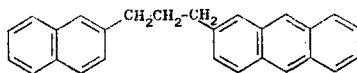
In view of this, luminophors of the greatest interest are those in which the luminescence spectrum of the donor fluorophor is well overlapped by the absorption spectrum of the acceptor fluorophor. In this case, an indispensable condition for the transfer of energy is satisfied, and takes place more effectively than in mixtures of compounds modeling the donor and the acceptor. A particularly large difference between the transfer of energy within the molecule of a bifluorophor and in a mixture of the luminophors is observed in dilute solutions where the probability of close contact of the luminophor molecules composing the mixture is greatly decreased. Luminophors with unconjugated fluorophoric groupings are, in the majority of cases, more soluble than their analogs with conjugated fluorophors.

Symmetrical Bifluorophors with "Isolating" Groups. In their spectral-luminescent properties, bifluorophors with bridge groupings preventing conjugation between the symmetrical parts of the molecule are close to the monofluorophoric compounds. Thus, for example, in the disalicylidene derivatives of 4,4'-diaminodiphenylmethane and of 4,4'-diaminodiphenyl oxide (XXIV, X = CH₂, O), the absorption and luminescent spectra are sharply shifted in the short-wave direction as compared with the bisazomethine derivatives of benzidine in the molecules of which there are no isolating bridges [47].



An analogous picture is observed in the series of dipyrazolines (XXV) with CH₂, CH₂-CH₂ and O bridges preventing conjugation between the nuclei in the biphenyl grouping. These compounds are very similar in their spectral-luminescent properties to triphenylpyrazoline. The intensity of their luminescence in toluene is approximately 1.5 times lower than in the absence of the isolating groups [48].

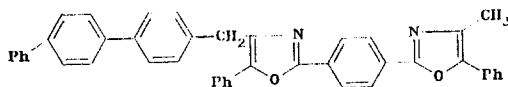
Unsymmetrical Bifluorophors with "Isolating" Bridges. One of the simplest examples of such compounds that can be given is the well-known molecular system (XXVI), consisting of naphthalene and anthracene nuclei separated by methylene groups.



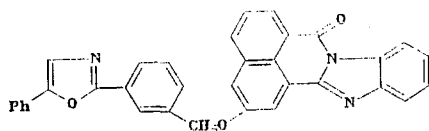
XXVI

In this system a transfer of the energy of electronic excitation is observed. The energy donor is the naphthalene fragment and the acceptor is the anthracene fragment. When the naphthalene group is excited, because of an effective transfer of energy, an intense emission band of the anthracene part of the molecule appears in the fluorescence spectrum [49].

Recently, great attention has been devoted to this group of bifluorophors in connection with the use of dye lasers. Luminophor (XXVII), including para-terphenyl and methyl-substituted POPOP groupings separated by a methylene group has been proposed [50]. The luminescence spectrum of this compound coincides in the position of its maximum with the spectrum of the second fluorophor, but the intensity of fluorescence for the bifluorophor is higher than for the substituted POPOP in a solution of the same concentration.



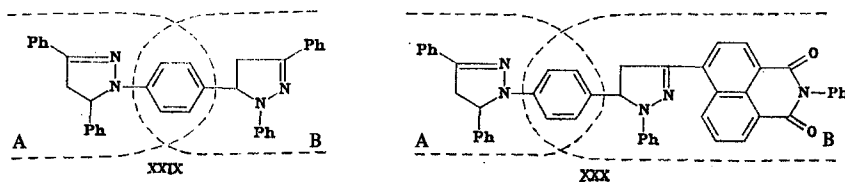
XXVII



XXVIII

A compound giving a yellow-green fluorescence synthesized in our laboratory (XXVIII) [51] contains 2,5-diphenyl-1,3,4-oxadiazole and 7H-benzimidazo[1,2-b]benz[de]isoquinolin-7-one residues. The bridge preventing conjugation between the fluorophors is an oxymethylene group. Characteristic for this luminophor is an effective transfer of the energy of electronic excitation to the fluorophoric grouping of the 7H-benzimidazo[1,2-b]benz[de]isoquinolin-7-one.

An example of a compound in which the "separating" atom is included in one of the fluorophors is the luminophor (XXIX) [52].

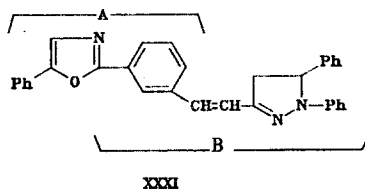


This compound contains two triphenylpyrazoline residues not included in a common chain of conjugation, which is interrupted by a saturated carbon atom of one of the heterocycles (fragment B). Its absorption spectrum shows complete additivity with respect to the spectrum of triphenylpyrazoline: the maxima coincide and the intensity of absorption is twice that for 5-phenylpyrazoline. The luminescence spectra are also close, the positions of their maxima coinciding and the absolute quantum yields of the two compounds being the same.

The same "separating" atom is present in the molecule of the luminophor (XXX) with a more complicated structure. The additional complication as compared with the preceding compound is that fragment B now consists of the conjugated bifluorophor (XIII) already mentioned in a preceding section of this review. In the absorption spectrum of this orange-fluorescing luminophor the bands due to both fluorophors can be well seen. But the luminescence spectra contain only the band corresponding to the luminescence of the fragment with the longer-wave emission. The absence of the short-wave band from the luminescence spectrum

is connected with the intramolecular radiationless transfer of energy in which fragment A is the donor and fragment B the acceptor of energy. This conclusion has been confirmed by an investigation of the spectral-luminescent properties of a mixture of model compounds analogous in structure to fragments A and B [52].

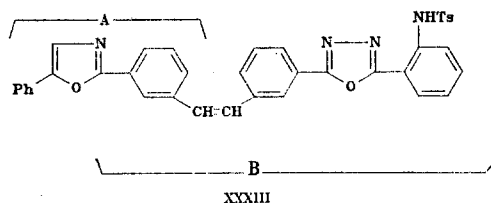
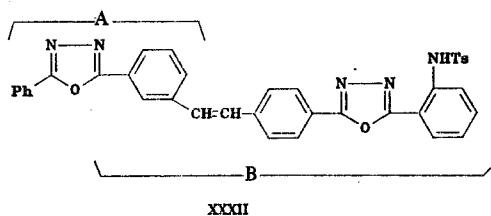
Bifluorophors with Common Aromatic Nuclei. A large number of bifluorophors of this type has been described in the literature [38, 53-55], the structural grouping of 2,5-bi-phenyloxazole having been used as one of the fluorophors in all cases; the second fluorophors were groupings with various structures. Without dwelling in detail on a description of the numerous compounds of this type, we may give as a characteristic example the bifluorophor (XXXI) containing unconjugated 2,5-diphenyloxazole and 1,5-diphenyl-3-styryl-2-pyrazoline groupings with a common aromatic nucleus [53].



In this, as in other cases when unconjugated fluorophors have a common phenylene group, the chain of conjugation is interrupted as a consequence of the meta arrangement of the fluorophoric residues on it. Apparently, in these circumstances an induction interaction between the fluorophors should appear. But the investigations mentioned above showed that the disengagement of the fluorophors in such molecular systems is quite sufficient for an effective transfer of electronic excitation energy from the donor fluorophor to the acceptor fluorophor.

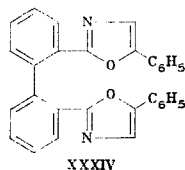
The absorption spectrum of luminophor (XXXI) in toluene and in poly(methyl methacrylate), just like that of luminophors containing bridges completely interrupting conjugation, is additive with respect to the component chromophores A and B but the luminescence spectrum is characteristic for fluorophor B. This indicates an intramolecular transfer of excitation energy from the structural grouping of diphenyloxazole to the diphenylstyrylpyrazoline grouping.

We may mention one more luminophor of a similar type (XXXII) in which an intramolecular radiationless transfer of energy to an acceptor fluorophor (fragment B) has been recorded [56].



In the case of compound (XXXIII), where the vinylene group is not conjugated with either of the azole rings, the absorption maximum of a toluene solution occupies an intermediate position between the maxima of the individual fluorophors. An interesting feature of this luminophor is the large Stokes shift ($\Delta\nu = 9272 \text{ cm}^{-1}$) due to the presence of an intramolecular hydrogen bond between the o-tosylamino group and the oxadiazole ring. The possibility of the formation of such a bond, leading to a considerable increase in the Stokes shift has been shown previously in a comparative study of the luminescence of o- and p-hydroxy-substituted 2,5-diphenyl-1,3,4-oxadiazoles [57]. It is interesting that in the case of compound (XXXII), no anomalous deviation in the magnitude of the Stokes shift was detected [56].

Sterically Hindered Bifluorophors. Another of our papers [58] contains information on another type of bifluorophor in which, in spite of the formal presence of a chain of conjugation between the fluorophors, there is practically no electronic interaction between them. These include compounds (XXXIV) the molecule of which consists of doubled 2,5-diphenyloxazole molecules.

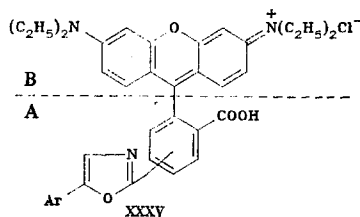


Formally, the aryloxazole groupings in this compound make a single conjugated system with the benzene rings of the biphenyl moiety. However, the introduction of such large substituents may create considerable steric hindrance when the aryloxazole groups are in the trans position with respect to the biphenyl nucleus and even more when they are in the cis position.

In actual fact, a comparison of the absorption spectra of ethanolic solutions of compound (XXXIV) and of 2,5-diphenyloxazole taken in double the concentration showed their analogy; the two solutions had practically identical absorption maxima and similar optical densities. This indicates the absence of conjugation between the diaryloxazole fragments of the bifluorophor and their autonomous behavior and, at the same time, the retention by each of them of the spatial configuration of 2,5-diphenyloxazole. The phenylene groups forming the biphenyl nucleus, being present in mutually perpendicular planes, do not interfere with the arrangement of the aromatic rings and the heterocycle of each of the diphenyloxazole groupings in one plane or in positions close to planar.

In the investigation of luminescence, attention is attracted by an increase of the Stokes shift in compound (XXXIV) as compared with 2,5-diphenyloxazole by $\sim 2400 \text{ cm}^{-1}$. This is possibly connected with some flattening of the bifluorophor molecules on their passage into the excited state. The conjugation then arising between the diphenyloxazole fragments leads to a shift of the luminescence in the long-wave direction and to some increase in its intensity.

Aryloxazolyl-substituted derivatives of Rhodamine C (XXXV) also belong to the spatially hindered bifluorophors, but now they are unsymmetrical ones [59].



The positions of the aryloxazole residues in relation to the carboxy groups in these compounds have not been accurately determined but, in view of the fact that the visible coloration and the fluorescence of the rhodamines are due to the structure of the xanthene part of their molecule, which is in a perpendicular plane with respect to the carboxyphenyl group [60], the isomers should not differ substantially from one another in their spectral-luminescent properties. The diaryloxazole fragment A does not interact appreciably with the remaining part of the molecule B, and the position of the long-wave absorption band responsible for fluorescence does not depend on its structure. Thanks to this, in molecules of type (XXXV) a transfer of excitation energy from fragment A to fragment B is possible. For the molecule with the fluorophor A of simplest structure ($\text{Ar} = \text{C}_6\text{H}_5$), the luminescent spectrum of which does not overlap with the absorption spectrum of fragment B, such transfer is excluded. This effect is achieved by a long-wave shift of the luminescent band of fragment A through the interaction of a p-methoxy group into the phenyl radical or through its replacement by a 2-naphthyl radical.

The possibility of increasing the intensity of fluorescence of Rhodamine C in polycondensation polymers, by dissolving in them binary mixtures of luminophors used to obtain daylight-fluorescing pigments in which a transfer of energy from a donor luminophor to the rhodamine takes place, has been shown in [61]. This gave us [59] the incentive to investigate the luminescent properties of solid solutions of compounds of type (XXXV) and their mixtures with the phenylimide of 4-aminonaphthalic acid (a luminophor with yellow-green fluorescence) in a melamino-toluenesulfonamido-formaldehyde polymer with a polarity close to that of ethanol that is widely used as pigment base. What was in view here was that the long-wave absorption band of the phenylimide is located between the absorption bands of fragments A and B of compounds (XXXV) and the excited singlet state of these compounds can be deactivated by the transfer of excitation energy to the phenylimide molecule before radiationless transfer takes place in the fluorophor A. This may lead to a cascade transfer of energy from the fluorophor A to the phenylimide, and then to the fluorophor B. In actual fact, the intensity of fluorescence of compound (XXXV, Ar = C₆H₅) in such a composition rose by a factor of ~3 in comparison with the luminescence of the individual compound.

The introduction of compounds of the type (XXXV) into a melamino-toluenesulfonamido-formaldehyde polymer permits the production of bright purple daylight-fluorescing pigments and enamel paints from them.

*

We have considered heterocyclic bifluorophors in all their diversity and have given typical examples of the most important of them. The construction of fluorophors, their use in various combinations, the determination of a definite form of the links between them, and, finally, the introduction into their aromatic and heterocyclic nuclei substituents of different electronic natures provide the possibility of varying the visible color and the color and intensity of the fluorescence of the luminophors and their solubility and other physical and chemical properties within wide limits. All this is opening up wide prospects for the directed synthesis of effective organic luminophors among the series of bifluorophoric compounds.

LITERATURE CITED

1. B. M. Krasovitskii, V. B. Smelyakova, and R. N. Nurmukhametov, *Opt. Spektrosk.*, 17, 558 (1964).
2. Yu. M. Vinetskaya, Author's dissertation for Candidate of Chemical Sciences [in Russian], NIOPIK, Moscow (1969).
3. B. M. Krasovitskii, N. I. Mal'tseva, and R. N. Nurmukhametov, *Ukr. Khim. Zh.*, 31, 828 (1965).
4. B. M. Krasovitskii, N. F. Levchenko, N. I. Mal'tseva, A. I. Nazarenko, V. B. Smelyakova, and L. Sh. Afanasiadi, in: *Azomethines* [in Russian], Izd. RGU, Rostov-on-Don (1967), p. 21.
5. E. E. Baroni and K. A. Kovyrzina, *Zh. Obshch. Khim.*, 33, 583 (1963).
6. B. M. Krasovitskii and B. M. Bolotin, *Organic Luminophors* [in Russian], Khimiya, Leningrad (1976).
7. B. M. Krasovitskii and V. B. Smelyakova, *Ukr. Khim. Zh.*, 33, 79 (1967).
8. B. M. Krasovitskii and A. I. Nazarenko, *Ukr. Khim. Zh.*, 31, 942 (1965).
9. L. L. Nagornaya, V. D. Bezuglyi, and N. P. Demchenko, *Opt. Spektrosk.*, 13, 518 (1962).
10. V. I. Grigor'eva and B. M. Krasovitskii, *Khim. Geterotsikl. Soedin.*, No. 4, 761 (1967).
11. B. M. Krasovitskii and V. I. Grigor'eva, *Khim. Geterotsikl. Soedin.*, No. 6, 1127 (1968).
12. V. I. Grigor'eva, R. S. Mil'ner, and B. M. Krasovitskii, in: *Single Crystals, Scintillators, and Organic Luminophors* [in Russian], VNII Monokristallov, Khar'kov, No. 4, (1968), p. 98.
13. B. M. Krasovitskii, V. I. Grigor'eva, L. P. Snagoshchenko, and L. D. Shcherbak, in: *Scintillators and Organic Luminophors* [in Russian], VNII Monokristallov, Khar'kov, No. 2 (1973), p. 56.
14. B. M. Krasovitskii, V. M. Shershukov, V. L. Volkov, and L. Sh. Afanasiadi, *Zh. Org. Khim.*, 19, 2459 (1983).
15. B. M. Krasovitskii, V. L. Volkov, V. M. Shershukov, and S. A. Verezubova, in: *The Physics and Chemistry of Single Crystals and Scintillators* [in Russian], VNII Monokristallov, Khar'kov, No. 7 (1981), p. 134.
16. A. M. Kuznetsov, B. M. Krasovitskii, E. A. Shevchenko, and G. F. Slezko, USSR Inventor's Certificate No. 309,036; published in *Byull. Izobret.*, No. 22 (1971).

17. A. M. Kuznetsov, S. A. Petrova, and B. M. Krasovitskii, in: Scintillators and Organic Luminophors [in Russian], VNII Monokristallov, Khar'kov, No. 1 (1972), p. 74.
18. S. E. Kovalev, B. M. Krasovitskii, and É. A. Shevchenko, USSR Inventor's Certificate No. 327,226; Byull. Izobret., No. 5 (1972).
19. S. E. Kovalev, B. M. Krasovitskii, and V. M. Shershukov, Khim. Geterotsikl. Soedin., No. 10, 1331 (1973).
20. S. E. Kovalev, B. M. Krasovitskii, and N. A. Popova, in: Scintillators and Organic Luminophors [in Russian], VNII Monokristallov, Khar'kov, No. 2 (1973), p. 3.
21. B. M. Krasovitsky [Krasovitskii], E. A. Shevchenko, D. G. Pereyaslova, A. M. Kuznetsov, G. F. Slesko, S. Ye. Kovalev, and E. G. Jushko [E. G. Yushko], J. Luminescence, 8, 44 (1973).
22. V. V. Gruzinskii, V. I. Danilova, T. N. Kopylova, and G. V. Maier, Zh. Prikl. Spektrosk., 33, 931 (1980).
23. É. A. Shevchenko, V. B. Distanov, and L. I. Bogdanova, USSR Inventors' Certificate No. 804,640; Byull. Izobret., No. 6 (1981).
24. B. M. Krasovitskii, É. A. Shevchenko, and V. B. Distanov, Zh. Org. Khim., 19, 1305 (1983).
25. B. M. Krasovitskii and V. M. Shershukov, Khim. Geterotsikl. Soedin., No. 1, 35 (1979).
26. M. N. Meisel', V. E. Barskii, M. P. Podglazova, B. M. Krasovitskii, V. M. Shershukov, and É. G. Yushko, Dokl. Akad. Nauk SSSR, 273, 987 (1983).
27. B. M. Krasovitskii, É. G. Yushko, and D. G. Pereyaslova, USSR Inventor's Certificate No. 196,873; Byull. Izobret., No. 12 (1967).
28. V. D. Orlov, A. I. Roberman, É. I. Rybachenko, and V. F. Lavrushin, Khim. Geterotsikl. Soedin.; No. 11, 1538 (1977).
29. V. V. Ivanov, V. M. Shershukov, V. B. Distanov, and B. M. Krasovitskii, in: Abstracts of Lectures at a Conference on Quantum Chemistry [in Russian], Dnepropetrovsk (1983), p. 39.
30. B. M. Krasovitskii and É. A. Shevchenko, USSR Inventor's Certificate No. 179,324; Byull. Izobret., No. 5 (1966).
31. B. M. Krasovitskii and É. A. Shevchenko, Khim. Geterotsikl. Soedin., No. 5, 756 (1968).
32. N. F. Levchenko, V. M. Solomonov, É. A. Shevchenko, and B. M. Krasovitskii, in: Single Crystals, Scintillators, and Organic Luminophors [in Russian], VNII Monokristallov, Khar'kov, No. 4 (1968), p. 186.
33. British Patent No. 1,392,670.
34. L. A. Kutulya, A. E. Shevchenko, and L. A. Terekhina, in: Scintillators and Organic Luminophors [in Russian], VNII Monokristallov, Khar'kov, No. 4 (1975), p. 54.
35. L. A. Kutulya, A. E. Shevchenko, V. F. Morina, and A. F. Korunova, Zh. Prikl. Spektrosk., 29, 365 (1978); Dep. at VINITI, reg., No. 1619-78. Dep.
36. B. M. Krasovitskii, L. A. Kutulya, A. E. Shevchenko, L. Sh. Afanasiadi, N. P. Egorova, and A. L. Shvorina, Khim. Geterotsikl. Soedin., No. 5, 656 (1977).
37. B. M. Krasovitskii, L. A. Kutulya, L. Sh. Afanasiadi, A. E. Shevchenko, and N. P. Egorova, Zh. Prikl. Spektrosk., 29, 272 (1978).
38. B. M. Krasovitskii, L. D. Pchelina, L. Sh. Afanasiadi, A. E. Shevchenko, and L. A. Kutulya, Izv. Akad. Nauk SSSR, Ser. Fiz., 42, 640 (1978).
39. S. E. Kovalev, B. M. Krasovitskii, N. A. Popova, and V. M. Shershukov, in: Scintillators and Organic Luminophors [in Russian], VNII Monokristallov, Khar'kov, No. 3 (1974), p. 23.
40. É. A. Shevchenko, D. G. Pereyaslova, and E. G. Solomakha, in: Scintillators and Organic Luminophors [in Russian], VNII Monokristallov, Khar'kov, No. 2 (1973), p. 31.
41. V. K. Matveev, USSR Inventor's Certificate No. 112,670; Byull. Izobret., No. 5 (1958).
42. V. K. Matveev, in: Methods of Luminescent Analysis. Proceedings of the VIIIth Conference on Luminescence [in Russian], Izd-vo AN BSSR, Minsk (1960), p. 75.
43. B. M. Krasovitskii, I. V. Lysova, L. Sh. Afanasiadi, M. B. Stryukov, M. I. Knyazhanskii, and Yu. M. Vinetskaya, Zh. Prikl. Spektrosk., 33, 434 (1980).
44. D. G. Pereyaslova, É. G. Yushko, and B. M. Krasovitskii, Zh. Org. Khim., 2, 134 (1966).
45. N. F. Levchenko, G. F. Slezko, and V. M. Solomonov, USSR Inventor's Certificate No. 231,794; Byull. Izobret., No. 36 (1968).
46. L. Sh. Afanasiadi and N. F. Levchenko, Zh. Prikl. Spektrosk., 11, 358 (1969).
47. B. M. Krasovitskii and N. I. Mal'tseva, Zh. Org. Khim., 2, 894 (1966).
48. D. G. Pereyaslova, V. E. Bondarenko, and B. M. Krasovitskii, Khim. Geterotsikl. Soedin., No. 1, 114 (1969).
49. O. Schnepf and M. Levy, J. Am. Chem. Soc., 84, 172 (1962).
50. B. Liphardt and W. Lüttke, Ann. Chem., No. 6, 118 (1981).

51. L. D. Shcherbak and L. Sh. Afanasiadi, in: Scintillators and Organic Luminophors [in Russian], VNII Monokristallov, Khar'kov, No. 4 (1975), p. 16.
52. B. M. Krasovitskii, T. P. Zubanova, and Yu. M. Vinetskaya, Khim. Geterotsikl. Soedin., No. 9, 1248 (1982).
53. V. I. Grigor'eva, L. D. Shcherbak, and B. M. Krasovitskii, in: Scintillators and Organic Luminophors [in Russian], VNII Monokristallov, Khar'kov (1972), p. 100.
54. V. F. Morina, L. D. Shcherbak, V. I. Grigor'eva, and B. M. Krasovitskii, Zh. Prikl. Spektrosk., 21, 653 (1974).
55. B. M. Krasovitskii, L. D. Shcherbak, and V. F. Morina, Izv. Akad. Nauk SSSR, Ser. Fiz., 39, 1851 (1975).
56. B. M. Krasovitskii, I. N. Tur, L. D. Pchelinova, and L. Sh. Afanasiadi, Khim. Geterotsikl. Soedin., No. 9, 1188 (1982).
57. B. M. Krasovitskii, L. M. Kutsyna, L. D. Kornilovskaya, N. F. Levchenko, and N. I. Mal'tseva, Zh. Prikl. Spektrosk., 9, 485 (1968).
58. B. M. Krasovitskii, S. G. Shapiro, and E. G. Yushko, Khim. Geterotsikl. Soedin., No. 2, 184 (1985).
59. B. M. Krasovitskii, V. M. Shershukov, D. G. Pereyashlova, and Yu. M. Vinetskaya, Khim. Geterotsikl. Soedin., No. 8, 1037 (1982).
60. F. P. Schafer, Dye Lasers, Springer, New York (1976).
61. D. G. Pereyaslova, V. E. Bondarenko, and V. T. Skripkina, Ukr. Khim. Zh., 45, 553 (1979).

π -AROMATIC COMPLEXES OF METAL CARBONYLS IN THE
PYRYLIUM SALT SERIES

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UDC 541.49:547.812.5'818'821.3'13.07

By the reaction of lithium derivatives of cyclopentadienylmagnesiumtricarboxyl, cyclopentadienylrhodiumtricarboxyl, and benzenechromiumtricarboxyl with 2,6-disubstituted pyrylium salts the corresponding 4H-pyrans have been synthesized, and the oxidative dehydration of these has given pyrylium cations containing the stated organometallic groups in position 4. It has been shown that the π -complexes obtained readily exchange the oxygen of the pyrylium ring for other heteroatoms with the formation of heterocyclic compounds with metallocarbonyl substituents.

Recently, the investigation of π -complexes of transition metals with heterocyclic compounds has received considerable development [1, 2]. At the same time, π -complexes based on pyrylium salts have been studied less than others and are represented by only individual examples of the formation of ferrocene- and cymantrene-containing derivatives [3-7]. The introduction of organometallic substituents into pyrylium cations, which are distinguished by a diversity of transformations, opens up possibilities for the investigation of the mutual influence of these groupings and for the production of new metal-containing heterocyclic compounds.

In view of this, we have obtained previously unknown pyrylium cations containing in the γ -position π -aromatic ligands coordinated with carbonyls of Mn, Re, and Cr and have studied some of their properties. To synthesize the π -complexes mentioned we used the general method of alkylating γ -unsubstituted pyrylium cations with organometallic compounds leading to substituted 4H-pyrans followed by their dehydrogenation to the corresponding pyrylium salts. Thus the action of cymantrenyllithium on 2,6-disubstituted pyrylium cations gives the 4H-pyrans (I) and (II) in high yield.

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