SYNTHESIS AND STUDY OF ORGANIC LUMINOPHORS CONTAINING ONE OR TWO PYRAZOLINE RINGS

D. G. Pereyaslova, V. E. Bondarenko, and B. M. Krasovitskii

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 1, pp. 114–117, 1969

UDC 547.778.4.07:668.8

A series of new organic luminophors with blue and yellow-green fluorescence containing two 1, 3, 5-triaryl-2-pyrazoline groupings has been obtained and their optical characteristics have been studied. Doubling the molecule of 1, 3, 5-triphenyl-2-pyrazoline causes a considerable bathochromic effect in the absorption and luminescence and sharply increases the intensity of absorption. The introduction of various bridge groupings weakening or interrupting the chain of conjugation between the two pyrazoline rings leads to a displacement of the absorption and luminescence spectra in the shortwave direction and to a lowering of the relative light yield of photoluminesence.

1, 3, 5-T[illegible]yl-2-pyrazoline and a number of its derivatives [illegible]inesce intensively in the crystalline state and in [illegible]n [1]. Many of them have been investigated as [illegible]escing additives for liquid [1–4] and plastic [5] [illegible]illators.

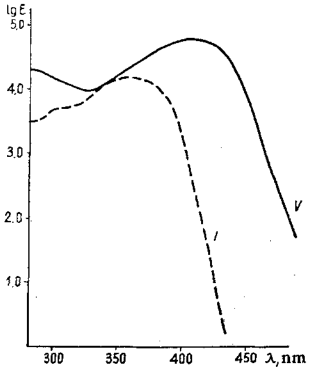
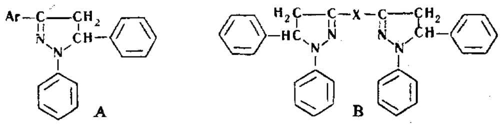


Fig. 1. Absorption spectra of compounds I and V.

We have studied the absorption and luminescence spectra of a number of luminophors of types A and B containing one or two pyrazoline rings in the molecule. The majority of them have not been described previously.



Ar = C_6H_5; C_6H_5—C_6H_4; C_6H_5—C_6H_4—C_6H_4;
X — various bridge groupings

The new pyrazoline derivatives were obtained by condensing the corresponding unsaturated monoketones and diketones with phenylhydrazine in acetic or ethanolic alkali with subsequent cyclization of the arylhydrazones formed.

It is interesting to trace the influence of conjugation in the molecules of the compounds on their absorption and luminescence spectra. The results of the measurements are given in Tables 1–3.

The absorption spectra of all the compounds studied have two well-defined bands differing considerably in their intensities: a less intense shortwave band with a maximum absorption at 290–310 nm and a more intense long-wave band (K band) the position of which varies according to the conjugation existing in the molecules (see Tables 1 and 2).

Lengthening the chain of conjugated double bonds in the aryl radical of compounds I–III leads to a long-wave shift of the maximum and to an increase in the intensity of absorption, while with an increase in the number of aromatic nuclei this effect becomes smaller.

Doubling the molecule of I and passing to V (see Table 2) causes a considerable bathochromic effect and greatly increases the intensity of absorption (Fig. 1).

All the compounds containing two pyrazoline rings included in a single π-electron system (Table 2) absorb and luminesce in a region of longer waves than compounds with one pyrazoline ring (Fig. 2).

In spite of the fact that on passing from IV to VI the chain of conjugation lengthens, absorption shifts in the shortwave direction. This is apparently due to a weakening of the mutual influence of the pyrazoline rings as a consequence both of the increased distance between them and of the noncoplanarity of the bridge groupings connecting them. Similar changes in absorption spectra have been observed previously in a study of diazo dyes [6] and bis(azomethine)s [7] containing the same bridge groupings between two chromophoric systems.

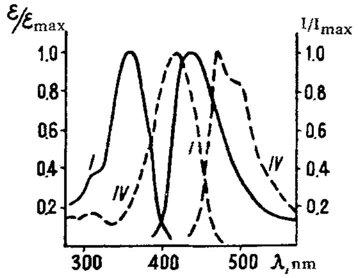


Fig. 2. Absorption and luminescence spectra of compounds I and IV.

Breaking the chain of conjugation between the heterocycles through separation by one or two methylene bridges (Table 3) causes a shift in the absorption maxima to the shortwave region of the spectrum. In the position of their absorption maxima, compounds VII and VIII are close to 1, 3, 5-triphenyl-2-pyrazoline, which shows the almost complete absence of

Table 1

Absorption and Luminescence Spectra of Compounds of Type A

Compound	Ar	UV absorption spectra		Luminescence spectra	
		λ_{max}, nm	$\varepsilon \cdot 10^{-4}$	λ_{max}, nm	Relative luminescence yield
I	C_6H_5—	360	1.62	440	1.0
II	C_6H_5—C_6H_4—(*p*)	380	2.59	454	1.08
III	C_6H_5—C_6H_4—C_6H_4—(*p*)	385	2.99	456	1.20

Table 2

Absorption and Luminescence Spectra of Compounds of Type B

Compound	X	UV absorption spectra		Luminescence spectra	
		λ_{max}, nm	$\varepsilon \cdot 10^{-4}$	λ_{max}, nm	Relative luminescence yield
IV	—C_6H_4—	420	4.34	475, 495	1.00
V	—C_6H_4—C_6H_4—(*p*)	405	6.19	465, 485 (inflection)	1.08
VI	—C_6H_4—C_6H_4—C_6H_4—(*p*)	396	7.18	460, 480 (inflection)	1.09

Table 3

Absorption and Luminescence Spectra of Compounds of Type B with a Disturbance of the Conjugation Between the Pyrazoline Rings

Compound	X	UV absorption spectra		Luminescence spectra	
		λ_{max}, nm	$\varepsilon \cdot 10^{-4}$	λ_{max}, nm	Relative luminescence yield
V	—C_6H_4—C_6H_4—(*p*)	405	6.19	465, 485	1.00
VII	—C_6H_4—CH_2—C_6H_4—(*p*)	368	4.21	442	0.73
VIII	—C_6H_4—CH_2—CH_2—C_6H_4—(*p*)	365	4.11	438	0.79
IX	—C_6H_4—O—C_6H_4—(*p*)	372	4.42	444	0.84
X	—C_6H_4—S—C_6H_4—(*p*)	390	4.70	450	0.78

Table 4

Characteristics of the Compounds Synthesized for the First Time

Compound	Conditions of preparation		Mp, °C	Solvent for crystallization	Empirical formula	N, %		Yield, %
	medium	time of heating, hr				found	calculated	
III	Alkaline	10	266—268	Dimethylformamide	$C_{33}H_{26}N_2$	6.22	6.22	50
VII	„	10	210—212	Ethanol, dimethylformamide	$C_{43}H_{36}N_4$	9.60	9.21	30
VIII	Acid	4	275—276	Chlorobenzene, dimethylformamide	$C_{44}H_{38}N_4$	8.82	9.00	28
IX	Alkaline	12	220—222	Dimethylformamide	$C_{42}H_{34}N_4O$	9.29	9.18	57
X	Acid	4	211—213	Xylene (activated carbon, two crystallizations)	$C_{42}H_{34}N_4S$	8.92	8.94	30

interaction between the two halves of their molecules, but the intensity of the absorption of VII and VIII is somewhat higher than that of I.

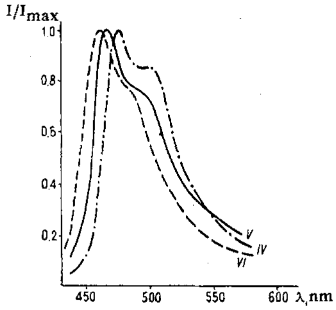


Fig. 3. Luminescence spectra compounds IV–VI.

A comparison of the spectral characteristics of compounds containing bridges of oxygen and sulfur atoms shows that in compounds IX and X the conjugation between the pyrazoline rings is disturbed. At the same time, the displacement of the absorption maximum in the long-wave direction in IX and, to a still greater extent, in X (as compared with VII) shows that the unshared pairs of electrons of the oxygen and sulfur atoms, enhancing the electron-donating nature of the bridges, play a definite role here.

There is a single band in the luminescence spectra of all the compounds apart from IV–VI. In the pyrazolines IV–VI, which contain a continuous chain of conjugated double bonds between the heterocycles, in addition to the main luminescence band, there is a second band, which has a longer wavelength and is less intense (Fig. 3). This is shown most clearly in IV, in the molecule of which interaction between the pyrazoline rings is shown more strongly. As this interaction weakens, the second band becomes less intense, and in the p-terphenyl derivative (VI) only a scarcely detectable inflection in the region of the luminescence maximum remains.

Otherwise, the same features are observed for the luminescence spectra as for the absorption spectra.

EXPERIMENTAL

Preparation of pyrazolines in an alkaline medium. A boiling suspension of 0.007 mole of a monoketone in 100 ml of ethanol was treated with 0.04 mole of phenylhydrazine and 0.4–0.5 g of caustic potash, and the mixture was reheated to the boil. After cooling, the precipitate was filtered off, washed with water until the wash-waters were neutral to litmus, treated with boiling propanol (to remove the excess of phenylhydrazine), dried, recrystallized from suitable organic solvents, and chromatographed in benzene solution on a column of alumina.

Preparation of pyrazolines in an acetic acid medium. A boiling solution of 0.01 mole of an unsaturated diketone in 150 ml of glacial acetic acid was treated with 0.25 mole of phenylhydrazine and the solution was boiled again. The precipitate that deposited when the solution was cooled was filtered off and purified in the same way as in the preparation of the pyrazolines in an alkaline medium. The conditions of obtaining the new substances and their characteristics are given in Table 4.

Absorption and luminescence spectra. The absorption spectra were measured on an SF-4 spectrophotometer in toluene at room temperature and the luminescence spectra, also in toluene, on an apparatus consisting of a ZMR-3 monochromator at the outlet of which, as a radiation receiver, was placed an FEU-18 photomultiplier working through a sensitive M-95 microammeter. The excitation of photoluminescence was performed with an SVDSh-500 lamp from the spectrum of which monochromatic light with a wavelength of 365 nm was isolated.

REFERENCES

1. V. G. Tishchenko, E. T. Verkhovtseva, L. M. Kutsyna, and B. G. Distanov, collection: Scientillators and Scintillation Materials [in Russian], Khar'kov, no. 2, p. 126, 1963.

2. R. Wiley, C. Jarboe, and F. Hayes, J. Org. Chem., 23, 732, 1958.

3. D. Rosahl, Ann. Phys., 12, 35, 1953.

4. USSR patent no. 161827, 1964; Byull. izobr., 8, 1964.

5. L. L. Nagornaya, A. P. Kilimou, B. G. Distanov, and L. M. Podgornaya, PTE, 2, 48, 1960.

6. B. M. Krasovitskii, Dissertation [in Russian], Khar'kov, 1960.

7. B. M. Krasovitskii, N. I. Mal'tseva, and R. N. Nurmukhametov, Ukr. khim. zhurn., 31, 828, 1965.

24 October 1966

All-Union Scientific-Research Institute for Monocrystals, Scintillation Materials, and Particularly Pure Chemical Substances, Khar'kov

Khar'kov State University