PYRYLOCYANINES. 12.* UNSYMMETRICAL PYRYLO-2-CYANINES

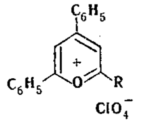
M. A. Kudinova, N. A. Derevyanko,
G. G. Dyadyusha, A. A. Ishchenko,
and A. I. Tolmachev

UDC 547.812.5'813:541.651:668.8

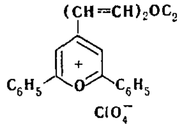
Unsymmetrical 4,6-diphenylpyrylo-2- and 2,6-diphenylpyrylo-4-carbo- and -dicarbocyanines, as well as the analogous pyridocyanines containing 3-ethylbenzothiazolium and 1,3,3-trimethyl-3H-indolium residues, were synthesized. The pyrylo-2-cyanines are more deeply colored than the corresponding 4 isomers, and their absorption bands are distinguished by lower intensities and greater widths. On the basis of data on the increase in the width of the absorption bands of unsymmetrical dyes as the length of their polymethine chain increases it is concluded that the α-pyran system has greater electron-donor character than the γ-pyran system. The regularities observed in the pyridocyanine series are just the opposite of these.

Symmetrical 2,6,2',6'-tetraphenyl-substituted pyrylo-2-cyanines and their sulfur- and nitrogen-containing analogs were described in a previous communication [1]. For a more detailed study of the effect of the structures of pyrylo- and pyridocyanines on their color in the present research we synthesized a number of isomeric unsymmetrical carbo- and dicarbocyanines in which pyrylium or pyridinium residues are connected to the polymethine chain in the 2 or 4 positions (Table 1).

The starting compounds for the synthesis were 2-methyl-4,6-diphenylpyridinium (I) and 2-(4-ethoxy-1,3-butadien-1-yl)-4,6-diphenylpyrylium (II) perchlorates, as well as the isomeric III salt.



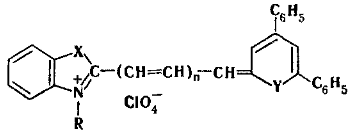
I, II



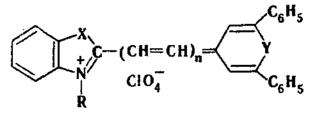
III

I $R = CH_3$; II $R = (CH{=}CH)_2OC_2H_5$

The unsymmetrical (pyrylo-2) (indo)-and (-pyrylo-2) (thia)- trimethylidynecyanines IVa and VIa were obtained by condensation of pyrylium salt I with, respectively, 1,3,3-trimethyl-2-(formylmethylene)indoline and 2-(formylmethylene)-3-ethylbenzothiazoline, while the unsymmetrical pentamethylidynecyanines Va,b and VIIa,b were obtained by the reaction of, respectively, intermediates II and III with 1,2,3,3-tetramethyl-3H-indolium and 2-methyl-3-ethylbenzothiazolium salts. The unsymmetrical pyrylo-4-trimethylidynecyanines IVb and VIb were synthesized as described in [2]. Pyridocarbo- and -dicarbocyanines VIIIa,b-XIa,b were obtained by treatment of dyes IVa,b-VIIa,b with methylamine. Unsymmetrical (pyrylo-2) (pyrylo-4)pentamethylidynecyanine XII was obtained by condensation of 2,6-diphenyl-4-methylpyrylium perchlorate with ethoxybutadienyl derivative II.



IV a – XI a



IV b – XI b

---

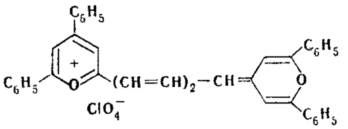
* See [1] for Communication 11.

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 903-908, July, 1980. Original article submitted August 6, 1979, revision submitted February 11, 1980.

0009-3122/80/1607-0696$07.50

TABLE 1. Characteristics of the Long-Wave Absorption Bands of Dyes IVa,b-XIa,b in CH_2Cl_2

Compound	X	Y	R	n	λ_{max}, nm	M^{-1}, nm	D_M, nm	lg ε	f	σ, cm^{-1}	γ_1	γ_2	F
IVa	$C(CH_3)_2$	O	CH_3	1	654, 682	641,1	−8,3	4,71; 4,63	0,76	1450	0,89	1,5	0,031
IVb					595, 632	593,0	2,6	4,87; 4,95	0,85	1253	1,15	2,3	0,048
Va	$C(CH_3)_2$	O	CH_3	2	750, 796	740,2	−5,8	4,97; 4,87	1,18	1280	0,86	1,3	0,030
Vb					685, 740	691,0	11,2	4,97; 5,15	1,29	1238	1,24	2,8	0,065
VIa	S	O	C_2H_5	1	658, 708	636,9	5,5	4,73; 4,53	0,84	1530	0,84	1,3	0,029
VIb					588, 625	586,4	18,7	4,91; 5,00	1,13	1296	1,13	2,1	0,059
VIIa	S	O	C_2H_5	2	748, 815	721,0	21,1	4,91; 4,74	1,14	1540	1,00	1,8	0,042
VIIb					676, 735	670,2	39,7	4,88; 4,97	1,18	1453	1,18	2,3	0,060
VIIIa	$C(CH_3)_2$	NCH_3	CH_3	1	550	538,0	27,3	4,84	0,72	1160	1,17	2,8	0,046
VIIIb					562	552,3	24,7	4,84	0,69	930	1,03	2,0	0,033
IXa	$C(CH_3)_2$	NCH_3	CH_3	2	630	607,3	58,3	4,91	0,93	1290	1,35	3,4	0,058
IXb					646	622,7	60,0	4,81	0,74	1210	1,24	2,7	0,048
Xa	S	NCH_3	C_2H_5	1	575	558,5	16,4	4,98	0,88	1040	1,16	2,7	0,055
Xb					585	572,4	14,1	5,10	0,92	910	1,34	3,8	0,059
XIa	S	NCH_3	C_2H_5	2	660	638,3	35,0	5,06	1,08	1140	1,36	3,4	0,058
XIb					676	654,4	36,0	5,07	1,18	1090	1,48	4,2	0,061



XII

XII λ_{max} 862 nm (lg ε 5.14), M^{-1} = 807.6 nm D_M = −0.4 nm.

The maxima of the long-wave absorption bands of the dyes, the logarithms of the extinctions, the average positions (M^{-1}), the deviations (D_M) determined from the M^{-1} values of the unsymmetrical and corresponding symmetrical dyes,* and the oscillator forces are presented in Table 1. In addition, the characteristics of the forms of the bands, viz., the widths (σ) and the coefficients of asymmetry (γ_1), excess (γ_2), and the fine structure (F), which characterize, respectively, the degree of slope, the degree of peaked character, and the degree of structured character of the bands [3], are also presented. It is apparent from Table 1 that, like dyes with symmetrical structures [1], all of the synthesized unsymmetrical pyrylo-2-cyanines are somewhat more deeply colored than their 4 isomers, while the pyrido-2-cyanines, on the other hand, are somewhat more highly colored. Greater widths, lower intensities, and lower values of the γ_1, γ_2, and F coefficients are observed for the bands of pyrylo-2-cyanines than for the bands of their 4 isomers. A similar regularity is also observed in the absorption of the isomeric (pyrido) (thia)cyanines. On the other hand, in the case of the (pyrido) (indo)cyanines contraction of the absorption bands on passing from the α to the γ isomers is accompanied by a change in the extinctions, oscillator forces, and γ_1, γ_2, and F coefficients in the same direction.

It is known that in polymethine dyes the pyridine rings connected to the chromophore in the 2 and 4 positions have almost identical electron donor character ("basicity") [4]. A similar regularity evidently should also hold for pyran rings. In fact, in the case of dicarbocyanine XII deviations determined from the moments of the absorption bands are virtually absent, although the absorption of the dicarbocyanines is more sensitive to a change in the "basicity" of the heterocyclic residues than in the case of the carbocyanines [5, 6].

It has been shown [2] that the greater the electronic asymmetry of the polymethine dye, the more intense the maxima that correspond to transitions to the vibrational sublevels in its long-wave absorption band. It follows from Fig. 1, in which the absorption spectra of isomeric (pyrylo) (indo)- and (pyrylo) (thia) carbocyanines (IVa, b and VIa, b) are compared, that this regularity is observed both in series of unsymmetrical α-pyrylocyanines and in series of their γ isomers. In fact, since the 2-benzothiazoline ring is a greater electron donor than the indoline ring, dyes VIa and VIb have correspondingly greater electronic asymmetry than IVa and IVb. However, on the basis of the fact that transitions with a change in the vibrational quantum number occur with a higher probability in the molecules of the α isomers (IVa, VIa) than in the molecules of the γ isomers (IVb, VIb), one cannot conclude that the heteroring attached to the polymethine chain in the 2 position has a smaller degree of electron-donor character than the same ring bonded to the 4 position, since the regularity presented above is valid only for structurally monotypic molecules. One could hope to solve this problem by the method of deviations in the case of unsymmetrical pyrylocyanines IVa,b-VIIa,b.

---

*The M^{-1} values of the symmetrical indo- and thiacarbocyanine dyes are 526.0 and 545.1 nm, while the M^{-1} values of the corresponding dicarbocyanines are 629.3 and 644.7 nm.

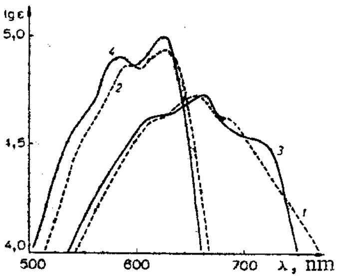


Fig. 1. Absorption spectra in CH_2Cl: (pyrylo-2)(indo)trimethylidynecyanine (IVa); 2) (pyrylo-4)(indo)trimethylidynecyanine (IVb); 3) (pyrylo-2)(thia)trimethylidynecyanine (Via); 4) (pyrylo-4)(thia)trimethylidynecyanine (VIb).

From an analysis of the deviations it may be concluded that the oxygen heteroring in pyrylo-2-cyanines has greater electron-donor character than in pyrylo-4-cyanines. In fact, the D_M values for unsymmetrical pyrylo-2-cyanines IVa-VIIa are smaller than for their 4 isomers VIb-VIIb. In both series of dyes replacement of the indolium residue by a benzothiazolium residue, which leads to an increase in the electronic asymmetry of the dye, and lengthening of the polymethine chain are accompanied, as expected, by an increase in the deviation. Nevertheless, the conclusion drawn above cannot be considered to be a rigorous one. In fact, the deviations for dyes IVa andVa have negative values. The theoretical possibility of the latter was demonstrated in [7]. In the calculation of the deviations the arithmetic mean of the analogous characteristic of the corresponding symmetrical dyes was adopted as the theoretical value of the wavelength of the absorption maximum of the unsymmetrical dye. This estimate is sufficiently accurate only if the absorption maxima of the symmetrical dyes lie in one spectral region. If, however, the absorption maxima differ by hundreds of nanometers, as in the case under consideration, the deviation may reach tens of nanometers. One cannot draw a distinct conclusion regarding the electron-donor character of the pyridine ring attached to the chromophore in the 2 or 4 positions on the basis of the deviations of the unsymmetrical pyridocyanines. In fact, whereas the deviations for (pyrido-2)carbocyanines VIIa and Xa are greater than for their 4 isomers VIIIb and Xb, there are virtually no deviations in the case of the isomeric pyridodicarbocyanines IXa and XIa and IXb and XIb.

In [6] it was shown that the greater the deviation in the "basicities" of the terminal heterocyclic groups, the smaller the vinylene shift. However, these characteristics differ little from one another (only 1-2 nm) for the examined series of unsymmetrical dyes.

We were able to draw more reliable conclusions regarding the basicities of the terminal heterocyclic residues in isomeric dyes on the basis of data on the change in the width of the bands (σ) as the length of the polymethine chain increases. As demonstrated in [6], the σ values for dyes with symmetrical structures or slightly asymmetrical structures should decrease as the length of the polymethine chain increases, whereas, on the other hand, they should increase for markedly asymmetrical structures. It is apparent from Table 1 that a 170 cm^{-1} contraction of the band is observed in the (pyrido-2)(indo)cyanine series IVa and Va as the length of the polymethine chain increases, whereas the contraction is only 15 cm^{-1} in the series of their 4 isomers IVb and Vb. This regularity confirms the higher "basicities" in dyes of the α-pyran system as compared with the γ-pyran system. In the (pyrylo)(thia) cyanine series, as a consequence of the increase in the electronic asymmetry of these dyes as compared with (pyrylo)(indo)cyanines, on passing from carbo- to dicarbocyanines one does not observe a contraction but rather broadening of the bands; in accordance with the higher basicity of the α-pyran system, this broadening is less pronounced (10 cm^{-1}) in the α series than in the γ series (157 cm^{-1}).

In contrast to the pyrylocyanines, significant broadening of the bands as the length of the polymethine chain increases is observed for all of the unsymmetrical pyridocyanines. This broadening is greater, on the one hand, for (pyrido)(indo)cyanines than for the corresponding (pyrido)(thia)cyanines because of the higher "basicities" in the examined dyes, and on the other hand, it is greater for dyes of the α series than for the corresponding dyes of the γ series. The latter indicates the lower "basicity" of the pyridine ring in pyrido-2-cyanines as compared with pyrido-4-cyanines.

The conclusion regarding the relative electron-donor character of the α and γ derivatives that was

TABLE 2. Characteristics of Dyes IV-XII

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		Cl	N	S		Cl	N	S	
IVa	188^{b}	6,6	—	—	$C_{31}H_{28}ClNO_5$	6,7	—	—	84
Va	172^{c}	6,3	—	—	$C_{33}H_{30}ClNO_5$	6,4	—	—	56
Vb	142^{d}	6,2	—	—	$C_{33}H_{30}ClNO_5$	6,4	—	—	56
VIa	$188—189^{b}$	6,6		5,7	$C_{29}H_{24}ClNO_5S$	6,6	—	6,0	38
VIIa	179^{c}	6.2		5,6	$C_{31}H_{26}ClNO_5S$	6,3	—	5,7	78
VIIb	$137—138^{e}$	6.2		5,5	$C_{31}H_{26}ClNO_5S$	6,3	—	5,7	57
VIIIa	$136—138^{f}$	6,5	5,2	—	$C_{32}H_{31}ClN_2O_4$	6,5	5,2	—	71
VIIIb	236^{f}	6,4	5,2	—	$C_{32}H_{31}ClN_2O_4$	6,5	5,2	—	61
IXa	198^{b}	5,9	4,7	—	$C_{34}H_{33}ClN_2O_4$	6,2	4,9	—	56
IXb	$208—209^{f}$	6,1	5,0	—	$C_{34}H_{33}ClN_2O_4$	6,2	4,9	—	71
Xa	225^{g}	—	5,1	5,6	$C_{30}H_{27}ClN_2O_4S$	—	5,1	5,9	15
Xb	146^{f}	6,6	5,2	5.7	$C_{30}H_{27}ClN_2O_4S$	6,5	5,1	5,9	72
XIa	$203—204^{h}$	5.9	4,7	—	$C_{32}H_{29}ClN_2O_4S$	6,2	4,9	—	67
XIb	$196—197^{f}$	6,2	—	5,5	$C_{32}H_{29}ClN_2O_4S$	6,2	—	5,6	74
XII	210^{c}	5,7	—	—	$C_{39}H_{23}ClO_6$	5.7	—	—	63

---

[a] The compositions of dyes IVa and Va,b were also confirmed by determination of the C and H content. [b] From ethanol. [c] From acetic anhydride. [d] From acetonitrile. [e] From a mixture of acetonitrile with 20% $HClO_4$. [f] From a mixture of ethanol with methylamines. [g] From a mixture of methanol with methylamine. [h] From a mixture of acetonitrile with alcohol (1: 1).

drawn on the basis of the spectral data is in agreement with the theoretical evaluation of this character starting from the calculated (by the Hückel MO method) energies of the upper filled and lower vacant orbitals [8] of the isomeric symmetrical dyes. Thus the theoretical electron-donor character expressed in degrees was 54.7 and 53.2° for pyrylo-2- and pyrylo-4-carbocyanines and 62.3 and 62.4° for pyrido-2- and pyrido-4-carbocyanines. Although the numerical values obtained differ little for the α and γ derivatives, they should accurately reflect qualitatively the regularities in the change in the electron-donor character, since the calculation for the isomeric dyes was made with the same set of parameters.

EXPERIMENTAL

The moments of the absorption bands were determined as in [1] on the basis of the absorption spectra recorded with an SF-4A spectrophotometer. The error in the measurement of the absorption spectra of solutions of dyes IVb-XIb was no less than two orders of magnitude (in intensity), as compared with no less than 1.5 orders of magnitude in the case of IVa-XIa. The numerical values in Table 1 are presented with an accuracy that corresponds to the error in the measurements of the absorption spectra of the dyes. The quantum-chemical calculations of the electron-donor character were made from an "ÉLA" program with the following set of coulombic (α) and resonance (β) integrals: $\alpha_O = \alpha_C + 2.4\beta$; $\alpha_N = \alpha_C + 1.1\beta$; $\beta_{CC} = \beta$; $\beta_{CO} = 1.05\beta$; $\beta_{CN} = 0.83\beta$; $\beta_{C\text{-}Ph} = 0.5\beta$ for the C_2–Ph and C_4–Ph bonds of the pyridine ring, while $\beta_{C\text{-}Ph} = 0.8\beta$ in the remaining cases. The purity of the preparations was monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates (elution with acetonitrile).

1,3,3-Trimethyl-2-[3-(4,6-diphenyl-2-pyranylidene)prop-1-en-1-yl]-3H-indolium Perchlorate (IVa). This compound was obtained from 0.173 g (0.5 mmole) of salt I and 0.105 g (0.5 mmole) of 1,3,3-trimethyl-2-formylmethyleneindoline by heating in 3 ml of a mixture of acetic acid and acetic anhydride (1: 1) at 100°C for 30 min (Table 2).

1,3,3-Trimethyl-2-[5-(4,6-diphenyl-2-pyranylidene)penta-1,3-dien-1-yl]-3H-indolium Perchlorate (Va). A mixture of 0.214 g (0.5 mmole) of salt II and 0.137 g (0.5 mmole) of 1,2,3,3-tetramethyl-3H-indolium perchlorate in 3 ml of acetic anhydride containing one drop of pyridine was refluxed for 5 min, after which the dye was precipitated from the reaction mixture with an aqueous solution of sodium perchlorate and was purified by reprecipitation from a mixture of acetonitrile with alcohol (1:) by the addition of an aqueous solution of sodium perchlorate.

1,3,3-Trimethyl-2-[5-(2,6-diphenyl-4-pyranylidene)penta-1,3-dien-1-yl]-3H-indolium Perchlorate (Vb). This compound was obtained from perchlorates III and 1,2,3,3-tetramethyl-3H-indolium perchlorate under conditions similar to those in the preparation of Va and was purified by chromatography in acetonitrile on aluminum oxide.

2-[3-(4,6-Diphenyl-2-pyranylidene)prop-1-en-1-yl]-3-ethylbenzothiazolium Perchlorate (VIa). This compound was obtained by heating 0.173 g (0.5 mmole) of salt I and 0.102 g (0.5 mmole) of 2-(formylmethylene)-3-ethylbenzothiazoline in 3 ml of acetic anhydride at 90-100°C for 30 min.

2-[5-(4,6-Diphenyl-2-pyranylidene)penta-1,3-dien-1-yl]-3-ethylbenzothiazolium Perchlorate (VIIa). This compound was obtained from perchlorate II and 2-methyl-3-ethylbenzothiazolium perchlorate under conditions similar to those in the preparation of Va.

2-[5-(2,6-Diphenyl-4-pyranylidene)penta-1,3-dien-1-yl]-3-ethylbenzothiazolium Perchlorate (VIIb). This compound was obtained from perchlorate III and 2-methyl-3-ethylbenzothiazolium perchlorate under similar conditions and was purified by chromatography in acetonitrile on aluminum oxide.

1-Methyl-2-[3-(1,3,3-trimethyl-2-indolinylidene)prop-1-en-1-yl]-4,6-diphenylpyridinium Perchlorate (VIIIa). A mixture of 0.4 g (0.75 mmole) of pyrylotrimethylidynecyanine IVa and 0.5 ml (1 mmole) of a 7.5% methanol solution of methylamine in 5 ml of acetonitrile was maintained at room temperature for 30 min, after which the dye was precipitated from the reaction mixture by the addition of a saturated aqueous solution of sodium perchlorate.

1-Methyl-2,6-diphenyl-4-[3-(1,3,3-trimethyl-2-indolinylidene)prop-1-en-1-yl]pyridinium Perchlorate (VIIIb). This compound was obtained by refluxing a solution of 0.265 g (0.5 mmole- of pyrylotrimethylidynecyanine IVb in 2 ml (5 mmole) of a 7.5% methanol solution of methylamine for 5 min. The precipitated dye was removed by filtration and washed on the filter with a drop of alcohol and ether.

1-Methyl-2-[5-(1,3,3-trimethyl-2-indolinylidene)penta-1,3-dien-1-yl]-4,6-diphenylpyridinium Perchlorate (IXa). This compound was obtained from pyrylopentamethylidynecyanine Va under conditions similar to those in the preparation of Va and was purified by chromatography on aluminum oxide in acetonitrile.

1-Methyl-2,6-diphenyl-4-]5-(1,3,-trimethyl-2-indolinylidene)penta-1,3-dien-1-yl]pyridinium Perchlorate (IXb). A suspension of 0.205 g (0.37 mmole) of pyrylocyanine Vb in 2 ml of acetonitrile and 1 ml (2.5 mmole) of a 7.5% methanol solution of methylamine was refluxed for 5 min. The dye was precipitated with an aqueous solution of sodium perchlorate, washed on the filter with alcohol and ether, and reprecipitated from acetonitrile by the addition of water.

1-Methyl-2-[3-ethyl-2-benzothiazolinylidene)prop-1-en-1-yl]-4,6-diphenylpyridinium Perchlorate (Xa). A 0.5-ml (1 mmole) sample of a 7.5% methanol solution of methylamine was added to 0.1 g (0.19 mmole) of pyrylotrimethylidynecyanine VIa in 4 ml of methanol, and the mixture was heated to the boiling point and allowed to stand at room temperature for 12 h. The precipitated dye was removed by filtration.

1-Methyl-2,6-diphenyl-4-[3-(3-ethyl-2-benzothiazolinylidene)prop-1-en-1-yl]pyridinium Perchlorate (Xb). A mixture of 0.27 g (0.5 mmole) of pyrylotrimethylidynecyanine VIb in 4 ml of dimethylformamide (DMF) containing 1 ml (2.5 mmole) of a 7.5% methanol solution of methylamine was heated at 50-60°C for 1 h, after which the dye was precipitated from DMF by the addition of an aqueous solution of sodium perchlorate.

1-Methyl-2-[5-(3-ethyl-2-benzothiazolinylidene)penta-1,3-dien-1-yl]-4,6-diphenylpyridinium Perchlorate (XIa). This compound was obtained from pyrylopentamethylidenecyanine VIIa under conditions similar to those in the preparation of VIIIa.

1-Methyl-2,6-diphenyl-4-[5-(3-ethyl-2-benzothiazolinylidene)penta-1,3-dien-1-yl]pyridinium Perchlorate (XIb). A mixture of 0.12 g (0.21 mmole) of pyrylopentamethylidynecyanine VIIb, 2 ml of acetonitrile, and 1 ml (2.5 mmole) of a 7.5% methanol solution of methylamine was refluxed for 5 min, after which the pyridocyanine was isolated from the hot solution in the form of golden crystals.

2-[5-(2,6-Diphenyl-4-pyranylidene)penta-1,3-dien-1-yl]-4,6-diphenylpyrylium Perchlorate (XII). A mixture of 0.107 g (0.25 mmole) sample of the perchlorate of the ethoxybutadienyl derivative (II) and 0.087 g (0.25 mmole) of 2,6-diphenyl-4-methylpyrylium perchlorate in 3 ml of acetic anhydride was refluxed in the presence of 0.1 ml of pyridine for 5 min, after which the dye was isolated in the form of bronze crystals.

LITERATURE CITED

1. M. A. Kudinova, N. A. Derevyanko, G. G. Dyadyusha, A. A. Ischenko, and A. I. Tolmachev, Khim. Geterotsikl. Soedin., No. 7, 898 (1980).
2. A. I. Tolmachev, M. A. Kudinova, and N. A. Derevyanko, Khim. Geterotsikl. Soedin., No. 1, 53 (1974).
3. G. G. Dyadyusha and A. A. Ischenko, Zh. Prikl. Spektrosk., 30, 1037 (1979).
4. L. Brooker, Rev. Modern. Phys., 14, 275 (1942).
5. A. I. Tolmachev, N. A. Derevyanko, E. F. Karaban, and M. A. Kudinova, Khim. Geterotsikl. Soedin., No. 5, 612 (1975).
6. G. G. Dyadyusha, A. A. Ischenko, N. A. Derevyanko, E. F. Karaban, and A. I. Tolmachev, Ukr. Khim. Zh., 46, No. 11 (1980, in press).
7. G. G. Dyadyusha, Ukr. Khim. Zh., 31, 1293 (1965).
8. G. G. Dyadyusha and A. D. Kachkovskii, Ukr. Khim. Zh., 44, 948 (1978).
9. Yu. A. Kruglyak, V. S. Kvakush, G. G. Dyadyusha, and V. I. Khil'chenko, Methods of Calculations in Quantum Chemistry [in Russian], Naukova Dumka, Kiev (1967).

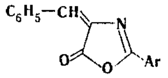
SYNTHESIS AND SPECTRAL-LUMINESCENCE PROPERTIES OF 2-ARYL-4-BENZYLIDENE-5-OXAZOLONES

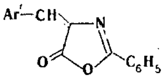
B. M. Krasovitskii, I. V. Lysova,
and L. Sh. Afanasiadi

UDC 547.787.2.07:535.37:542.953

A number of 2-aryl-4-benzylidene-5-oxazolones was obtained by condensation of benzaldehyde with N-acylglycines. The absorption and fluorescence spectra in chloroform at 77°K were measured. The spectral characteristics of the investigated and previously synthesized 2-phenyl-4-arylidene-5-oxazolones are compared.

In connection with the search for organic luminophores among 5-oxazolone derivatives we synthesized 2-aryl-4-benzylidene-5-oxazolones (I), traced the dependence of the change in their spectral-luminescence properties on the structure of the 2-aryl group, and compared these properties with the properties of 2-phenyl-4-arylidene-5-oxazolones (II) [1].


I a-h


II a-g

$ArCONHCH_2COOH$

III a-f

I a $Ar = C_6H_5$, b $Ar = 4\text{-}CH_3OC_6H_4$, c $Ar = 4\text{-}(CH_3)_2NC_6H_4$, d $Ar = 4\text{-}O_2NC_6H_4$, e $Ar = 4\text{-}CHF_2SO_2C_6H_4$, f $Ar = 4\text{-}C_6H_5C_6H_4$, g $Ar = 1\text{-}C_{10}H_7$, h $Ar = C_6H_5CH{=}CH$; II a $Ar' = 4\text{-}CH_3OC_6H_4$, b $Ar' = 4\text{-}(CH_3)_2NC_6H_4$, c $Ar' = 4\text{-}O_2NC_6H_4$, d $Ar' = 4\text{-}CHF_2SO_2C_6H_4$, e $Ar' = 4\text{-}C_6H_5C_6H_4$, f $Ar' = 1\text{-}C_{10}H_7$, g $Ar' = C_6H_5CH{=}CH$; III a $Ar = 4\text{-}CH_3OC_6H_4$, b $Ar = 4\text{-}(CH_3)_2NC_6H_4$, c $Ar = 4\text{-}CHF_2SO_2C_6H_4$, d $Ar = 4\text{-}C_6H_5C_6H_4$, e $Ar = 1\text{-}C_{10}H_7$, f $Ar = C_6H_5CH{=}CH$

All of the investigated compounds were obtained in the form of trans isomers [2] by condensation of aromatic aldehydes with substituted hippuric acids (III- in acetic anhydride in the presence of anhydrous sodium acetate.

Compounds III were synthesized by acylation of hippuric acid with the chlorides of the corresponding aromatic acids. In those cases in which the acid chlorides were liquid substances, the acylation was carried out in an aqueous alkali medium at room temperature by the method in [3]. In the case of solid acid chlorides substituted hippuric acids were synthesized by two methods, viz., in glacial acetic acid at 50-60°C (method A)

All-Union Scientific-Research Institute of Single Crystals, Scintillation Materials, and Ultrapure Chemical Substances, Kharkov 310059. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 909-911, July, 1980. Original article submitted September 19, 1979.