1630, 1610, 1600, 1140 cm^{-1}. PMR spectrum: 3.80 (s, 30CH$_3$), 3.82 (s, OCH$_3$), 5.05 (s, 2H), 6.15 (s, 1H), 6.62-7.17 ppm (m, 5H, arom.). The isochromene III obtained was unstable during chromatography with a column (Al$_2$O$_3$, CHCl$_3$, SiO$_2$, CHCl$_3$), and a large part of it underwent resinification during fusion under the conditions used to obtain keto acid VII.

LITERATURE CITED

1. I. V. Shcherbakova, S. V. Verin, and E. V. Kuznetsov, Khim. Prir. Soedin., No. 1, 75 (1989).
2. Yu. A. Zhdanov, S. V. Verin, I. V. Korobka, and E. V. Kuznetsov, Khim. Geterotsikl. Soedin., No. 9, 1185 (1988).
3. E. V. Kuznetsov, D. V. Pruchkin, A. I. Pyshchev, and G. N. Dorofeenko, Khim. Geterotsikl. Soedin., No. 10, 1320 (1978).
4. V. M. Vlasov, Zh. Vses. Khim. Obshch., 15, 708 (1978).
5. A. T. Balaban, Tetrahedron Lett., 599 (1978).
6. M. G. Farooq, W. Rahman, and M. Ilyas, Chem. Ber., 92, 2555 (1959).
7. J. W. Bunting, Adv. Heterocycl. Chem., 25, 1 (1979).
8. L. Jurd, Tetrahedron, 28, 493 (1972).
9. T. Omoto, J. Pharm. Soc. Jn., 80, 137 (1960).
10. J. M. Hornback, J. Org. Chem., 45, 3524 (1980).
11. G. N. Dorofeenko, G. P. Safaryan, and E. V. Kuznetsov, Khim. Geterotsikl. Soedin., No. 8, 1013 (1970).

SYNTHESIS AND SPECTRAL-LUMINESCENCE PROPERTIES OF 2,7-DIAMINO-BENZOPYRYLIUM TETRAFLUOROBORATES

M. A. Kirpichëok, S. K. Gorozhankin,
D. S. Yufit, Yu. T. Struchkov, P. B. Kurapov,
and I. I. Grandberg

Stable 2,7-diaminobenzopyrylium tetrafluoroborates were obtained by the successive treatment of 7-diethylaminocoumarin, 4-methyl-7-diethylaminocoumarin, and 9-methyl-1H,5H-quinolizino[9,9a,1-gh]coumarin with triethyloxonium tetrafluoroborate and amines, viz., diethylamine, piperidine, morpholine, benzylamine, and aniline. The spectral-luminescence characteristics of the synthesized compounds were investigated. The data from the ^{13}C NMR spectra and x-ray diffraction analysis confirm the greater participation of the 2-amino group as compared with the 7-amino group in stabilization of the positive charge of the pyrylium system.

In [1] we demonstrated that the successive treatment of 7-dialkylaminocoumarins with triethyloxonium tetrafluoroborate and C nucleophiles — sodium derivatives of compounds that have an active methylene group — leads to the synthesis of substituted 2-alkylidene-7-dialkylaminobenzopyrans; the reactions proceed through a step involving the formation of unstable 2-ethoxybenzopyrylium salts.

In the present research we studied the reactions of a number of 7-dialkylaminocoumarins — 7-diethylaminocoumarin (I), 4-methyl-7-diethylaminocoumarin (II), and 9-methyl-1H,5H-quinolizino[9,9a,1-gh]coumarin (III) — with triethyloxonium tetrafluoroborate and N-nucleophilic reagents — primary and secondary amines (diethylamine, piperidine, morpholine, benzylamine, and aniline). 2,7-Diaminobenzopyrylium tetrafluoroborates are formed as a result of these reactions. The interest in benzopyrylium salts was due to their potential luminescence properties [2, p. 335]. In addition, it seemed of interest to ascertain the electron and geometrical structures of aminobenzopyrylium salts, including the question of the delocalization of the positive charge in the molecules.

The synthesis of 2,7-diaminobenzopyrylium salts IV-XII* (Table 1) was carried out via the scheme
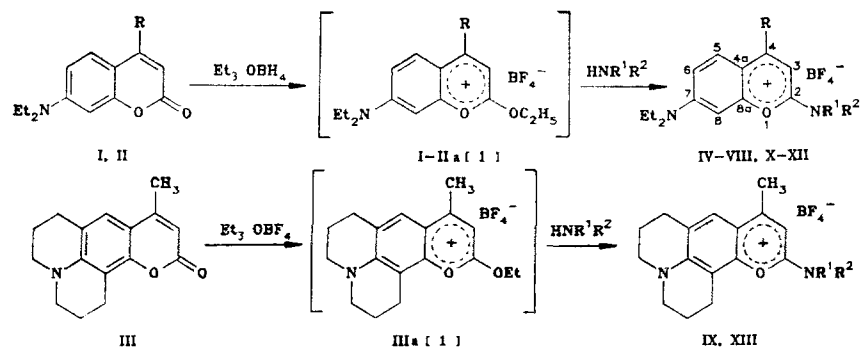
I R=H; II R=CH₃; IV R=CH₃, R¹=R²=C₂H₅; V R=H, R¹R²=—(CH₂)₅—; VI R=CH₃, R¹R²=—(CH₂)₅—; VII R=H, R¹R²=—(CH₂)₂O(CH₂)₂—; VIII R=CH₃, R¹R²= =—(CH₂)₂O(CH₂)₂; IX R=CH₃, R¹R²=—(CH₂)₅—; X R=CH₃, R¹=H, R²=CH₂C₆H₅; XI R=R¹=H, R²=C₆H₅; XII R=CH₃, R¹=H, R²=C₆H₅; XIII R=CH₃, R¹=H, R²=C₆H₅

Salts IV-XIII are yellow, orange, or red substances that are resistant to heating and photochemical action. Peaks of $[M - BF_4]^+$ ions, which have relative intensities of 20-100%, are recorded in their mass spectra (Table 2). The fragmentation of salts IV-VIII and X-XII, which contain a 7-diethylamino group, proceeds with the formation of $[M - BF_4 - CH_3]^+$ (5-60%) and $[M - BF_4 - CH_3 - C_2H_5]^+$ (10-30%) ions as in the fragmentation of 7-diethylaminocoumarins [3, 4]. In salts IX and XIII the substituent in the pyran part of the molecule is primarily destroyed. Thus, for example, peaks of $[M - BF_4]^+$ (25%), $[M - HBF_4]^+$ (26%) and then $[M - HBF_4 - C_6H_5CN]^+$ (100%) ions are present in the spectrum of XIII. Intensive processes involving the detachment of hydrogen atoms in different (with respect to degree) steps of the fragmentation are a distinctive feature of the mass-spectral fragmentation of all of the investigated compounds, as evidenced by the intensive (50-100%) peaks of $[M - HBF_4]^+$, $[M - HBF_4 - CH_3]^+$, and other ions. A similar principle is also valid for other pyrylium salts [5].

A long-wave band at 430-475 nm is present in the absorption spectra of tetrafluoroborates IV-XIII (Table 3). The presence of a methyl group in the 4 position in IV, VI, and VIII leads to a hypsochromic shift of this band as compared with 4-unsubstituted analogs V, VII, and XI of ~10 nm. The fixing of the 7-dialkylamino group in six-membered rings in IX and XIII, on the other hand, leads to a 20-30 nm bathochromic shift. The substituents attached to the nitrogen atom of the 2-amino group have a substantially smaller effect on the position of the long-wave absorption maximum. The same principles are characteristic for 7-aminocoumarins [6] and make it possible to classify the indicated absorption in the spectra of salts IV-XIII as a charge-transfer band.

The electronic absorption spectra of salts X-XIII, in contrast to the remaining synthesized tetrafluoroborates, reveal a dependence on the pH of the medium (see Fig. 1). The form of the graph and the presence of isobestic points (at 259, 329, and 414 nm) provide evidence for the existence at pH 2.5-11.5 of two forms of XII; the transition from one to the other is reversible. Similar dependences were obtained for X, XI, and XIII (Table 4). The most likely explanation for the observed principles is an acid—base equilibrium with the participation of salts X-XIII and the corresponding 2-iminocoumarins Xa-XIIIa.

*In accordance with the IUPAC rules of nomenclature IX and XIII should be called 1H,5H-[1]benzopyrano[6,7,8-ij]-quinolizinium salts; however, in order to retain integrity in the exposition of the material and for convenience in comparing the properties of analogous structural fragments in the present paper we retained a unified nomenclature and monotypic numbering (see the scheme) of the investigated salts as benzopyrylium salts. In addition, the additional designations $N_{(1)}$ and $N_{(2)}$ were introduced for the nitrogen atoms of the 2- and 7-amino groups, respectively.

TABLE 1. Physicochemical Characteristics of Salts IV-XIII

Com-pound	Empirical formula	mp, °C	IR spectrum, cm⁻¹		Yield, %	Degree of con-version, %
			C=C	BF₄⁻		
IV	$C_{18}H_{27}BF_4N_2O$	158	1635	1050	67	58
V	$C_{18}H_{25}BF_4N_2O$	208	1641	1045	71	51
VI	$C_{19}H_{27}BF_4N_2O$	170	1640	1070	82	70
VII	$C_{17}H_{23}BF_4N_2O_2$	195	1642	1065	65	69
VIII	$C_{18}H_{25}BF_4N_2O_2$	195 (dec.)	1638	1050	78	70
IX	$C_{21}H_{27}BF_4N_2O$	180 (dec.)	1635	1045	73	60
X	$C_{21}H_{25}BF_4N_2O$	142	1650	1050	65	68
XI	$C_{19}H_{21}BF_4N_2O$	118	1640	1070	45	53
XII	$C_{20}H_{23}BF_4N_2O$	134	1641	1075	69	58
XIII	$C_{22}H_{23}BF_4N_2O$	175 (dec.)	1640	1075	70	66

TABLE 2. Characteristic Peaks in the Mass Spectra of Salts IV-XII

Compound	m/z value (I_{rel}, % relative to the maximum peak)*					
	$[M-BF_4]^+$	$[M-HBF_4]^+$	$[M-BF_4-CH_3]^+$	$[M-HBF_4-CH_3]^+$	$[M-BF_4-CH_3-C_2H_5]^+$	$[M-HBF_4-CH_3-C_2H_5]^+$
IV	287 (44)	286 (81)	272 (5)	271 (17)	243 (18)	242 (10)
V	285 (51)	284 (100)	270 (6)	—	241 (11)	—
VI	299 (28)	298 (100)	283 (9)	—	254 (15)	—
VII	287 (54)	286 (100)	272 (5)	—	243 (11)	—
VIII	301 (54)	300 (53)	286 (16)	285 (53)	257 (16)	256 (51)
IX	323 (55)	322 (100)	—	—	—	—
X	321 (42)	320 (58)	306 (15)	305 (59)	—	—
XI	293 (60)	292 (59)	278 (60)	277 (61)	249 (32)	248 (54)
XII	307 (45)	306 (100)	292 (15)	291 (59)	263 (8)	262 (18)
XIII	331 (25)	330 (100)	—	—	—	—

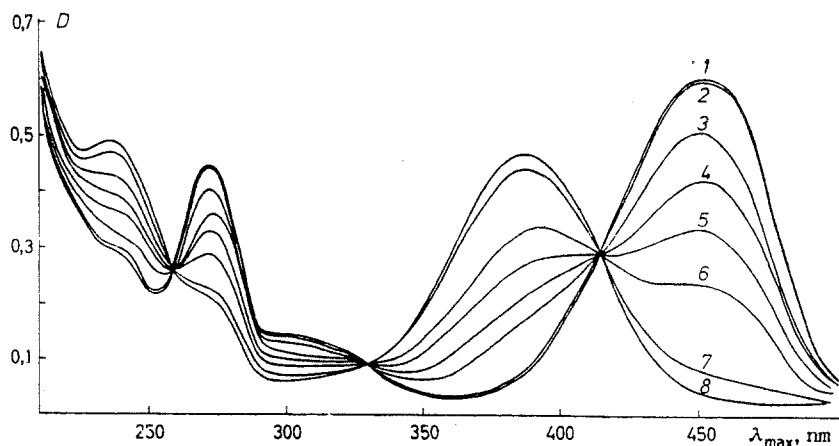*The peaks with $I_{rel} \geq 5\%$ are presented.

Fig. 1. Dependence of the absorption spectra of aqueous ethanol (1:1) solutions of salt XII on the pH of the medium: 1) pH 2.50; 2) pH 3.54; 3) pH 5.60; 4) pH 5.80; 5) pH 6.20; 6) pH 6.32; 7) pH 6.90; 8) pH 11.42.

TABLE 3. Spectral-Luminescence Properties of Salts IV-XIII

Com-pound	Solvent	UV spectrum, λ_{max}, nm (log ε)	Luminescence		Relative quantum yield*
			λ_{exc}	λ_{max}	
IV	C$_2$H$_5$OH	221 (4,45), 260 (4,34), 296 (3,78), 321 (3,58), 435 (4,53)	435	500	0,13
	CH$_3$CN	221 (4,45), 258 (4,31), 296 (3,75), 321 (3,58), 430 (4,54)	430	500	0,10
V	C$_2$H$_5$OH	221 (4,56), 261 (4,37), 300 (3,78), 327 (3,68), 444 (4,64)	440	515	<0,10
	CH$_3$CN	222 (4,43), 260 (4,22), 300 (3,64), 327 (3,57), 442 (4,53)	440	515	<0,10
VI	C$_2$H$_5$OH	259 (4,23), 296 (3,64), 432 (4,42)	430	502	<0,10
	CH$_3$CN	258 (4,34), 296 (3,88), 428 (4,38)	430	502	<0,10
VII	C$_2$H$_5$OH	220 (4,37), 263 (4,15), 304 (4,15), 324 (3,85), 448 (4,36)	445	515	<0,10
	CH$_3$CN	220 (4,44), 263 (4,25), 300 (3,75), 326 (3,61), 446 (4,52)	445	520	<0,10
VIII	C$_2$H$_5$OH	221 (4,35), 261 (4,28), 298 (3,75), 322 (3,54), 440 (4,47)	445	512	<0,10
	CH$_3$CN	223 (4,29), 262 (4,22), 298 (3,70), 322 (3,49), 438 (4,43)	445	514	<0,10
IX	C$_2$H$_5$OH	230 (4,42), 269 (4,21), 303 (3,79), 455 (4,48)	445	525	0,54
	CH$_3$CN	230 (4,51), 268 (4,26), 304 (3,86), 453 (4,55)	445	525	0,41
X	C$_2$H$_5$OH**—H$_2$O, 1 : 1	218 (4,45), 260 (4,29), 290 (3,79), 310 (3,60), 322 (3,54), 429 (4,44)	415	500	<0,10
	CH$_3$CN	214 (4,47), 251 (4,26), 290 (3,74), 310 (3,52), 322 (3,46), 429 (4,42)	415	506	<0,10
XI	C$_2$H$_5$OH**—H$_2$O, 1 : 1	224 (4,29), 240 (4,21), 273 (4,39), 310 (3,85), 327 (3,80), 460 (4,54)	460	534	<0,10
	CH$_3$CN	230 (4,21), 274 (4,24), 310 (3,77), 328 (3,79), 390 (3,98), 466 (4,29)	460	525	<0,10
XII	C$_2$H$_5$OH**—H$_2$O, 1 : 1	240 (4,06), 272 (4,23), 307 (3,73), 452 (4,36)	460	516	<0,10
	CH$_3$CN	235 (4,24), 271 (4,42), 305 (3,97), 447 (4,51)	450	524	<0,10
XIII	C$_2$H$_5$OH**—H$_2$O, 1 : 1	234 (4,18), 244 (4,08), 281 (4,22), 310 (3,80), 474 (4,35)	470	540	0,30
	CH$_3$CN	233 (4,15), 246 (4,03), 281 (4,14), 312 (3,77), 474 (4,28)	470	530	0,16

*Fluorescein was used as the standard.
**The spectra were obtained for solutions with pH 2.5.

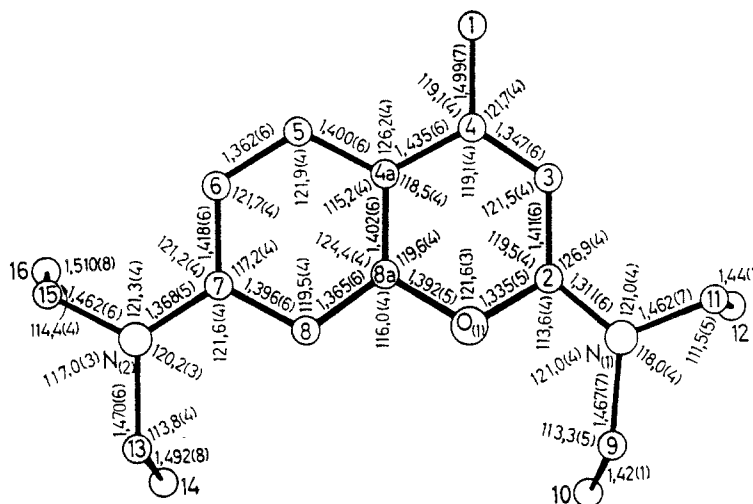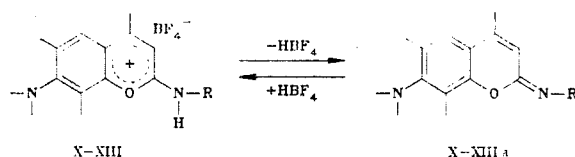| Compound	pH	λ_{max}, nm (lg ε)	pK_a	Compound	pH	λ_{max}, nm (lg ε)	pK_a
X	2,34	429 (4,44)	8,31	XII	2,50	452 (4,36)	6,15
Xa	10,75	365 (4,32)	—	XIIa	11,42	386 (4,25)	—
XI	2,94	460 (4,54)	5,62	XIII	2,34	474 (4,35)	6,74
XIa	11,21	391 (4,46)	—	XIIIa	8,45	399 (4,29)	—

Fig. 2. Bond lengths and bond angles in the cation of salt IV.

X, Xa R=$CH_2C_6H_5$; XI—XIII, XIa—XIIIa R=C_6H_5

The increase in the pK_a values in the series of salts XI < XII < XIII < X (see Table 4) should be symbatic with respect to the decrease in the positive charge on the N(1) atom, which, in turn, increases with an increase in the electron-acceptor character of the benzopyrylium fragment and the substituents attached to the N(1') atom. On the basis of a comparison of the data in Table 4 it was concluded that the electron-donor effect of the 4-methyl group is quite appreciable (compare XI and XII) and that the electron-donor character of the fixed amino group in XIII is greater than in XII. The absorption of iminocoumarins in a shorter-wave region than in the case of pyrylium salts is in agreement with the decrease in the intramolecular charge transfer in Xa-XIIIa. For the definitive elucidation of the problem, from salt XIII as a result of treatment with triethylamine we obtained and identified iminocoumarin XIIIa. The spectral characteristics of XIIIa were in complete agreement with the short-wave part in the absorption spectra of alkaline solutions of salt XIII, and thus the examined equilibrium can be regarded as proved.

A study of the PMR spectrum (see the experimental section) showed that in solution in deuterochloroform iminocoumarin XIIIa exists in the form of an equilibrium mixture of Z and E isomers in a ratio of 3:5. The E structure was assigned to the predominant isomer on the basis of the large weak-field shift of the 10-H proton (6.12 ppm) and the protons of the 9-CH3 group (2.21 ppm); the deshielding effect of the N-phenyl substituent on these protons is absent in the Z isomer (weak-field shifts of 5.80 and 2.09 ppm, respectively).

Tetrafluoroborates IV-XIII luminesce at 500-550 nm (Table 3); salts IX and XIII luminesce most intensely (φ 0.2-0.5). On the whole the emission bands of the investigated salts are subject to the same principles as the long-wave asbsorption bands, i.e., they experience

TABLE 5. PMR Spectra of Salts IV-XIII in $CDCl_3$

Compound	δ, ppm (J, Hz)							
	3-H	4-R	5-H	6-H, d,d	8-H, d	7-NCH$_2$	7-NCH$_2$CH$_2$R	Other protons
IV	6,53 s	2,59 s	7,63 d (9,3)	6,84 (9,3; 2,5)	6,69 (2,5)	3,49 q (7,0)	1,22 t (7,0)	1,35 (3H, t, $J=7,0$, 2-NCH$_2$CH$_3$); 1,40 (3H, t, $J=7,0$, 2-NCH$_2$CH$_3$); 3,74 (2H, q, $J=7,0$, 2-NCH$_2$); 3,84 (2H, q, $J=7,0$, 2-NCH$_2$)
V	6,79 d (9,7)	7,96 d (9,7)	7,42 d (9,1)	6,78 (9,1; 2,5)	6,68 (2,5)	3,47 q (7,0)	1,22 t (7,0)	1,79 (6H, m, 2-NCH$_2$CH$_2$CH$_2$); 3,80 (2H, m, 2-NCH$_2$); 4,05 (2H, m, 2-NCH$_2$)
VI	6,98 s	2,61 s	7,80 d (9,0)	7,04 (9,0; 2,5)	7,02 (2,5)	3,60 q (7,0)	1,26 t (7,0)	1,87 (6H, m, 2-NCH$_2$CH$_2$CH$_2$CH$_2$); 4,01 (2H, m, 2-NCH$_2$); 4,12 (2H, m, 2-NCH$_2$)
VII	6,75 d (9,6)	7,94 d (9,6)	7,48 d (9,2)	6,78 (9,2; 2,6)	6,69 (2,6)	3,47 q (7,0)	1,22 t (7,0)	3,99 (6H, m, O(CH$_2$)$_2$; NCH$_2$); 4,05 (2H, m, NCH$_2$)
VIII	6,72 s	2,56 s	7,58 d (9,0)	6,79 (9,0; 2,7)	6,75 (2,7)	3,47 q (7,0)	1,22 t (7,0)	3,98 (6H, m, O(CH$_2$)$_2$; NCH$_2$); 4,05 (2H, m, NCH$_2$)
IX	6,65 s	2,52 s	7,19 s	—	—	3,35 t (6,5)	1,99 quint (6,5); 2,04 quint (6,5)	1,81 (6H, m, 2-NCH$_2$CH$_2$CH$_2$); 2,81 (2H, t, $J=6,5$, 8-CH$_2$); 2,85 (2H, t, $J=6,5$, 6-CH$_2$); 3,89 (2H, m, 2-NCH$_2$); 3,92 (2H, m, 2-NCH$_2$)
X	6,54 s	2,40 s	7,52 d (9,4)	6,79 (9,4; 2,6)	6,61 (2,6)	3,45 q (7,0)	1,21 t (7,0)	4,75 (2H, d, $J=7,6$, 2-NCH$_2$); 7,24 (1H, t, $J=7,8$, p-C$_6$H$_5$); 7,30 (2H, t, $J=7,8$, m-C$_6$H$_5$); 7,45 (2H, d, $J=7,8$, o-C$_6$H$_5$); 9,41 (1H, t, $J=7,6$, NH)
XI	6,87 d (9,2)	7,93 d (9,2)	7,64 d (9,4)	7,04 (9,4; 2,6)	6,66 (2,6)	3,50 q (7,0)	1,24 t (7,0)	7,31 (2H, t, $J=7,5$, p-C$_6$H$_5$); 7,50 (2H, t, $J=7,5$, m-C$_6$H$_5$); 7,55 (1H, d, $J=7,5$, o-C$_6$H$_5$); 7,95 (1H, d, $J=7,5$, o-C$_6$H$_5$); 10,35 (1H, s, NH)
XII	6,63 s	2,62 s	7,72 d (9,1)	7,08 (9,1; 2,4)	6,82 (2,4)	3,57 q (7,0)	1,32 t (7,0)	7,42 (1H, t, $J=7,8$, p-C$_6$H$_5$); 7,57 (2H, t, $J=7,8$, m-C$_6$H$_5$); 7,89 (2H, d, $J=7,8$, o-C$_6$H$_5$); 10,90 (1H, s, NH)
XIII*	6,73 s	2,49 s	7,20 s	—	—	3,37 m	1,92 m	2,80 (4H, m, 6-CH$_2$, 8-CH$_2$); 7,28 (1H, d, $J=7,9$, p-C$_6$H$_5$); 7,40 (2H, t, $J=7,9$, p-C$_6$H$_5$); 7,53 (2H, m-C$_6$H$_5$); 10,22 (1H, s, NH)
E-XIII**	6,77 s	2,52 s	7,20 s	—	—	3,39 m	1,99 m	2,82 (4H, m, 6-CH$_2$, 8-CH$_2$); 7,31 (1H, t, $J=7,9$, p-C$_6$H$_5$); 7,43 (2H, t, $J=7,9$, m-C$_6$H$_5$); 7,55 (2H, d, $J=7,9$, o-C$_6$H$_5$); 10,40 (1H, s, NH)
Z-XIII**	6,30 s	2,49 s	7,19 s	—	—	3,85 m	2,24 m	2,82 (2H, m, 6-CH$_2$); 3,02 (2H, m, 8-CH$_2$); 7,31...7,55 (5H, m, C$_6$H$_5$); 10,21 (1H, s, NH)

*The PMR spectrum was recorded at 20°C.
**The PMR spectrum was recorded at −60°C.

626

TABLE 6. ^{13}C NMR Spectra of Salts VIII, IX, and XIII and 7-Aminocoumarins

Compound	Chemical shift, δ, ppm (SSCC, $J^{13}C{-}^1H$, Hz) in $CDCl_3$									
	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(4a)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	$C_{(8a)}$	Other carbon atoms*
II** III**	161,4 s 162,2	108,2 107,8	152,1 150,8	109,2 108,6	125,4 121,4	109,0 117,6	150,4 145,4	97,8 106,4	156,1 152,7	12,6 (NCH₂CH₃); 18,4 (4-CH₃); 44,7 (NCH₂); 18,2 (4-CH₃); 20,2 (8-CH₂); 20,4 (8-CH₂); 21,3 (8-CH₂CH₂); 27,4 (6-CH₂CH₂); 49,2 (8-CH₂CH₂CH₂); 49,6 (6-CH₂CH₂CH₂);
VIII	160,4 s	99,5 dq (173,9; 4,7)	154,2 d (7,0)	109,2 m	126,9 d (161,6)	112,0 dd (161,5; 4,4)	152,9 m	96,7 d (162,3)	159,1 s	12,3 (q, J=126,6, 7-N-CH₂CH₃); 19,1 (q, J=128,0; 4,4, 4-CH₃); 45,0 (t, J=135,9, 7-NCH₂); 45,4 (t, J=146,3, 2-NCH₂); 45,7 (t, J=147,3, 2-NCH₂); 66,0 (J=147,3, O(CH₂)₂)
IX	159,6 s	98,9 dq (173,6; 5,3)	149,2 d (9,8)	109,9 s	121,6 d (162,5)	122,7 s	148,2 s	105,4 t (6,7)	158,1 s	19,3 (q, J=130,5, 4-CH₃); 19,8 (t, J=129,4, 8-CH₂); 20,2 (t, J=131,2, 6-CH₂); 20,8 (t, J=131,0, 8-CH₂—CH₂); 20,8 (t, J=130,3, 2-NCH₂CH₂CH₂); 23,4 (t, J=132,2, 2-NCH₂CH₂); 25,7 (t, J=130,3, 2-N—CH₂CH₂); 27,7 (t, J=130,3, 6-CH₂CH₂); 46,5 (m, 2-NCH₂); 48,1 (2-NCH₂); 49,5 (t, J=138,1, 8-CH₂CH₂CH₂); 50,1 (t, J=139,7, 6-CH₂CH₂CH₂)
XIII	160,5 d (4,0)	101,3 d (172,5)	149,3 d (10,0)	109,9 s	122,4 d (162,9)	122,6 t (5,4)	148,6 m	105,5 t (5,2)	158,5 s	19,1 (q q, J=129,2; 4,7, 4-CH₃); 19,8 (t, J=131,0, 8-CH₂); 20,3 (t, J=130,9, 6-CH₂); 20,6 (t, J=130,8, 8-CH₂CH₂); 27,6 (q t, J=130,1; 4,1, 6-CH₂CH₂); 49,5 (t, J=138,8, 8-CH₂CH₂CH₂); 50,1 (t, J=130,1, 6-CH₂CH₂CH₂); 122,8 (d, J=160,3, C(₆) and C(₅) in C₆H₅NH); 127,2 (t, d, J=162,5; 7,2, C(₃) in C₆H₅NH); 129,5 (d, d, J=162,6; 7,7, C(₄) in C₆H₅NH); 134,3 (m, α-C in C₆H₅NH)

*The form of the signal in the monoresonance spectrum (J, Hz) and the assignment of the signal are presented in parentheses.

**The data from [8] are presented.

TABLE 7. Coordinates of the Atoms in Salt IV

Atom	Coordinates of the nonhydrogen			Atom	(Coordinates of the H atoms $(\cdot 10^3)$)		
	x	y	z		x	y	z
$F_{(1)}$	1021(5)	−1977(3)	−5849(4)	$H_{(1,1)}$	103(4)	407(3)	9(4)
$F_{(2)}$	1822(6)	−2654(4)	−7543(4)	$H_{(1,2)}$	292(4)	420(3)	21(4)
$F_{(3)}$	−65(5)	−3858(5)	−7348(4)	$H_{(1,3)}$	192(4)	480(3)	106(4)
$F_{(4)}$	2295(7)	−3575(4)	−5923(4)	$H_{(3)}$	209(4)	395(3)	299(4)
$O_{(1)}$	2143(3)	1141(2)	2513(3)	$H_{(5)}$	177(4)	204(3)	−117(4)
$N_{(1)}$	2151(4)	2410(3)	4389(3)	$H_{(6)}$	191(4)	−1(3)	−216(4)
$N_{(2)}$	2025(4)	−1980(3)	−1305(3)	$H_{(8)}$	216(4)	−90(3)	104(4)
$C_{(1)}$	1986(6)	4143(4)	614(6)	$H_{(9,1)}$	130(4)	48(3)	413(4)
$C_{(2)}$	2141(5)	2320(4)	3182(4)	$H_{(9,2)}$	168(4)	129(3)	545(4)
$C_{(3)}$	2120(5)	3314(4)	2560(5)	$H_{(10,1)}$	383(4)	146(3)	634(4)
$C_{(4)}$	1991(5)	3088(4)	1274(4)	$H_{(10,2)}$	357(4)	22(3)	591(4)
$C_{(4a)}$	1955(4)	1817(4)	541(4)	$H_{(11,1)}$	161(4)	409(3)	490(4)
$C_{(5)}$	1836(5)	1426(4)	−792(4)	$H_{(11,2)}$	178(4)	345(3)	586(4)
$C_{(6)}$	1874(5)	202(4)	−1386(4)	$H_{(12,1)}$	473(4)	409(3)	633(4)
$C_{(7)}$	2015(4)	−749(4)	−691(4)	$H_{(13,1)}$	184(4)	−372(3)	−116(4)
$C_{(8)}$	2108(5)	−380(3)	632(4)	$H_{(13,2)}$	144(4)	−287(3)	0(4)
$C_{(8a)}$	2058(4)	853(4)	1195(4)	$H_{(14,1)}$	462(4)	−213(3)	68(4)
$C_{(9)}$	2108(7)	1280(5)	4889(5)	$H_{(14,2)}$	490(4)	−314(3)	−13(4)
$C_{(10)}$	3650(10)	1001(7)	5476(8)	$H_{(14,3)}$	390(4)	−349(3)	60(4)
$C_{(11)}$	2184(7)	3637(5)	5273(5)	$H_{(15,1)}$	205(4)	−315(3)	−287(4)
$C_{(12)}$	3796(9)	4255(6)	6132(9)	$H_{(15,2)}$	146(4)	−192(3)	−304(4)
$C_{(13)}$	2277(5)	−2930(4)	−543(5)	$H_{(16,1)}$	449(4)	−240(3)	−218(4)
$C_{(14)}$	3986(6)	−2852(5)	283(6)	$H_{(16,2)}$	422(4)	−103(3)	−230(4)
$C_{(15)}$	2157(5)	−2325(4)	−2622(5)	$H_{(16,3)}$	382(4)	−209(3)	−336(4)
$C_{(16)}$	3811(6)	−1930(5)	−2620(5)	$H_{(10,3)}$	415(4)	96(3)	497(4)
$B_{(1)}$	1314(8)	−2984(5)	−6653(6)	$H_{(12,2)}$	364(4)	472(3)	668(4)
				$H_{(12,3)}$	382(4)	494(3)	602(4)

a bathofluoric shift as the electron-donor properties of the aminobenzene and electron-acceptor properties of the pyran fragment become more inense. Data on the luminescence of salts X-XIII were obtained in acidic aqueous ethanol solutions, which were used in order to exclude the formation of iminocoumarins Xa-XIIIa, which have virtually no luminescence.

An intense absorption band of the tetrafluoroborate anion is observed in the IR spectra of salts IV-XIII (Table 1) at 1020-1100 cm^{-1}. The characteristic absorption of the benzopyrylium system of multiple bond [7] appears at 1610-1640 cm^{-1}, which is usually accompanied by intense absorption at 1560-1590 cm^{-1}.

Signals of aromatic protons of the benzopyrylium fragment, which, as compared with the analogous signals of the starting 7-aminocoumarins I-III [8], experience a weak-field shift, are quite distinguishable in the PMR spectra of IV-XIII (Table 5). The strongest shift ($\Delta \sim$ 0.5-0.9 ppm) is observed for the signals of the 3-H protons, which show up at 6.5-6.9 ppm. In the case of X-XIII, which have unsymmetrical substitution at the $N_{(1)}$ atom, one observed substantial broadening of the signals of the 3-H protons; this recalls the behavior of 2-alkylidene-7-aminobenzopyrans [1, 9]. This phenomenon may be associated with rapid rotation of the 2-amino group around the $C_{(2)}-N_{(2)}$ bond. The existence of rotation of the dialkylamino groups in IV-IX is confirmed by the "smoothed out" broad structure of the signals of the protons in the α position relative to the $N_{(1)}$ atom. The chemical shifts of these protons are found at 3.7-4.1 ppm, usually in the form of two signals (Table 5); this constitutes evidence for their different chemical environments.

In order to obtain a more definite confirmation of the intramolecular rotation of the 2-amino group in solutions we investigated the low-temperature PMR spectrum of XIII. At −60°C in deuterchloroform we were able to record the PMR signals of the Z and E isomers (Table 5), the ratio between which was ~1:10. The chemical shift of the 3-H proton, which in the case of the E isomer (6.77 ppm) is under the deshielding influence of the phenyl group and is found at weaker field as compared with the Z isomer (6.30 ppm), undergoes the most pronounced change in the low-temperature spectrum. The preponderance of the E isomer in solution is in agreement with the analogous principle in iminocoumarin XIIIa and is evidently determined by the more effective conjugation of the E substituent with the benzopyran part of the molecule [9].

The chemical shifts of the 5-H, 6-H, and 8-H protons in IV-XIII are shifted 0.1-0.5 ppm to weak field as compared with coumarins I-III but also retain their relative positions in the order 5-H > 6-H > 8-H. The protons of the 4-methyl group, the 4-H proton ($\Delta \sim$ 0.4 ppm), and the protons in the α position relative to the $N_{(2)}$ atom ($\Delta \sim$ 0.1-0.2 ppm) experience an appreciable weak-field shift ($\Delta \sim$ 0.1-0.3 ppm) as compared with the starting coumarins. The weak-field shift of the protons in the $N_{(2)}-CH_2$ fragment indicates a certain

increase in the positive charge in the 7 position. On the other hand, the chemical shifts of the protons of the substituents attached to this atom constitute evidence for substantial localization of the positive charge on the $N_{(1)}$ atom. Thus, for example, in the spectrum of XIII the chemical shifts of the protons of the phenyl ring are found between the chemical shifts of the analogous protons in aromatic amines and the chemical shifts of the corresponding onium compounds [10, p. 272]; in the spectrum of X the weak-field shift of the $N(1)-CH_2$ protons is ~0.4 ppm as compared with N-benzylaniline, etc.

Also of interest to us was the principle of delocalization of the positive charge in salts IV-XIII. For this we investigated the ^{13}C NMR spectra of salts VIII, IX, and XIII (see Table 6). It is known [11] that the ^{13}C NMR chemical shifts correlate well with the π-electron densities on the carbon atoms; in particular, this has been used repeatedly for such evaluations in series of pyrylium and related salts [12]. Most of the signals in the spectra of VIII, IX, and XIII were assigned on the basis of the characteristic $^1J^{13}C-H$ and $^3J^{13}C-H$ constants [8, 12], as well as a result of comparison with the available data [13]. Thus the signal of the $C_{(3)}$ atom is distinguished by the maximal $^1J^{13}C-H$ constant (173-174 Hz) in the monoresonance spectrum [8], the signal of the $C_{(7)}$ atom has a characteristic multiplet structure that is due to the quadrupole moment of the $N_{(2)}$ atom [8], etc. It is interesting that appreciable broadening of the signal of the $C_{(3)}$ atom ($\Delta h_{\frac{1}{2}} = 23$ Hz) as a consequence of the above-examined rotation of the 2-amino group is observed in the spectrum of salt XIII. Several conclusions can be drawn on the basis of the data in Table 6. The chemical shifts of the $C_{(8)}$ (Δ~—7 to −9 ppm), $C_{(8a)}$ (Δ~3-6 ppm), $C_{(6)}$ (Δ~ 3-5 ppm), and $C_{(7)}$ (Δ~3 ppm) atoms in salts VII, VIII, and XIII undergo the most pronounced changes as compared with 6-aminocoumarins II and III. On the other hand, the chemical shifts of the $C_{(10)}$, $C_{(8)}$, $C_{(5)}$ and $C_{(4)}$ atoms, as well as the $C_{(2)}$ atom, change only slightly (Δ~ 0 ± 2 ppm).

For the rational explanation of these (at first glance) chaotic changes one should bear in mind that the formation of the benzyopyrylium system disrupts the usual pathway of transmission of the π-electron effect in 7-aminocoumarins. In fact, compensation of the positive charge on the $C_{(2)}$ atom through involvement of one of the unshared pairs of the $O_{(1)}$ atom should lead to localization of the $O_{(1)}-C_{(2)}$ or $O_{(1)}-C_{(8a)}$ π bond and, consequently, primary fixation of the remaining π bonds in accordance with the types represented by formulas A, B, and C. This fixation should lead to restriction of the regions of the p-donor effect of the 2-and 7-amino groups, which exist in a competitive relationship with one another.
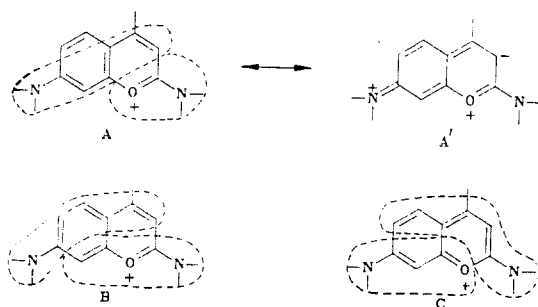
The realization of structures A and B, in which the positive charge is concentrated mainly between the $O_{(1)}$ and $N_{(1)}$ atoms vis-a-vis retention of the extended conjugation chain with the participation of the 7-amino group, is most preferable. In a comparison of the two alternative pathways of the p-electron effect of the 7-amino group in structures A and B) encircled by dash lines) one might expect more effective conjugation in the A system , in which the $C_{(7)}-C_{(8)}-C_{(8a)}-C_{(4a)}-C_{(4)}-C_{(3)}$ conjugation chain is situated along the direction of charge transfer. Within the limit charge transfer in structure A gives rise to form A'. In this case for 2,7-diaminobenzopyrylium salts one should expect increased localization of the $C_{(5)}-C_{(6)}$ double bond and pronounced localization of the $O_{(1)}-C_{(2)}$ double bond as compared with 7-aminocoumarins. From the point of view of the ^{13}C NMR chemical shifts within the framework of the proposed model the weak-field chemical shift of the $C_{(8a)}$ atom, which is deshielded as a result of π bonding of the unshared pair of the $O_{(1)}$ atom, and the weak-field shift of the signal of the $C_{(3)}$ atom become understandable. The small weak-field shift of the signals of the $C_{(5)}$ and $C_{(6)}$ atoms in this case can be explained by their location within the pathway of the p-electron effect of the 7-amino group.

To verify this hypothesis and establish the structures of 2,7-diaminobenzopyrylium salts we subjected tetrafluoroborate IV to an x-ray diffraction study. The selection of salt IV was dictated by the desire to more accurately evaluate the effect of two identical but competitive (with respect to the electronic effect) amino groups on the geometry of the cationic part.

The structure of the cationic part of salt IV is shown in Fig. 2; the BF_4^- anion has the usual close-to-tetrahedral geometry. Great scatter in the B—F bond lengths and low accuracy in the determination of the geometrical parameters of the ethyl groups are characteristic for tetrafluoroborate IV; this is associated with the strong thermal vibrations of the F atoms and the peripheral carbon atoms. Short interionic contacts are absent in structure IV (Table 7).

We have previously [9] investigated the structures of 2-acetylcarbethoxymethylene-(XIV) and 2-cyanocarbethoxymethylene-4-methyl-7-diethylaminobenzopyran (XV), one of the peculiarities of which is partial intramolecular charge separation in the molecules, which leads, in particular, to delocaliztion of the $C_{(3)}$—$C_{(4)}$ double bond in the pyran ring. The principal difference in the geometry of the two-ring system of the planar cation of salt IV from that found in alkylidenebenzopyrans XIV and XV consists in the substantially smaller length of the $O_{(1)}$—$C_{(2)}$ bond [1.335(5) Å] than in starting coumarin II (1.383 Å) [14], which is characteristic for the O—C bonds in pyrylium salts [15], while the length of the $O_{(1)}$—$C_{(8a)}$ bond [1.392(5) Å] is even somewhat greater than in XIV, XV, and II. Considering that the $N_{(1)}$—$C_{(2)}$ bond [1.311(6) Å] is substantially shorter than the $N_{(2)}$—$C_{(7)}$ bond [1.368(5) A] one may conclude that the positive charge of the cation is primarily localized on the $O_{(1)}$—$C_{(2)}$—$N_{(1)}$ triad. Evidence for this is also provided by the certain decrease (as compared with the value found in the XIV and XV molecules) in the length of the $C_{(3)}$—$C_{(4)}$ double bond [1.347(6) Å], i.e., the charge delocalization over the heteroring in the cation of salt IV is small; however, it does, nevertheless, exist, since in starting coumarin II the length of this bond is 1.322 Å. On the other hand, one must note the similar (to that found in the XIV and XV molecules) geometry of the 7-diethylamino group and benzene ring in the cation with a characteristic decrease in the lengths of the $C_{(5)}$—$C_{(6)}$ and $C_{(8)}$—$C_{(8a)}$ bonds as compared with the rest of the bond lengths in the ring. This effect can be considered to be a consequence of the certain contribution of structure A'. The participation of structure A' should lead to an increase in the negative charge on the $C_{(3)}$ atom and the positive charge on the $C_{(7)}$ atom and increased localization of the $C_{(8)}$—$C_{(8a)}$ double bond.

Thus the description of the molecules of the benzopyrylium salts within the framework of formulas A and A' is in good agreement with the ^{13}C NMR spectral data, is virtually completely confirmed by the x-ray diffraction study, and, despite its simplicity, makes it possible to understand in greater depth the detailed scheme of the electronic effect of the substituents.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a Jasco spectrometer. The UV and luminescence spectra of solutions in ethanol, 50% aqueous ethanol, or acetonitrile were recorded with a Hitachi EPS-3T spectrophotometer with a G-3 luminescence adapter. The relative fluorescence quantum yields were determined with respect to 3-aminophthalimide by the method in [16, p. 510]. The PMR and ^{13}C NMR spectra were recorded with a Bruker WM-250 spectrometer [with hexamethyldisiloxane (HMDS) as the internal standard]. The mass spectra were obtained with a Varian MAT-311A mass spectrometer (ionizing voltage 70 eV).

The pK_a values were determined spectrophotometrically in 50% ethanol. Hydrochloric acid served as the proton donor. The pH values were measured with an OR-401/1 titer pH meter with glass and calomel electrodes.

General Method for Obtaining Salts IV-XIII. A solution of 4.0 mmole of triethyloxonium tetrafluoroborate in 10 ml of CH_2Cl_2 was added with stirring in a nitrogen atmosphere to a solution of 4.0 mmole of starting 7-aminocoumarin in 20 ml of absolute CH_2Cl_2, after which the reaction mixture was stirred for another 20-30 min at 30°C. A 20-mmole sample of the corresponding amine was added, and the mixture was refluxed for 2-3 h. The organic solution was washed with water (three 10-ml portions) and evaporated to a volume of 5 ml, and 25 ml of ether was added to the concentrate. When necessary, the precipitated salt was recrystallized from hexane—acetone (1:1).

The physicochemical characteristics of the synthesized salts are presented in Tables 1-6.

X-Ray Diffraction Study. The crystals of salt IV ($C_{18}H_{27}N_2O^+BF_4^-$) were triclinic and had the following parameters at 20°C: a = 9.008(1) Å, b = 10.959(1) Å. c = 11.032(1) Å, α = 103.10(1)°, β = 109.13 (1)°, γ = 95.56(1)°, Z = 2, and space group P1. The cell parameters and the intensities of 2416 independent reflections, 2200 of which with I ≥ 2 σ were used in decoding and refining the structure, were measured with a Hilger—Watts automatic diffractometer ($\lambda CuK\alpha$, graphite mono-chromator, $\theta/2\theta$ scanning, $\theta \le 66$°). The structure was decoded by the direct method and refined by means of the total-matrix method of least squares (MLS) within the anisotropic approximation for all of the nonhydrogen atoms. All of the H atoms were revealed from the differential series and refined with fixed B_{iso} = 5 Å². The final divergence factors R = 0.088 and R_w = 0.100. The BF⁴⁻ anion is evidently disordered; however, an attempt to take this disorderliness into account led to unlikely values of both the populations of the positions and the geometrical parameters of the anion. All of the calculations were made with an Eclipse S/200 computer by means of INEXTL programs [17]. The coordinates of the atoms of salt IV are presented in Table 7.

9-Methyl-11-N-Phenylamino-1H,5H-quinolizino[9,9a,1-gh]-benzopyran (XIIIa, $C_{22}H_{22}NO$). This compound was obtained by treatment of 0.42 g (1.0 mmole) of salt XIII in 15 ml of dioxane with 5 ml of triethylamine. After evaporation of the organic solvent, the residue was chromatographed on Silpearl UV-254 silica gel with hexane—acetone (2:1) as the eluent. The fraction with Rf 0.32 was collected and worked up to give 0.17 g (52%) of XIIIa with mp 168°C (from hexane—acetone). PMR spectrum of the E isomer (in CDCl₃): 1.8-2.0 [4H, m, $C_{(6)}H_2$, $C_{(2)}H_2$], 2.21 (3H, s, 9-CH₃), 2.72 [4H, t, J = 6.5 Hz, $C_{(1)}H_2$, $C_{(7)}H_2$], 3.20 [4H, m, $C_{(3)}H_2$, $C_{(5)}H_2$], 6.12 (1H s, 10-H), 6.8-7.3 ppm (6H, m, 8-H, C_6H_5). PMR spectrum of the Z isomer (in CDCl₃): 1.8-2.0 [4H, m, $C_{(2)}H_2$, $C_{(6)}H_2$], 2.09 (3H, s, 9-CH₃), 2.55 [2H, t, J = 6.5 Hz, $C_{(7)}H_2$], 2.90 [2H, t, J = 6.5 Hz, $C_{(1)}H_2$], 3.20 [4H, m, $C_{(3)}H_2$, $C_{(5)}H_2$], 5.80 (1H, s, 10-H), 6.8-7.3 ppm (6H, m, 8-H, C_6H_5). IR spectrum (in KBr): 1645 (C=N), 1602, 1585 cm⁻¹ (C=C). UV spectrum (in ethanol), λ_{max} (log ε): 220 (4.37), 234 (4.37), 280 (3.99), 334 (3.67), 396 nm (4.31).

LITERATURE CITED

1. M. A. Kirpichenok, S. K. Gorozhankin, and I. I. Grandberg, Khim. Geterotsikl. Soedin., No. 6, 751 (1988).
2. M. Maeda, Laser Dyes, Academic Press, New York (1984).
3. S. K. Gorozhankin, M. A. Kirpichenok, N. A. Klyuev, and I. I. Grandberg, Izv. Timiryazev. Skh. Akad., No.4, 151 (1986).
4. S. K. Gorozhankin, M. A. Kirpichenok, N. A. Klyuek, and V. G. Zhil'nikov, Izv. Timiryazev. Skh. Akad., No. 5, 181 (1987).
5. G. Hvistendahl, P. Gyorosi, and K. Undheim, Org.Mass Spectrom., 90, 80 (1974).
6. G. Jones, W. R. Jackson, Ch.-yoo Choi, and W. R. Bergmark, J. Phys. Chem., 89, 294 (1985).
7. A. T. Balaban, G. D. Mateescu, and M. Elian, Tetrahedron, 18, 1083 (1962).
8. M. A. Kirpichenok, I. I. Grandberg, L. K. Denisov, and L. M. Mel'nikova, Izv. Timiryazev. Skh. Akad., No. 3, 173 (1985).
9. M. A, Kirpichenok, D. S. Yufit, Yu. I. Struchkov, S. K. Gorozhankin, and I. I. Grandberg, Khim. Geterotskl. Soedin., No. 8, 1028 (1988).
10. B. I. Ionin, B. A. Ershov, and A. I. Kol'tov, NMR Spectroscopy in Organic Chemistry [in Russian], Khimiya, Leningrad (1983).
11. G. J. Martin, M. L. Martin, and S. Odiot, J. Org. Magn. Reson., 7, 2 (1975).
12. A. T. Balaban and V. Wray, J. Org. Magn. Reson., 9, 16 (1977).
13. M. Th. Chenon, S. Sib, and M. Simalty, J. Org. Magn. Reson., 12, 71 (1979).
14. J. C. Messager and Y. Delugeard, Cryst. Struct. Commun., 3, 391 (1974).
15. A. V. Goncharvo, D. S. Yufit, and Yu. T. Struchkov, Summaries of Papers Presented at the 5th All-Union Conference on Organic Crystal Chemistry [in Russian], Chernogolovka (1987), p. 86.
16. S. Parker, Photoluminescence of Solutions [Russian translation], Mir, Moscow (1972).
17. R. G. Gerr, A. I. Yanovskii, and Yu. T. Struchkov, Kristallografiya, 28, 1029 (1983).