of petroleum ether and ethyl acetate to give the oxide II (51 mg, 78.4%) with mp 80.5-82°C (from ethanol); $[\alpha]_D^{22}$ –8.7° (c = 1.3, $CHCl_3$). The compound was identified by spectral and chromatographic comparison of an authentic sample [15].

B. Using conditions described in method A, fluorosulfonic acid (175 mg, 1.75 mmoles) was added to a mixture of the alcohols IX (87 mg, 0.35 mmole). Treatment as before, and chromatography gave oxide II (64 mg, 73.6%).

LITERATURE CITED

1. P. F. Vlad, *Usp. Khim.*, **51**, 1129 (1982).
2. P. F. Vlad and M. N. Koltsa, *Synthesis and Use of Fragrant Substances from Laboratory-Made Diterpenes* [in Russian], Shtiintsa, Kishinev (1988), p. 182.
3. G. Buchi and H. Wüest, US Patent No. 4,677,233; *Ref. Zh. Khim.*, 6P576P (1988).
4. M. L. Mihailovič, N. Orbovič, and D. Marinkovič, *Bull. Soc. Chim. Beograd*, **44**, 597 (1979).
5. P. F. Vlad, N. D. Ungur, and V. B. Perutskii, *Khim. Priv. Soedin.*, No. 4, 514 (1986).
6. P. F. Vlad, N. D. Ungur, and V. B. Perutskii, *Khim. Priv. Soedin.*, No. 6, 793 (1986).
7. D. V. Banthorpe, P. A. Boullier, and W. D. Fordham, *J. Chem. Soc., Perkin 1*, 1637 (1974).
8. D. V. Banthorpe and P. A. Boullier, *J. Chem. Soc., Perkin 1*, 114 (1977).
9. G. Carr, C. Dean, and D. Whittaker, *J. Chem. Soc., Perkin 2*, 351 (1988).
10. G. Staiger and A. Macri, Claim (Request) DE 3,240,054 A-1 FRG; *Ref. Zh. Khim.*, 8R523P (1985).
11. P. Dietrich and E. Lederer, *Helv. Chim. Acta*, **35**, 1148 (1952).
12. M. M. Emel'yanov, A. V. Lozanova, A. M. Moiseenkov, V. A. Smit, and A. V. Semenovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2788 (1982).
13. V. E. Sibirtseva, S. D. Kustova, and V. Ya. Tokareva, *Oil Industry*, No. 12, 25 (1979).
14. E. J. Corey, H. J. Hess, and S. Prostkow, *J. Am. Chem. Soc.*, **85**, 3979 (1963).
15. P. F. Vlad and N. D. Ungur, *Synthesis* (1983), p. 216.

PYRYLOCYANINS.

26.* SYMMETRICAL DI-tert-BUTYLDIPHENYL-SUBSTITUTED PYRYLO-2-CYANINS

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Isomeric 2-methyl-4-phenyl-6-tert-butylpyrylium and 2-methyl-4-tert-butyl-6-phenylpyrylium salts and their sulfur analogs were synthesized. From these, symmetrical α-pyrylium and α-thiopyrylium carbo- and dicarbocyanins were obtained. α-Pyrylocyanins were converted into symmetrical α-pyridocyanins. From a comparison of the experimental spectral characteristics of the above dyes with the results of quantum-chemical calculations of the average positions of the absorption bands and the quadratic changes of the bond orders during excitation, the influence of the phenyl substituent in the 2- and 4-positions of the heteroresidue on the color was analyzed.

We have previously described [2, 3] the synthesis and studied the patterns of color formation of symmetrical tetraphenyl- and tetra-tert-butyl-substituted pyrylo-2-cyanins and their heteroanalogs. The aim of the present work was to study similar

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*See [1] for Communication 25.

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TABLE 1. Characteristics of Long-Wave Absorption Bands of Dyes V-XVI

Compound	Solvent*	λ_{max}, nm	lg ε	M^{-1}, nm	*f*	σ	γ_1	γ_2	*F*
V	MC	670,734	4,81; 5,03	687,6	0,87	1135	1,24	2,3	0,078
	A	674,734	4,81; 4,93	681,4	0,88	1240	1,20	2,3	0,066
VI	MC	765,844	4,92; 5,17	790,2	1,20	1061	1,28	2,5	0,073
	A	764,838	4,90; 5,01	769,3	1,13	1294	1,31	2,8	0,070
VII	MC	814	4,91	776,8	0,80	1032	1,08	1,8	0,046
	A	804	4,79	758,2	0,77	1238	1,13	2,3	0,046
VIII	MC	858,948	4,96; 5,06	868,9	1,31	1010	1,02	1,7	0,049
	A	840,928	4,91; 4,88	817,3	1,32	1573	1,10	2,1	0,050
IX	MC	620	4,95	599,5	0,81	1050	1,23	2,8	0,053
	A	620	4,92	593,3	0,85	1190	1,26	2,8	0,056
X	MC	722	5,21	699,9	1,14	950	1,40	3,6	0,062
	A	712	5,10	681,8	1,13	1170	1,49	3,9	0,073
XI	MC	670,725	4,68; 4,81	676,3	0,65	1192	1,26	2,7	0,063
	A	672,721	4,75; 4,77	667,5	0,71	1268	1,10	2,1	0,052
XII	MC	754,829	4,75; 4,89	764,8	0,87	1227	0,82	0,9	0,040
	A	742,812	4,75; 4,77	740,2	0,90	1363	0,72	0,8	0,030
XIII	MC	808	4,83	769,1	0,76	1158	1,00	2,0	0,037
	A	773	4,72	744,5	0,68	1243	0,88	1,3	0,031
XIV	MC	926	4,93	850,5	0,96	1187	1,17	2,4	0,056
	A	828,876	4,81; 4,78	793,8	1,00	1600	0,96	1,4	0,042
XV	MC	584	4,85	563,1	0,56	1040	1,17	2,5	0,060
	A	580	4,81	556,0	0,60	1170	1,19	2,6	0,065
XVI	MC	685	5,12	667,3	0,79	950	1,41	3,6	0,063
	A	674	4,99	648,9	0,77	1160	1,51	4,0	0,074

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*MC – Methylene chloride; A – acetonitrile.

TABLE 2. Results of Quantum-Chemical Calculations of M_{theor}^{-1} and δ of Dyes V-XVI and Their Tetraphenyl-Substituted Analogs (TPSA)*

X	*n*	Compounds V-X		Compounds XI-XVI		TPSA*	
		M_{theor}^{-1}, nm	δ	M_{theor}^{-1}, nm	δ	M_{theor}^{-},	δ
O	1	673 (594)	0,1701	681 (592)	0,1796	730	0,1723
O	2	779 (701)	0,1360	786 (694)	0,1425	837	0,1408
S	1	766	0,1480	750	0,1547	798	0,1509
S	2	880	0,1234	861	0,1269	911	0,1268
NCH_3	1	541	0,1669	501	0,1678	554	0,1693
NCH_3	2	622	0,1276	589	0,1291	633	0,1296

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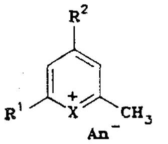
*Compounds V-X, $R^1 = C(CH_3)_3$, $R^2 = C_6H_5$; XI-XVI, $R^1 = C_6H_5$, $R^2 = C(CH_3)_3$; TPSA, $R^1 = R^2 = C_6H_5$.

patterns in isomeric α,α'-di-tert-butyl-γ,γ'-diphenyl- and α,α'-diphenyl-γ,γ'-di-tert-butyl-substituted dyes of this type. In pyrylo-2-cyanins and their hetero analogs, the α,α'- and γ,γ'-positions in the hetero residues are not equivalent. Therefore, the examination of the absorption spectra of these dyes should give more comprehensive information on the nature of the color of substituted pyrylocyanins.

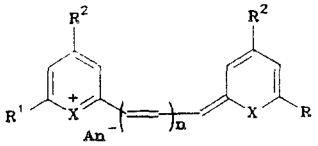
To obtain di-tert-butyldiphenyl-substituted dyes, we synthesized the isomeric 2-methyl-4-phenyl-6-tert-butylpyrylium (I) and 2-methyl-4-tert-butyl-6-phenylpyrylium salts (II) and the sulfur analogs of these salts (III, IV).

Salt I was obtained by the condensation of 1-phenyl-4,4-dimethylpent-2-en-3-one with acetone in the presence of boron trifluoride etherate. The isomeric salt II was synthesized according to [4] from 2-methyl-6-phenyl-4H-pyran-4-one. By reaction with sodium hydrosulfide, salts I and II were converted into thio-analogs III and IV (see scheme on following page).

Pyrylo- and thiopyrylocarbocyanins V, VII, XI, and XIII were synthesized by the condensation of salts I-IV, respectively, with ethyl orthoformate. The corresponding dicarbocyanins VI, VIII, XII, and XIV were obtained from these salts and phenyl-



I - IV



V - XVI

I, III, V—X $R^1=C(CH_3)_3$, $R^2=C_6H_5$; II, IV, XI—XVI $R^1=C_6H_5$, $R^2=C(CH_3)_3$; I, II, V, VI, XI, XII X=O, III, IV, VII, VIII, XIII, XIV X=S; IX, X, XV, XVI $X=NCH_3$; I, V, VI $An=BF_4$, II—IV, VII—XVI $An=ClO_4$; V, VII, IX, XI, XIII, XV $n=1$; VI, VIII, X, XII, XIV, XVI $n=2$

[(3-phenylamino)-2-propenylidene]ammonium chloride. Treatment of pyrylocyanins V, VI, XI, and XII with methylamine gave symmetrical carbo- and dicarbopyridocyanins IX, X, XV, and XVI.

For solutions of the synthesized dyes in a slightly polar methylene chloride and in strongly polar acetonitrile, in addition to λ_{max} and log ε, using the moments method as in [2, 3], we determined the average positions of the absorption bands M^{-1}, the oscillator forces f, and the characteristics of the forms of the bands – the width σ, the asymmetry γ_1, excess γ_2, and the fine structure coefficients F (Table 1).

Table 1 shows that the dyes V-X containing phenyl substituents in the γ,γ'-positions are more deeply colored than their isomers XI–XVI with the same substituents at the α,α'-positions. Thus, the differences in the values of the average positions of the bands in the series of pyrylo-, thiopyrylo-, and pyridocarbocyanins in a methylene chloride solution are equal to 11.3, 7.7, and 33.9 nm and in acetonitrile 13.9, 13.7, and 27.7 nm, respectively. A similar tendency is also observed with respect to the absorption maxima in the two solvents. However, it is expressed much more distinctly with respect to the M^{-1} values than with respect to λ_{max} values. This is because the forms of the absorption bands of the dyes studied differ sharply. Being the centers of gravity of the bands, the values of M^{-1} permit a more objective comparison of the curves of any of the forms.

The redistribution of the intensities in the spectra of the dyes studied is manifested in the greater differences of the σ, γ_1, γ_2, and F values of the isomeric compounds. Thus, pyrylo- and thiopyrylocyanins V-VIII have narrower bands in the two solvents than the isomeric dyes XI-XIV. In methylene chloride, the bands of the former dyes are generally asymmetric with sharp apices and more structurized (higher values of γ_1, γ_2, and F) than in the latter. In the strongly solvating acetonitrile, the change in coefficients γ_1, γ_2, and F is much less regular. In the isomeric pyridocyanines IX, X and XV, XVI, the width and the form characteristics of the dyes do not differ very much.

It is characteristic that dyes XI-XIV containing two phenyl groups in the α,α'-positions of the hetero residue have broader absorption bands than their tetraphenyl analogs substituted in the α,α', γ, γ'-positions (Table 1 and [2]). Judging by the color, the two types of isomers occupy an intermediate position between tetra-tert-butyl-substituted and tetraphenyl-substituted dyes – compounds V-XVI are more deeply colored than the former and have a higher color than the latter (Table 1, [2, 3]).

To interpret the patterns of the position and form of the absorption bands of the synthesized dyes we carried out quantum-chemical calculations of their average positions M_{theor}^{-1} and of quadratic changes in the bond orders δ [3] (Table 2). The calculations were carried out by a simple Hückel MO method, using the same approximations and parameters as in [3]. For compounds V-X, the resonance integrals β of the $C–C_6H_5$ bonds were taken as equal to 0.8. In dyes XI-XVI, they were selected in analogy to [5] according to the rotation angles of the phenyl groups, depending on the nature of the hetero atom [6]. For comparison, we calculated the same parameters for tetraphenyl-substituted dyes (Table 2).

The data of quantum-chemical calculations of M_{theor}^{-1} show that taking into account the phenyl groups in both the α,α'- and γ,γ'-positions leads to deepening of the color, compared with the corresponding tetra-tert-butyl-substituted pyrylocyanins and their hetero analogs (Table 2 [3]). At the same time, the M_{theor}^{-1} of diphenyl-substituted dyes is lower than the corresponding value for the tetraphenyl-substituted compounds (Table 2). These data indicate that the phenyl groups elongate the chromophore of the synthesized dyes. This leads to the deepening of their color in comparison with tetra-tert-butyl-substituted compounds. Compounds V-XVI have a shorter chromophore than the tetraphenyl-substituted analogs and, therefore, they are more highly colored than the latter compounds.

In the isomeric dyes V-X and XI-XVI, the length of the chromophore is the same. However, the values of their λ_{max} and M^{-1} parameters differ appreciably (Table 1). hence it can be concluded that the phenyl groups in α,α'- and γ,γ'-positions conjugate to a different degree with the main chromophore. The data of quantum-chemical calculations (Fig. 1) show that in the hetero residues of the dyes studied a strong bond alternation takes place even at the same values of β ($\beta_{C=C} = \beta_{C-C} = 1$). The $C_{(5)}–C_{(6)}$ and $C_{(6)}–O$ bond orders thereby differ from one another more considerably than the orders of the $C_{(3)}–C_{(4)}$ and $C_{(4)}–$

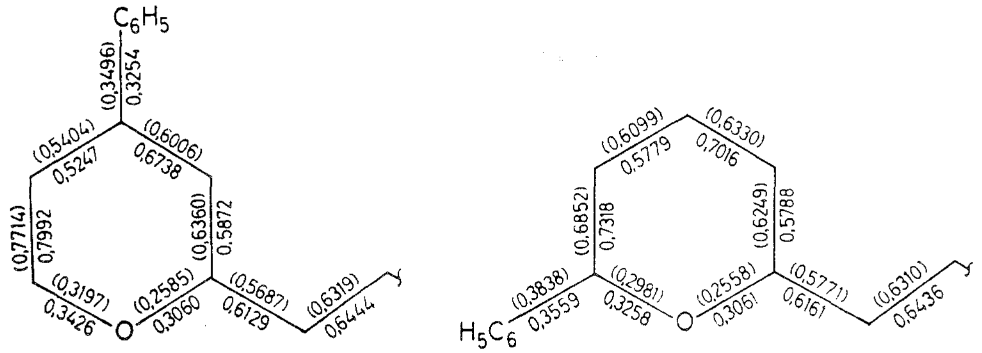


Fig. 1. Results of quantum-chemical calculations of π-bond orders in the ground and excited (numerals in brackets) states in pyrylocyanin cations V and XI.

$C_{(5)}$ bonds, and deviate to a greater extent from a bond order of an ideal polymethine state of the dyes (0.6366 [7]). Hence it follows that the phenyl groups in the α,α'-positions conjugate more weakly than those in the γ,γ'-positions, and this should lead to a higher color on transition from compounds V, VI to XI, XII. In fact, even a rough modeling in the calculations of the bond alternation in the hetero residues by assigning the value of $\beta = 1.1$ for bonds with an increased order ($C_{(3)}$–$C_{(4)}$ and $C_{(5)}$–$C_{(6)}$) and the value of $\beta = 0.9$ for bonds with a decreased order ($C_{(2)}$–$C_{(3)}$ and $C_{(4)}$–$C_{(5)}$) leads to a higher color in α,α'-diphenyl-substituted pyrylocyanins compared with their isomers.

In thiopyrylocyanins VII, VIII and XIII, XIV, the bonds in the hetero residues are more leveled than in the oxygen-containing analogs (the alternation parameters of the bond orders in the ground state and in the hetero residues, calculated according to [8], for compounds V and VII are equal to 0.1478 and 0.1372, respectively). It can be expected on this basis that the difference in the influence of phenyl; groups in the α,α'- and γ,γ'-positions will be lower in compounds VII, VIII than in XIII, XIV. However, the transition from pyrylo- to thiopyrylocyanin is also accompanied by an increase in the rotation angle of the phenyl groups in the α,α'-positions because of an increase in the steric hindrance from the side of the hetero atom [6], which runs counter to the intensification of conjugation of these groups due to weakening of the bond alternation. As a result, the average positions of the isomeric oxygen-containing dyes V, VI and XI, XII differ by practically the same value as the M^{-1} values of their sulfur analogs VII, VIII and XIII, XIV.

In pyridocyanins XV, XVI, the phenyl groups deviate from the plane of the chromophore much more strongly than in the corresponding pyrylo- and thiopyrylocyanins [6]. This fact plays a decisive role in the increase in color on transition from compounds IX, X to XV, XVI, and also causes a considerably greater difference in the colors of the isomeric pyridocyanins, compared with their oxygen- and sulfur-containing analogs.

In the weakly nucleophilic methylene chloride, the experimental band widths of the dyes studied change symbatically with the calculated δ, which serves as a quantitative measure of the vibronic interactions (VIn) ([3], Tables 1 and 2). This shows that in this solvent the course of the band widths in the series of compounds V-XVI is preferentially determined by the VIn. Analysis of changes in the orders ΔP of the individual bonds during excitation showed that in the phenyl groups of the isomers (and even of the tetra-phenyl-substituted dyes) these changes are slight and practically equal. They make an approximately 2% contribution to the overall value of δ. Hence, it follows that the difference in the rotation angles of phenyls in the α,α'- and γ,γ'-positions of compounds V-XVI, unlike the color, does not decisively influence the width of the bands of the isomeric dyes. In fact, the δ of pyrylocyanins V, VI and XI, XII differ substantially, although their $\beta_{C-C_6H_5}$ values are the same (Table 2).

We have previously shown that in pyrylo-2-cyanins and their hetero analogs the changes in the bond orders of the six-membered heterocycle, in particular of the $C_{(3)}$–$C_{(4)}$ bond, introduce the main contribution to the VIn of the cation of the dye [9]. Introduction of phenyl groups appreciably influences the ΔP of these bonds (Fig. 1). The point is that the order of the C–C_6H_5 bond in both the α,α'- and γ,γ'-diphenyl-substituted dyes in the excited state increases according to the quantum-chemical calculations. This should lead to a decrease during excitation of the orders of bonds of the heterocyclic ring adjacent to the C–C_6H_5 bond, which in turn causes a redistribution of orders of other bonds. Since the $C_{(6)}$–O and $C_{(5)}$–$C_{(6)}$ bonds become elongated on excitation, the introduction of phenyls into the α,α'-positions intensifies this process. The above-described changes, in their turn, promote a considerable shortening during the excitation of the $C_{(4)}$–$C_{(5)}$ bond, since it is located between strongly elongating $C_{(3)}$–$C_{(4)}$ and $C_{(5)}$–$C_{(6)}$ bonds. As a result, in dyes XI-XVI, not only the ΔP of the $C_{(3)}$–$C_{(4)}$ bond, but also that of the above-mentioned bonds of the heterocyclic ring introduce a considerable contribution to the overall value of δ (Fig. 1).

TABLE 3. Characteristics of Synthesized Compounds

Compound	Empirical formula	mp, °C*	Compound	Yield, %	Empirical formula	mp, °C*	Yield, %
I**	$C_{16}H_{19}ClO_5$	213...214	17	IX	$C_{35}H_{41}ClN_2O_4$	170...171	27
II	$C_{16}H_{19}ClO_5$	243...245	40	X	$C_{37}H_{43}ClN_2O_4$	229...231	41
III	$C_{16}H_{19}ClO_4S$	221...223	54	XI	$C_{33}H_{35}ClO_6$	243...245	50
IV	$C_{16}H_{19}ClO_4S$	193...195	55	XII	$C_{35}H_{37}ClO_6$	145...147	49
V	$C_{33}H_{35}BF_4O_2$	237...238	46	XIII	$C_{33}H_{35}ClO_4S_2$	158...160	46
VI	$C_{35}H_{37}BF_4O_2$	171...173	25	XIV	$C_{35}H_{37}ClO_4S_2$	221...222	59
VII	$C_{33}H_{35}ClO_4S_2$	252...253	44	XV	$C_{35}H_{41}ClN_2O_4$	185...188	36
VIII	$C_{35}H_{37}ClO_4S_2$	193...195	35	XVI	$C_{37}H_{43}ClN_2O_4$	198...200	31

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*Compounds I-IV and VI were recrystallized from acetic acid; V, VII, X-XIII, and XVI from a tert-butanol–ethanol (1:1) mixture; VIII, IX, and XIV from an ethanol–ether (2:1) mixture.

**The compound was analyzed in the form of a perchlorate.

Compared with the α,α'-positions, in the γ,γ'-positions the phenyl groups have an opposite influence on the change in the bond orders in the hetero residue. They promote a greater elongation of the $C_{(3)}$–$C_{(4)}$ bond, but considerably counteraction to the shortening of the $C_{(4)}$–$C_{(5)}$ bond (Fig. 1). The last feature hinders the $C_{(5)}$–$C_{(6)}$ bond with a strongly elevated order in the ground state, to elongate substantially in the excited state. Similar hindrances also arise in the $C_{(6)}$–O bond. As a result, the hetero-residue bonds in dyes V-X introduce a smaller contribution to the overall value of δ than the bonds in XI-XVI. For example, the share of the pyrylium ring bonds in compound V is made up of 79.7% of VIn of the cation, and that of dye XI of 82.7%; therefore, the transition from cyanins V-X to the isomeric compounds XI-XVI is accompanied by an intensification of the VIn and broadening of the bands.

In tetraphenyl-substitute pyrylo-2-cyanins and their hetero analogs, the phenyl groups in the γ,γ'-positions decrease the change in the bond orders during excitation, caused by similar groups in the α,α'-positions (the share of the pyrylocarbocyanin ring is made up of 80.4% of the VIn of the cation) and, therefore, these bands have narrower absorption bands than the corresponding α,α'-diphenyl-substituted dyes.

In pyrido-2-cyanins IX, X and XV, XVI, the carbon–carbon bonds of the hetero residue, as in the case of tetra-tert-butyl and tetraphenyl analogs [2, 3] take a considerably smaller part in the conjugation than in the case of oxygen- and sulfur-containing dyes. As a result, the ΔP of the pyridinium ring is less sensitive to the position of the phenyl substituents, and the widths of the bands in the isomeric and tetraphenyl-substituted dyes are similar to one another.

The widths of the absorption bands of the dyes studied are determined not only by the VIn of their cations, but also by solvation effects.

In acetonitrile, the broadening of the bands on transition from compounds V-VIII to XI-XIV is much smaller than in methylene chloride. This indicates a weakening of the nucleophilic solvation. As follows from [10], it weakens on increase in the uniformity of the charge distribution in the cations of the dyes. In unsubstituted pyrylo-2-cyanins and their hetero analogs, a considerable positive charge is concentrated in the α,α'-positions. In these positions of dyes XI-XIV, the phenyl groups noticeably decrease this charge. As a result, in compounds XI-XIV a higher uniformity of charge distribution is achieved than in compounds V-VIII. This is indicated by the overall positive charges in the hetero-residue and in the polymethine chain (the closer these values are, the more uniform is the charge distribution [10]). For example, in pyrylocyanin V, these values are equal to 1.1203 and 0.2209, and, in its isomer XI, 1.0982 and 0.2273.

Thus, on transition from dyes V-X to their isomeric compounds XI-XVI, the increase in color is caused mainly by a decrease in conjugation of the phenyl groups in the α,α'-positions, compared with the γ,γ'-positions. In this series of dyes, the broadening of the absorption bands is caused by the intensification of the VIn, preferentially occurring due to redistribution of bond orders in the hetero residues.

EXPERIMENTAL

The moments of the absorption bands were determined similarly as in [2, 3] from the absorption spectra taken on an SF-3A spectrophotometer in methylene chloride stabilized by 1% absolute ethanol, and in acetonitrile. The UV spectra were run on the same apparatus in methylene chloride. The dyes were thoroughly purified up to the establishment of a constant absorption curve. The purity of the preparations was monitored by TLC on Silufol UV-254 plates using acetonitrile as eluent. The PMR spectra were determined on a Bruker WP-200 spectrometer (200.132 MHz) at 25°C, in CD_3CN, using HMDS as internal standard.

The characteristics of compounds I-XVI are given in Table 3. The results of the elemental analysis for C, H, Cl(F), and N(S) correspond to the calculated data.

2-Methyl-4-phenyl-6-tert-butylpyrylium Tetrafluoroborate (I). A mixture of 47 g (250 mmoles) of 1-phenyl-4,4-dimethylpent-2-en-3-one, 4.85 g (83 mmoles) of acetone and 24.5 g (173 mmoles) of boron trifluoride etherate was stirred at 40°C for 12 h. After cooling, the mixture was diluted with ether. UV spectrum, λ_{max} (log ε): 248 (3.61), 304 (3.99), 342 nm (4.27). PMR spectrum, δ: 1.47 [9H, s, $C(CH_3)_3$], 2.86 (3H, s, CH_3), 7.57-7.79 (3H, m, Ar–H), 8.02-8.07 (2H, m, Ar–H), 8.09 (1H, d, J = 1.6 Hz, β-H), 8.13 ppm (1H, d, J = 1.6 Hz, β'-H).

2-Methyl-4-tert-butyl-6-phenylpyrylium perchlorate (II) was obtained in a similar way as the salt described in [4], from 2-methyl-6-phenyl-4H-pyran-4-one. UV spectrum, λ_{max} (log ε): 252 (4.09), 360 nm (4.32). PMR spectrum, δ: 1.40 [9H, s, $C(CH_3)_3$]; 2.88 (3H, s, CH_3); 7.52-7.73 (3H, m, Ar–H), 7.85 (1H, d, J = 2 Hz, β-H), 8.17 (2H, m, Ar–H), 8.24 ppm (1H, d, J = 2 Hz, β'-H).

2-Methyl-4-phenyl-6-tert-butylthiopyrylium Perchlorate (III). A solution of 0.34 g (6 mmoles) of anhydrous sodium hydrosulfide in 6 ml of absolute ethanol was added to a solution of 0.684 g (2 mmoles) of salt I in 8 ml of acetonitrile. The mixture was stirred for 20 min, then was filtered, and 3.5 ml (41 mmoles) of 70% $HClO_4$ and 100 ml of ether were added to the filtrate. The precipitate was filtered off, dissolved in CH_2Cl_2, sodium perchlorate was filtered off, and the solvent was evaporated. UV spectrum, λ_{max} (log ε): 317 (4.05), 360 nm (4.33). PMR spectrum, δ: 1.57 [9H, s, $C(CH_3)_3$], 3.04 (3H, s, CH_3), 7.57-7.70 (3H, m, Ar–H), 7.91-8.00 (2H, m, Ar–H), 8.55 (1H, d, J = 2 Hz, β-H), 8.66 ppm (1H, d, J = 2 Hz, β'-H).

2-Methyl-4-tert-butyl-6-phenylthiopyrylium perchlorate (IV) was obtained in a similar way as compound III from salt II. UV spectrum, λ_{max} (log ε): 260 (4.20), 370 nm (4.10). PMR spectrum, δ: 1.46 [9H, s, $C(CH_3)_3$], 3.04 (3H, s, CH_3), 7.60-7.90 (5H, m, Ar–H), 8.52 (1H, d, J = 2 Hz, β-H), 8.63 ppm (1H, d, J = 2 Hz, β'-H).

2-[3-(4-Phenyl-6-tert-butylpyranylid-2-ene)prop-1-en-1-yl]-4-phenyl-6-tert-butylpyrylium Tetrafluoroborate (V). A mixture of 0.314 g (1 mmole) of salt I and 1.5 g (10 mmoles) of ethyl orthoformate in 3 ml of acetonitrile was boiled for 5 min in the presence of 0.090 g (1.1 mmoles) of pyridine, then was cooled and poured into 20% HBF_4. The dye was filtered and washed with water.

2-[5-(4-Phenyl-6-tert-butylpyranylid-2-ene)-1,3-pentadien-1-yl]-4-phenyl-6-tert-butylpyrylium Tetrafluoroborate (VI). A mixture of 0.157 g (0.5 mmole) of salt I and 0.128 g (0.5 mmole) of phenyl[(3-phenylamino)-2-propenylidene]ammonium chloride in 0.8 ml of acetic anhydride was boiled for 1 min, and then a mixture of 0.157 g (0.5 mmole) of salt I and 0.110 g (1.34 mmoles) of anhydrous sodium acetate in 1 ml of acetic anhydride was added. The mixture was boiled for 5 min, then was cooled and poured into an aqueous solution of ammonium tetrafluoroborate. The dye was filtered and washed with water.

2-[3-(4-Phenyl-6-tert-butylthiopyranylid-2-ene)prop-1-en-1-yl]-4-phenyl-6-tert-butylthiopyrylium Perchlorate (VII) was synthesized in a similar way as V, starting from salt III and using 20% $HClO_4$.

2-[5-(4-Phenyl-6-tert-butylthiopyranylid-2-ene)-1,3-pentadien-1-yl]-4-phenyl-6-tert-butylthiopyrylium perchlorate (VIII) was synthesized in a similar way as VI, using salt III and sodium perchlorate.

1-Methyl-2-[3-(1-methyl-4-phenyl-6-tert-butyl-1,4-dihydropyridinylid-2-ene)prop-1-en-1-yl]-4-phenyl-6-tert-butylpyridinium Perchlorate (IX). A mixture of 0.078 g (0.142 mmole) of pyrylocyanin V and 0.6 ml of a 10% methanolic solution of methylamine in 1.5 ml of DMSO was heated at 100°C for 2 h. The dye was precipitated by an aqueous solution of sodium perchlorate.

1-Methyl-2-[5-(1-methyl-4-phenyl-6-tert-butyl-1,4-dihydropyridinylid-2-ene)-1,3-pentadiene-1-yl]-4-phenyl-6-tert-butylpyridinium perchlorate (X) was obtained in a similar way as IX, using pyrylocyanin VI.

2-[3-(4-tert-Butyl-6-phenylpyranylid-2-ene)prop-1-en-1-yl]-4-tert-butyl-6-phenylpyrylium perchlorate (XI) was obtained in a similar way as V, using salt II and $HClO_4$.

2-[5-(4-tert-Butyl-6-phenylpyranylid-2-ene)-1,3-pentadien-1-yl]-4-tert-butyl-6-phenylpyrylium perchlorate (XII) was obtained in a similar way as compound VI, using salt II and $NaClO_4$.

2-[3-(4-tert-Butyl-6-phenylthiopyranylid-2-ene)prop-1-en-1-yl]-4-tert-butyl-6-phenylthiopyrylium perchlorate (XIII) was obtained in a similar way as compound V, using salt IV and $HClO_4$.

2-[5-(4-tert-Butyl-6-phenylthiopyranylid-2-ene)-1,3-pentadien-1-yl]-4-tert-butyl-6-phenylthiopyrylium perchlorate (XIV) was obtained in a similar way as compound VI, using salt IV and $NaClO_4$.

1-Methyl-2-[3-(1-methyl-4-tert-butyl-6-phenyl-1,4-dihydropyridinylid-2-ene)-prop-1-en-1-yl]-4-tert-butyl-6-phenylpyridinium perchlorate (XV) was obtained in a similar way as IX, using pyrylocyanin XI.

1-Methyl-2-[5-(1-methyl-4-tert-butyl-6-phenyl-1,4-dihydropyridinylid-2-ene)-1,3-pentadien-1-yl]-4-tert-butyl-6-phenylpyridinium perchlorate (XVI) was obtained a similar way as IX from pyrylocyanin XII.

LITERATURE CITED

1. M. A. Kudinova, V. V. Kurdyukov, and A. I. Tolmachev, *Khim. Geterotsikl. Soedin.*, No. 2, 167 (1988).
2. M. A. Kudinova, N. A. Derevyanko, G. G. Dyadyusha, A. A. Ishchenko, and A. I. Tolmachev, *Khim. Geterotsikl. Soedin.*, No. 7, 898 (1980).
3. V. V. Kurdyukov, A. A. Ishchenko, M. A. Kudinova, and A. I. Tolmachev, *Khim. Geterotsikl. Soedin.*, No. 6, 760 (1987).
4. K. Dimroth, *Angew. Chem.*, **72**, 331 (1960).
5. I. M. Gavrilyuk, A. A. Ishchenko, M. A. Kudinova, and A. I. Tolmachev, *Khim. Geterotsikl. Soedin.*, No. 11, 1486 (1984).
6. A. I. Tolmachev, M. Yu. Kornilov, L. M. Shulezhko, and A. V. Turov, *Teor. Éksp. Khim.*, **11**, 556 (1975).
7. C. A. Coulson and H. C. Longuet-Higgins, *Proc. R. Soc. A*, **191**, No. 1, 39 (1947).
8. A. A. Ishchenko, V. A. Svidro, N. A. Derevyanko, Yu. L. Slominskii, and A. I. Tolmachev, *Opt. Spektrosk.*, **65**, 100 (1988).
9. G. G. Dyadyusha, A. A. Ishchenko, N. A. Derevyanko, and A. I. Tolmachev, *Zh. Prikl. Khim.*, **41**, 998 (1984).
10. A. A. Ishchenko, N. A. Derevyanko, V. M. Zubarovskii, and A. I. Tolmachev, *Teor. Éksp. Khim.*, **20**, 443 (1984).

EFFECT OF ELECTRONIC FACTORS ON THE DIMERIZATION AND ISOMERIZATION OF SUBSTITUTED NITRILE OXIDES OF THE THIOPHENE SERIES

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Sterically hindered, stable 3-thiophenecarbonitrile oxides containing electron-accepting groups (SO_2R, Br) in the 2- or 4-position are converted to substituted 4,5-dithienylfuroxanes when boiled in benzene or toluene, whereas trialkyl-substituted 3-thiophenecarbonitrile oxides isomerize quantitatively to the corresponding isocyanates.

It is known that heating nitrile oxides above the limit of their thermal stability leads to two concurrent reactions: dimerization to furoxanes and isomerization to isocyanates [1]. Here the isomerization to the isocyanate characteristically predominates for sterically hindered, aromatic nitrile oxides [1].

In the present work we have studied the effect of the nature of the substituent on the direction of these conversions in sterically hindered, stable 3-thiophenecarbonitrile oxides Ib-j containing electron-donor or electron-acceptor substituents in the 2, 4, and 5 positions [2, 3] and also in nitrile oxide II [3].

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