8. S. Hünig, G. Kieblich, D. H. Quast, and D. Schentzow, Ann. Chem., No. 2, 310 (1973).
9. E. M. Engler and V. V. Patel, Tetrahedron Lett., No. 5, 423 (1976).
10. V. Y. Lee, E. M. Engler, R. R. Schumaker, and S. S. P. Parkin, Chem. Commun., No. 5, 235 (1983).
11. J. A. Pople and G. A. Segal, J. Chem. Phys., 44, 3289 (1966).
12. H. L. Hase and A. Schweig, Theor. Chim. Acta, 14, 206 (1969).

PYRYLOCYANINES.

21.* UNSYMMETRICAL α-PYRYLO- AND α-PYRIDOCYANINES

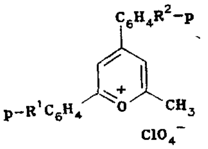
I. M. Gavrilyuk, A. A. Ishchenko,
M. A. Kudinova, and A. I. Tolmachev

UDC 547.812'821.3'753:541.651:668.819

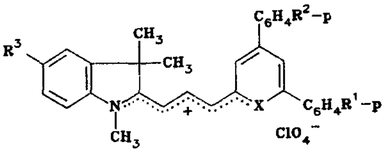
(2-Pyrylo)- and (2-pyrido)(indo)trimethinecyanines containing both electron donor and electron acceptor substituents in the heterocyclic rings have been synthesized. It has been shown that the 4,6-diphenyl-2H-pyran nucleus confers less basicity (electron donor characteristics) than the 1,3,3-trimethylindoline segment. It has also been shown that the introduction of substituents to the heterocyclic residues of unsymmetrical dyes allows one to manipulate their electronic asymmetry over a wide range up to a change in the distribution of charge from one ring to another.

The pyran ring constitutes one of the largest and most important groups, in a practical sense, of polymethine dyes, namely, the pyrylocyanines. Nevertheless, up to this time, the electron donating ability of the heterocyclic residues in these dyes has not been addressed in the literature. On the basis of the work in [2], which has appeared in a monograph [3], the 4,6-diphenyl-2H-pyran residue would be expected to exhibit more electron donating ability than the 1,3,3-trimethylindoline residue; on the other hand, on the basis of [4], just the opposite is predicted. In order to resolve this controversy, the present work describes, in analogy with [5-7], the properties of unsymmetrical dyes containing both electron donating and electron withdrawing substituents in the heterocyclic residues. This approach is well suited to accomplish the stated goal, inasmuch as the introduction of substituents does not alter the structural characteristics or conformation of the dye. Consequently, any change in the electron donating properties of the heterocyclic residues will depend only on the electronic nature of the substituents.

The unsymmetrical (2-pyrylo)(indo)trimethinecyanines IIa-f were synthesized via the condensation of nitro- and methoxy-substituted pyrylium salts Ia-d with 1,3,3-trimethyl-2-formylmethyleneindoline or its 5-nitroderivative. In addition, in order to elucidate analogous mechanisms for substituted (2-pyrido)(indo)trimethinecyanines, the compounds IIIa-f were prepared by treatment of the dyes IIa-f with methylamine.



Ia-d



IIa-f, IIIa-f

I—III a $R^1=NO_2$; c, d, f $R^1=OCH_3$; b, d, f $R^2=OCH_3$; e, f $R^3=NO_2$; II X=O; III X=NCH_3; if not specified, R^1, R^2, R^3 =H

The following parameters have been evaluated for solutions of the synthetic dyes (except IIIa, which could not be isolated in analytically pure form) in both the weakly polar solvent

---

*For Communication No. 20, see [1].

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 44-48, January, 1985. Original article submitted February 10, 1984.

0009-3122/85/2101-0034$09.50 © 1985 Plenum Publishing Corporation

methylene chloride, and the strongly polar solvent acetonitrile: λ_{max}, log ε, the midpoint of the absorption band (M^{-1}), the oscillator strength f, the deviation D_m, and other characteristics of the absorption band — its width σ, coefficient of asymmetry γ_1, excess γ_2, and the fine structure F. These parameters are presented in Table 1, along with values for the unsubstituted dyes II and III.

It is immediately obvious that no conclusions regarding the relative electron donating abilities of the heterocyclic residues in the pyrylocyanines IIa-f can be inferred from the values of the absorption band maxima, since the ratio of the intensities of the vibrational and fundamental transition maxima, just as in the case of the unsymmetrical (flavilo)(indo)-carbocyanines [6], is strongly dependent on the nature of the substituents, even though the form characteristics of the band (γ_1, γ_2, and F) change very little.

The data in Table 1 do show, however, that the introduction of an electron withdrawing nitro group into the oxygen-containing ring of (2-pyrylo)(indo)trimethinecyanine II is accompanied by a hypsochromic shift and widening of the absorption band. In contrast, an electron donating methoxy group in the same ring induces a bathochromic shift and a narrowing of the absorption band relative to the unsubstituted dye II. These spectral changes can only be rationalized if the 4,6-diphenyl-2H-pyran nucleus confers less electron donating ability than the 1,3,3-trimethyleneindoline residue. This conclusion is confirmed by the observation that a decrease in the electron donating ability of the 1,3,3-trimethyleneindoline fragment via the incorporation of a nitro group (compound IIe) manifests itself in a more intense color and nar-

TABLE 1. Characteristics of the High Wavelength Absorption Bands for Solutions of the Dyes IIa-f and IIIa-f

Dye	X	R^1	R^2	R^3	Solvent*	λ_{max}, nm	M^{-1}, nm	lg ε	D_m	f	σ, cm^{-1}	γ_1	γ_2	F
IIa	O	NO_2	H	H	1	640, 676	637,1	4,65; 4,67	—	0,86	1889	1,12	2,5	0,056
					2	634, 666	625,0	4,63; 4,62	—	0,84	2012	1,18	2,8	0,067
II	O	H	H	H	1 [4]	654, 682	641,1	4,71; 4,63	−8,3	0,76	1450	0,89	1,5	0,031
					2	650	627,9	4,63	−7,2	0,67	1594	1,21	3,3	0,046
IIb	O	H	OCH_3	H	1	660, 702	648,9	4,77; 4,73	−9,0	0,81	1387	1,14	2,5	0,046
					2	656	636,4	4,73	−8,7	0,78	1505	1,19	3,0	0,044
IIc	O	OCH_3	H	H	1	662, 706	655,3	4,75; 4,71	−10,0	0,77	1352	1,00	1,8	0,037
					2	660	642,1	4,73	−10,7	0,78	1482	1,02	2,1	0,037
IId	O	OCH_3	OCH_3	H	1	664, 700	654,9	4,78; 4,79	−7,2	0,81	1324	1,26	3,0	0,054
					2	662	642,8	4,78	−8,0	0,81	1414	1,19	3,0	0,045
IIe	O	H	H	NO_2	1	648, 676	646,7	4,84; 4,88	−1,1	0,86	1094	0,93	1,4	0,033
					2	646	635,6	4,88	−0,8	0,93	1223	0,87	1,5	0,028
IIf	O	OCH_3	OCH_3	NO_2	1	670	645,8	4,95	14,8	0,85	1037	1,14	2,4	0,042
					2	650	634,6	4,85	14,4	0,80	1189	0,95	1,9	0,035
IIIa	NCH_3	NO_2	H	H	1	566								
					2	544								
III	NCH_3	H	H	H	1 [4]	550	538,0	4,84	27,3	0,72	1160	1,17	2,8	0,046
					2	536	519,0	4,74	40,4	0,76	1527	1,13	2,9	0,069
IIIb	NCH_3	H	OCH_3	H	1	552	534,6	4,89	31,4	0,81	1206	1,14	2,7	0,047
					2	534	515,4	4,78	44,5	0,83	1514	1,13	2,8	0,053
IIIc	NCH_3	OCH_3	H	H	1	554	537,0	4,90	30,0	0,86	1254	1,14	2,9	0,048
					2	536	518,2	4,81	42,2	0,88	1517	1,12	2,8	0,053
IIId	NCH_3	OCH_3	OCH_3	H	1	550	532,0	4,86	35,0	0,80	1278	1,19	3,0	0,052
					2	532	513,5	4,80	46,9	0,89	1547	1,16	2,9	0,056
IIIe	NCH_3	H	H	NO_2	1	532	507,8	4,79	70,4	0,84	1545	1,35	3,4	0,075
					2	520	495,8	(4,81)	77,7	(1,02)	1848	1,48	4,0	0,084
IIIf	NCH_3	OCH_3	OCH_3	NO_2	1	524	499,6	4,74	80,3	0,81	1659	1,38	3,5	0,083
					2	512	487,9	4,69	86,6	0,83	1940	1,30	3,5	0,089
Astrofloxine					1	550	526,0	5,13	—	1,10	1092	1,31	3,0	0,064
					2	542	519,8	5,14	—	1,12	1048	1,24	1,9	0,059
5,5'-Dinitroastrofloxine					1	568	551,7	5,24	—	1,09	879	1,15	1,8	0,063
					2	568	548,0	5,16	—	1,04	980	1,40	3,2	0,076

*1) Methylene chloride; 2) acetonitrile.

rowing of the absorption band. We note also, that the differences in the electron donating abilities of the heterocycles cannot be associated with varying degrees of solvation for the dyes in question, since the spectral changes described above arise in both the relatively nonpolar solvent methylene chloride, as well as in the strongly polar solvent acetonitrile (Table 1).

Similar rules governing the changes in the position and width of the absorption band were observed for the effects of substituents in the (flavilo)(indo)trimethinecyanine series [6]. It is significant that in the series of dyes of type II the introduction of methoxy groups in the para positions of both phenyl substituents (dye IId) induces a smaller bathochromic shift than the introduction of a single methoxy group to the ring in position 6 of the pyran nucleus (dye IIc). The introduction of two methoxy groups to the pyran nucleus of dye IIe, which already contains a nitro group in the indoline ring, results not in a bathochromic, but rather a very small hypsochromic shift (dye IIf). A similar substitution in the (flavilo)(indo)trimethinecyanine series leads to a larger bathochromic shift of the absorption band. The observed effects can be explained if the electron donating ability of the oxygen-containing heterocyclic residue in both the (2-pyrylo)- and (flavilo)(indo)trimethinecyanines is less than that of the indoline residue. The difference in the electron donating abilities of the end groups is smaller, however, in the case of the type II dyes. As a result, the introduction of a methoxy group in the pyran residue or a nitro group in the indoline nucleus of II balances the electron donating abilities of the two heterocyclic residues, and the dye becomes symmetrical. The introduction of a second methoxy group to the pyran nucleus renders that group more electron donating than the indoline group, which once again increases the electronic asymmetry of the dye, resulting in a more intense color as well as a change in the distribution of charge along the bonds. The introduction of a nitro group in the indoline residue of dye IId further increases the charge distribution in the direction of the pyran ring and induces a hypsochromic shift of the absorption maximum. The change from IId to IIf also increases the intensity of the absorption maximum. However, the band width does not increase as expected, but rather is constricted (cf. Table 1). This latter observation follows apparently from the fact that the introduction of a nitro group by itself into the indoline portion of the dye, as evident in the case of the symmetrical indotrimethinecyanine, is accompanied by a significant decrease in the absorption band width (Table 1). It follows then, that the changes in the absorption band width for the dyes II-IIf are comparable to the changes observed in the parent dyes. For the compounds of type II it is impossible to reach a conclusion regarding the electron donating abilities of the heterocyclic components based only on the values for σ.

We note also, that the values for the deviation (D_M) were inadequate to resolve the question about the relative electron donating abilities of the heterocyclic residues in the dyes II-IIf. Apparently, in the present case, just as in [2, 6], these values may be attributed to large differences in the absorption bands of the parent dyes (ca. 190-240 nm, based on M^{-1}).

For the unsymmetrical pyridocyanines III, IIIa-f the absorption bands of the parent dyes differ far less than in the pyrylocyanines, and the ratio of the intensities of the fundamental and vibrational maxima does not depend to as large an extent on the nature of the substituents. As a result, accurate conclusions for these compounds can be drawn from the values for λ_{max}; the values for the deviation (D_M) also reflect changes in the electron donating abilities of the heterocyclic residues. As can be seen from a comparison of λ_{max} and M^{-1} for the substituted (2-pyrido)(indo)trimethinecyanines IIIa-f and the unsubstituted compound III, the introduction of an electron withdrawing nitro group to the pyridine residue leads to an increased color intensity. Electron donating methoxy groups in the pyridine ring do not influence λ_{max} values for the dyes, although the absorption bands are displaced toward the short wavelength region of the spectrum, as evidenced by the values for M^{-1}. A larger hypsochromic shift occurs in the case of dye IIIe, which contains a nitro group on the 1,3,3-trimethylindoline ring; further introduction of two methoxy groups to the pyridine nucleus shifts the band maximum even more in this direction. A comparison of the deviations for the substituted (2-pyrido)(indo)trimethinecyanines vs. the unsubstituted analog III leads one to the conclusion that these dyes are characterized by a significant electronic asymmetry, which is increased when methoxy groups are added to the pyridine residue or nitro groups are added to the trimethylindoline fragment. The absorption band widths also increase in this direction. These results are consistent with a greater electron donating ability for the six-membered heterocyclic ring (pyridine) than for the five-membered indoline ring in these dyes.

In this way, the addition of electron donating and electron withdrawing substituents to the heterocyclic residues of unsymmetrical dyes allows one to manipulate their electronic asym-

TABLE 2. Properties of the Synthetic Dyes

Compound	bp,* °C	Found, %			Molecular formula	Calc., %			Yield, %
		C (OCH$_3$)	H (N)	Cl		C (OCH$_3$)	H (N)	Cl	
Ia	251—252	55,5	3,6	9,0	$C_{18}H_{14}ClNO_7$	55,2	3,6	9,1	3,5
IIa	258—259		(5,0)	6,2	$C_{31}H_{27}ClN_2O_7$		(4,9)	6,2	25
IIb	185—186	68,6	5,5	6,2	$C_{32}H_{30}ClNO_6$	68,8	5,4	6,4	63
IIc	172—173	69,1	5,4	6,3	$C_{32}H_{30}ClNO_6$	68,8	5,4	6,4	56
IId	167—168	(10,6)		6,4	$C_{33}H_{32}ClNO_7$	(10,5)		6,0	80
IIe	>300		(5,2)	6,1	$C_{31}H_{27}ClN_2O_7$		(4,9)	6,2	75
IIf	262—263	(9,6)		5,5	$C_{33}H_{31}ClN_2O_9$	(9,9)		5,6	82
IIIb	160—162		(4,8)	6,0	$C_{33}H_{33}ClN_2O_5$		(4,9)	6,2	60
IIIc	255—256		(5,2)	6,1	$C_{33}H_{33}ClN_2O_5$		(4,9)	6,2	58
IIId	197—199		(4,7)	5,7	$C_{34}H_{35}ClN_2O_6$		(4,7)	5,9	50
IIIe	217—218		(7,3)	6,0	$C_{32}H_{30}ClN_3O_6$		(7,2)	6,1	41
IIIf	172—173		(6,3)	5,4	$C_{34}H_{34}ClN_3O_8$		(6,5)	5,5	36

*Compounds IIa-d were crystallized from CH_3COOH; IIe, f from CH_3CN; IIIb-f from C_2H_5OH; and Ia from $CH_3CN—CH_3COOH$ (1:1).

metry over a wide range, up to a change in the distribution of charge from one ring to another. At the same time, this method can be used to assess the relative electron donating abilities of the heterocyclic residues.

EXPERIMENTAL

The absorption band characteristics were determined in an analogous manner to [1, 4] on the basis of the spectra obtained on an SF-4A spectrophotometer in methylene chloride (stabilized with 1% C_2H_5OH) and acetonitrile. UV spectra were recorded on this spectrophotometer in acetonitrile. PMR spectra were recorded on a Tesla BS-487-B spectrometer (60 MHz) at 20°C in CF_3COOH with HMDS as internal standard. The purity of the compounds was monitored by TLC on Silufol UV-254 plates with acetonitrile eluent.

2-Methyl-4-phenyl-6-(4-nitrophenyl)pyrylium Perchlorate (Ia). To a solution of 4.8 g (34 mmole) of benzalacetone in 30 ml of absolute ether was added 4.1 ml (50 mmole) of 70% $HClO_4$ dropwise; the temperature was maintained at 0 ± 3°C. Acetic anhydride (22 ml) was then added in small portions at the same temperature. A crystalline residue was deposited. The cold reaction mixture was treated with 5.9 g (36 mmole) of 4-nitroacetophenone and then heated on a water bath until the solid phase had completely dissolved. The salt Ia separated out of the reaction mixture after 3-4 h at room temperature (Table 2). UV spectrum, λ_{max} (log ε): 261 (4.19), 352 (4.38), 418 nm (4.08). PMR spectrum: 2.60 ppm (3H, s, CH_3).

1,3,3-Trimethyl-2-{3-[4-phenyl-6-(4-nitrophenyl)pyranylidene-2]-1-propenyl}-3H-indoline Perchlorate (IIa). A mixture of 0.392 g (1 mmole) Ia, 0.204 g (1.1 mmole) 1,3,3-trimethyl-2-formylmethyleneindoline, and 1.0 ml of acetic anhydride was boiled vigorously for 5-7 min. The mixture was cooled and the resulting precipitate was removed by filtration.

Perchlorate Salts of 1,3,3-Trimethyl-2-{3-[4-(4-methoxyphenyl)-6-phenylpyranylidene-2]-1-propenyl}-3H-indoline (IIb), 1,3,3-Trimethyl-2-{3-[4-phenyl-6-(4-methoxyphenyl)pyranylidene-2]-1-propenyl}-3H-indoline (IIc), and 1,3,3-Trimethyl-2-{3-[4,6-di(4-methoxyphenyl)pyranylidene-2]-1-propenyl}-3H-indoline (IId). These were obtained in an analogous manner from salts Ib [1], Ic [1], and Id [8], respectively, and purified by chromatography on Al_2O_3 in chloroform.

Perchlorate Salts of 1,3,3-Trimethyl-5-nitro-2-[3-(4,6-diphenylpyranylidene-2)-1-propenyl]-3H-indoline (IIe) and 1,3,3-Trimethyl-5-nitro-2-{3-[4,6-di(4-methoxyphenyl)pyranylidene-2]-1-propenyl}-3H-indoline(IIf). These were obtained in an analogous manner to IIa from 2-methyl-4,6-diphenylpyrylium perchlorate or salt Id [8], respectively, and 1,3,3-trimethyl-5-nitro-2-formylmethyleneindoline [9].

1-Methyl-2-[3-(1,3,3-trimethylindolinylidene-2)-1-propenyl]-4-phenyl-6-(4-nitrophenyl)-pyridinium Perchlorate (IIIa). The dye IIa (0.172 g, 0.3 mmole) was dissolved in 2-3 ml of DMF, 1 ml (ca. 25 mmole) of a 7.5% methanolic solution of methylamine was added, and the solution was heated at 50-60°C for 1.5 h. The mixture was cooled, and the resulting salt was washed with water.

Perchlorate Salts of 1-Methyl-2-[3-(1,3,3-trimethylindolinylidene-2)-1-propenyl]-4-(4-methoxyphenyl)-6-phenylpyridine (IIIb), 1-Methyl-2-[3-(1,3,3-trimethylindolinylidene-2)-1-propenyl]-4-phenyl-6-(4-methoxyphenyl)pyridine (IIIc), 1-Methyl-2-[3-(1,3,3-trimethylindolinylidene-2)-1-propenyl]-4,6-di(4-methoxyphenyl)pyridine (IIId), 1-Methyl-2-[3-(1,3,3-trimethyl-5-nitroindolinylidene-2)-1-propenyl]-4,6-diphenylpyridine (IIIe), and 1-Methyl-2-[3-(1,3,3-trimethyl-5-nitroindolinylidene-2)-1-propenyl]-4,6-di(4-methoxyphenyl)pyridine (IIIf). These were obtained in an analogous manner to IIIa from the dyes IIb-f, respectively.

LITERATURE CITED

1. I. M. Gavrilyuk, A. A. Ishchenko, M. A. Kudinova, and A. I. Tolmachev, Khim. Geterotsikl. Soedin., No. 11, 1486 (1984).
2. G. A. Reynolds and J. A. Van Allan, J. Heterocycl. Chem., 12, 367 (1975).
3. T. H. James, Theory of the Photographic Process, MacMillan (1977).
4. M. A. Kudinova, N. A. Derevyanko, G. G. Dyabusha, A. A. Ishchenko, and A. I. Tolmachev, Khim. Geterotsikl. Soedin., No. 7, 903 (1980).
5. I. M. Gavrilyuk, A. A. Ishchenko, M. A. Kudinova, and A. I. Tolmachev, Khim. Geterotsikl. Soedin., No. 9, 1189 (1983).
6. I. M. Gavrilyuk, M. A. Kudinova, A. A. Ishchenko, and A. I. Tolmachev, Dokl. Akad. Nauk SSSR, Ser. B, No. 6, 28 (1983).
7. I. M. Gavrilyuk, A. A. Ishchenko, M. A. Kudinova, and A. I. Tolmachev, Ukr. Khim. Zh., 50, 1101 (1984).
8. G. N. Dorofeenko and S. V. Krivun, Ukr. Khim. Zh., 29, 1058 (1963).
9. J. Mee and D. Heseltine, Patent 1,562,912 (France) [Cl.C091, C071], 1969; Chem. Abstr., 73, P110914r.

CHEMISTRY OF HETEROCYCLIC QUINONIMINES.

6.* DIRECT AMINATION OF BENZO[*a*]PHENOTHIAZIN-5-ONE WITH AROMATIC AMINES

G. B. Afanas'eva, V. I. Vysokov,
O. N. Chupakhin, and I. S. Ufimtseva

UDC 547.869.2:542.953

The reaction of benzo[*a*]phenothiazin-5-one with aromatic amines proceeds under mineral acid activation of the substrate to generate 6-arylamino derivatives exclusively. N-Alkylanilines give, in addition to the corresponding 6-N-alkyl-N-arylaminobenzo[*a*]phenothiazin-5-ones, the dealkylation product, namely 6-anilinobenzo[*a*]phenothiazin-5-one.

The potential utilization of aryl(alkyl)aminobenzo[*a*]phenothiazin-5-ones as laser agents [2], dyes [3], or biologically active compounds [4] has stimulated a need for the development of straightforward methods for their synthesis. At the present time they are synthesized via difficult multistep cyclization procedures based on the initial introduction of appropriate substituents into the synthons [5, 6]. The direct amination of heterocyclic quinonimines (HQI) which are benzoannelated on the quinonimine fragment has not been described in the literature. The simple introduction of O- and S-nucleophilic residues into benzo[*a*]phenothizain-5-one (I) has recently been reported [1].

In the present paper we describe the nucleophilic amination of benzo[*a*]phenothiazin-5-one with the following aromatic and aliphatic-aromatic amines: aniline, p-chloro-, p-bromo-, p-methyl-, p-methoxy-, N-methyl-, and N-ethylaniline.

It has previously been demonstrated [7] that the method of activation of the reagents significantly influences the ease of nucleophilic substitution of hydrogen in HQI. Without prior activation benzo[*a*]phenothiazin-5-one does not react, even at reflux, with any of the amines

---

*For Communication No. 5, see [1].

S. M. Kirov Ural Polytechnic Institute, Sverdlovsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 49-52, January, 1985. Original article submitted May 3, 1984.

0009-3122/85/2101-0038$09.50 © 1985 Plenum Publishing Corporation