SPIROPYRANS OF THE PHENANTHRIDINE SERIES

É. R. Zakhs, V. P. Martynova,
and L. S. Éfros

The relative stabilities of the cyclic and open forms of spiropyrans of the phenanthridine series depend on the character and position of the substituents in the chromene ring and also on the polarity of the media. The structure of the open forms of the spiropyrans is closer to the limiting dipolar structure. The open forms of the carboxy derivatives of the spiropyrans are stabilized in alcohol solutions due to proton transfer to the phenoxide oxygen.

The ease of dark and photoinduced reversible transformations of the open and spiran forms of spiropyrans based on five-membered nitrogen heterocycles depends to a considerable extent on the presence of substituents and their character [1, 2]. We have previously established that 6-(o-oxidostyryl)derivatives (I) of the N-methylphenanthridinium ion are capable of undergoing intramolecular cyclization to give colorless spiropyrans (II) [3].
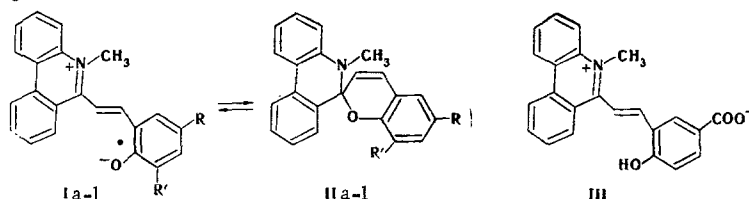
In order to ascertain the effect of substituents on the properties of spiropyrans of the phenanthridine series, we synthesized a number of compounds of this type with substituents in the chromene ring (Table 1). Like the previously described first representatives [3], they were obtained by condensation of 5,6-dimethylphenanthridinium methosulfate with salicylaldehyde derivatives in the presence of excess piperidine. The condensation products were isolated from the reaction mass in either the spiran (IIa-e,k,l) or merocyanine (If-j) from, depending on the nature of R and R'. The stability of the spiran form decreases as the electron-acceptor properties of the substituents become stronger. The dibromo (If, R = R' = Br) and nitromethoxy (Ig, R = NO$_2$, R' = OCH$_3$) derivatives, like the previously described nitro derivative (R = NO$_2$, R' = H) [3], are isolated as merocyanines (I) in the condensation in alcohol. When they are heated in solvents of low polarity they are converted to the corresponding spiropyrans (IIf,g), which can be isolated in the crystalline state.

A colorless spiropyran form (IIh) cannot be isolated for compounds with stronger acceptor substituents — the bromonitro derivative (Ih, R = NO$_2$, R' = Br). However, solutions of Ih in benzene and dioxane (two absorption maxima of identical intensity at 395 and 590 nm are observed immediately after dissolving the compound) are quite rapidly decolorized as a consequence of the formation of spiropyran IIh in solution, as shown by the similarity in the absorption spectrum of the decolorized solution (λ_{max} 330 nm) and the spectra of the remaining spyrans (Tables 1 and 2). The decolorization is sharply accelerated during irradiation with sunlight. The rate of dark cyclization depends markedly on the polarity of the solvent. Thus the time required for half conversion of Ih to IIh at 20° C in dioxane is ~30 min, as compared with ~315 min (at 30°) in a 5% solution of alcohol in benzene.

We were also unable to isolate spiropyrans with NO$_2$ and COOH groups in the 8' position (IIi, j), although the isomeric 6' derivatives are completely stable in the crystalline state. It is, of course, true that

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TABLE 1. 5-Methyl-6'-R-8'-R'-spiro(5,6-dihydrophenanthridine-6,2'-[2H]chromenes) (II) and 5-Methyl-6-(2-oxido-3-R'-5-R-styryl)phenanthridinium Salts (I)

Compound	R	R'	Decomp. point, °C	Empirical formula	N, %† found	N, %† calc.	λ_{max}, nm (lg ε)*	Yield, %
IIa	Cl	H	206—207	$C_{22}H_{16}ClNO$	4,0	4,1	237, 267, 328 (4,71; 4,24; 3,91)	87
IIb	Br	H	220—225	$C_{22}H_{16}BrNO$	3,6	3,2	240, 265*, 326 (4,82; 4,38; 3,98)	95
IIc	CH₃	H	216—219	$C_{23}H_{19}NO$	4,5	4,3	240, 260*, 332 (4,68; 4,30; 3,96)	91
IId	OCH₃	H	222—223	$C_{23}H_{19}NO_2$	4,2	4,1	245, 263*, 332 (4,66; 4,30; 3,99)	57
IIe	H	OCH₃	181—185	$C_{23}H_{19}NO_2$	4,0	4,1	232, 267, 332 (4,65; 4,32; 3,88)	91
IIf	Br	Br	93—97	$C_{22}H_{15}Br_2NO$	3,4	3,0	240, 272*, 332 (4,63; 4,17; 3,82)	61
IIg	NO₂	OCH₃	215—217	$C_{23}H_{18}N_2O_4$	7,0	7,2	245, 340 (4,55; 4,16)	82
Ig	NO₂	OCH₃	224—226	$C_{23}H_{18}N_2O_4$	7,2	7,2	245, 340 (4,55; 4,16)	91
Ih	NO₂	Br	225—230	$C_{22}H_{15}BrN_2O_3$	6,6	6,4	247, 265*, 330, 590 (4,50; 4,31; 4,00; ~2,5)	82
Ii	H	NO₂	105—111	$C_{22}H_{16}N_2O_3$	7,9	7,9	270*, 328, 340, 360*, 610 (4,24; 3,87; 3,69; ~2,5)	60
Ij	H	COOH	193—195	$C_{23}H_{17}NO_3$	4,0	3,9	252, 320, 358, 375, 530 (4,65; 1,00; 0,75; 0,72; 0,51)	83
IIk	COOH	H	205—207	$C_{23}H_{17}NO_3$	4,2	3,9	249, 265*, 325 (4,76; 4,26; 3,78)	90
Il	COOCH₃	H	219—221	$C_{24}H_{19}NO_3$	3,9	3,8	248, 265*, 323 (4,78; 4,28; 3,76)	94

*The UV spectra of Ii, j were recorded with chloroform solutions, while the UV spectra of the remaining compounds were recorded with dioxane solutions. The intensities of the absorption relative to the absorption at 320 nm are indicated for Ij instead of log ε. The spectrum of Ih was measured 2 h after it had been dissolved. The asterisks denote the shoulders and inflection points.
†Satisfactory results of elementary analysis for C and H or for halogen were also obtained for all of the compounds.

TABLE 2. Absorption Spectra of I and II in Alcohol

Compound	λ_{max}, nm (lg ε)*
IIf	242, 270*, 330, 384*, 545 (4,73; 4,29; 3,98; 3,56; 3,42)
Ig, IIg	252, 327, 394, 420, 517 (4,59; 4,12; 4,19; 4,20; 4,14)
Ih	252, 270*, 322, 395, 475 (4,62; 4,31; 4,21; 4,25; 4,16)
Ii	242, 251, 270*, 322, 335*, 360*, 505 (4,61; 4,61; 4,28; 4,01; 3,95; 3,80; 3,78)
Ij	250, 317, 375, 412 (4,58; 3,87; 3,76; 3,81)
IIk	247, 265*, 320, 405 (7,92; 3,59; 1,00; 0,45)
IIl	248, 265*, 290—300, 510 (6,45; 2,48; 1,00; 0,04)

* The intensities of the absorption relative to the absorption at 300–320 nm are indicated instead of log ε for IIk and IIl. The shoulders and inflection points are indicated by asterisks.
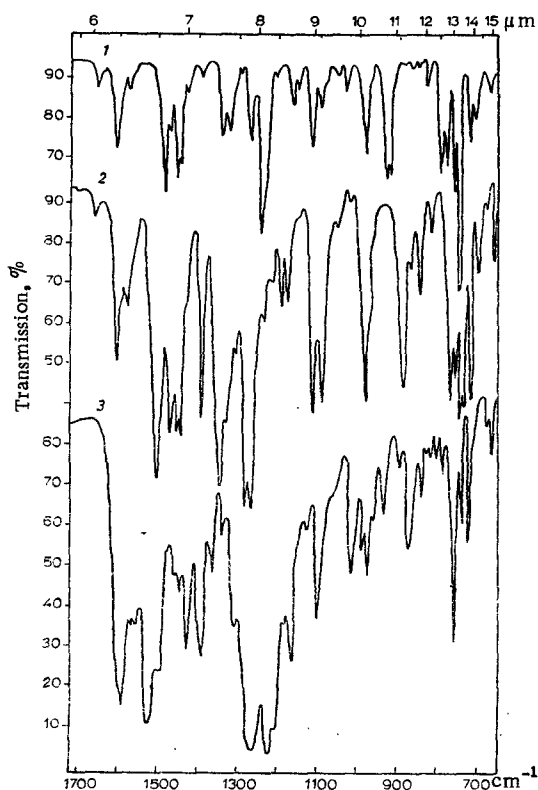

Fig. 1. IR spectra (in KBr): 1) 5-methyl-spiro(5,6-dihydrophenanthridine-6,2'-[2H] chromene); 2) 5-methyl-6'-nitro-8'-methoxyspiro(5,6-dihydrophenanthridine-6,2-[2H]chromene) (IIg); 3) 5-methyl-6-(2-oxido-3-methoxy-5-nitrostyryl)phenathridinium salt (Ig).

Ii, j exist primarily as spiropyrans (IIi, j) in chloroform solutions, but the absorption in the visible region attests to the presence of appreciable amounts of the open forms.

Considering the pronounced stabilization of the open forms in polar media, it might be assumed that the impossibility of isolating crystalline spiropyrans IIh-j is due to strong polar interaction in the crystal lattices of these compounds. Molecules of such compounds are stable in the cyclic form only when they are shielded from one another by a solvate shell from the molecules of the nonpolar solvent.

The structure of the open forms of the spiropyrans is close to dipolar (I), inasmuch as pronounced negative solvatochromism is peculiar to them [4]. The long-wave maximum of Ih is shifted from 590 nm in dioxane solution to 575 and 545 nm when ethanol is added, (up to 2 and 10% concentration), but it is found at 480 nm in alcohol; in the case of Ij, the long-wave maximum is shifted from 530 nm in chloroform to 458 nm when ethanol is added (up to a 10% concentration). These hypsochromic shifts are much greater than those previously observed for the indoline analogs [5]. At the same time, the absorptions of the shorter-wave maximum of the open form and the long-wave maximum of the closed form depend only slightly on the solvent.

The dipolar structure of the open forms is in agreement with their IR spectra (Fig. 1), in which a carbonyl absorption band is absent. For the open forms of the nitro derivative the absorption in the region of the stretching vibrations of the nitro group and the aromatic ring is very similar to the absorption of sodium p-nitrophenoxide. The greatest difference in the IR spectra in these same regions is observed on passing to the corresponding spiropyrans.

The behavior of the 8'- and 6'-carboxy derivatives in alcohol solution is peculiar. In contrast to 6-carbomethoxyspiran IIl, which is very slightly colored with an absorption maximum in the usual region for open forms at ~510 nm, solutions of these compounds have intense absorption, but in the shorter-wave region (~410 nm) characteristic for solutions in acidic media. Moreover, the relative intensity of the long-wave absorption of Ij is approximately twice that of the 6'-isomer. The reason for the difference in the spectra of Ij, k and the spectra of the remaining spirans can only be proton transfer from the carboxyl group to the phenoxide oxygen of the open form to give a structure of the merocyanine salt type (III), which

apparently occurs readily intramolecularly. This sort of proton transfer or, at least, the formation of a hydrogen bond in Ij should therefore also occur in the solid phase. The presence of a structure of the III-type is confirmed by the fact that when excess ammonia is added to an alcohol solution of Ik, the latter initially becomes crimson-colored as a consequence of the formation of the open form with R = COO⁻ and is then decolorized. The spectrum of the solution becomes practically the same as that of spiropyran IIk in dioxane. Thus when the carboxyl group ionizes, the spiran form proves to be stable even in alcohol solution; this is in agreement with the absence of electron-acceptor properties for this group.

EXPERIMENTAL

The aldehydes used in the synthesis and the spiropyrans were obtained by literature methods.

5-Methyl-6'-R-8'-R'-spiro(5,6-dihydrophenanthridine-6,2'-[2H]chromenes) (IIa-f,k,*l*) and 5-Methyl-6-(2-oxido-3-R'-5-R-styryl)phenanthridinium Salts (Ig-j). These compounds were obtained by refluxing an alcohol solution (20 ml of alcohol per millimole; 70% aqueous alcohol was used in the preparation of If) of equimolecular amounts of 5,6-dimethylphenathridinium methosulfate and the appropriate aldehyde in the presence of 2 equivalents of piperidine for 30 min. Compounds IIa-e,k,*l* were isolated as the colorless spiropyrans, while If-j were isolated in the open form. Compound Ij was isolated from the reaction mixture by the addition of hydrochloric acid up to pH 6. The reaction products were removed by filtration, and washed successively with alcohol and ether. Compound IIf was obtained by the addition of an equal volume of water to a hot solution of If in alcohol (1:100). Heating of Ig in chlorobenzene (1:50) gave a green solution, from which IIg was isolated on cooling. All of the spiropyrans except IIf were only slightly soluble in alcohol, hexane, and ether, but more soluble in aromatic or chlorinated hydrocarbons. Compounds IIa, c, e, *l* were purified by crystallization from toluene (1:20; 1:60 for II*l*), while IIb was purified by crystallization from benzene (1:30), IId was purified by crystallization from m-xylene (1:30), IIg was purified by crystallization from chlorobenzene (1:50), and IIk was purified by crystallization from dimethylformamide (DMF) (1:20). Compound Ii was precipitated from alcohol solution (1:120) by the addition of a twofold quantity of water, while compounds Ih, j were precipitated from DMF solution (1:50) by the addition of a fourfold amount of ether. All of the I compounds had intense colors in the crystalline state: If was dark blue, Ig and Ii were dark brown, Ih was orange-red, and Ij was orange-yellow.

LITERATURE CITED

1. E. Berman, R. E. Fox, and F. D. Thomson, J. Amer. Chem. Soc., 81, 5605 (1959).
2. R. Gautron, Bull. Soc. Chim. France, 3190 (1968).
3. V. P. Martynova, N. E. Shelepin, N. S. Loseva, É. R. Zakhs, L. E. Nivorozhkin, V. I. Minkin, and L. S. Éfros, Khim. Geterotsikl. Soedin., 167 (1971).
4. A. I. Kiprianov, Usp. Khim., 29, 1336 (1960).
5. M. A. Gal'bershtam, L. M. Mikheeva, and N. P. Samoilova, Khim. Geterotsikl. Soedin., 1534 (1972).