PHOTOCHROMIC AND THERMOCHROMIC SPIRANS.

IX.* PREDICTION OF THE STABILITIES OF SPIROPYRAN STRUCTURES AND THE ELECTRONIC ABSORPTION SPECTRA OF THEIR PHOTOCOLORED AND THERMOCOLORED ISOMERS

B. Ya. Simkin, V. I. Minkin,
and L. E. Nivorozhkin

The self-consistent-field (SCF) molecular orbital (MO) Pariser—Parr—Pople (PPP) methods within the Dewar σ,π parametrization for the calculation of the properties of the ground states and variable β for the description of the excited states were used to estimate the relative stabilities of the spiropyran forms in spiran—merocyanine valence–tautomeric equilibria and to predict the electronic spectra of the photocolored and thermocolored forms of spirans. A correlation was found between the energies of anionic localization of the heterocation and the electron charge in the hypothetical position of spirocyclization and the experimental data on the stability of the spiropyran form. Another correlation links the calculated differences in the energies of the pyran and quinoneallide systems with the tendency of the latter to undergo cyclization. The stabilities of a large number of spiropyrans with different structures are predicted on the basis of the correlations obtained. The effect of various structural factors on the absorption spectra of the merocyanine forms of spiropyrans was studied. 2H-Naphtho[2,3-b]-pyran systems are recommended as promising photochromic compounds.

Compounds of the spiropyran series (A) are among the most promising organic photochromic materials and are distinguished by their high resolving power, ease of recording and reading information, and other valuable properties [2-4]. In this connection, we studied the photochemical behavior and spectral properties of an extremely large number of spiropyrans with different structures [2-6]. It is sufficient to note that information on more than 1000 spiropyrans representing ∿75 different structural types was presented in a review by Bertelson in 1971 [2].

The mechanism of the photocoloration and thermocoloration of spiropyran compounds is due to A⇌B, valence tautomerization, respectively, in the electronically exicted or ground states with subsequent isomerization to the most stable merocyanine trans structure C:
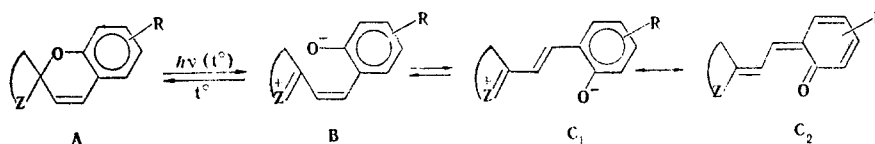
The long-wave absorption band of the C form is one of the most practically important characteristics of the spiropyrans and is usually found at 500-600 nm [2, 5, 6]. At present the requirements of technology have created the need for the preparation of spiropyrans whose merocyanine forms absorb light in the longer-wave portion of the spectrum. This task, together with other practically important tasks (increasing the photostabilities and quantum yields of photoreactions, decreasing the rate of the dark process, etc.), continues to stimulate the development of research on the synthesis of new types of spiropyran compounds and the structural modification of previously investigated compounds. The major question that primarily arises in the course of these studies is the problem of the relative stabilities

*See [1] for communication VIII.

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of the spiropyran and merocyanine forms. An obligatory requirement for photochromic spiropyrans is evidently the **energetic preferableness of cyclic form** A as compared with merocyanines B and C and inversion of the energy levels of these forms in the electronically excited state, whereas in attempts to obtain a large number of spiropyrans from pyridinium [7], quinolinium [8, 9], benzimidazolium [18], and other salts (see Table 1), it was found that the open merocyanine structures C are more stable than spiropyrans A. Consequently, the search for photochromic spiropyrans should begin with a study of the relative stabilities of structures A and C.

The tasks of the present research consisted of: 1) finding correlations between the energy characteristics obtained by means of quantum-mechanical calculations and the data on the electron distribution in the heterocyclic and pyran fragments of spiropyrans A, on the one hand, and the experimental data on the state of the A⇌C thermal equilibria, on the other, and 2) extrapolation of the correlations thus obtained to previously unknown spiropyrans in order to predict their stable forms; 3) a theoretical study of the nature and energetics of the lower singlet electron transitions in merocyanines of the C type during extensive variation of their structures in order to ascertain the structural factors that are capable of ensuring the desired spectral shifts.

To solve the indicated problems we calculated the energy characteristics and the spectra of an extensive series of previously described compounds of the spiropyran type and a number of new structures by means of the self-consistent-field (SCF) MO method within the Pariser—Parr—Pople (PPP) approximation with different parametrizations for the ground and excited states. The results of the calculations are discussed below.

1. Correlation of the Relative Stabilities of the Spiran

and Merocyanine Forms of Spirobenzopyrans

The results of theoretical calculations [11] and the experimental data on the ^{1}H and ^{13}C NMR spectra of the merocyanine forms of benzothiazoline spiropyrans of the C type [12] indicate strong polarization of their molecules corresponding to a large contribution of dipolar structure C_l. Considering this, the B→A thermal cyclization can be regarded as intramolecular nucleophilic addition to the α position of the corresponding heterocyclic cation. In this case one might expect that the equilibrium of the B and A forms would be shifted to an even greater extent to favor the latter, the lower the energy of anionic localization of the α position of the heterocyclic cation (L_α^-) or the higher the positive charge (q_α) in the α position of the cation. In fact, calculations by Veksler and coworkers [13] by the Hückel MO method for a series of cations of nitrogen heterocycles demonstrated that there is a certain threshold value of the localization energy (L_α^-) above which the products of condensation of α-methyl-substituted heterocyclic cations with aromatic o-hydroxy aldehydes do not undergo cyclization to spiropyrans A when they are treated with bases and are stable in merocyanine form C. Correlations between the q_α values and the order of the heteroatom—α-carbon atom bond and the tendency to form a spiropyran have also been established.

The number of heterocyclic cations has been expanded substantially in the present research. We performed calculations of virtually all of the heterocyclic nitrogen-, sulfur-, and oxygen-containing cations included in the compositions of the heretofore known types of spiropyrans: I-VI, VIII-XV, XXI, XXIII, and XXIV. A number of new structures of cations (VII, XVI-XX, XXII, XXV, XXVI) that hold promise for the **preparation of spiropyrans from** them were also calculated.

The results of the calculations are presented in Table 1. An analaysis of these results leads to the following principal conclusions.

1. There is an extremely definite correlation between the experimental data on the relative stabilities of the A and C isomers and the charges and energies of anionic localization for the corresponding positions of the heterocyclic cations. It is apparent from Fig. 1 that almost all of the heterocycles form the spiro[2H-1-benzopyran] structures obtained on the basis of the corresponding C-methyl cations and salicylaldehyde if the energy of anionic localization of the spiro position in the cation is lower than 6.2 eV and the charge is higher than +0.18 e. The exceptions (with respect to L_α^-) pertain to the series of benzothiazoline spiropyrans of the IX type, for which the merocyanine form is preferable when there is no substituent in the 3 position of the benzopyran fragment, and to perimi-

TABLE 1. Charges (q_α), Energies of Anionic Localization (L_α^-), and Orders of the π Bonds (pzc_α) in the Spirocyclization Positions for Heterocyclic Cations I–XXVI and Experimental Data [2] on the State of the $A \rightleftharpoons C$ Equilibrium in Solutions*

Cation			q_α	$p\,zc_\alpha$	L_α^-	Thermally stable form in the $A \rightleftharpoons C$ equilibrium	
designation in Fig. 1	type	Z or R (spirocyclization position)				exptl.	prediction
1	2	3	4	5	6	7	8
1		O (2)	0,161	0,518	6,14	—†	Sp⇌Mc
2		(4)	0,191	—	6,02	—	Sp
3	I	N (2)	0,104	0,578	6,63	Mc [2,13]	
4		(4)	0,159	—	6,49	Mc [13]	
5		S (2)	0,174	0,467	4,52	—	Sp
6		(4)	0,233	—	5,09	—	Sp
7		O (2)	0,193	0,538	5,90	Sp	
8		(4)	0,207	—	5,68	Sp	
9	II	N (2)	0,138	0,616	6,36	Mc [2,9]	
10		(4)	0,173	—	6,09	Mc [14]	
11		S (2)	0,198	0,461	4,43	Sp [15]	
12		(4)	0,251	—	4,94	—	Sp
13		O (1)	0,201	0,559	5,76	—	Sp
14		(3)	0,071	0,452	6,91	—	Mc
15	III	N (1)	0,138	0,633	6,22	Mc⇌Sp[10]	
16		(3)	0,026	0,501	7,30	Mc[10]	
17		S (1)	0,230	0,517	4,19	—	Sp
18		(3)	0,070	0,343	5,43	—	Sp
19		O	0,156	0,514	6,16	Sp	
20	IV	N	0,106	0,588	6,60	—	Mc
21		S	0,155	0,421	4,69	Sp [15]	
22		O	0,229	—	5,28	Sp [2,16]	
23	V	N	0,196	—	5,60	Sp	
24		S	0,270	—	4,89	Sp	
25		O	0,253	0,564	5,49		Sp
26	VI	N	0,174	0,665	6,07	Sp [17]	
27		S	0,252	0,518	4,13	—	Sp
28		O	0,315	0,594	5,56	—	Sp
29	VII	N	0,260	0,709	6,11	—	Sp⇌Mc
30		S	0,262	0,499	4,12	—	Sp
31		O	0,116	0,664	7,21	Mc	
32	VIII	N	0,051	0,626	7,70	—	Mc
33		S	0,168	0,720	5,68	—	Sp ‡
34		O	0,153	0,680	6,82	Mc	
35	IX	N	0,091	0,636	7,23	Mc[18]	
36		S	0,194	0,742	5,74	Mc[8]	
37		O	0,370	0,631	5,27	Sp[19]	
38	X	N	0,298	0,742	5,90	Sp[20]	
39		S	0,323	0,570	3,79	—	Sp
40	XI		0,187	0,654	6,30	Sp[1]	
41	XII		0,309	0,838	4,46	Sp	
42	XIII		0,286	0,827	4,52	Sp	
43	XIV		0,278	0,627	4,21	Sp[21,22]	
44	XV		0,313	0,677	4,88	Sp [23]	

TABLE 1 (Continued)

45	XVI		0,224	0,599	6,32	—	Mc
46	XVII		0,278	0,665	4,99	—	Sp
47	XVIII		0,266	0,663	5,01	—	Sp
48	XIX		0,412	0,644	6,10	—	Sp⇌Mc
49	XX		0,327	0,586	6,63	—	Mc
50	XXI	H	0,275	0,588	5,54	Sp[24]	
51		Ph	0,219	0,557	5,51	—	Sp
52	XXII	H	0,270	0,593	5,61	—	Sp
53		Ph	0,218	0,564	5,57	—	Sp
54	XXIII		0,296	0,674	4,71	Sp[20]	
55	XXIV		0,353	0,566	4,34	Sp[25]	
56	XXV		0,442	0,855	3,51	—	Sp
57	XXVI		0,140	0,658	6,10	—	Sp⇌Mc

*Experimental data for spirobenzopyrans obtained from the given heterocycle and salicylaldehyde (Sp indicates spiropyran, and Mc indicates merocyanine).
†The dashed line indicates that no experimental data are available. These spiropyrans or their corresponding merocyanines have not been synthesized.
‡According to the data in [8], the spectrum of the product of condensation of the indicated cation with 2-hydroxy-naphthaldehyde corresponds to the merocyanine form.
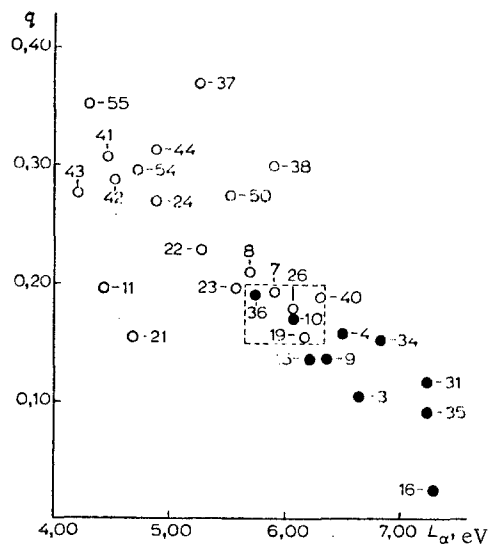

Fig. 1. Correlation of the q_α and L_α^- values with the experimental data on the relative stabilities of the spiropyran and merocyanine forms: ●) merocyanines; ○) spirans. The dashed line outlines the "region of uncertainty" of the theoretical prediction, the location of a point within which corresponds to probable energetic equivalence of structures A and C. The serial numbers from Table 1 were used to designate the heterocyclic cations.

dine spiropyran XI. The correlation with respect to charge has more exceptions, but, on the whole, as one can see from Fig. 1, one can rather accurately isolate the region of stability of the spiropyrans and merocyanine forms and the intermediate region with limits q_α = 0.15-0.19 e and L_α^- = 5.8-6.3 eV, in which approximately equal stabilities of the A and C structures are expected, on the basis of the calculated data. The correlation with the $Z-C_\alpha$ bond orders is less reliable for the prediction of the positions of the $A \rightleftharpoons C$ equilibria.
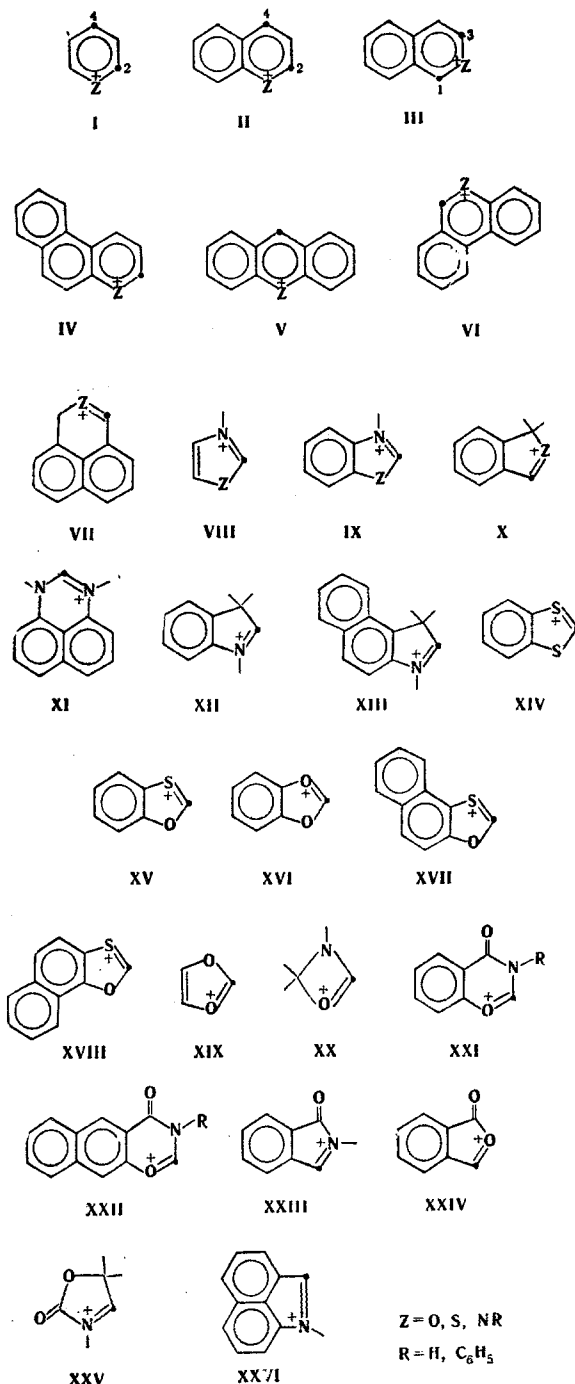
2. The correlation presented above makes it possible to sufficiently validly predict a number of new structures of the type A spiropyran (see Table 1). Particularly stable spiropyran structures can be obtained on the basis of the heterocyclic system XXV, for which sufficiently simple methods for the preparation of a methylene base that is the conjugate base of the α-methyl cation have been described [26].

On the other hand, the results of the calculations indicate the inexpediency of attempts to synthesize spiropyrans from a number of heterocyclic structures (for example, XVI, XX, etc.).
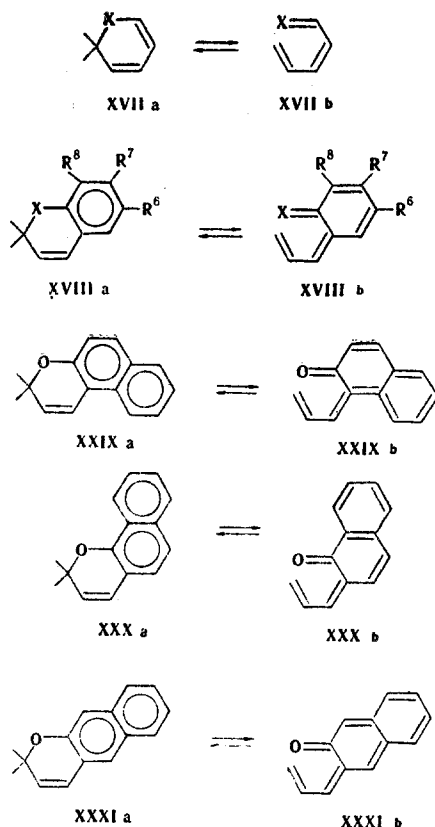
3. The results of calculations for cations I-X with variable heteroatom Z = NR, O, S show that the stability of the corresponding spiropyran form A increases in this order. This tendency is in agreement with the available experimental data. However, it must be noted that the calculations evidently somewhat overestimate the tendency of sulfur-containing systems to exist in the form of a spiropyran structure. It is precisely for this reason that an important group of benzothiazoline spirans (based on IX cations with Z = S) deviate from the general correlation. The reasons for this deviation are evidently associated with the incompletely satisfactory parametrization for the sulfur atom, as noted in [27].
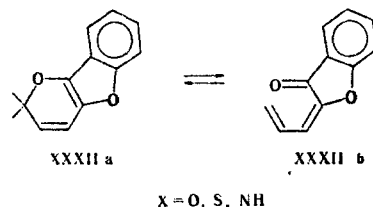
4. The correlations of the stabilities of spiropyran structures do not take into account the electronic and steric effects of the substituents in the fragments of the molecule. A knowledge of the latter is extremely important. Thus the introduction of substituents (for example, an alkyl group) in the 3 position of the benzopyran ring very greatly stabilizes spiran structure A [2, 5]. When there is a nitro group in the 5 and 6 positions of the benzimidazole, even benzimidazole spirans (L_{α}^{-} value of the cation 7.2 eV) exist in the form of spiropyrans A [18]. The introduction of a methyl group in the 3 position of the quinoline cation (II, Z = NR) also leads to a shift of the $A \rightleftarrows C$ equilibrium to favor the spiropyran form [28].

Thus the "critical" L_{α}^{-} value of 6.2 eV and the order of stabilities of the spiropyran tautomers as a function of the type of heterene fragment have meaning as relative characteristics in the case of a constant pyran fragment. The role of the electronic factors of the structure of the conjugated system of the pyran portion of the molecule can be taken into account separately.

2. Effect of the Electronic Structure of the Pyran Fragment on the Relative Stabilities of the Spiran and Merocyanine Forms

This effect can be estimated by calculating the relative energies of the valence tautomers in the equilibria depicted below by means of the PPP method with the Dewar σ,π parametrization [29]:

XVII a   XVII b

XVIII a   XVIII b

XXIX a   XXIX b

XXX a   XXX b

XXXI a   XXXI b

XXXII a   XXXII b

X = O, S, NH

Assuming an additive contribution of the heterene fragments to the relative energies of the indicated equilibria, one can trace the effect of annelation and the nature of heteroatom X and the substituents on the relative stabilities of forms a and b. The results of the calculations are presented in Table 2, according to the data from which the conclusions below can be drawn.

1. The transition from the benzopyran derivatives to pyran derivatives markedly increases the stability of the open form with a XXVIIb fragment. This result is confirmed by a number of unsuccessful attempts, such as, for example [30], the attempted preparation of cyclic spiro[2H-pyran] derivatives.

2. Annelation of an additional benzene ring to benzopyran XXVIII ($R^6 = R^7 = R^8 = H$) in structures of the 3H-naphtho[2,1-b]pyran (XXIX) and 2H-naphtho[1,2-b]pyran (XXX) types, like transition to heterocyclic structures of the XXXII type, promotes an increase in the stabilities of the quinoneallide structures and, consequently, a shift in the $A \rightleftarrows C$ equilibria to favor the merocyanine form. These results are in complete agreement with the numerous experimental data [2].

3. Replacement of salicylaldehyde by thiosalicylaldehyde (XXVIII, X = S) should lead to a shift in the equilibrium to favor the open structure, according to the theoretical prediction. The transition to o-aminobenzaldehyde (XXVIII, X = NH), for example, leads to predominance of the closed spiran form. Virtually no experimental data are available for these systems.

4. The effect of donor (the NH_2 group was used as a model) and acceptor (CHO) substituents is expressed less markedly than the effect of annelation and the nature of the heteroatom, and donor substituents have a smaller effect than acceptor substituents. Donors (in the 7 and 8 positions) and acceptors (in the 6 and 8 positions) promote a shift in the equilibrium to favor the merocyanine structure. Donor substituents in the 6 position and acceptor substituents in the 7 position lead to the opposite effect. These conclusions are in agreement with the voluminous experimental data [31-33] on the effect of substituents in the benzopyran ring of spiropyrans on the position of the $A \rightleftarrows C$ equilibrium.

TABLE 2. Relative Energies of the Pyran (a) and Quinone-allide (b) Structures (in kcal/mole)*

Structure	ΔE	Structure	ΔE
XXVII, X=O	16,1	XXXI	−8,6
XXVII, X=S	28,1	XXXII	13,0
XXVII, X=NH	−1,6	XXVIII, X=O, $R^6=R^7=H$, $R^8=NH_2$	0,3
XXVIII, X=O $R^6=R^7=R^8=H$	0,0	XXVIII, X=O; $R^6=R^8=H$, $R^7=NH_2$	0,4
XXVIII, X=S, $R^6=R^7=R^8=H$	9,7	XXVIII, X=O, $R^7=R^8=H$, $R^6=NH_2$	−0,1
XXVIII, X=NH $R^6=R^7=R^8=H$	−17,7	XXVIII, X=O, $R^6=R^7=H$, $R^8=HCO$	2,6
XXIX	6,9	XXVIII, X=O, $R^6=R^8=H$, $R^7=HCO$	−1,7
XXX	7,2	XXVIII, X=O, $R^7=R^8=H$, $R^6=HCO$	1,4

*A positive sign designates a shift in the equilibrium to favor the open (quinoneallide) form. The ΔE value for the XXVIII$_a$ (X = O) $\rightleftarrows$ XXVIII$_b$ (X = O) equilibrium was adopted as the point of reference.

It should be noted that conclusions 1 and 2 can be easily understood from the point of view of the concepts regarding the effect of the aromatic character of the conjugated cyclic system on the state of the tautomeric equilibria possible for it [34].

3. Calculation of the Electronic Absorption Spectra of the Merocyanine
Forms of Spiropyrans

A joint analysis of the data presented in sections 1 and 2 of this paper makes it possible to specifically select the heterene and pyran portions of the spiropyran molecule in order to satisfy the necessary condition of the photochromic system — stabilization of the spiran structure. Another no less important part of the problem of obtaining a photochromic material with the necessary properties is absorption of the photocolored form in the spectral region determined by the corresponding technical requirements [3, 4].

A rather large number of calculations [11, 35, 36] in which the PPP method was used have been devoted to the theoretical study of the absorption spectra of spiropyrans — merocyanines of the **B** and **C** types. In the case of suitable parametrization [11] [the two-electron coulombic integrals were calculated from the formula in [37], and the geometry and resonance integrals (β) corresponded to a dipolar structure], the PPP method extremely accurately reproduces the most important long-wave portion of the spectrum. This method was used in the present research to calculate the long-wave portion of the spectra of an extensive series of merocyanine forms of spiropyrans (XXXIII-XC). The calculations pursued two principal objectives: 1) the establishment of the effect of various structural modifications of the merocyanine molecule on the position of the absorption bands in its electronic spectrum and 2) the establishment of those structural factors that are capable of leading to a considerable bathochromic shift of the long-wave absorption bands of merocyanines.

Only the most stable trans configuration of the **C** type was taken into account for all merocyanines XXXIII-XC, since previous calculations [11, 35, 36] have shown that the spectra of the various possible conformers of merocyanines differ extremely slightly from one another. The results of the calculations, which are presented in Table 3, make it possible to draw the following conclusions regarding the effect of the structure on the spectra of merocyanines **C**.

XXXIII (1-12)   XXXIV (1,2)

XXXV   XXXVI (1-4)

XXXVII (1-8)   XXXVIII

XXXIX   XC

X = S, CO; Z = O, S, NR
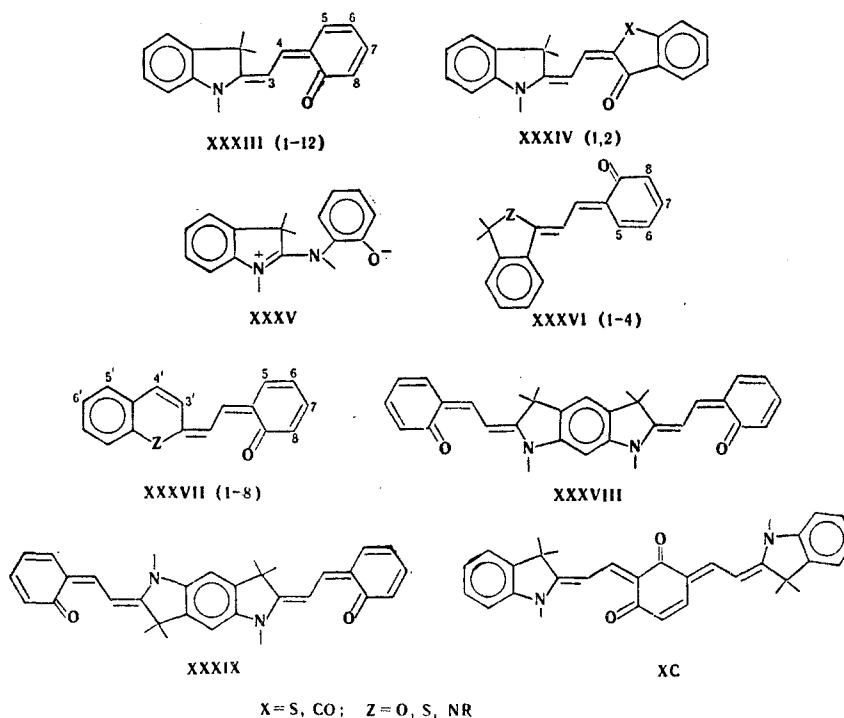
1. Annelation of the benzene and naphthalene rings at any of the possible faces of the quinoneallide ring (except for the pair at 6 and 7 positions) leads only to a very small and usually **hypsochromic** shift of the long-wave absorption band. This conclusion follows from the results of calculations with respect to annelated indoline systems (XXXIII), as well as

TABLE 3. Spectral Characteristics of the Merocyanine Forms of Spiropyrans

Compound	Annelation* or substitution	Calc.			Exptl. [2]	
		ε, eV	λ, nm	f	ε, eV	λ, nm
1	2	3·	4	5	6	7
XXXIII-1		2,10 3,12 3,92	591 397 316	0,48 0,21 0,08	2,11 3,10	588 400
XXXIII-2	6,7-Benzo	1,64 2,59 3,31	754 478 374	0,25 0,41 0,08	—	—
XXXIII-3	5,6-Benzo	2,27 3,00 3,54	546 413 350	0,56 0,08 0,16	2,22 3,10 3,49	558 400 355
XXXIII-4	7,8-Benzo	2,20 3,38 3,66	564 367 339	0,63 0,13 0,12	2,19	567
XXXIII-5	7,8-(2,3-Naphtho)	2,14 3,08 3,43	579 403 361	0,76 0,11 0,00	—	—
XXXIII-6	7,8-(1,2-Naphtho)	2,05 3,05 3,63	604 406 342	0,61 0,19 0,04	—	—
XXXIII-7	5,6-(2,1-Naphtho)	2,20 2,83 3,43	564 438 362	0,56 0,17 0,14	—	—
XXXIII-8	5,6-(2,3-Naphtho)	2,24 2,96 3,28	552 419 378	0,58 0,00 0,24	—	—
XXXIII-9	6-N†	2,08 3,02 4,02	597 410 308	0,31 0,14 0,02	—	—
XXXIII-10	7-N†	2,08 3,24 3,83	597 383 324	0,24 0,11 0,03	—	—
XXXIII-11	3-N†	2,33 3,46 4,06	533 358 305	0,18 0,19 0,08	—	—
XXXIII-12	4-N†	1,92 2,92 4,42	646 426 280	0,57 0,12 0,02	—	—
XXXIV-1	X=S	2,66 3,44 3,67	466 360 338	0,43 0,21 0,38	—	—
XXXIV-2	X=CO	2,61 2,76 4,17	475 449 297	0,37 0,37 0,00	—	—
XXXV	—	2,30 3,56 3,87	539 348 320	0,43 0,18 0,00	—	—
XXXVI-1	Z=O	2,05	606	0,40	2.05	606[19]
XXXVI-2	Z=O,5,6-Benzo	2,20	564	0,34	2,30	539[19]
XXXVI-3	Z=NR	1,96	634	0,68	2,10	590[20]
XXXVI-4	Z=NR, 5,6-Benzo	2,07	599	0,70	—	—
XXXVII-1	Z=O	1,98	626	0,71	1,93	642
XXXVII-2	Z=O, 5,6-Benzo	2,10	590	0,75	2,17	572
XXXVII-3	Z=O,5',6'-Benzo	1,88	660	0,74	—	—
XXXVII-4	Z=O,5,6,5',6'-Dibenzo	2,00	620	0,57	—	—
XXXVII-5	Z=S	2,02	614	0,78	—	—
XXXVII-6	Z=S, 5,6-Benzo	2,13	582	0,80	2,18	570
XXXVII-7	Z=S, 5',6'-Benzo	1,92	645	0,83	—	—
XXXVII-8	Z=S,5,6,5',6'-Dibenzo	2,04	608	0,67	—	—
XXXVIII	—	2,01 2,26 2,76 2,81	616 550 449 441	0,78 0,21 0,00 0,00	—	—

TABLE 3 (Continued)

XXXIX	—	1,89	657	1,01	—	—
		2,25	552	0,00		
		2,82	440	0,00		
		2,98	416	0,15		
XC	—	2,14	580	0,94	—	—
		2,24	553	0,05		
		2,51	495	0,21		
		2,84	437	0,13		

*The positions of the merocyanine rings and the annelated ring at which annelation is realized are indicated.
†The =CH— group is replaced in the indicated position by =N—.

merocyanines XXXVI and XXXVII. The available experimental data are in agreement with this general conclusion in all cases (Table 3).

2. Aza substitution of the methylidyne groups in the quinoid ring and the polymethylidyne chain (XXXIII, 9-12) also has a slight effect on the spectra, although 4-substitution, which is achieved by the use of o-hydroxynitrosophenols in place of o-hydroxy aldehydes in the synthesis of spirans (for example, see [38]), ensures a certain bathochromic shift.

3. The inclusion of a heteroatom or a carbonyl group in place of a CH=CH bond (XXXIV and XXXV) leads to a strong hypsochromic shift of the long-wave absorption band. The reasons for this follow from an examination of the nature of the electronic shifts in the corresponding excited state, which shows that in the case of compounds of the XXXIV type the electron transition is localized exclusively in the polyenone chain. Thus attempts to obtain a bathochromic shift of the absorption bands in photoisomers of spiropyrans by preparation of them with the use of heterocyclic hydroxy aldehydes in place of carbocyclic hydroxy aldehydes are evidently inexpedient.

4. The conclusions regarding the role of annelation and other structural modifications of the quinoneallide portion of the merocyanine on its absorption spectrum do not depend on the structure of the heterene portion (see the data on the XXXIII and XXXVII structural types and the results of our earlier calculations [39]).

In the present research we did not attempt to make a theoretical study of the effect of substituents in the benzopyran portion of the molecule on the spectrum of the photoisomer because of the voluminous experimental data that has been accumulated in this area [2]. The introduction of a nitro group in the 6 or 8 position of the quinoneallide ring when donor substituents are additionally introduced in these positions ensures a shift of the long-wave band in the spectra of indoline and benzothiazoline spiropyrans to 635 nm [40]. Other attempts at a further bathochromic shift of the spectra of merocyanines were based on the additional introduction of auxochromic groups [41] or the preparation of bis-(spiropyrans) of the XXXVII and XXXIX type [42].

The latter case is of particular interest if the photoinduced opening involves both spiropyran rings. In this case one expects the possibility of application of the semiquantitative theory of interaction of conjugated chromophores [43], which predicts splitting of the levels of the excited states. This effect should lead to the appearance of a new long-wave band. Malkin and co-workers [42] assigned the absorption bands observed at 590 nm in toluene solutions of spiropyrans XXXVIIIA and XXXIXA (with 8-nitro substituents) to bis-merocyanine forms (XXXVIII and XXXIX). However, the results of the calculations (Table 3) compel one to assume that opening of only one spiropyran ring was most likely observed in these experiments. If two rings can open simultaneously during photoirradiation (this does not happen in the case of flash photolysis of liquid solutions of XXXVIIIA and XXXIXA [44]), when methoxy and nitro groups are introduced in the 6 and 8 positions, the XXXIX system may, according to the results of the calculations, have a long-wave absorption band. At the same time, bis(spiropyrans) obtained from aromatic dihydroxy aldehydes and having merocyanine forms of the XC type probably hold little promise.

The results of the calculation of the spectrum of the merocyanine form of spiropyran XXXIII-2, the long-wave band of which should be shifted bathochromically (160 nm) relative to merocyanine XXXIII-1, are extremely important. This effect is equivalent to replacement of the oxygen atom in the quinoneallide system by sulfur [45]. Taking into account the fact that, according to the calculated data presented in section 2 of this paper, the use of

2-hydroxy-3-formylnaphthalene in the synthesis of spiropyrans should lead to systems that are stable in the spiropyran form, research involving the 2H-naphtho[2,3-b]pyran series is extremely promising.

COMPUTATIONAL METHODS

The calculations relative to the stabilities and electronic absorption spectra of spiropyran and merocyanine structures were made with the programs and methods described in [27, 46, 47].

The localization energy (L_α^-) was calculated as the difference in the π-electron energies of structures a and b, (for example, the 2 position for I).

I a   I b

In the calculations of the effect of the pyran fragment on the relative stabilities of the spiran and merocyanine structures (section 2) the geometry of the quinoneallide fragments (b) was assumed to be analogous to the geometry of fragment a, i.e., all were assumed to have cis structures, although structure c is apparently the most stable structure (for example, for XXVII):

XXVII c
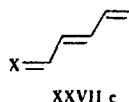
In accordance with [11], a geometrical structure corresponding to the merocyanine form was selected for the calculation of the absorption spectra, and the resonance integrals (β) were not varied. Twenty singly-excited configurations closest to the ground state were taken into account in the construction of the configuration interaction matrix. An increase in the number of configurations to 63 (the maximally possible number of configurations for the program) led to a slight change in the energies of the transitions. Thus the first singlet transition for the XXXIII-1 structure is shifted 0.04 eV bathochromically, and the second is shifted 0.07 eV.

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