PHOTOCHROMIC AND THERMOCHROMIC SPIRANS

V.* A THEORETICAL STUDY OF THE ELECTRONIC STRUCTURE AND SPECTRAL PROPERTIES OF THE PHOTO-COLORED FORMS OF INDOLINE SPIROPYRANS, SPIRODIPYRANS, AND SPIROTHIOPYRANOPYRANS

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

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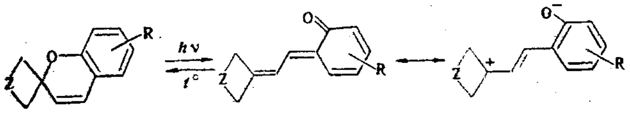
By means of the SCF MO LCAO method in the π-electronic approximation (PPP), the electronic structures and spectral characteristics of indoline spiropyrans, spirodipyrans, and spirothiopyranopyrans have been calculated. The calculated spectral characteristics of the photo-colored forms of the spiropyrans agree best with the experimental results when a geometric configuration corresponding to a bipolar structure is taken. The diffuseness of the long-wave absorption band is not connected with a difference in the spectral characteristics of the stereoisomers. It has been shown that the long-wave electronic transition is localized in the allylidenecyclohexadienone fragment of the molecule. An explanation of the mechanism of the opening up of the spirothiopyranopyrans at the C—O bond is given. The existence of spirothiopyranopyrans in which the thiopyran fragment must be opened is predicted.

Compounds of the spiropyran series form one of the most important classes of organic photochromes [2-4]. The nature of the photochromic properties of the spiropyrans is determined by valence isomerization initiated by irradiation in the absorption band of the spiran form A.



A B₁ B₂

Z — heterene residue, R— substituents, arene nuclei

A large number of publications have been devoted to experimental investigations of the spectral properties and photochromism of the spirans (see the reviews [2-6]), but attempts to study the electronic structures and spectra of compounds A and B with the aid of the methods of quantum chemistry have not been made. Nevertheless, considering the considerable difficulties that are not infrequently encountered in the study of the spectral properties of the unstable photo-colored forms B, the frequent necessity for an extremely complex synthesis preceding the investigation of the properties mentioned, the value of which does not always justify the efforts involved, and also considering the fairly high accuracy achieved in the most improved semi-empirical methods of calculating spectral properties, the problem of a theoretical description and prediction of electronic structures and spectra of the pyrans must be considered as very urgent.

In the present paper, with the aid of the SCF MO method in the Pariser—Parr—Pople (PPP) method, we investigate the electronic structures of the ground and the singlet and triplet excited states, and also the spectra of the open forms (I-V) of a series of pyrans.

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* For Communication IV, see [1].

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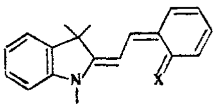
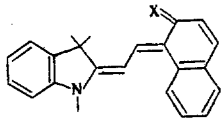


I



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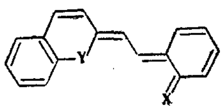

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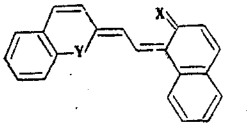

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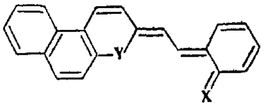
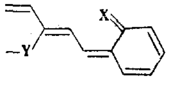


V

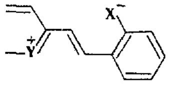
X, Y = O, S

The calculations were performed by the PPP method taking configurational interaction (CI) into account. In the construction of the CI matrix, the 20 singly-excited configurations closest to the ground state were considered. An increase in the number of configurations considered has practically no effect on the energies of the spectral transitions and their intensities. Two-electronic Coulomb integrals were calculated by the method of Mataga and Nishimoto [7]. The resonance integrals $\beta_{\mu\nu}$ were calculated as functions of the interatomic distance $r_{\mu\nu}$ from the formulas of Allinger and Miller [8]. The energies of transition into triplet states were calculated with the use of the special parametrization proposed by Zahradnik et al. [9]. The oscillator force calculated by a well-known formula [10] was then halved, following Bailey's prescriptions [11]. The technique of the calculations has been given in more detail elsewhere [12, 13].

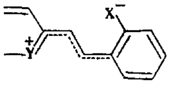
The calculations of the spectral characteristics of α,ω-substituted polyenes has shown that they depend substantially on the sequence of alternation of ordinary and double bonds, and also on the alternation value [14]. In the case of the spiropyrans, a similar problem arises. Qualitatively, the structure of the open form of a spiropyran can be given by two structures: a quinoid (B_1) and a bipolar (B_2) form, in which different polyenic configurations (different molecular geometries) exist; for example, for (III):



III B_1



III B_2



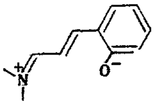
III C

In addition, the complete equivalence of the lengths of the bonds of the four-carbon chain connecting the two nuclei (structure IIIC) may be assumed.

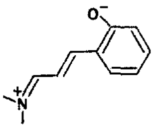
We performed the calculations with a consideration of the geometries or all the possible structures (B_1, B_2, and C) of compounds (I) (X = O) and (III) (X = Y = O). The results of calculations for (III) are given in Table 1 together with the experimental values. The length of an ordinary bond was taken as 1.43 Å and that of a double bond as 1.37 Å. In calculating the structure of (IIIC), the lengths of the bonds of the four-carbon chain were taken as 1.40 Å. The other geometric parameters were similar to those used in previous work [12, 13].

The figures of Table 1 show that the spectral characteristics of the bipolar structure (IIIB_2) practically coincide with the experimental figures. The results of calculations for compound (I) (X = O) are similar to those given. This result confirms the conclusion [15] of the predominant contribution of the bipolar structure in the open forms of the spiropyrans.

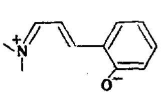
The Indoline Spiropyrans (I and II). The complex structure of the long-wave absorption band of the colored forms of the indoline spiropyrans is generally connected with the existence of four stereoisomers the equilibrium between which depends on the temperature and the solvent [15-17]. All these isomers (Ia-Id) possess the trans configuration relative to the central bond. Steric factors for them are approximately the same, and therefore the stabilities of the isomers are connected with the distances between the N and O atoms [18-20]. The stable isomer (Ic) must have the shortest-wave absorption [15, 21].



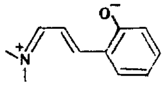
Ia



Ib



Ic



Id

TABLE 1. Spectral Characteristics of Various Structures of Compound (III) (X = Y = O)

Structure	IIIB$_1$			IIIB$_2$			IIIC		
ΔE, eV*	2,83	3,76	4,21	1,93	2,78	3,32	2,33	3,21	3,82
f	0,64	0,05	0,04	0,71	0,18	0,06	0,76	0,04	0,04

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*The calculated figures are given. The experimental figures are: 1.93 and 2.85 eV in isopentane–isopropanol (7 : 2).

TABLE 2. Spectral Characteristics of Compounds (I-V)

Characteristics	Ia	Ib	Ic	Id	Ie	I (X=S)
E_{calc}, eV	2,18 3,22 3,82	2,22 3,25 3.85	2,24 3,23 3,87	2,21 3,24 3,83	2,33 3,74 4,62	1,74 2,81 3,18
f	0,42 0,20 0,02	0,51 0,21 0,04	0,50 0,20 0,03	0,44 0,20 0,04	0,07 0,19 0,02	0,24 0,02 0,36
E_{exp}, eV			2,11 3,10^a		2,26^b	1,66 2,80^c
	I (X=O)	II (X=S)	III (X=Y=O)	III (X=O, Y=S)	III (Y=O, X=S)	IV (X=Y=O)
E_{calc}, eV	2,41 3,08 3,59	1,95 2,67 3,02	1,98 2,78 3,32	2,02 2,70 3,00	1,63 2,72 3,13	2,10 2,84 3,34
f	0,56 0,08 0,16	0,32 0,01 0,36	0,71 0,18 0,06	0,76 0,10 0,08	0.46 0,15 0,40	0,75 0,06 0,10
E_{exp}, eV	2,22 3,10 3,49^g		1,93 2,85^e			2,17^f
	IV (Y=S, X=O)	IV (Y=O, X=S)	V (X=Y=O)	V (Y=S, X=O)	V (Y=O, X=S)	
E_{calc}, eV	2,13 2,76 3,25	1,74 2,69 3,08	1,88 2,68 3,03	1,92 2,57 2,98	1,53 2,67 3,01	
f	0,80 0,05 0,03	0,46 0,07 0,10	0,74 0,18 0,09	0,83 0,08 0,02	0,48 0,17 0,14	
E_{exp}, eV	2,18^g					

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[a] In a mixture of methylcyclohexane and 2-methylpentane (2 : 1) [23]. [b] In benzene [15]. [c] In 3-methylpentane [28]. [d] In mixture of ethanol and toluene (1 : 1) [24]. [e] In a mixture of isopentane and propan-2-o- (7 : 2). [f] In a mixture of ethanol and methanol [25]. [g] In isopentane.

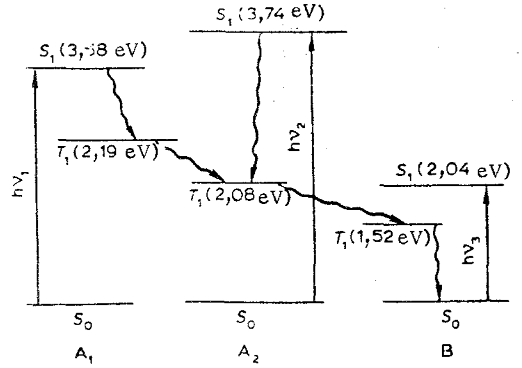


Fig. 1. Diagram of the energy levels of the spirothiopyranopyran (VI): A_1 and A_2 – the 2H-thiopyran and 2H-pyran moieties of the molecule of (VI), respectively; B – the opened pyran fragment of the molecule.

It is assumed [15, 18] that when the C–O bond is cleaved the colored molecule is converted into an unstable form which is most probably the nonplanar cis isomer (Ie) with a nuclear configuration close to the spiran structure. The absorption of the isomer (Ie) must be at shorter wavelengths than that of (Ia–Id).

To confirm this hypothesis, we have made calculations of the isomers (Ia–Ie) (Table 2). The calculated spectral characteristics of the isomers (Ia–Id) scarcely differed from another and agreed well with the experimental figures. Of the four isomers, (Ic) actually has the shortest-wave absorption, but the difference, of 0.04 eV, is not significant. The presence of a broad absorption band for the open forms of the spiropyrans is possibly connected with features of the appearance of a vibrational structure or with intermolecular interactions. The long-wave maximum of the nonplanar cis isomer (Ie), retaining the geometry of the spiran, is shifted hypsochromically relative to the trans isomers, which is in harmony with the results of experiment [15].

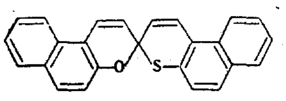
In a preceding communication [1], we showed that the fusion of a benzene nucleus at positions 5, 6, of chromene or thiochromene leads to a hypsochromic shift of the long-wave absorption band of the open forms. This result also proves to be correct for the spiropyrans, as can be established by comparing the long-wave maxima of compounds (I) and (II) (Table 2). The same change in the spectrum is observed experimentally [22].

Spirodipyrans and Spirothiopyranopyrans. For the open forms of the spirodipyrans and spirothiopyranopyrans, just as for the indoline spiropyrans, four trans isomers are possible. The calculated energies of the long-wave transitions of all the trans isomers practically coincide (difference of not more than 0.05 eV), and therefore we give the calculation of only one of them. The energies of the singlet–singlet transitions are in satisfactory agreement with experiment, as can be seen from Table 2. The replacement of oxygen by sulfur in the benzo- and naphthopyran nucleus has practically no effect on the spectral characteristics of the open forms. At the same time, an analogous substitution in the allylidenecyclohexadienone part strongly shifts the long-wave maximum bathochromically, by approximately 120–130 nm (0.35 eV). Benzo-fusion in position 3,4 of the allylidenecyclohexadienone nucleus (compound (IV) leads to a hypsochromic shift of the long-wave maximum, while benzo-fusion in position 5,6 of the 2H-chromene (thiochromene) nucleus [compound (V)] shifts the long-wave transition bathochromically. These facts can be used to establish the method of opening up of unsymmetrical spirodipyrans and spirothiopyranopyrans.

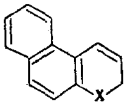
TABLE 3. Calculated Energies of Singlet–Triplet Transitions (S_0-T_1) of Compounds (I–V)

Compound	ΔE, eV	Compound	ΔE, eV
I X=O	0,40 2,34 3,17	III Y=O, X=S	0,35 2,12 2,35
I X=S	0,21 2,13 2,79	III Y=S, X=O	0,97 2,05 3,00
II X=O	0,54 2,40 3,07	IV X=Y=O	1,21 2,00 2,76
III X=Y=O	1,08 1,93 2,84	V X=Y=O	0,99 1,98 2,89

In the spirothiopyrans that we have studied [26], on photoexcitation only the pyran and not the thiopyran ring opens. This result can be explained by making use of the diagram of molecular levels that we calculated on the basis of the mechanism proposed by Bercovic and others [22, 23, 27]. The diagram of levels (Fig. 1) was constructed on the basis of the figures of Tables 2 and 5 of the preceding paper [1]. In view of the absence of appreciable spiroconjugation effects between the spiro-linked nuclei [29], the diagram of levels of the spirothiapyranopyran (VI) can be constructed additively from results for the energy level of 2H-chromene and 2H-thiochromene (VII, X = O, S).

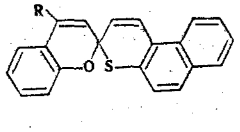


VI



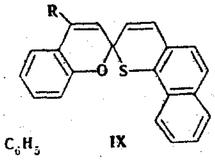
VII X = O,S

The first triplet state of the closed form of thiochromene is 0.15 eV higher than the triplet state of chromene (see Table 5 of the preceding paper [1]). In view of this, the rapid internal conversion into the triplet state of chromene will be prevented by the population of the triplet level of the thiochromene. Consequently, only the triplet level of the chromene is populated, which leads to the opening of the spiropyran at the C–O bond. For the spirothiopyranopyran to open at the C–S bond, the first triplet state of the thiopyran moiety of the molecule must be lower than the triplet state of the pyran moiety. Making use of the figures of Table 5 of the preceding paper [1] it is possible to predict some spirothiopyranopyrans (VIII, IX) in which the thiopyran fragment should open.



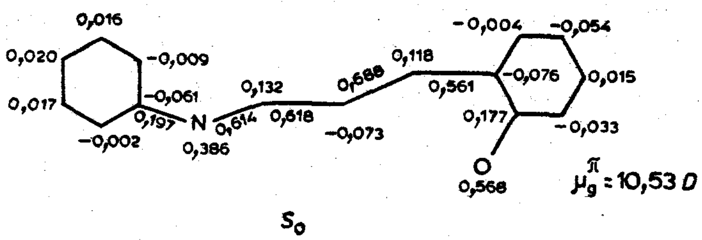
VIII

R = H, C_6H_5

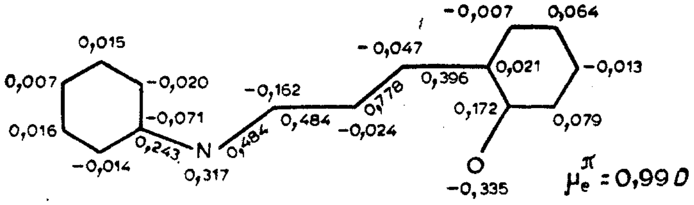


IX

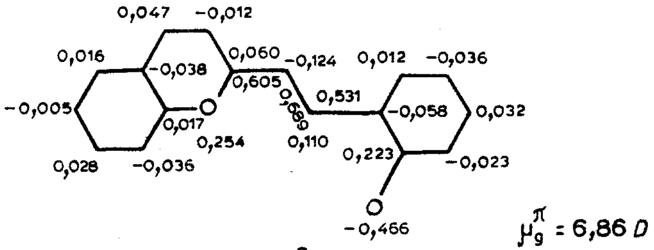
Nature of the Long-Wave Absorption. The π-electronic charges and bond orders of the four-carbon chain in the ground (S_0) and first excited singlet (S_1) states of the indoline spiropyran (I, X = O), the spirodipyran (III, X = Y = O), and the spirothiopyranopyran (III, X = O, Y = S) are shown in the molecular diagrams.



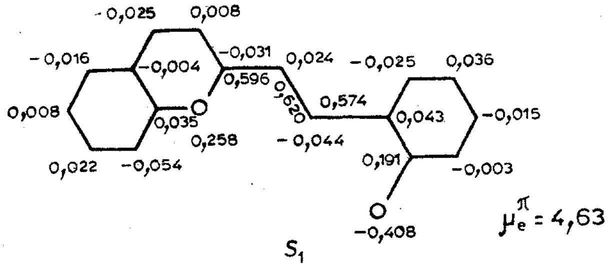
S_0



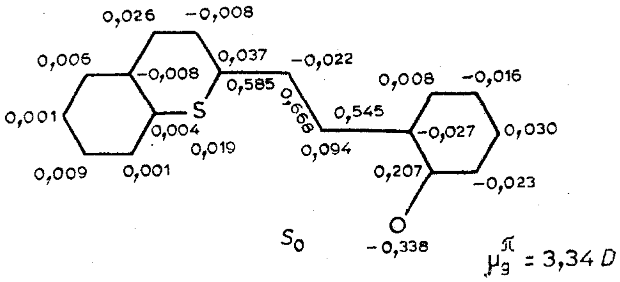
S_1



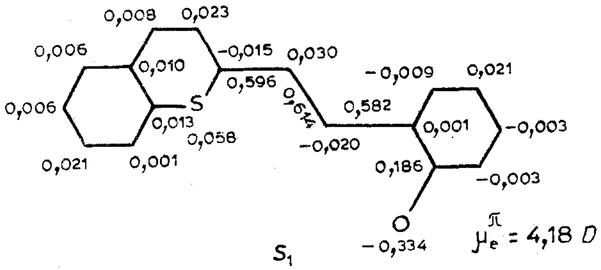
S_0



S_1



S_0



S_1

From a comparison of the charges and a consideration of the form of the most important MOs of the ground and excited states, it may be concluded that the electronic transition is localized in the allylidenecyclohexadienone component of the molecule of the spiropyran. It becomes understandable why the replacement of oxygen by sulfur in the benzo- and naphthopyran nuclei has practically no effect on the spectral properties of the open forms of the spiropyrans [26]. The similar reaction to the benzo-fusion of the long-wave absorption band of the spiropyran and of the chromene corresponding to it is also understandable. It follows from the results presented that structural modifications having the aim of substantially changing the spectral properties of the spiropyrans must affect the allylidenecyclohexadienone part of the molecule.

A consideration of the orders of the π bonds of the four-carbon chain shows a bipolar structure (B_2) of the ground state of the spiropyrans, while the charge distribution does not correspond to complete polarization. For the indoline spiropyran in the first excited state, the dipole moment decreases by almost 10 D, which leads to a hypsochromic shift of the corresponding absorption band on passing to polar solvents [15]. The dipole moments of the spiropyran and of the spirothiopyranopyran scarcely change on passing to the excited state. This explains the absence of solvatochromy that is actually observed.

The energies of the singlet–triplet transitions of some spiropyrans are given in Table 3. The first triplet state of the open forms of the spiropyrans (I, X = O, S, and III, X = S, Y = O) is located very close to the ground state, which must hinder its observation. The absence of experimental results on the position of the triplet levels of the open forms of the spiropyrans does not yet enable the correctness of the calculations to be checked.

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