PHOTOCHROMIC AND THERMOCHROMIC SPIRANS

IV.* A THEORETICAL STUDY OF THE ELECTRONIC STRUCTURE AND SPECTRA OF THE VALENCE ISOMERS OF 2H-CHROMENES, THIOCHROMENES, AND 1,2-DIHYDROQUINOLINES

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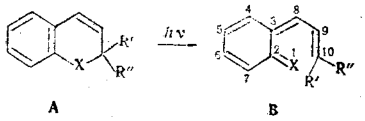
By means of the SCF MO LCAO method in the π-electronic (PPP) and all-valence (CNDO) approximations the electronic structures and spectral characteristics of the valence isomers of 2H-chromenes, thiochromenes, and 1,2-dihydroquinolines have been calculated. On the basis of a consideration of the electronic configuration of various excited states, an explanation has been given of the mechanism of the photochromism of the chromenes and their analogs. A hypothesis has been put forward concerning the possibility of thermochromism in 1,2-dihydronaphthalene. It has been shown that the diffuseness of the long-wave absorption band of the open forms of the compounds investigated is not connected with the existence of several stereoisomers. The influence of the heteroatom and of benzo-fusion on the long-wave absorption has been analyzed. The nature of the electronic transition responsible for the long-wave absorption of the photo-colored forms has been explained.

Compounds of type A – the chromenes (X = O) [2, 3], thiochromenes (X = S) [4], the selenochromenes (X = Se) [1], the dihydroquinolines (X = NR) [5, 6], and the dihydronaphthalenes (X = CH_2) [7, 8] – undergo valence isomerization on irradiation.



A B

The reaction explains the nature of the thermochromism and photochromism of compounds of the spiropyran series (R', R'' together represent a heterene residue) [9, 10]. It also attracts attention since it possibly determines the capacity of green plants containing chromene alkaloids for accumulating solar energy [2]. To understand the mechanism of the photochemical cleavage of a σ bond on irradiation and to describe and predict photoreaction routes, information is necessary on the electronic structure of the ground and excited states and the nature of the low-lying electronic transitions. With these aims, we have performed a calculation of the electronic structure, energy states, and spectra of the valence isomers of a number of 2H-chromenes, thiochromenes, and 1,2-dihydroquinolines, and of 1,2-dihydronaphthalene (I-XI) in the π-electronic and all-valence approximations of the SCF MO method.

The calculations of the electronic structure and the spectra of the cyclic (A) and open (B-E) isomers of the compounds investigated were performed by means of the Pariser–Parr–Pople (PPP) method and a method taking into account all the valence orbitals in the approximation of complete neglect of differential overlap (CNDO) [11]. There is no information in the literature on the molecular geometry of the chromenes

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*For Communication III, see [1].

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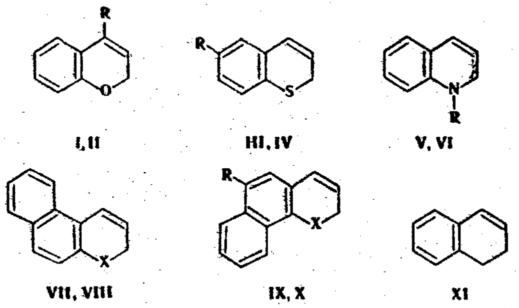
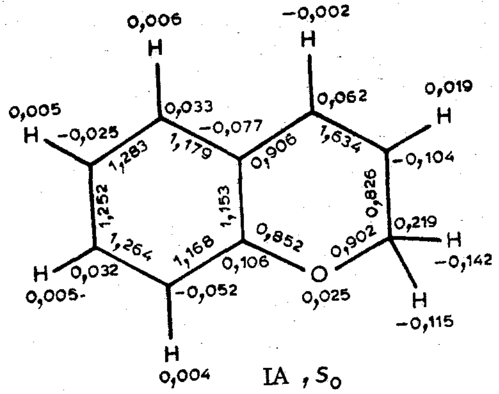
and their analogs. Consequently, we used the standard values of the valence angles and bond lengths taking into account the hybrid states of the atoms [11]. The calculations by the PPP method were performed in the "variable β" approximation [12], and for the C–S bonds we used the constants that we obtained previously [13]. The two-electron Coulomb repulsion integrals were calculated by means of the Mataga–Nishimoto formula. In the construction of the matrix of the configurational interaction, 20 singly excited configurations were taken into account. To calculate the energy of the triplet levels the parametrization introduced specially for these purposes was used [14]. The oscillator force was calculated by a well-known formula [21] with the subsequent introduction of the coefficient 0.5 in agreement with Bailey [22]. More details of the calculations by the PPP method are given elsewhere [13].

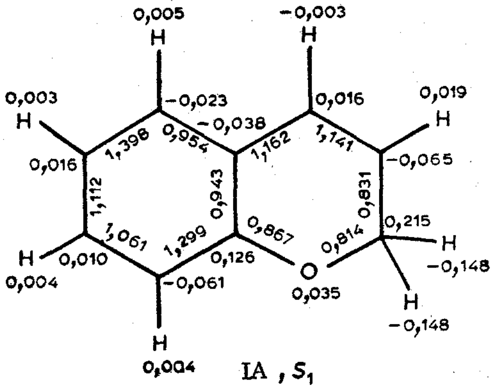


I, III, V, X R = H; II R = C_6H_5; IV, IX R = OCH_3; VI R = COR′; VII, IX X = O; VIII, X X = S

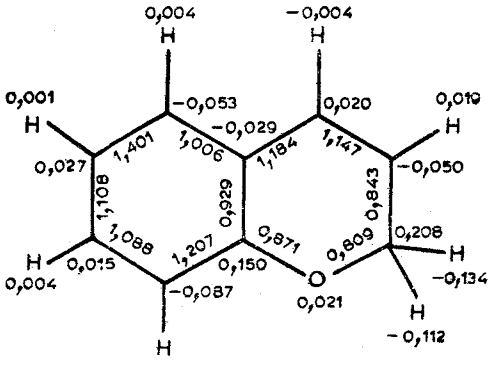
The CNDO method was applied in the parametrization proposed for the calculation of spectral characteristics [15]. Forty singly-excited configurations were taken into account. The calculations by the CNDO method were performed according to a program written and modified by I. I. Zakharov for a BÉSM-6 computer. The results of the calculations are given in Tables 1-5.



IA, S_0



IA, S_1



IA , T_1

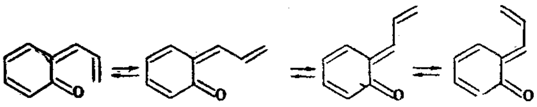
The Closed Forms (A). Table 1 gives the spectral characteristics of the closed forms of the compounds investigated calculated by the PPP and CNDO methods. The calculated and experimental values agree satisfactorily. The calculation correctly reproduces the observed bathochromic shift of the long-wave band on passing from 2H-chromene (I) to 2H-thiochromene (III) and 1,2-dihydroquinoline (V). A similar change in the spectrum is observed on passing from the chromene (I) and the thiochromene (III), respectively, to the benzochromenes (VII, IX) and benzothiochromenes (VIII, X). Calculations by the CNDO method show that $\pi\pi^*$ transitions are responsible for the first three excited states of 2H-chromene (I), of 1,2-dihydroquinoline (V), and of 1,2-dihydronaphthalene (XI).

The molecular diagrams give the total ($\sigma + \pi$) charges on the atoms and the bond indices of 2H-chromene (I) calculated according to Wiberg [16] in the ground (S_0) and in the first excited singlet (S_1) and triplet (T_1) states. In the S_1 and T_1 states, the C_2–O bond is the most loosened, as can be seen from the value of the bond index. In addition, on excitation there is a considerable equalization of the C_3–C_4 and the C_4–C_{4a} bonds in the pyran ring, which are strongly localized in the ground state. Thus, on passing to the first excited states (S_1 and T_1) the perturbation of the electronic structure of the pyran ring strongly favors the electrocyclic ring-opening reaction. We obtained the same result for 1,2-dihydroquinoline (V) and so has Tinland [23] for 1,2-dihydronaphthalene (XI).

Figure 1 shows graphically the highest occupied molecular orbitals (HOMO) of the ground (S_0) and first triplet (T_1) excited states of the closed and open forms (A and B) of 2H-chromene (I) and of 1,2-dihydronaphthalene (XI) obtained by the CNDO method. All these orbitals are of the π type. It is easy to see that the HOMOs of the ground states of the closed and open forms of the chromenes do not correlate. Because of this, the electrocyclic reaction of the opening of the pyran ring does not take place in the ground state even on heating. At the same time, the HOMOs of the triplet states of the A and B forms practically coincide, and as a result the opening of the pyran ring becomes a permitted process. Thus, the transition from the open form (A) into the closed form (B) of chromene must take place through excited states with the participation of triplet levels of both the closed and the open forms.

In the case of 1,2-dihydronaphthalene, the HOMOs of the closed (A) and open (B) forms correlate both in the ground state (S_0) and in the first triplet state (T_1) (Fig. 1). On this basis, it may be concluded that the cleavage of the C_1–C_2 bond is permitted in the ground and in the excited states, i.e., 1,2-dihydronaphthalene should possess photochromic and thermochromic properties. Unlike its photochromism [7, 8], the thermochromism of 1,2-dihydronaphthalene has never been investigated.

The Open Forms (B–E). The presence of a broad structural absorption band in the 400–500 nm region for the open forms of the chromenes, thiochromenes, and dihydroquinolines is connected [5, 10] with the existence of several stereoisomers the equilibrium between which depends on the temperature and the solvent.



IB (cis-s-cis) IC (cis-s-trans) ID (trans-s-trans) IE (trans-s-as)

We have performed a calculation of the spectra of all four allylidenecyclohexadienone isomers of chromene (IB–IE) by the PPP method. The calculated energies of the long-wave spectral transition are

TABLE 1. Singlet – Singlet Electronic Transitions of the Closed Forms (A) of 2H-Chromenes, Thiochromenes, and 1,2-Dihydroquinolines

Compound	Calculation		Experiment		
	ΔE, eV	f	ΔE, eV	f	solvent
I	4,17	0,07	4,00	0,02[a]	Isopentane [2]
	4,90	0,11	4,68	0,03	
	5,85	0,16			
I[b]	4,38	0,09	4,00	0,02[a]	Isopentane [2]
	4,52	0,02	4,68	0,03	
	5,36	0,02			
II	4,12	0,07	—		
	4,63	0,00			
	4,73	0,09			
III	3,92	0,02	3,82	0,02	Isopentane, propan-2-ol [4]
	4,54	0,01	4,35	0,01	
	5,11	0,00			
IV	3,78	0,04	—		
	4,42	0,01			
	5,00	0,03			
V	3,85	0,08	3,58	0,10[c]	Dioxane [5]
	4,75	0,04			
	5,59	0,05			
V[b]	4,21	0,10	3,58	0,10[c]	Dioxane [5]
	4,45	0,01			
	4,78	0,01			
VI	4,15	0,06	4,05	0,04	Dioxane[d]
	4,57	0,09			
	5,44	0,46			
VII	3,74	0,13	3,57	0,08	Ethanol [24]
	4,16	0,08	3,95	0,04	
	4,98	0.04			
VIII	3,58	0,05	3,40	0,01	Ethanol [1]
	4,10	0,07	3,93	0,01	
	4,32	0,18	4,39	0,06	
IX	3,61	0,08	3,47	0,07	3-Methylpentane [3]
	4,06	0,06			
	4,79	0,46	4,50	0,21	
X	3,51	0,04	—		
	3,98	0,01			
	4,50	0,03			
XI[b]	3,91	0,12	4,20	0,09	3-Methylpentane [17]
	4,26	0,01			
	4,66	0,02			

[a] The absorption and intensities of the bands are taken from information on the spectrum of 2,2-diethylchromene. [b] Calculated by the CNDO method; for (I) and (V) all transitions of the $\pi\pi^*$ type. The other calculations by the PPP method. [c] The absorption and intensities of the bands were taken from information on the spectrum of 2,2,4-trimethyl-1,2-dihydroquinoline. [d] The absorption and intensities of the bands were taken from the spectrum of N-acetyl-2,2,4-trimethyl-1,2-dihydroquinoline.

TABLE 2

Isomer	IB	IC	ID	IE
ΔE, eV	2,77	3,05	3,08	3,04
f	0,10	0,22	0,28	0,23

given in Table 2. The results of the calculations show that the isomers IC–IE are indistinguishable in the region of the long-wave absorption, and the isomer IB must undergo rapid s-cis-trans isomerization because of its steric hindrance. In view of this, the diffuseness of the long-wave absorption band of the photo forms of the chromenes must be connected either with features of the appearance of a vibrational structure or with intermolecular effects. The calculated spectral characteristics (the energies of the transitions and their intensities) of the isomers B and C are given in Table 3, together with the available experimental results. The agreement between the values calculated by both the methods used and the experimental values is fairly good. The first two singlets of the open form of chromene (I) and of 1,2-dihydroquinoline (V)

TABLE 3. Singlet–Singlet Electronic Transitions of the Open Forms (B and C) of the 2H-Chromenes, Thiochromenes, and 1,2-Dihydroquinolines

Compound	Calculation				Experiment	
	isomer B		isomer C		ΔE, eV	solvent
	ΔE, eV	f	ΔE, eV	f		
I	2,77 3,82 4,82	0,10 0,06 0,10	3,05 4,00 5,04	0,22 0,16 0,18	2,68^{a} 3,52	Isopentane [2]
I^{b}	2,68 3,49 3,89	0,06^{c} 0,01^{c} 0,04^{c}	3,00 4,01 4,88	0,20^{c} 0,22^{c} 0,00^{d}	2,68^{a} 3,52	Isopentane [2]
II	2,60 3,79 4,24	0,19 0,17 0,13	2,81 3,86 4,13	0,37 0,12 0,01	—	
III	1,85 3,11 3,64	0,05 0,04 0,03	2,36 3,38 3,52	0,19 0,06 0,03	2,18 3,10 3,44	Isopentane, propan-2-ol [4]
IV	1,85 2,85 3,39	0,06 0,04 0,02	2,27 2,99 3,45	0,16 0,05 0,08	—	
V	2,71 3,83 4,61	0,09 0,03 0,08	3,02 4,06 4,25	0,24 0,08 0,15	3,02; 3,26^{e} 3,72	Dioxane [5]
V^{b}	—		2,90 4,07 4,55	0,21^{c} 0,16^{c} 0,00^{d}	3,02; 3,26^{e} 3,72	Dioxane [5]
VI	2,44 3,62 4,27	0,10 0,06 0,02	2,69 3,81 4,45	0,22 0,16 0,02	2,84; 2,95^{f}	Dioxane
VII	3,12 3,57 4,36	0,06 0,03 0,20	3,35 3,71 4,40	0,22 0,11 0,30	3,16	3-Methylpentane [3]
VIII	2,05 2,95 3,64	0,06 0,08 0,18	2,53 3,12 3,63	0,20 0,14 0,10	—	
IX	2,68 3,83 4,11	0,14 0,01 0,12	2,91 4,05 4,31	0,32 0,02 0,19	2,91 3,88	3-Methylpentane [3]
X	1,76 3,13 3,25	0,06 0,01 0,04	2,23 3,46 3,52	0,24 0,08 0,09	—	
XI^{b}	2,20 2,74 3,59	0,00^{g} 0,09^{c} 0,01^{c}	2,29 2,86 3,77	0,00^{g} 0,32^{c} 0,01^{c}	3,02	Isopentane [7]

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[a] The absorption and the intensities of the bands were taken from information on the spectrum of 2,2-diethylchromene. [b] Calculation by the CNDO method, the other calculations being by the PPP method. [c] $\pi\pi^*$ transition. [d] $\pi\sigma^*$ transition. [e] The absorption and intensities of the bands were taken from information on the spectrum of 2,2,4-trimethyl-1,2-dihydroquinoline. [f] The absorption and intensities of the bands were taken from information on the spectrum of N-acetyl-2,2,4-trimethyl-1,2-dihydroquinoline. [g] $\sigma\pi^*$ transition.

TABLE 4. π-Electronic Charges of the Ground (S_0) and First Singlet Excited (S_1) States of the Open Forms of Chromene, 1,2-Dihydroquinoline, and Thiochromene Obtained by the PPP Method

Structure No.	IB		VB		IIIB	
	S_0	S_1	S_0	S_1	S_0	S_1
1	−0,428	−0,418	−0,274	−0,259	−0,415	−0,084
2	0,232	0,153	**0,142**	0,076	0,131	0,055
3	−0,022	−0,015	−0,014	−0,006	−0,011	−0,018
4	0,011	0,083	0,008	0,054	0,019	0,016
5	−0,011	0,104	−0,006	0,069	−0,003	0,014
6	0,040	−0,001	0,028	0,000	0,044	0,017
7	−0,011	0,122	−0,007	0,081	0,007	0,049
8	0,119	−0,072	0,078	−0,048	0,130	−0,055
9	0,018	0,039	0,010	0,026	0,020	0,025
10	0,052	0,005	0,036	0,008	0,077	−0,020

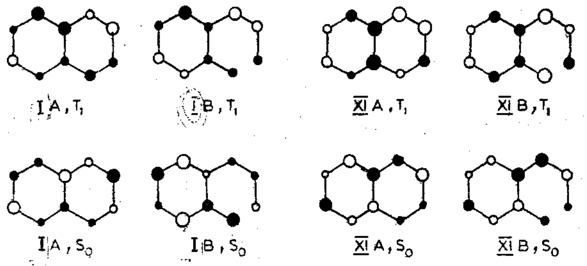


Fig. 1. The highest occupied molecular orbitals of the ground (S_0) and first triplet (T_1) excited states of the closed and open forms of 2H-chromene (IA and IB) and of 1,2-dihydronaphthalene (XIA and XIB). The open circles correspond to positive and the filled-in circles to negative values of the coefficients for the atomic orbitals. The area of each circle is proportional to the value of the coefficient.

TABLE 5. Singlet–Triplet (S_0-T_1) Electronic Transitions of Chromenes, Thiochromenes, 1,2-Dihydroquinolines, and 1,2-Dihydronaphthalene

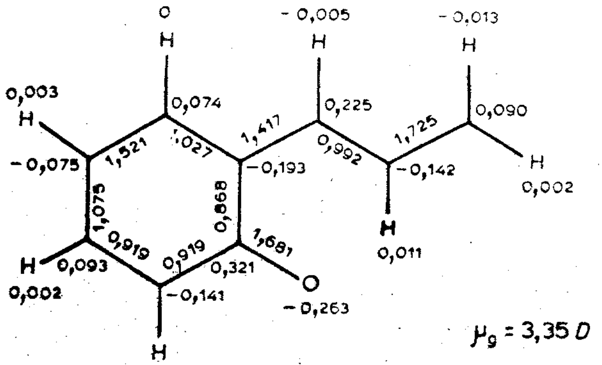
Characteristics	ΔE, eV		Characteristics	ΔE, eV	
	Formula A	formula C		formula A	formula C
I	2,43 3,33 3,51	1,01 2,39 3,24	VI	2,56 3,48 3,81	0,92 2,38 3,36
I[a]	2,82[b] 3,80[b] 3,96[b]	1,49[b] 2,44[b] 3,30[c]	VII	2,08 3,11 3,58	1,52 2,45 3,48
II	2,34 3,29 3,47	0,94 2,36 3,21	VIII	2,19 3,18 3,63	0,51 2,04 3,71
III	2,56 3,60 3,89	0,22 2,21 2,87	IX	1,95 2,58 3,24	1,43 2,56 3,19
IV	2,50 3,48 3,76	0,24 2,18 2,81	X	2,04 2,82 3,41	0,41 2,00 3,36
V	2,42 3,32 3,57	0,89 2,44 3,40	XI	2,57 3,63 3,98	0,69 2,49 3,01
V[a]	2,64[b] 3,76[b] 3,92[b]	1,24[b] 2,47[b] 3,31[c]	XI[a]	2,36[b] 3,55[b] 3,81[b]	0,38[b] 2,29[b] 2,93[b]

[a] Calculation by the CNDO method; other calculations by the PPP method. [b] $\pi\pi^*$ transition. [c] $\pi\sigma^*$ transition. [d] $\sigma\pi^*$ transition.

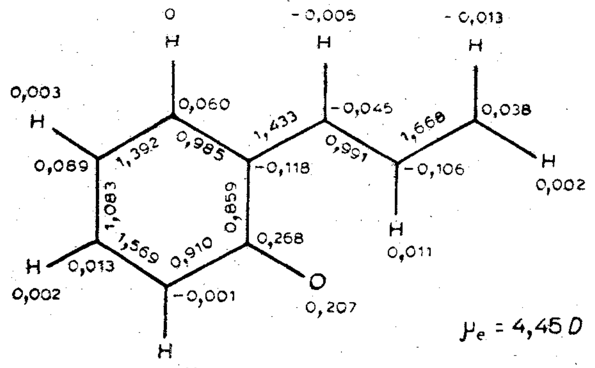
relate $\pi\pi^*$ transitions, which follows from the calculations by the CNDO method. In the case of 1,2-dihydronaphthalene (XI), a forbidden $\sigma\pi^*$ transition is responsible for the first singlet state. The second and third singlets relate to $\pi\pi^*$ states. In all the isomers of type C, the calculated absorption band maximum is shifted hypsochromically by 0.3–0.4 eV relative to the isomer B.

When in the open forms of type B oxygen is replaced by sulfur and selenium, the long-wave maximum shifts bathochromically by 100–120 nm [1, 4]. Calculation correctly predicts these features of the absorption spectra. The results of the calculations also permit an explanation of the unexpected hypsochromic shift in the spectrum of 5,6-benzo-2H-chromene and 5,6-benzo-2H-thiochromene (VII, VIII) as compared with (I, III). At the same time, the fusion of a benzene nucleus in the 7,8 position (compounds (IX) and (X)) leads to a bathochromic shift of the long-wave maximum.

The nature of the long-wave absorption of the open forms is of special interest, since it is just this absorption that determines the properties of the photochromic system. The molecular diagrams show the ($\sigma+\pi$)-electronic charges and the bond indices of the ground (S_0) and the first singlet excited (S_1) states of the isomer C of the open form of the chromene (I) calculated by the CNDO method. On S_0-S_1 excitation, a transfer of electron density (about 0.25 of an electron) from the benzene ring to the α-carbon atom of the side chain takes place. The dipole moment varies insignificantly on excitation, which leads to the absence of solvatochromism.



IC, S_0



IC, S_1

The influence of the heteroatom X on the first electronic transition can be determined by making use of the figures of Table 4, which gives the π-electronic charges of the ground and first singlet excited states of 2H-chromene, 2H-thiochromene, and 1,2-dihydroquinoline. On $S_0 - S_1$ excitation, the charge on the oxygen atom (for chromene) and the nitrogen atom (for 1,2-dihydroquinoline) scarcely changes. At the same time, on excitation, the sulfur atom (in the case of thiochromene) loses 0.35 unit of electron density actively participating in conjugation, which leads to a bathochromic shift of the long-wave maximum of 2H-thiochromene relative to 2H-chromene and 1,2-dihydroquinoline.

The energies of the singlet–triplet transitions of the open and closed forms of the compounds investigated as calculated by the CNDO and PPP methods are given in Table 5. A knowledge of the absorption and the nature of the triplet states is particularly important since, according to the point of view accepted at the present time, valence isomerism of the A → B type takes place by a $^1A_0 \to {}^1A_1 \to {}^3A_1 \to {}^1B_0$ mechanism, i.e., through an intercombinational conversion from the triplet state of the cyclic form A [18, 19]. In the case of the chromenes, apart from those containing a nitro group in the nucleus [20], fluorescence is absent. Therefore the experimental possibilities of determining the positions of the triplet levels are limited.

As can be seen from Table 5, the energy of the $S_0 - T_1$ transitions calculated by the CNDO method are 0.3-0.4 eV higher than those obtained in the π-electron approximation. The first two triplets of all the compounds investigated with the exception of 1,2-dihydronaphthalene (XI) belong to the $\pi\pi^*$ type. The second triplet state of 1,2-dihydronaphthalene is a $\sigma\pi^*$ transition.

The first triplet state of the closed form of the thiochromene (III) lies 0.15 eV above that for the chromene (I). This result is extremely important in the analysis of the photochromic behavior of the spiropyranothiopyrans considered in the following paper [25].

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