

# A QUANTUM CHEMICAL STUDY OF THE ELECTRON SPECTRA OF PHOTOCROMIC CHROMENES AND SPIROPYRANES

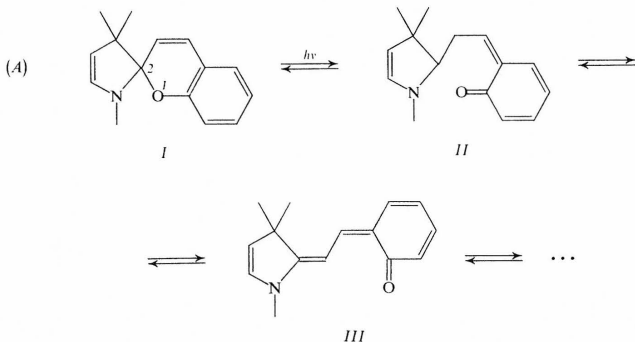
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The electron spectra of substituted 2H-chromenes are discussed on the basis of CNDO/2S theoretical calculations. The nature of the absorption bands and the emission properties of 6-NO<sub>2</sub> and 6-CHO substituted chromenes are essentially different from chromenes bearing electron-donor substituents. Electron-acceptor substituents with non-bonding electrons are important for an effective intersystem crossing and raise the phosphorescence of the <sup>3</sup>(ππ\*) type.

Photochromic systems most in use for technical purposes are systems of organic compounds in which photoinduced reversible changes in the geometry of the molecule take place. *Cis-trans* isomerism of stilbenes in the excited state is a typical example. As regards technical applications, however, spiroopyranes *I* appear to be the most suitable<sup>1</sup> compounds. The functional unit of spiroopyranes is the chromene part, *i.e.* the 2 H-benzopyrane part of the molecule, in which excitation in the UV region leads to the heterolytic splitting of the single 1,2-bond of the pyrane ring<sup>2</sup> followed by the formation of *cis-cis* *II*, *cis-trans* *III* and other *o*-quinoid structures absorbing in the visible region.



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In spite of the vast amount of patent literature reporting the use of spiropyranes for technical purposes, no systematic attempts have been made — at least, as far as we know — to offer a theoretical analysis of the suggested mechanism of photochromism<sup>3</sup> represented in scheme (A). The indole part of the spiropyran molecule serves mainly for the stabilization of coloured open structures and has no substantial influence on the primary photoinitiated process of splitting of the —O—C<sub>spiro</sub>-bond; hence, to interpret the process of reversible photochemical reactions in spiropyranes one must know, in the first place, the character of electron transitions in the chromene part of the molecule, which is orthogonal to the indole part and the interaction of which with the latter due to spiroconjugation can be neglected.

It has been the objective of this work to investigate the electron structure of some substituted chromenes and to employ the results thus obtained in an interpretation of their absorption and emission spectra and in the characterization of the effect of the electron-donor and electron-acceptor substituents on the character and relative position of the lowest triplet and singlet electron transitions.

### METHOD OF CALCULATION

The electron structure of molecules can be examined by using appropriate quantum chemical methods. In this work we have employed the reparametrised CNDO/2S method<sup>3,4</sup>, suitable for calculations of the transition energies of conjugated systems. We believe that the usefulness of this method is not affected to any important degree by the presence of substituents, such as the —NO<sub>2</sub>, —CHO and —OCH<sub>3</sub> groups. The assumption is in accord with the results obtained with other substituted conjugated systems<sup>3-5</sup>.

To calculate the electron properties of molecules, one must know their geometry. Since no crystallographic data on the structure of chromenes are known, the geometry of chromenes

TABLE I  
Geometrical Model of the Pyrane Ring — Atom Coordinates in Å  
Atoms Numbered as in Formula IV.

Atoms		x	y	z
Carbon atoms	C <sub>2</sub>	1.539	2.543	0.000
	C <sub>3</sub>	0.030	2.473	0.000
	C <sub>4</sub>	-0.666	1.333	0.000
	C <sub>9</sub>	1.394	0.000	0.000
	C <sub>10</sub>	0.000	0.000	0.000
Hydrogen atoms	H <sub>2</sub>	1.883	3.058	0.876
	H <sub>2</sub> '	1.883	3.058	-0.876
	H <sub>3</sub>	-0.522	3.405	0.000
	H <sub>4</sub>	-1.749	1.379	0.000
Oxygen	O	2.020	1.207	0.000

had to be determined approximatively. Standard bond lengths and valence angles<sup>6</sup> are too rough data for our purpose. We therefore employed extended Hückel method<sup>7</sup> in order to ascertain the geometry of a molecule possessing the lowest energy in the space of the cartesian coordinates as a function of the magnitude of the valence angles in the pyrane ring; the interatomic distances in chromene and other valence angles were estimated using the known molecular structures of geometrically similar compounds<sup>8</sup>. The model geometry of the pyrane ring is given in Table I. The geometries of the other substituted chromenes were derived from the model geometry of 2 H-benzopyrane. All molecules are considered to be planar, with the exception of hydrogen atoms on saturated carbon atoms.

## RESULTS AND DISCUSSION

In the literature the quantum chemical study of chromenes has so far been restricted only to calculations of the electron structure of 2 H-chromene<sup>9,10</sup>. Table II gives the transition energies and oscillator strengths calculated by using the reparametrized CNDO/2 S method for the Ohno and Mataga-Nishimoto approximation of the calculation of two-centre coulomb integrals. The values obtained have been compared with calculations carried out by Tinland and coworkers<sup>9</sup>, and by Minkin and coworkers<sup>10</sup> for standard geometries.

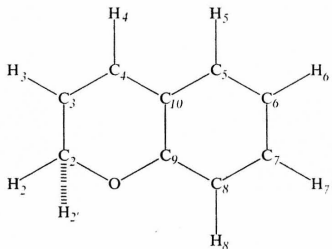
The electron properties of chromenes greatly resemble those of the benzopyrane parts in spiropyranes. Even though there exist weak interactions between the indole and pyrane chromophores, which cause a small red shift ( $\sim 10$  nm) in the long-wave band of chromenes with respect to indolinospiryranes, an experimental proof has been given of the additivity of spectra of the indoline and chromene parts<sup>12,13</sup>, *i.e.*

TABLE II  
Absorption Spectrum of 2 H-Chromene — Observed and Calculated  
Calculated Oscillator Strengths are Given in Brackets.

$\lambda_{\text{obs}}$ , eV	$\lambda_{\text{calc}}$ , eV			
	Ref. <sup>9,11</sup>	Ref. <sup>9</sup>	ref. <sup>10</sup>	Ohno approx. Mat.-Nish. approx.
$S_1$ 4.00		3.67 (0.12)	4.38 (0.09)	4.03 (0.132) 4.07 (0.126)
$S_2$ 4.63		4.16 (0.001)	4.52 (0.02)	4.38 (0.006) 4.54 (0.104)
$S_3$ 5.64		5.23 (0.06)	5.36 (0.02)	5.47 (0.299) 5.62 (0.000)
$S_4$				6.27 (0.000) 5.67 (0.003)
$S_5$				6.28 (1.186) 5.76 (1.237)
$T_1$	2.04		2.82	2.76 1.94
$T_2$	3.43		3.80	3.47 2.72
$T_3$	3.70		3.96	3.77 3.39

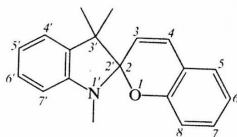
the effect of spiroconjugation of the orthogonal molecular fragments on the electron spectra is negligible. This is why it was possible, in the calculations of the electron spectra of substituted chromenes, to use a comparison with experimental data concerning the respective indolinospiropyranes.

Table III summarizes the spectral properties of chromenes and of substituted 1',3',3'-trimethylindolinobenzospiropyranes



IV

The transition energies calculated by the CNDO/2 S (ref.<sup>3,4</sup>) method for the Ohno approximation of the two-centre coulomb integrals are compared with the spectra observed.



V

An interpretation of the absorption spectra is not simple, because in most cases long-wave transitions ( $n\pi^*$ ) cannot be observed, owing to overlapping with the intensive ( $\pi\pi^*$ ) bands. Fluorescence, which could help in the interpretation of spectra, has not been found with the chromenes and spiropyranes under investigation. Also, an interpretation of the photochemically active and lowest phosphorescence triplet state is difficult because of the lack of experimental data. In this case, it is mainly data on the polarization of phosphorescence that are missing; if available, they would help to distinguish the nature of the  $^3(n\pi^*)$  and  $^3(\pi\pi^*)$  transitions. Thus, the important

thing for the interpretation of the absorption and emission spectra is the knowledge of the character of electron transitions based on a theoretical model. Theoretical results are consistent with the existing experimental data.

TABLE III

Absorption Spectra of Chromenes (observed and calculated) in nm,  $f$  is the Oscillator Strength

2 H-Chromene substituent	Singlets			Triplets	
	$\lambda_{\text{obs}}$	ref.	$\lambda_{\text{calc}}$	$f$	$\lambda_{\text{calc}}$
Unsubst.	310	9,11	308( $\pi\pi^*$ )	0.13	450( $\pi\pi^*$ )
	268		284( $\pi\pi^*$ )	0.01	358( $\pi\pi^*$ )
	220		227( $\pi\pi^*$ )	0.30	330( $\pi\pi^*$ )
6-CHO-	(350) <sup>d</sup>	14	367( $n\pi^*$ )	0.00	420( $\pi\pi^*$ )
	328	15	304( $\pi\pi^*$ )	0.11	367( $\pi\pi^*$ ) <sup>b</sup>
	315		286( $\pi\pi^*$ )	0.02	347( $\pi\pi^*$ )
	—		230( $\pi\pi^*$ )	0.60	313( $\pi\pi^*$ )
6-OCH <sub>3</sub> -	337	15	317( $\pi\pi^*$ )	0.13	451( $\pi\pi^*$ )
	—		299( $\pi\pi^*$ )	0.04	426( $\pi\pi^*$ )
	—		235( $\pi\pi^*$ )	0.43	355( $\pi\pi^*$ )
	—		203( $\pi\pi^*$ )	0.86	297( $\pi\pi^*$ )
6-NO <sub>2</sub> -	373	12	331( $n\pi^*$ )	0.00	375( $\pi\pi^*$ )
	345	16	314( $n\pi^*$ )	0.00	366( $\pi_0\pi^*$ )
	(295) <sup>c</sup>		293( $\pi\pi^*$ )	0.09	333( $\pi\pi^*$ )
	266		276( $\pi\pi^*$ )	0.03	331( $n\pi^*$ ) <sup>b</sup>
	238		222( $\pi\pi^*$ )	0.55	314( $n\pi^*$ ) <sup>b</sup>
6-NO <sub>2</sub> - <sup>d</sup>	373	12	417( $n\pi^*$ )	0.00	627( $\pi_0\pi^*$ )
	345	16	391( $n\pi^*$ )	0.00	472( $\pi\pi^*$ )
	(295) <sup>c</sup>		297( $\pi\pi^*$ )	0.08	417( $n\pi^*$ ) <sup>b</sup>
	266		285( $\pi\pi^*$ )	0.13	391( $n\pi^*$ ) <sup>b</sup>
	238		236( $\pi\pi^*$ )	0.81	385( $\pi\pi^*$ )
5,6-Benzo-	358	15	353( $\pi\pi^*$ )	0.23	—
	314		317( $\pi\pi^*$ )	0.00	—
6,7-Benzo-	347	17	328( $\pi\pi^*$ )	0.05	496( $\pi\pi^*$ )
	314		324( $\pi\pi^*$ )	0.07	391( $\pi\pi^*$ )
	—		253( $\pi\pi^*$ )	0.69	348( $\pi\pi^*$ )
	—		237( $\pi\pi^*$ )	0.05	338( $\pi\pi^*$ )
	—		222( $\pi\pi^*$ )	1.74	305( $\pi\pi^*$ )

<sup>a</sup>  $^1S(n\pi^*)$  in 2-naphthaldehyde<sup>14</sup> (cf. below). <sup>b</sup> If monocentric exchange integrals are neglected, ( $n\pi^*$ ) transition has zero-singlet-triplet splitting. <sup>c</sup> Intensive band at 295 nm observed with indolinobenzospiropyranes is sometimes attributed to the indole part of the molecule<sup>12</sup>. However, a less intensive transition localized on substituted parts of chromene can also be found in this region. <sup>d</sup> Mataga-Nishimoto approximation of two-centre coulomb integrals.

2 H-Chromene, 6-OCH<sub>3</sub>-2 H-chromene, 5,6-benzo-2 H-chromene and 6,7-benzo-2 H-chromene. The calculated transition energies are in good agreement with the absorption spectra observed. Long-wave electron transitions are interpreted as transitions of the ( $\pi\pi^*$ ) type.

6-CHO-2 H-Chromene. The calculated lowest singlet state is of the ( $n\pi^*$ ) type. Even if there is no experimental proof of the existence of such state in the UV spectrum, one may assume that it nevertheless exists, but is overlapped by an intensive ( $\pi\pi^*$ ) band at 330 nm. In ref.<sup>18</sup>, phosphorescence was observed between 435 and 555 nm with the lifetime  $\tau_{ph} = 0.2$  s and was interpreted as the  $^3(n\pi^*)$  transition, while in ref.<sup>16</sup> it was interpreted as the  $^3(\pi\pi^*)$  transition. The absorption spectrum of unsubstituted chromene (310, 268, and 220 nm) is similar to that of naphthalene (313, 274, and 220 nm); it may be assumed, therefore, that the absorption spectrum of 6-CHO-2 H-chromene too will be analogous to that of 2-naphthaldehyde. In ref.<sup>14</sup>, the first singlet state ( $n\pi^*$ ) of 2-naphthaldehyde was found at 350 nm,  $T_1(\pi\pi^*) = 478$  nm, and  $T_2(n\pi^*) = 382$  nm, in other words, in the same region as the calculated values of 6-CHO-2 H-chromene. One may assume, therefore, that the calculated scheme of energy levels represented in Table III, i.e.  $^3(\pi\pi^*) < ^3(n\pi^*) < ^1(n\pi^*) < ^1(\pi\pi^*)$ , is correct; here, phosphorescence is interpreted as a transition of the  $^3(\pi\pi^*)$  type.

6-NO<sub>2</sub>-2 H-Chromene. It was assumed in ref.<sup>16</sup>, that the lowest singlet excited state at 370 nm was of the ( $\pi\pi^*$ ) type. On the other hand, however, the excitation phosphorescence spectrum<sup>13</sup> and the absorption spectrum of 6-nitro-1',3',3'-trimethyl-5'-Cl-indolinospiropyrane at 77 K exhibited<sup>12</sup> a weak long-wave transition, similar to the weak shoulder also observed in the excitation spectrum of phosphorescence of 2-nitronaphthalene and assigned<sup>19</sup> to a transition of the  $^1(n\pi^*)$  type. Typical of a case when the lowest singlet state is of the  $^1(n\pi^*)$  type is the effective intersystem crossing,  $^1(n\pi^*) \rightarrow ^3(\pi\pi^*)$  and the fact that no fluorescence is observed. There was indeed no fluorescence, but phosphorescence was observed instead. Balny and coworkers<sup>18</sup> and Tyler and Becker<sup>12</sup> interpreted the observed phosphorescence as the  $^3(n\pi^*)$  emission; in ref.<sup>16</sup> it is interpreted as the  $^3(\pi\pi^*)$  transition. Thus, the question of interpretation of the lowest-energy triplet states resembles a situation arising with nitro-substituted aromatic hydrocarbons. The lowest triplet state of nitrobenzene was proved to be of the ( $n\pi^*$ ) character<sup>20</sup>, while in 2-nitrosubstituted naphthalene phosphorescence exhibits the ( $\pi\pi^*$ ) character. The observed in-plane polarization of phosphorescence in nitronaphthalene<sup>19</sup>, however, indicates the complexity and ambiguity of the energy scheme of the excited states; a more detailed study of luminescence in nitroaromatic molecules<sup>22</sup> strongly favours the assumption that the lowest singlet state is  $^1(n\pi^*)$ , and that the phosphorescence triplet is of the  $^3(\pi\pi^*)$  type. The results reported in this work also show that the lowest singlet state is of the  $^1(n\pi^*)$  type, and that the transition involved in phosphorescence is probably

a  $^3(\pi\pi^*)$  transition, namely, transition of a delocalized  $\pi$ -electron system or transition between  $\pi$ -electrons localized on the oxygen atoms of the nitro group (nonbonding  $\pi$ -orbital – in Table III denoted as  $\pi_0$ ). With the Ohno approximation of coulomb integrals, the two lowest triplet states of the  $^3(\pi\pi^*)$  and  $^3(\pi_0\pi^*)$  type are almost degenerated, while in the Mataga–Nishimoto approximation the triplet state  $^3(\pi_0\pi^*)$  is lower by 0.65 eV than the energy of the state  $^3(\pi\pi^*)$ . The energy of the phosphorescent state lies between the lowest values of the triplet states calculated by using the two approximations. We believe, therefore, that the phosphorescence from the lowest triplet state in the range 455–625 nm in toluene is a transition of the non-bonding  $\pi_0$ -electrons, which explains the well-distinguished vibrational structure of phosphorescence and the lifetime of phosphorescence being 0.1 s. Both the calculated and experimentally determined  $S$ - $T$  splitting is too large to allow an explanation of the observed phosphorescence as  $^3(n\pi^*)$  transition. Also, the observed  $\tau_{ph}$  is longer than  $\tau_{ph}$  typical of the  $^3(\pi\pi^*)$  transitions, *i.e.*  $10^{-4}$ – $10^{-2}$  s. Using calculations by means of the CNDO/2 S method, the energy scheme of the lowest excited states in 6-NO<sub>2</sub>-2 H-chromene and in 6-nitro-1',3',3'-trimethylindolinospiropyrane is interpreted as follows:  $^3(\pi_0\pi^*) < ^3(\pi\pi^*) < ^3(n\pi^*) < ^1(n\pi^*) < ^1(\pi\pi^*)$ . The probability of a fluorescence from the  $^1(n\pi^*)$  state is very low, but the intersystem crossing into the triplet state  $^3(\pi\pi^*)$  or directly into the state  $^3(\pi_0\pi^*)$ , also localized on the nitro group, is very effective. The shorter phosphorescence time  $\tau_{ph}$  of nitrosubstituted spiropyranes compared with  $\tau_{ph}$  typical of the  $^3(\pi\pi^*)$  transitions, *i.e.* 0.1–100 s, may also be explained by a considerable influence of non-radiative transitions, but the effect of the non-bonding  $\pi_0$ -orbital and of its local character on the phosphorescence time seems to be more likely.

The theoretical results obtained may be summarized as follows: in molecules of chromene bearing electron-acceptor substituents, —NO<sub>2</sub> and —CHO, one observes the lowest singlet states of the  $^1(n\pi^*)$  type. From these states there is a very effective transition into triplet states, which is documented by the phosphorescence observed<sup>18</sup> in 6-NO<sub>2</sub> and 6-CHO-derivatives of 1',3',3'-trimethylindolinospiropyrane. On the other hand, in molecules containing electron-donor substituents (1',3',3'-trimethylindolinospiropyrane and its 6-methoxy and 5,6-benzo derivatives) no phosphorescence could be observed. The intensity of phosphorescence of spiropyranes is closely related to their colourability. The photocolorability of nonphosphorescent compounds is weak<sup>18</sup>, while that of phosphorescent compounds is pronounced. It seems probable, therefore, that photoinitiated splitting of the pyrane ring also occurs in the triplet state.

The triplet states play an important role in the photochemistry of phosphorescent chromenes and spiropyranes, because numerous experiments also indicate<sup>13,22</sup> that the formation of coloured open forms *II* from closed forms *I* can be sensitized by donors of the triplet energy. Moreover, some experimental data<sup>13</sup> show that phosphorescent and photochemically active triplet states possess a different electron char-

acter. To evaluate the photochemical activity of chromenes and spiropyranes in excited states, one should not only know the character of electron transitions, but also find a theoretical explanation of the change in the conformation of the molecule during excitation. An estimation of the probability of migration of atoms in excited states of substituted chromenes using a theoretical model based on the LCAO formalism is the object of a further study.

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