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A THEORETICAL CNDO CI STUDY OF THE ELECTRONIC SPECTRUM AND STRUCTURE OF A SPIROPYRAN

B. TINLAND,* R. GUGLIELMETTI† and O. CHALVET‡
Université de Lyon, 69 Villeurbanne, France

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Abstract—The electronic structure and spectrum of a model compound of a spiropyran were investigated using an all valence-electrons CNDO CI method. The $\pi \rightarrow \pi^*$ electronic excitations are localized on a given half of the molecule. The photochromic process is discussed on the basis of charge densities and bond orders.

Reversible, photoinduced, color changes of spiropyrans in solution were first described by Löwenbein.[1] Photochromism in spiropyrans involving the reversible process shown in Fig 1 is now well documented and has recently been reviewed[2-6] but only a few electronic state assignments have been made.[7,8] In order to understand the photochemical process, it is necessary to assign the number and nature of the transitions in the absorption spectrum and to determine whether these transitions are "total molecule" in character or restricted to a particular half of the molecule. Examination of the structure of indolinospiropyran indicates that the two halves are, topologically, essentially orthogonal. So it might be expected that the π-absorption spectrum could consist of localized transitions belonging to a particular half of the molecule rather than delocalized transitions belonging to the molecule as a whole. In order to determine the accuracy of this prediction, Becker *et al.* studied the absorption spectra of a series of indolinospiropyrans as well as those of chromenes and of an indoline, which were treated as models for the appropriate halves of the spiropyran. They concluded that the transitions are localized on a given half of the molecule and might be assigned as $\pi \rightarrow \pi^*$, except in the nitro derivatives where an $n \rightarrow \pi^*$ transition occurs.[8,9]

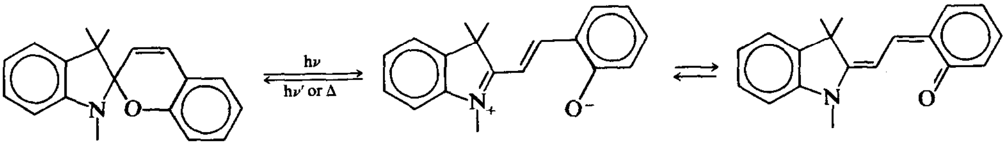

Fig 1. Photochromic process.

This elegant work was purely experimental. As far as we know, no theoretical study of the photochromism of indolinospiropyrans has been undertaken if one excepts the elementary work of Chaudé and Masse[10] using the simple HMO method, although quite a lot of experimental information is available about this molecule.

It is the intent of the present study to clear up the problem of the π-electron orthogonality of the constituent halves of the spiropyran as well as that of the primary act of the photochemical process itself in a purely quantum-mechanical way. Such a study is now possible because of the advent of quantum-mechanical methods which treat all valence-shell electrons in molecules. The method used here was the now classical CNDO CI procedure of Del Bene and Jaffé which was shown to be quite successful in predicting the electronic spectra of a variety of organic compounds.[11] Discussion of the formalism and parametrization has been given previously and will not be repeated here.[11] Because of the large size of the spiropyran system, we studied this molecule with no other substituents than hydrogens. Similarly, unsubstituted chromene and indoline were treated as models for the corresponding parts of the spiropyran (Fig 2). We do believe, however, that the main features of the computed electronic absorption spectra remain unaltered by this simplification. Configuration interaction calculations were per-

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*Section de Recherches de Mécanique Ondulatoire Appliquée, Université de Lyon I, 69 Villeurbanne, France.

†Département de Chimie, Université de Bretagne Occidentale 29 N Brest, France.

‡Centre de Mécanique Ondulatoire Appliquée, 23 rue du Maroc. Paris (19°), France.

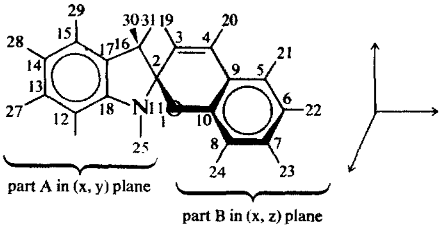

Fig 2. Coordinate axes and numbering scheme.

formed considering the 30 lowest excited singlet and triplet monoexcited configurations. The electronic states of spiropyran are listed in Table 1 together with the orbital transitions contributing predominantly to each excited state. Tables 2 and 3 present the electronic states of the chromene and indoline systems, respectively.

It is readily seen from these spectral results that the lowest singlet absorption band of spiropyran, located at 3·82 eV which is mainly involved in the photochromic process originates from the chromene half (part B) of the molecule and obviously corresponds to the absorption band at 3·67 eV exhibited by the chromene species. The $\pi \rightarrow \pi^*$ character of the near UV absorption bands of the three molecules considered is also quite well demonstrated since the first $\sigma \rightarrow \pi^*$ transition takes place only at about 6·5 eV in each case. Experimental absorption band energies for real neighbour compounds[12] are quoted in Table 1. No detailed comparison with the computed values is

Table 1. Electronic transitions of spiropyran (energies in eV)

Expt.	Singlet energies	Osc. strengths	Polarization coefficients x	y	z	Main C.I. coefficients on orbitals	Triplet energies	Main C.I. coefficients on orbitals
3·35	3·82	0·17	0·78	0·02	0·62	0·93 (44 → 45)	2·49	0·92 (44 → 45)
4·14	4·27	0·01	0·81	0·53	0·26	0·55 (43 → 46)	3·29	0·76 (43 → 48)
						0·52 (44 → 47)		0·36 (41 → 46)
						0·35 (42 → 45)		0·32 (43 → 47)
						0·34 (41 → 48)		0·21 (43 → 50)
						0·20 (44 → 48)		0·21 (42 → 46)
	4·42	0·01	0·84	0·54	0·02	0·59 (43 → 46)	3·59	0·58 (44 → 47)
						0·49 (44 → 47)		0·42 (43 → 46)
						0·33 (42 → 45)		0·41 (42 → 47)
4·36						0·24 (41 → 48)		0·27 (44 → 48)
						0·24 (44 → 48)		0·26 (44 → 49)
	4·53	0·05	0·80	0·60	0·01	0·69 (43 → 48)	3·62	0·80 (43 → 46)
						0·39 (41 → 46)		0·24 (43 → 47)
						0·37 (43 → 47)		0·23 (42 → 47)
						0·35 (43 → 45)		0·21 (44 → 47)
						0·20 (42 → 46)		

orbital number	41	42	43	44	45	46	47	48
TYPE	π_{AB}	π_{AB}	π_A	π_B	π^*	π^*	π^*	π^*

Table 2. Electronic transitions in chromene molecule (energies in eV)

Expt.	Singlet energies	Osc. strengths	Polarization coefficients x	y	z	Type	Triplet energies
3·99	3·67	0·12	0·70	0·0	0·72	$\pi \rightarrow \pi^*$	2·04
4·65	4·16	0·001	1·00	0·0	0·0	$\pi \rightarrow \pi^*$	3·43
5·66	5·23	0·06	0·79	0·0	0·61	$\pi \rightarrow \pi^*$	3·70

Table 3. Electronic transitions in indoline molecule (energies in eV)

Expt.	Singlet energies	Osc. strengths	Polarization coefficients x	y	z	Type	Triplet energies
4·15	4·22	0·02	0·85	0·53	0·0	$\pi \rightarrow \pi^*$	3·07
4·63	4·48	0·04	0·65	0·75	0·0	$\pi \rightarrow \pi^*$	3·46
5·9	6·17	0·31	0·47	0·88	0·0	$\pi \rightarrow \pi^*$	3·94

Table 4. Atomic electron charge densities in spiropyran

					Atom number							
State	1	2	3	4	5	6	7	8	9	10	11	16
S_0	6·223	3·736	4·003	4·095	4·023	4·046	4·015	4·060	4·002	3·842	5·247	4·014
S_1	6·150	3·719	4·081	4·070	4·096	4·002	4·074	4·099	3·999	3·800	5·212	4·000
T_1	6·149	3·719	4·083	4·078	4·092	4·002	4·078	4·104	3·996	3·789	5·217	4·000

Table 5. π Bond orders in spiropyran

State	1–2	2–3	3–4	4–9	5–9	5–6	6–7	7–8	8–10	1–10	9–10	2–11
S_0	0·056	0·146	0·913	0·329	0·634	0·671	0·661	0·664	0·647	0·281	0·602	0·040
S_1	0·096	0·176	0·585	0·572	0·457	0·723	0·547	0·590	0·662	0·354	0·404	0·043
T_1	0·097	0·178	0·566	0·563	0·458	0·734	0·534	0·584	0·670	0·358	0·401	0·042

possible because of the idealized molecular models used in the calculations. We may observe, however, that the general features of the experimental spectra are satisfactorily accounted for by the method used.

Let us consider now the atomic valence-electron densities summarized in Table 4 for the lowest electronic singlet and triplet states of spiropyran. At first sight, the breaking of the C_2—O_1 sigma bond as the result of $\pi \rightarrow \pi^*$ excitation seems somewhat surprising. The inspection of Table 4 indicates, however, that the oxygen becomes more positive by 0·073 electron whereas the other atoms linked to the spiro carbon 2 become more positive by much smaller amounts. The examination of these results shows a transfer of 0·090 electron from the atoms forming the C_2—O_1 bond to the rest of the molecule as a result of $S_0 \rightarrow S_1$ excitation. Having lost this amount of electrons, these atoms subsequently reorganize and attract some of the σ bonding electrons joining them. As a matter of fact, since the charge loss on the O atom equals four times that on the spiro carbon, the σ bonding electron pair moves towards the O atom, thus weakening the C_2—O_1 bond considerably. At the same time, the strong variations of the π bond orders of bonds C_3—C_4 and C_4—C_9 apparent from Table 5 corresponds, respectively, to an important lengthening and shortening of these bonds, changing from strongly localized bonds to more nearly aromatic ones. All these electronic and geometrical modifications strongly perturb the weakest bond in the chromene half of the molecule, i.e. the C_2—O_1 bond which can therefore be more easily broken than in the ground state.

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