Subchromophore Recognition in Some New Luminophores

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The character of electronic transitions in the UV-VIS spectra of some organic luminophores has been studied by means of the Pars Orbital Analysis (POA) of electronic excitation. The analysis allows to classify the compounds investigated as luminophores with stilbene (ST) or bis-styrylbenzene (BSB) subchromophores.

It has long been known that the 308, 296 and 232 nm bands in the UV spectra of trans- and cis-3-Phenylmethylene-1(3H)-isobenzofuranones, I, show a remarkable similarity to the absorption bands of trans- and cis-stilbene (ST). The spectra of 3-phenylisocoumarin, II, [1] and of 3-phenylcoumarin, II, [2] can also be characterized as stilbenoid. This means that for compounds I–III local excitation in the ST subchromophore are observed, the so-called "partial bands" (see [3]) which cause the similarity of some bands in the UV spectrum characterized by position, intensity and vibrational structure with those of ST. These considerations lead to the so-called composite model of molecules, in which a molecule is thought to be built up from two (or more) subunits; in the present case we consider a molecule (T + U) and choose the subunit T as ST and U as –COO–. This partitioning will be termed composite model A.

Usually, the subchromophores are recognized by chemical intuition, but in the last few years quantum chemical methods for the analysis of electronic transitions have also been used sometimes (see [3]). Without the knowledge of the experimental results mentioned above, chemical intuition would lead to another partitioning of the molecules I–III into subchromophores (composite model B): one would anticipate T = methylenephthalide (MPH), isocoumarin (ICU), or coumarin (CU), respectively, and U = phenyl. But the spectral bands of these subchromophores differ strongly in their intensity and shape from those of compounds I–III although they lie in the same range. The differences between the experimental results and the intuitive anticipation prompted us to use pars orbital analysis (POA) [4]. Along with II and III, which belong to the well-known isocoumarin and coumarin luminophores, we also studied the new luminophores I [5] and diarylidene benzodifurandione IV [6].

The UV spectra of I–IV are presented on Figure 1. The energies of the electronic transitions were calculated in the framework of the SCF-CI-PPP method using standard parametrization [7]. The calculations reproduce well the position of the absorption bands, whereas the oscillator strengths f are in some cases in disagreement with the experimental data; such discrepancies between the molar absorption coefficient ε and f are often encountered in semi-empirical quantum chemistry.

The results of POA pertaining to the composite models A and B of I–IV are presented in Table 1. Among several fragmentations of I–III studied by us, these two models yielded the best fits, i.e. the lowest values of dC (I), for all 10 electronic transitions which were calculated. Furthermore, in Table 1 the results for only those transitions $S_0 \rightarrow S_I$ are presented which are characterized by a pronounced localization of the excitation on a given subchromophore, i.e. dLT (I) or dLU (I) $\geqq 0.85$; the transition $S_0 \rightarrow S_1$ is also always presented, for comparison.

It is seen that the longest wavelength absorption band of compound I is caused by an electronic transition in which the excitation is delocalized over the whole conjugated system. In the 280–320 nm range lie two electronic transitions: the first, $S_0 \rightarrow S_2$, computed at 300 nm, can be assigned as excitation localized either on the MPH or on the ST subchromophore, whereas the second transition, $S_0 \rightarrow S_3$, computed at 289 nm, is unequivocally a local excitation solely in the ST subchromophore. The presence of two near-lying electronic transitions with localized

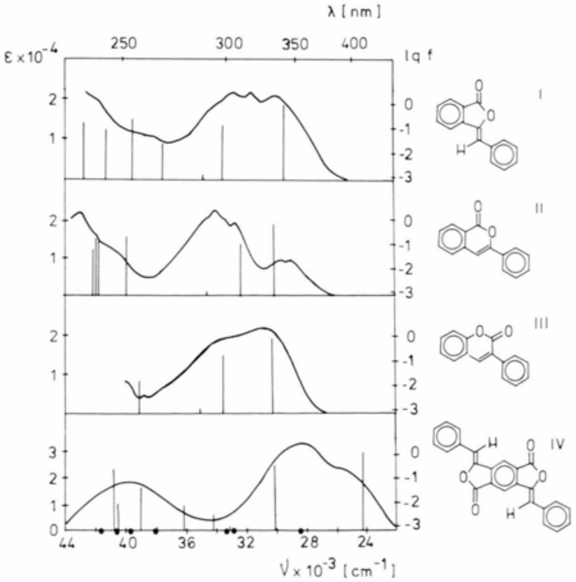

Fig. 1. UV spectra of the studied compounds. The computed transitions are marked by lines; the black dots mark $\lg f < -3$.

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Table 1. Pars Orbital Analysis of the investigated compounds; for IV (model B: dLU = = dL (U + V + W), T = I, U = −COO−, V = C=C, W = −Ph).

Com-pound	S_0-S_1		Model A				Model B		
	I	dLT	dLU	dCT	dC	dLT	dLU	dCT	dC
I	1	0.807	0.111	0.035 TU	0.047	0.754	0.142	0.076 UT	0.029
	2	0.888	0.038	0.036 UT	0.038	0.924	0.057	0.007 TU	0.013
	3	0.971	0.012	0.002 TU	0.014	0.095	0.849	0.040 UT	0.016
	7	0.869	0.042	0.056 TU	0.033	0.026	0.366	0.357 TU	0.017
II	1	0.819	0.025	0.093 UT	0.063	0.712	0.136	0.114 TU	0.038
	2	0.853	0.085	0.005 TU	0.057	0.947	0.036	0.002 UT	0.016
	3	0.986	−0.003	0.006 UT	0.011	0.083	0.855	0.039 TU	0.023
	5	0.859	0.093	0.007 UT	0.041	0.626	0.172	0.179 TU	0.024
III	1	0.759	0.069	0.112 AT	0.060	0.854	0.061	0.068 UT	0.016
	2	0.916	0.026	0.006 TU	0.052	0.783	0.068	0.135 UT	0.014
	3	0.980	−0.001	0.013 TU	0.009	0.036	0.769	0.183 UT	0.013
	8	0.834	0.085	0.034 UT	0.048	0.433	0.300	0.250 TU	0.016
IV	1	0.824	0.025	0.043 TU	0.108	0.636	0.241	0.059 UT	0.064
	3	0.877	0.021	0.066 UT	0.036	0.772	0.123	0.048 UT	0.057
	14	0.866	0.024	0.028 TU	0.083	0.484	0.351	0.091 UT	0.074

excitation on the ST subchromophore explains the stilbene-like absorption in this spectral range. The absorption band which would be caused by the $S_0 \rightarrow S_1$ transition of the MPH subchromophore is of much weaker intensity ($\varepsilon \approx 4000$) than that of the ST subchromophore ($\varepsilon \approx 29000$) [1, 5], and thus couldn't be observed as a "partial band" experimentally.

POA carried out for MPH itself shows that the $S_0 \rightarrow S_1$ transition at 304 nm (computed at 296 nm) can be considered to be an excitation localized mainly on the styrene subchromophore of MPH, dLT(1) = 0.809, which is, however, considerably perturbed by charge transfer dCT(1) = 0.109, from styrene to COO. The same holds for coumarin (CU) and isocoumarin (ICU).

POA provides similar results for the $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ transitions for compounds II and III (Table 1). It is seen that the oxygen atom (directly attached to the double bond in compounds I and II) perturbs more strongly the ST system in comparison with the C=O group (directly attached to the double bond in compound III), and, thus, decreases the localization of the excitation. For the $S_0 \rightarrow S_1$ transition, the excitation is delocalized over the whole molecule for I and II, whereas for III, this transition is to a large extent localized on the CU fragment (Table 1, IIIB). Indeed, the longest wavelength band in the UV spectrum of III (Fig. 1) is similar to that of CU. The small bathochromic shift is due to some delocalization, dC (1) = 0.016 and a charge transfer, dCT (1) = 0.07, from Ph to CU.

For I−III our calculations predict the presence of electronic transitions in the 230−240 nm range which are localized on the ST subchromophore according to POA. Experimentally is observed: $S_0 \rightarrow S_7$ at 232 nm for I, $S_0 \rightarrow S_5$ at 233 nm for II, and $S_0 \rightarrow S_8$ at 235 nm for III.

The $S_0 \rightarrow S_1$ transition of IV at about 410 nm is associated with a delocalized excitation over the whole conjugated system (Table 1). The second UV band of IV at 280−320 nm cannot be characterized experimentally, since both probable subchromophores − bisstyrylbenzene (BSB) (composite model A: T = BSB and $U_1 = U_2$ = COO) and I (composite model B: T = I, U = COO, V = /C=C/ and W = Ph) absorb in this range. The quantum chemical calculations and POA (Table 1) show that this band is caused mainly by the transition $S_0 \rightarrow S_3$, which is localized in the BSB subchromophore; the $S_0 \rightarrow S_1$ transition of BSB has a very high intensity, $\varepsilon \approx 45000$ [8], which corresponds to that of the second band of ÌV, $\varepsilon \approx 34920$ [6]. The band at 230−260 nm (Fig. 1, IV) is caused by the electronic transition $S_0 \rightarrow S_{14}$, which is also localized on the BSB subchromophore (Table 1, IV).

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