THEORETICAL PREDICTION OF THE DEACTIVATION PATHWAYS IN THE COUMARIN CLASS

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abstract; Semiempirical and ab initio calculations for coumarin and some 3-substituted derivatives were performed, in order to get an insight on the n-π^* or π-π^* nature of the first excited state and on the possible nonradiative deactivation pathways. The results indicate that both HOMO and LUMO are π-type orbitals, while the n orbital has a lower energy (HOMO-2 or deeper) and the nature of the first transition is π-π^*. The sequence of states calculated at the optimized geometry of the first excited singlet state indicates that substitution in position 3 determines changes of energy in the triplet manifold, meaning a change in the intersystem crossing (ISC) rate and thus the emission efficiency. The results correlate well with the experimental data on the Φ_P/Φ_F ratio.

Introduction

Owing to the wide applications of the compounds in the coumarin class and the importance of their photophysical properties, the sequence and nature of the first excited states of coumarin and its derivatives were widely discussed [1÷5].

On the basis of low temperature phosphorescence spectra it was reported that the first excited state of the unsubstituted coumarin corresponds to a π-π^* transition [4,5]. This result was also supported by MO semiempirical calculations using the PPP and CNDO methods. However, other literature data [1,2] consider that for coumarin itself the first excited singlet has an n-π^* character and for some of its derivatives there is a mixing of n-π^* and π-π^* states.

The dependence of the fluorescence quantum yields on the substituted positions and the type of the substituent was rationalized in terms of several deactivation processes like internal conversion (IC), intersystem crossing (ISC) or conformational change in the excited state with the formation of TICT (twisted intermolecular charge transfer) states [6].

In order to get an insight on the nature of the excited state and on the possibility to predict on a theoretical basis the nonradiative deactivation pathways, the sequence of the molecular orbitals in the ground state (S_0) and the energy of the excited states of the parent coumarin

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(C) and of some derivatives were calculated using several levels of configuration interaction. We have chosen the derivatives substituted in the same position of the ring (3), i.e. 3-Cl-, 3-CH$_3$-, 3-Phenyl-, 3-COOH-, characterized by different quantum yields and for which some data on the ratio of phosphorescence, fluorescence quantum yields (Φ_P/Φ_F) were available. The compounds are presented in Figure 1.

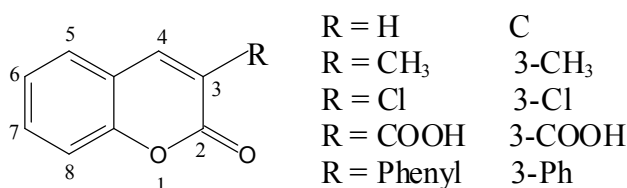|	
R = H	C
R = CH$_3$	3-CH$_3$
R = Cl	3-Cl
R = COOH	3-COOH
R = Phenyl	3-Ph

Fig. 1: *Molecular structure and numbering of the studied compounds*

Computational details

Semiempirical calculations were performed using the PC version of the MOPAC 7.0 package and the AMSOL program [7÷12]; SM5.4A solvent dependent optimizations were performed in cyclohexane (CHX) and methanol as models for nonpolar and polar protic solvents, respectively. For both in vacuo and solvent dependent calculations, the AM1 Hamiltonian [13,14] and Eigenvector Following and TRUSTE optimization procedures were used. The keywords for excited singlet states optimizations were OPEN(2,2), ROOT=2, SINGLET. Different levels of configuration interaction, C.I. = n (n = 2, 3, 4, 5) were used, depending on the degeneracy of the last occupied and first empty molecular orbitals. The singlet-triplet splitting was considered as the energy difference between the first singlet and the respective triplet, both calculated at the optimized geometry of the first singlet. Ab initio calculations (HF/6-31G*//HF/6-31G*) for the ground state were performed using the PC version of the GAMESS program [15].

Results and discussion

As was already mentioned, one of the main problem in the discussion of the emission properties in the coumarin class is the nature n-π^* or π-π^* of the first excited singlet state. In order to get an insight on this point, a survey of the molecular orbitals in coumarin, obtained in vacuo or in solvents with different polarities was necessary.

The results show that the highest occupied (*m, m-1*) as well as the lowest vacant orbitals (*m+1, m+2*) present a π character. The molecular orbital corresponding to the n electrons of the oxygen atoms is *m-2*. The same kind of orbitals are found in the other derivatives, excepting 3-COOH, in which, due to the presence of the carboxyl group, there are two orbitals, *m-2* and *m-3*, correlated with the nonbonding electrons of the oxygens. In fact, it can be stated that the considered derivatives and/or the substituted position do not perturb

to a great extent the frontier orbitals of the coumarin ring (Table 1). The same observation was made in our previous study on 3-phenylcoumarin [6].

The same conclusion on the insignificant role of substituents on the features of the frontier molecular orbitals can be drawn from the ab initio calculations. As it can be seen in Figure 2, the energies of the molecular orbitals are not changed to a great extent by substitution. The degree of localization of the highest occupied orbitals on different atoms, as reflected by the atomic populations for HOMO and the *m-3* orbital given in Table 2, supports this statement. The localization on the carbon atoms in the coumarin fragment was calculated by summing up the populations on all the atoms; then the atomic populations on the two oxygens in the coumarin and on the substituent are given.

Table 1. Sequence of the highest occupied molecular orbitals calculated at the semiempirical level

MO	Type	ε (eV)			
		C	3-CH3	3-Cl	3-COOH
m	π	-9.460	-9.109	-9.302	-9.553
m-1	π	-9.950	-9.739	-9.955	-10.166
m-2	n	-11.232	-10.886	-11.223	-11.082
m-3	n	-	-	-	-11.609
m-4	π	-11.851	-11.450	-11.463	-11.904

The features of the highest occupied molecular orbitals, *m* and *m-1*, are determined by the coumarin π system. The most interesting orbital for the nature of the excited state is the orbital corresponding to the nonbonding, n, electrons of the oxygen atoms in coumarin. This orbital is *m-3* in all the compounds except for the 3-carboxy derivative, in which, as a consequence of the presence of more oxygen atoms, there are several non-bonding orbitals, starting with *m*-3. The exact position of the n orbital is different from that predicted at the semiempirical level, an inversion being obtained between the n orbital and the π orbital, *m-3*.

The main result of semiempirical and ab intio calculations of the ground state properties is the fact that the n orbital in coumarin and these derivatives is deeply located, with a low probability to be implied in the first electronic transition. In order to elucidate the n-π^* or π-π^* nature of the first excited singlet state, ensuring the inclusion of the nonbonding electrons, the calculations were performed at the semiempirical level considering C.I.=5, i.e. 100 single and double excited configurations implying all the orbitals from *m*-2 to *m*+2. The geometry of the first excited singlet state was fully optimized for all the compounds and the sequence of state at the geometry of S_1 calculated. The results are presented in Figure 3.

The componence of the excited states reveals that the n orbital is implied in the formation of the third singlet in both CHX and methanol for coumarin and its 3-substituted derivatives.
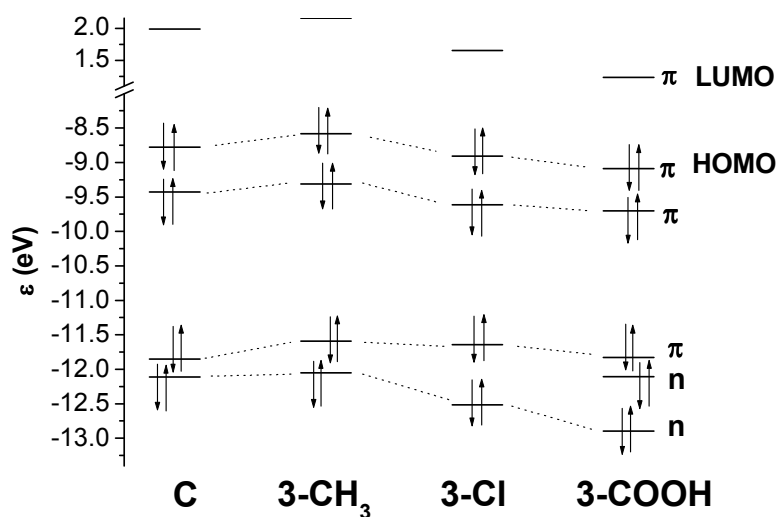
Fig.2 *Sequence of ab initio calculated frontier molecular orbitals*

Table 2. Ab initio atomic populations in HOMO and the highest n-type MOs

Orbital	Compound	ε (eV)	Coumarin Ring			Substituent
			Carbons	Oxygen (ring)	Oxygen (C=O)	
m	C	-8.78	1.644	0.000	0.166	-
	3-CH3	-8.58	1.698	0.000	0.145	0.000
	3-Cl	-8.91	1.612	0.000	0.136	0.000
	3-COOH	-8.91	1.620	0.095	0.163	0.000
m-3	C	-12.11	0.345	0.178	1.261	-
	3-CH3	-12.05	0.376	0.180	1.170	0.000
	3-Cl	-12.52	0.315	0.167	0.729	0.643
m-2	3-COOH	-11.83[*]	0.218	0.111	0.698	0.714
m-4		-12.90[*]	0.000	0.000	0.662	0.922
m-5		-13.94[*]	0.000	0.000	0.184	1.419

[*] *m*-2, the first n-type MO, located on COOH, and *m*-4, *m*-5 MOs.

The overall rate of the ISC nonradiative deactivation, k_{ISC}, can be expressed as the sum of the rates of the individual ISC processes, $k^j_{ISC}(S_1 \rightarrow T_j)$, [16]:

$$k_{ISC} = \sum_{j=1}^{n} k^j_{ISC}\left(S_1 \rightarrow T_j\right)$$

(1)

They decrease exponentially with the increasing of the singlet-triplet splitting by way of the Franck-Condon factor, according to the empirical Robinson-Frosch formula:

$$k_{ISC}^{j}\left(S_1 \rightarrow T_j\right) \cong 10^{12}\left(\beta_{S_1 T_j}\right)^2 \exp\left(-0,25\Delta E_{ST}^{0,4}\right)$$ (2)

where $\beta_{S1Tj} = \langle\Psi_{S1}|H_{so}|\Psi_{Tj}\rangle$ is the matrix element of the spin-orbit coupling operator of states S_1 and T_j, ΔE_{ST} stands for the singlet-triplet energetic gap, expressed in cm^{-1}. The exponential part represents the Franck-Condon factor.

The condition for an ISC process to occur with a non negligible rate is that the triplet be situated at a lower energy than the first singlet or above it, with no more than 1000 cm^{-1} [16]. A decrease in the singlet-triplet splitting thus determines a decrease in the experimental quantum yield, due to ISC deactivation. The crossing to a triplet higher in energy than S_1 is due to thermal activation on different vibrational levels of S_1, from which then ISC occurs.

The main results on the first excited levels are presented in the diagram (Figure 3) and also in Table 3. The negative values mean that the triplet is above S_1. For the sake of comparison the results previously obtained for 3-phenylcoumarin are included as well.
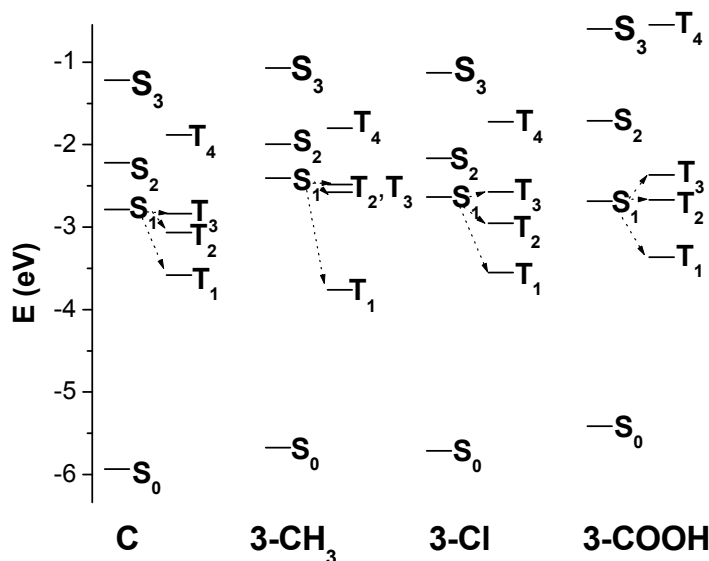

Fig.3. *Sequence of states calculated in methanol at the optimized geometry of the first excited singlet (C.I.=5).*

One can see that in the case of the unsubstituted coumarin, three triplet levels are found below the first excited singlet, S_1, contributing to the ISC nonradiative deactivation

pathways. Considering the S-T splittings, it is expected that ISC towards T_1 and T_2 has a lower probability. The high value of Φ_P/Φ_F can be explained by the high probability of the intersystem crossing process from S_1 to T_3, ensured by the small gap (471 cm^{-1}), the smallest value for all the series. In the case of the methyl derivative the larger splitting for the same states predicts a lower rate for this process; on the other hand, due to a large value of the S_1-T_1 gap, 12253 cm^{-1}, this ISC process can be ruled out, in agreement with the lower value for the Φ_P/Φ_F ratio. For 3-carboxycoumarin, the first triplet located below S_1 is T_1, with a gap of 5509 cm^{-1}. In this case, the presence of T_3, although above S_1, is very close to it (324 cm^{-1}), which ensures a deactivation channel. For the chloro-substituted derivatives there were no available experimental data. On the basis of the calculated S-T splittings one could expect a lower value for the phosphorescence to fluorescence quantum yields ratio than for the unsubstituted coumarin. The last compound, 3-phenyl coumarin, behaves differently. In this case, there is only one triplet below S_1 that could contribute to the ISC deactivation, but well separated, 10475 cm^{-1}. The other two, T_2 and T_3 are too high to be considered from this point of view.

It can be seen that the experimental data on the Φ_P/Φ_F ratio could be explained on grounds of the singlet-triplet splitting.

Table 3. Ratio of the phosphorescence and fluorescence quantum yield and relevant singlet-triplet gaps S_1-T_i calculated in methanol (cm^{-1}, a negative sign shows that the triplet state is above S_1)

Compound	C	3-Me	3-Cl	3-COOH	3-Phenyl[b]
Φ_P/Φ_F[a]	5.83	1.08	-	2.82	<0.05
S_1-T_1	7213	12256	7396	5509	10475
S_1-T_2	2530	1524	2896	-1994	-12602
S_1-T_3	471	700	-575	-324	-14871

[a] ref. [4], values in ethanol.

[b] ref. [6].

Conclusions

Semiempirical calculations on some 3-substituted coumarins were performed. The results on the frontier orbitals indicate that they present a π character, and, consequently the first excited singlet state has a π-π^* character. The nonbonding MO has a deeper position (*m*-2). Substitution doesn't modify the electronic structure of the coumarin, except for the carboxyl-substituted compound, which introduces some additional n orbitals, due to the nonbonding electrons of the carboxyl oxygens. The sequence of states calculated at the optimized geometry of the first excited singlet, i.e. the state responsible for the emission properties, was correlated to the probability of nonradiative ISC processes. It was found that the coumarin has three triplet states below S_1 and that the lowest S-T gap is very small (471 cm^{-1}), whereas substitution modifies the relative energy of the triplets, in such a way as to decrease the ISC probability. The results could explain the variation of the Φ_P/Φ_F ratio in the series found experimentally.

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