

The photodimerisation of coumarin

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Abstract

The photochemical dimerisation of coumarin can be rationalised on the basis of simple *ab initio* calculations. The direct reaction, that occurs through the first excited singlet state, gives the *syn* head-to-head dimer. This dimer can be obtained if the reaction occurs via a frontier orbitals control and if the reaction is concerted. The sensitised reaction gives the *anti* head-to-head dimer: this product can be obtained by assuming that the frontier orbitals control of the reaction is able to explain the observed regiochemical behaviour. The stereochemical behaviour can be explained on the basis of the formation of the most stable biradical intermediate.

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Some years ago we reported some experimental results on the photodimerisation of heteroaryl substituted acrylic derivatives [1–7]. More recently, we proposed an approach able to explain the observed photochemical behaviour [8,9]. In fact we noted that in sensitised reaction the formation of only head-to-head dimers could be explained assuming a frontier orbitals control of the reaction. Furthermore, the coupling reaction allowed the formation of the most stable biradical species. The following ring closure is determined by the activation energy of the reactions. In our cases, the reactions allow to obtain the most stable photodimers.

The photochemical dimerisation of coumarin is a well-known reaction in organic photochemistry [10–16]. The photodimerisation of coumarin is regioselective. Direct irradiation of **1** in ethanol gives the *syn* dimer (Scheme 1). The *syn* head-to-head dimer **2** was obtained from the singlet-excited state, perhaps via an excimer intermediate. Dimerisation does not occur in less polar solvents, such as benzene. Direct irradiation of a benzene solution induces self-quenching of the S_1 state. The *anti* head-to-head dimer **3** was found after benzophenone-sensitised population of the triplet state in both polar and non-polar solvent. Direct absorption of the light by coumarin induces a sensitised population of the singlet-excited state of benzophenone. Intersystem crossing and following energy transfer allow the population of the triplet state of coumarin.

In this paper, we want to show that the above reported description of the photodimerisation reaction can be used also in order to explain the formation of the products **2** and **3** in the dimerisation of coumarin.

1. Results and discussion

We performed some *ab initio* calculations using 6-31G** basis set on Gaussian 98, using UHF method. The calculations were usually done using Møller-Plesset perturbations (MP2). The Polak-Ribiere algorithm with gradient calculations was adopted for geometry optimisations. The open-shell states were treated at the same level of accuracy as the closed state states. We verified that the obtained structures were minima on the potential energy surfaces calculating the frequencies of the optimised structures.

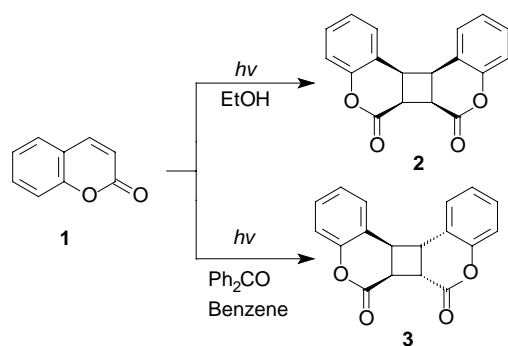
First we studied the reaction in the first excited singlet state through direct irradiation. The HOMO of the ground state is at -9.69 eV while the LUMO is present at -0.99 eV. The first excited singlet state showed an energy of 83 kcal mol $^{-1}$ in good agreement with the experimental 82 kcal mol $^{-1}$ [12]. The LSOMO showed an energy of -6.99 , while the HSOMO is at -3.56 eV. The best interaction is that between LSOMO of the first excited singlet state and the LUMO of the ground state. In Fig. 1 we report the atomic coefficients of these two orbitals.

We can see that there is a complete superposition between these two orbitals. This datum is in agreement with a possible concerted mechanism. On the other hand, the total super-

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Scheme 1.

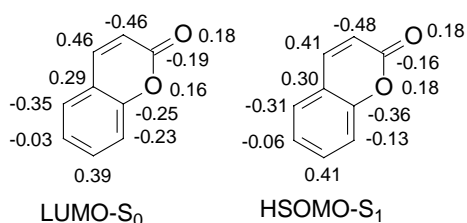


Fig. 1. Atomic coefficients involved in frontier orbitals in the direct photodimerisation reaction of coumarin.

position between these orbitals is in agreement with the fact that only a head-to-head product is obtained in this reaction. A concerted mechanism is able to explain also why compound **2** is the only product of this reaction. The direct coupling between two superimposed molecules can give only **2**.

In the sensitised reaction, the reaction has to occur through the first excited triplet state. The triplet state showed an energy of 60 kcal mol⁻¹, in good agreement with the experimental result (62 kcal mol⁻¹) [12]. The LSOMO of the triplet state is at -9.60 eV, while the HSOMO shows an energy of -8.78 eV. The best interaction with the ground state is obtained between the HOMO of the ground state and the LSOMO of the triplet state. In Fig. 2 we report the atomic coefficients of these two orbitals.

Also in this case, we observe good superposition between the frontier orbitals. The involved orbitals showed the same shape, even if the atomic coefficients in some positions are quite different. The superposition between the frontier orbitals can explain the formation of only head-to-head dimers, because, in the case of head-to-tail dimers, the same superposition is not allowed. While the frontier orbitals allow

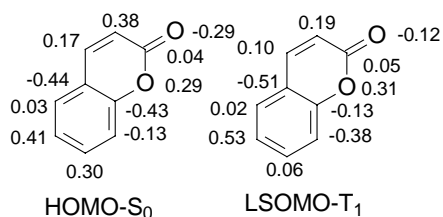


Fig. 2. Atomic coefficients of the frontier orbitals involved in the sensitised photodimerisation of coumarin.

Table 1
Radical intermediates in the sensitised photodimerisation of coumarin

Biradical	Total energy (kcal mol ⁻¹)
	-80491.167
	-80489.974
	-80481.452
	-80481.353

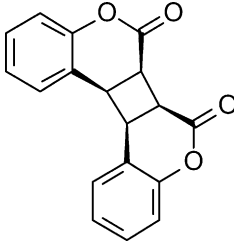
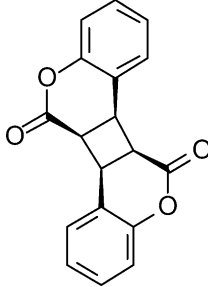
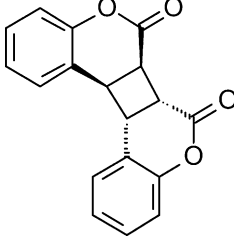
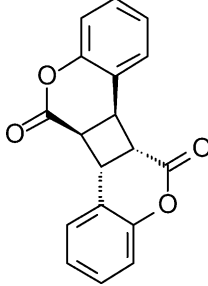
us to explain regiochemical behaviour of the photochemical reaction, the stereochemistry of the reaction cannot be explained on the basis of this theory.

The sensitised reaction involved the formation of biradical intermediates. The biradical favoured in this reaction determines the stereochemistry of the product, because the other two stereocenters formed in the cyclobutane ring closure are correlated to the first formed ones. In Table 1, we report the total energy of all the possible biradical intermediates.

The formation of head-to-head *trans* biradical is favoured. This is in agreement with the experimental results. In fact, the ring closure reaction on this biradical intermediate allows the formation of **3**.

It is noteworthy, that in this case, the reaction does not allow the formation of the thermodynamic more stable compound. In Table 2 we collected the results of the calculation of the total energy for all the possible dimers. We can

Table 2
Total energy of all the possible dimers of coumarin

Dimer	Energy (kcal mol ⁻¹)	Dimer	Energy (kcal mol ⁻¹)
	-80503.112		-80505.177
	-80508.979		-80510.317

see that the reaction allows the formation of the more stable head-to-head dimer, but it is not the most stable isomer (the corresponding head-to-tail dimer).

In conclusion, we have shown that our theoretical approach is able to explain the photochemical behaviour of coumarin. The approach described above has been previously used to explain the photodimerisation of heterocyclic substituted acrylic derivatives [8,9]. These results showed that this approach can be used to explain the photodimerisation of all aryl substituted acrylic derivatives.

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