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Intramolecular Triplet−Triplet Energy Transfer in Oxa- and Aza-di-π-methane Photosensitized Systems

Luis M. Frutos,* Unai Sancho, and Obis Castaño

Departamento de Química Física, Universidad de Alcalá, 28871 Alcalá de Henares, Madrid, Spain

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Two different mechanisms are proposed for the intramolecular triplet−triplet energy transfer in oxa- and aza-di-π-methane systems, one thermally induced and the other photoinduced. These mechanisms involve a key structure that corresponds to an avoided crossing. The triplet sensitized photochemistry of these compounds, focusing attention in the di-π-methane rearrangement, is discussed in light of these proposed mechanisms.

Intermolecular triplet−triplet energy transfer (TET) between a triplet sensitizer and an acceptor molecule is a common process to initiate organic reactions taking place in the triplet state. If the acceptor molecule contains several chromophore groups, after the energy transfer, intramolecular TET between these groups becomes feasible.

Intramolecular TET has been widely studied in several systems in which two chromophores in the same molecular system are kept apart.[1] The rate constant for the intramolecular TET is sensitive to the distance between the chromophores, and decays exponentially as the distance increases.[2] A close approach between the groups is necessary for the process to occur.

In this communication, we advance the principal results of a theoretical study of intramolecular TET in aza- and oxa-di-π-methane (aza- and oxa-DPM) systems. We propose, from potential energy surface computations, that intramolecular TET should occur in these systems through an avoided crossing between $T_2(n,\pi^*)$ and $T_1(\pi,\pi^*)$ states.[3] In addition, two possible mechanisms for these processes are discussed: the first thermally induced and the second photoinduced. Finally, we analyze their photochemical implications in triplet sensitized reactions according to the energy of the triplet sensitizer.

The first step in a triplet-sensitized di-π-methane rearrangement reaction is the triplet excitation of one of the chromophore groups. From this state, the DPM rearrangement to vinylcyclopropane can occur through thermal activation.[4] The most simple oxa- and aza-DPM systems (Figure 1) have two chromophore groups, a keto or imino and vinyl, which are separated by only a few Å units by an sp^3 carbon bridge. Due to this proximity, the triplet states corresponding to the excitation of each group are strongly electronically coupled, giving rise to repulsion between the diabatic potential energy surfaces (T_2/T_1 avoided crossing). This repulsion energy corresponds essentially to a pure electronic coupling (EC), since the vibronic contribution is negligible.[5] For this reason, it is expected that the crossing between surfaces (even being of the same spin multiplicity) corresponds to an avoided crossing rather than to a conical intersection. Furthermore, the energy gradient difference vector is collinear to the derivative coupling (for both studied cases), indicating the nonexistence of a conical intersection.

Figure 1. (**I**) oxa- and (**II**) aza-di-π-methane systems studied.

The potential energy surfaces of the above-mentioned di-π-methane systems have been studied with the CASPT2//CASSCF methodology.[6] The minimum energy structure fulfilling this avoided crossing condition between triplet states must be reached by the molecule in order to verify the intramolecular TET by thermal activation in the T_1 state. Also, the same avoided crossing is a minimum energy point on the PES which the system must reach after the excitation to T_2 in order to decay to T_1.

The oxa-DPM system (**I**) presents two triplet states ($T_1(\pi,\pi^*)$ and $T_2(n,\pi^*)$) that correspond to the vertical excitation (Franck−Condon, FC) of the C=C and C=O groups, respectively.[7] To determine the relaxation pathways after electronic excitation (triplet photosensitized), we have studied the corresponding minimum energy paths (MEP). If the system is excited to T_1, the energy is localized in the vinyl group, breaking the double bond (Figure 2).

Conversely, if the molecule is excited to T_2, the system relaxes vibrationally, reaching an avoided crossing point between the T_2 and T_1 states ($\Delta E_{\mathrm{CASPT2}} = 1473$ cm^{-1}), where the triplet energy is delocalized between the two groups (Figure 3a). As a result of the relatively large EC at this point, a short but finite lifetime for this structure is expected, making possible the redistribution of the vibrational energy.[8] Hence, in the decay to T_1, the two biradical minima, corresponding to C−C and C−O double bond cleavage, would be populated. Specifically, following the gradient difference (GD) vector (difference between T_2 and T_1 states) as the initial relaxation direction, the C−C is broken, and in the opposite direction (−GD), the keto group retains the triplet energy (Figure 3a).

The existence of this avoided crossing may result in a thermally activated (T_1) intramolecular TET process, which can be crucial in many systems. TET process for **I** does not compete

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* To whom correspondence should be addressed. E-mail: luisma.frutos@uah.es.

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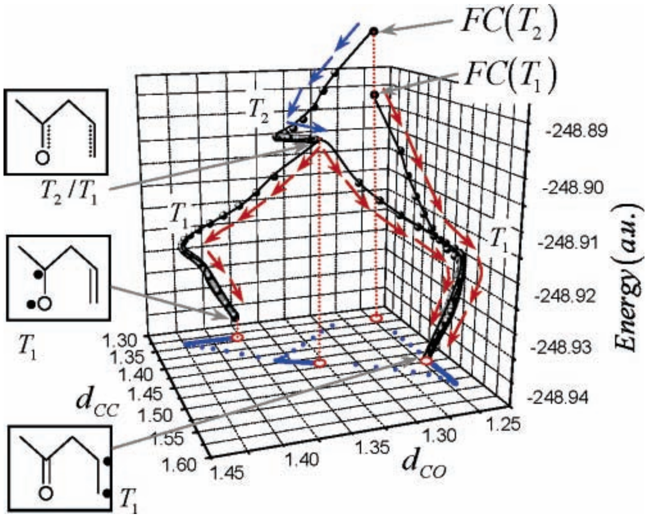

Figure 2. Representation of the energy (a.u.) vs the internal coordinates (C−O distance (carbonyl) and C−C distance (vinyl) in angstroms) for the MEP corresponding to the relaxation pathways (indicated by arrows) after the vertical excitation to T_1 and to T_2 and the later decay to T_1 through an (T_2/T_1) avoided crossing. Also, the projections of the MEP points onto the coordinates are indicated.

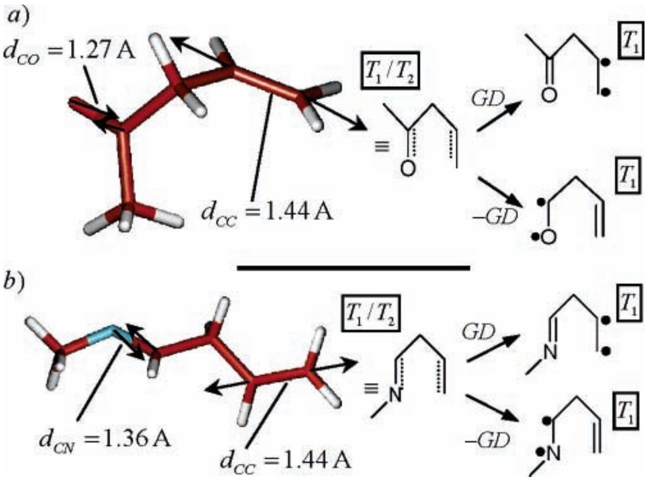

Figure 3. GD vector for the T_2/T_1 avoided crossing in the (a) oxa- and (b) aza-di-π-methane systems for the intramolecular TET process. Relaxation in the direction of GD implies localization of the triplet excitation in the C═C chromophore, while relaxation in the −GD direction localizes the excitation energy in the keto/imino group.

with the first step of DPM rearrangement (formation of the ciclopropane birradical[4b]) due to the high energy of activation of ca. 32.9 kcal/mol, compared with 30.0 kcal/mol for the rearrangement, and activationless for Z−E isomerization.[9]

The intramolecular TET processes in the aza-DPM system (**II**) are similar to those of **I**. In this case, the molecule shows two well differentiated FC triplet states ($T_1(\pi,\pi^*)$ and $T_2(n,\pi^*)$) corresponding to the excitation of the vinyl and imino groups, respectively. Therefore, after the excitation to T_1, the triplet energy is localized on the vinyl group. In contrast, by effecting excitation to T_2 using a triplet sensitizer with enough energy, the system undergoes vibrational relaxation to reach the avoided crossing point, $\Delta E[T_2 - T_1]_{\mathrm{CASPT2}} = 139\ \mathrm{cm}^{-1}$ (Figure 3.b).

The GD vector gives the two possible initial relaxation directions in the decay to the T_1 state through the avoided crossing. In one direction (GD), the C−C double bond is broken, localizing the triplet energy in this group, as the C−N bond is shortened to become a double bond. In the opposite relaxation direction (−GD), the converse occurs with the energy localized in the imino group (Figure 4). As in **I**, intramolecular TET in the T_1 state by thermal activation must be inefficient (E_a= 33.4 kcal/mol) compared with the first step of DPM rearrangement (formation of the ciclopropane birradical[4c,4d]) (E_a = 27.4 kcal/mol) and Z−E isomerization of the vinyl group (activationless but $T_1 \rightarrow S_0$ spin-forbidden transition).

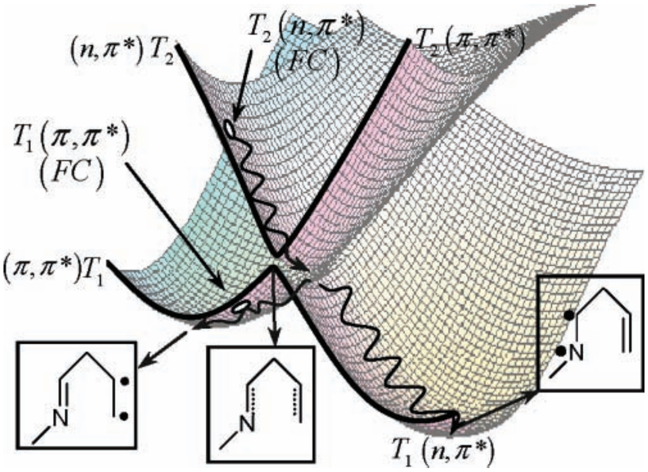

Figure 4. Schematic potential energy surface and relaxation pathways after the excitation to T_2 and T_1 in the aza-di-π-methane system. The decay to the T_1 state via an avoided crossing (T_2/T_1) is shown.

In conclusion, from the analysis of the triplet potential energy surfaces of **I** and **II**, we propose that an avoided crossing between two triplet states is responsible for the intramolecular TET process. Two mechanisms of intramolecular TET are possible. First, by excitation to the lowest energy triplet state T_1, once the triplet excitation in a chromophore group (i.e., C═C group in **I** and **II**) is localized, the energy could migrate to the other group (C═O and C═N in **I** and **II** respectively) overcoming the avoided crossing barrier. Therefore, by determining the electronic properties of the avoided crossing, it is possible, for example, to calculate the thermal energy of activation for the intramolecular TET. Second, by excitation to the higher energy triplet state (T_2), the molecule undergoes vibrational relaxation to reach the T_2/T_1 avoided crossing. Due to the large EC, the system decays to the T_1 state following two possible initial relaxation directions: those given by the GD vector (forward and reverse phases).

Consequently, if low energy triplet sensitizers are used, only the T_1 state can be populated and additional thermal energy is necessary to enable the intramolecular TET (which in the case of oxa- and aza-DPM systems does not compete with the rearrangement, due to the high energy of activation). In contrast, if a high energy triplet sensitizer is used, the T_2 state can be populated, and relaxation to T_1 allows approximately equal excitation of the two chromophore groups of the system. The excitation of the two chromophores may allow competition between several photochemical pathways. Indeed, activation of the vinyl moiety should be less effective for DPM rearrangement because of the possibility of Z−E isomerization, whereas excitation to T_2 should increase the efficiency of the DPM rearrangement.

Finally, these two mechanisms must be common to most intramolecular TET processes, and the study of the properties of the diabatic PES involved in the process, specifically the region near the avoided crossing, must give insight into the mechanism and kinetics of the process.

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(7) A study of the ground state (S_0) was made at the MP2/6-31+G-(d,p) level, to determine the most stable conformation for the oxa- and aza-DPM systems, which were taken to study all of the described processes.

(8) The lifetime of the T_2/T_1 structure is dictated by the dynamics of the process (for a recent review on ultrafast dynamics see Worth, G.; Cederbaum, L. S. *Annu. Rev. Phys. Chem.* **2004**, *55*, 127−158) which has not been studied here. Nevertheless, the large electronic coupling must ensures a significant population of both minima on T_1. Experimental indications of this fact are found for 1-phenyl-2-butene (see ref 3).

(9) Despite DPM rearrangement activation energy is close to that for intra-TET, the former process is less efficient due to the value of the transmission coefficient for the diabatic process ($\chi < 1$). Also, *Z*−*E* isomerization is an activationless but spin-forbidden transition ($S_0 \rightarrow T_1$).