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# Influence of the $S_0 - T_1$ structural changes on the triplet–triplet sensitization of dienes

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## Abstract

The triplet–triplet energy transfer properties of different dienes were examined through time-resolved laser spectroscopy, and the different structural changes between ground and triplet states were investigated by molecular modeling. It was found that these compounds exhibit very different behaviors depending on their molecular structure. The calculations of ground- and triplet-state potential energy surfaces (PESs) at the B3LYP/6-31+G(d) level clearly evidenced the crucial role of the thermal activation of a single bond torsion in order to decrease the energetic requirement for the transition. A recently developed model, that included the influence of such a torsional mode, was successfully used to support this hypothesis.

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## 1. Introduction

The triplet–triplet energy transfer reaction represents an important photochemical process and has received considerable attention [1–7]. A simple treatment, proposed by Sandros [1], allows the description of this reaction. Nowadays, this approach is routinely used as a guide for classical behavior and leads to the following equation for the observed rate constant of the energy transfer reaction ( $k_q$ ):

$$k_q = \frac{k_d}{1 + \exp(+\Delta G/RT)}, \quad (1)$$

where  $\Delta G$  represents the difference between the acceptor triplet energy  $E_T^A$  and the donor triplet energy  $E_T^D$  and  $k_d$  the rate constant of diffusion. From this equation, it can be seen that the rate constant drastically decreases in the endergonic region.

The so-called “non-vertical triplet excitation transfer (NVET)” represents a particular behavior in which unexpected large rate constants for endothermic reactions are observed [3–7]. This particular character has been already observed on different compounds such as *cis*-stilbene [2–7], biphenyl [8,9] or benzyl [10] derivatives, and can be detected on various other systems [11–20]. Some aspects of this phenomenon are really puzzling, the physical origin of this behavior remaining largely unclear although the importance of structural changes between ground and excited states has

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been emphasized: this NVET character is usually observed on compounds exhibiting large rearrangements with the transition. Simple structures must be examined to get more insights on this phenomenon.

The aim of this paper is to control by cyclization the geometry of elementary  $\pi$  systems (dienes) in order to investigate the particular effect of the molecular geometry on the energy transfer behavior. On these model compounds, the possibility to evidence the major molecular coordinate which is responsible for this character seems particularly interesting. The conclusions obtained on these dienes will be compared to those previously found on model oxime derivatives [20,21]. Moreover, the use of a recently proposed thermal activation model, that takes into account the contribution of the different populated ground state conformations [21], will be examined.

## 2. Experimental

### 2.1. Compounds

The studied compounds are shown in Scheme 1, together with the definition of the two dihedral angles  $\alpha(3, 2, 1, 5)$  and  $\beta(1, 2, 3, 4)$ . The dienes II–V are commercial products (Aldrich). Compound I was prepared by distillation of the corresponding dimer. The structures of these compounds were checked by NMR  $^1\text{H}$ ,  $^{13}\text{C}$ .

### 2.2. Laser setup

The nanosecond transient absorption setup was based on a pulsed Nd:YAG laser (Powerlite 9010, Continuum) that delivered pulses of 10 ns width at 355 nm. The transient absorption analysis system

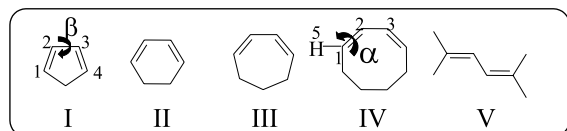
(LP900, Edinburgh Instruments) used a 450-W pulsed xenon arc lamp, a Czerny–Turner monochromator, a fast photomultiplier (risetime of ca. 2.2 ns) and a 100-MHz transient digitizer (TDS 340, Tektronix). This experimental setup was characterized by an instrumental response equal to 7 ns. Photoacoustic calorimetry (PAC) employed an experimental setup [22] that used the 355 nm attenuated YAG laser beam to irradiate the cell through a calibrated pinhole. The acoustic wave was detected by a piezoelectric element (Panametrics A603S) and recorded by a transient digitizer (TDS 3052, Tektronix). 2-Hydroxybenzophenone was used as a calorimetric reference. All the experiments were made in argon-saturated benzene solution (spectroscopic grade, Fluka).

### 2.3. Computational procedure

All quantum calculations were carried out using the Gaussian 98 suite of programs [23]. Density Functional Theory (DFT) was used to calculate the structure of the molecules. Relaxed ground and triplet states were fully optimized using the B3LYP functional with the 6-31+G(d) basis set. Potential Energy Surfaces (PESs) for the ground states were computed using the same method with a complete optimization of all geometrical parameters excepted the constrained dihedral angle ( $\alpha$  or  $\beta$ ). The corresponding spectroscopic triplet PESs were computed at both DFT and TDDFT levels (same basis set than for ground state) to get more confidence on the change of the spectroscopic triplet energies with these molecular coordinates.

## 3. Results and discussion

PAC was employed to measure the triplet energies of the dienes by using the following procedure. The benzophenone triplet state was quenched by the dienes through energy transfer at such a concentration that the triplet state was reduced down to 10 ns. This formed quantitatively the diene triplet state, and leads to an acoustic wave that propagates in the medium. For triplet state lifetimes longer than the integration time of



Scheme 1.

the PAC setup, the amplitude of the acoustic wave is proportional to all the non-radiative deactivation pathways, excepted the triplet state decay of the diene (Fig. 1). Therefore, triplet-state lifetimes shorter than 100 ns cannot be analyzed by this procedure. By comparison to the signal obtained for hydroxybenzophenone, a well-known calorimetric standard [24], the energy of the relaxed triplet state of the diene can be easily retrieved.

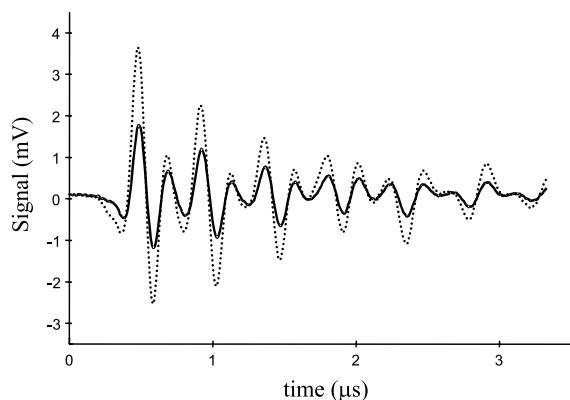


Fig. 1. PAC signals obtained for compound I (plain line) and hydroxybenzophenone (dot line).

The results, gathered in Table 1, are in good agreement with the values found in the literature. In the case of compounds IV and V, the short triplet state lifetimes prevent any analysis by our PAC experimental setup.

Sensitization experiments have been realized in benzene by using donors having well-known triplet energy [25]. The results are gathered in Table 1. The evolution of the rate constants of interaction,  $k_q$ , with the triplet energy of the donor is shown in Fig. 2. The quenching curves clearly evidence the large influence of the diene structure on the observed energy transfer properties. The experimental data obtained for the dienes I, II and V are well fitted by the Sandros model, demonstrating their classical ‘vertical’ behavior towards sensitization experiments. For these compounds, the slope of the quenching curve in the endergonic region is in good agreement with that expected from Eq. (1). However, for III and IV, this treatment poorly describes the experimental data, the slope of the quenching curve being lower than expected (0.17 mol/kJ, Fig. 2). These compounds are characterized by a manifest non-vertical behavior, which is more important in IV than in III.

Table 1

Triplet energies for the dienes  $E_T^{\text{PAC}}$  measured by PAC and  $E_T^{\text{lit}}$  from the literature, rate constants of interaction in benzene,  $\log(k_q)$ , between different donors and the studied dienes

	I	II	III	IV	V
$E_T^{\text{PAC}}$ (kJ/mol)	238	220	214	—	—
$E_T^{\text{lit}}$ (kJ/mol)	—	219 <sup>d</sup>	228 <sup>c</sup>	—	222 <sup>c</sup>
$\tau_T$ (ns) <sup>a</sup>	1800	6000	400	40	40
Donor ( $E_T^{\text{D}}$ kJ/mol) <sup>b</sup>			$\log k_q$		
Xanthone (310)	9.6 <sub>5</sub>			9.8	9.8
Benzophenone (287)	9.6	9.8	9.8	9.3	9.7 <sub>5</sub>
Phenanthrene (260)	9.5	9.7 <sub>5</sub>	9.6 <sub>5</sub>	8.8	9.5
4-Phenylbenzophenone (254)	9.3			8.67	
9-Cyanophenanthrene (243) <sup>c</sup>	8.8	9.7	9.5	8.4	9.5
Chrysene (239)	8.1	9.5	9.3	7.7 <sub>5</sub>	9.3
Benzyl (223)	6.4 <sub>5</sub>	8.9	8.1	6.2	8.8
1,2,3,4-Dibenzanthracene (213)		8.2	7.3	5.7	7.0
Pyrene (203)		6.1 <sub>5</sub>	6.3 <sub>5</sub>		5.7

<sup>a</sup> Lifetime measured by transient absorption spectroscopy.

<sup>b</sup> From Ref. [25].

<sup>c</sup> From Ref. [12].

<sup>d</sup> From Ref. [26].

<sup>e</sup> From Ref. [27].

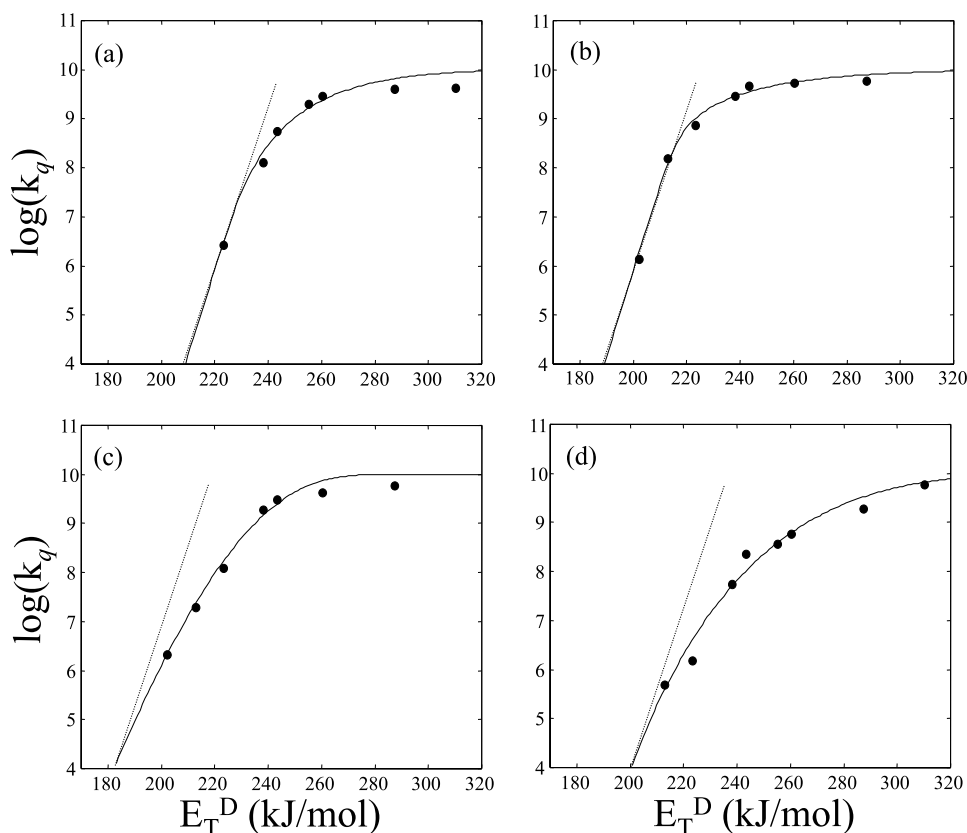


Fig. 2. Quenching rate constants  $k_q$  vs. the triplet energy of the donors for compounds (a) I, (b) II, (c) III and (d) IV. Slope of the quenching curve expected from Eq. (1) (dot lines). Fit of  $k_q$  (plain line) by using the thermal activation model (Eq. (4)).

### 3.1. Ground- and triplet-state equilibrium structures

In order to investigate the influence of the structural properties of the acceptor on the energy transfer reaction, the rearrangements associated with the transition from the ground to the relaxed triplet states of the dienes were studied by molecular calculations with DFT methods. These latter achieve significantly greater accuracy than the Hartree–Fock theory with just a modest increase of the computational cost. It has been shown that DFT methods reproduce quite well the energy difference between relaxed ground and triplet states and are in good agreement with the results obtained from high level electron correlated ab initio methods [28–31]. It can be seen from Table 2 that the triplet energies (computed as the difference between the relaxed triplet state and the equilib-

rium ground state) are in very good agreement with those obtained experimentally (Table 1). The deviation is less than 11 kJ/mol for all the molecules studied, and is particularly small for I. This gives confidence to both the functional and the basis set used for the calculations.

The geometrical properties obtained for these two states are gathered in Table 2 and schematically represented for I and IV in Fig. 3. From these results, different conformational changes can be noticed: (i) a  $\pi$  system flattening in the triplet state characterized by a decrease of  $\beta$  between ground and triplet states, (ii) a decrease of the C2–C3 bond length associated with an increase of the C1–C2 and C3–C4 bond lengths and (iii) a complete twist of the C1–C2 double bond for compounds IV and V. These different rearrangements arise from the promotion of an electron from the  $\pi$

Table 2

Structural parameters for the relaxed  $S_0$  and  $T_1$  states of the dienes calculated by using (U)B3LYP/6-31+G(d)

	$E_T^{\text{DFT}}$ (kJ/mol)	Electronic state	$\beta$ ( $^\circ$ )	$\alpha$ ( $^\circ$ )	C1–C2 ( $\text{\AA}$ )	C2–C3 ( $\text{\AA}$ )	C3–C4 ( $\text{\AA}$ )
I	234	$S_0$	0	180	1.352	1.470	1.352
		$T_1$	0	180	1.462	1.363	1.462
II	209	$S_0$	14.3	180	1.346	1.468	1.347
		$T_1$	2.0	170	1.452	1.366	1.452
III	216	$S_0$	0.2	177.7	1.349	1.466	1.349
		$T_1$	0	171.2	1.455	1.367	1.455
IV	209	$S_0$	51.2	178.2	1.347	1.467	1.347
		$T_1$	0.9	–96.3	1.467	1.394	1.396
V	211	$S_0$	180	180	1.354	1.456	1.354
		$T_1$	180	–90	1.476	1.393	1.398

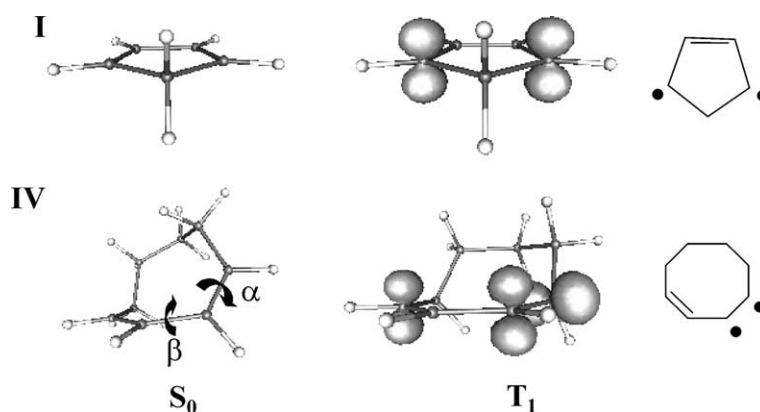


Fig. 3. Structural changes between ground and relaxed triplet states for I and IV (U)B3LYP/6-31+G(d). For the triplet state, the representation of the spin density is given together with a schematic representation of the biradical structure obtained.

bonding orbital (localized on the C1–C2 and C3–C4 bonds) to a  $\pi^*$  orbital (which possesses a bonding character along the C2–C3 bond) [32]. However, it is interesting to note that for different constrained molecules (I, II and III), the complete twist of a terminal double bond in the triplet state cannot occur. In this case, the cyclization of the chromophore strongly constrains the triplet state in a nearly planar structure. Therefore, compounds I–III exhibit a net 1,4 biradical character and compounds IV and V a 1,2 biradical structure. This is illustrated by the representation of the spin density in Fig. 3 for the relaxed triplet states of I and IV. The consequences of such structural changes on the energy transfer properties can be now discussed in details.

### 3.2. Thermal bond activation mechanism

The thermal bond activation mechanism recently developed [21] is schematically presented in Fig. 4. Some structures for which the transition energy is different from that of the equilibrium ground state structure (configuration *b* or *c*, compared to *a*) are thermally populated. When the triplet energy of the donor decreases, configuration *a* or *c* cannot be sensitized, and only a fraction of molecules are thermally populated (configuration *b* for example) in such a way that the reaction remains energetically feasible. Therefore, the quenching rate constants decrease much more slowly when one assumes a distribution of conformations, in contrast to the classical view that

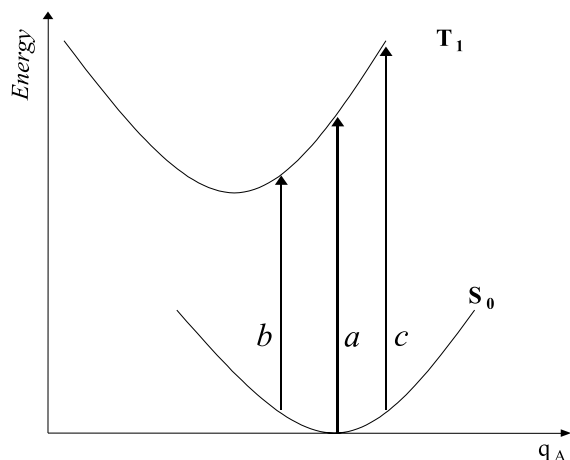


Fig. 4. Schematic representation of the thermal activation mechanism in vertical transitions originating from different configurations ( $a, b, c$ ).

considers only one acceptor structure at the equilibrium ground state. The determination of the molecular coordinate ( $q_A$ ) for which is associated such a distribution of spectroscopic triplet energy, remains a fascinating challenge.

In the present case, two molecular coordinates ( $\alpha$  and  $\beta$ ) lead to significant structural changes that can stabilize the triplet state. As a consequence, a large change of the spectroscopic triplet energy could be expected through a thermal population of the corresponding ground state molecules. Therefore, the potential energy surfaces (PESs) associated with these molecular coordinates were calculated at the (U)B3LYP/6-31+G(d) level. The energies given in Figs. 5 and 6 correspond to relative values with respect to the equilibrium ground state structure. The spectroscopic triplet energy

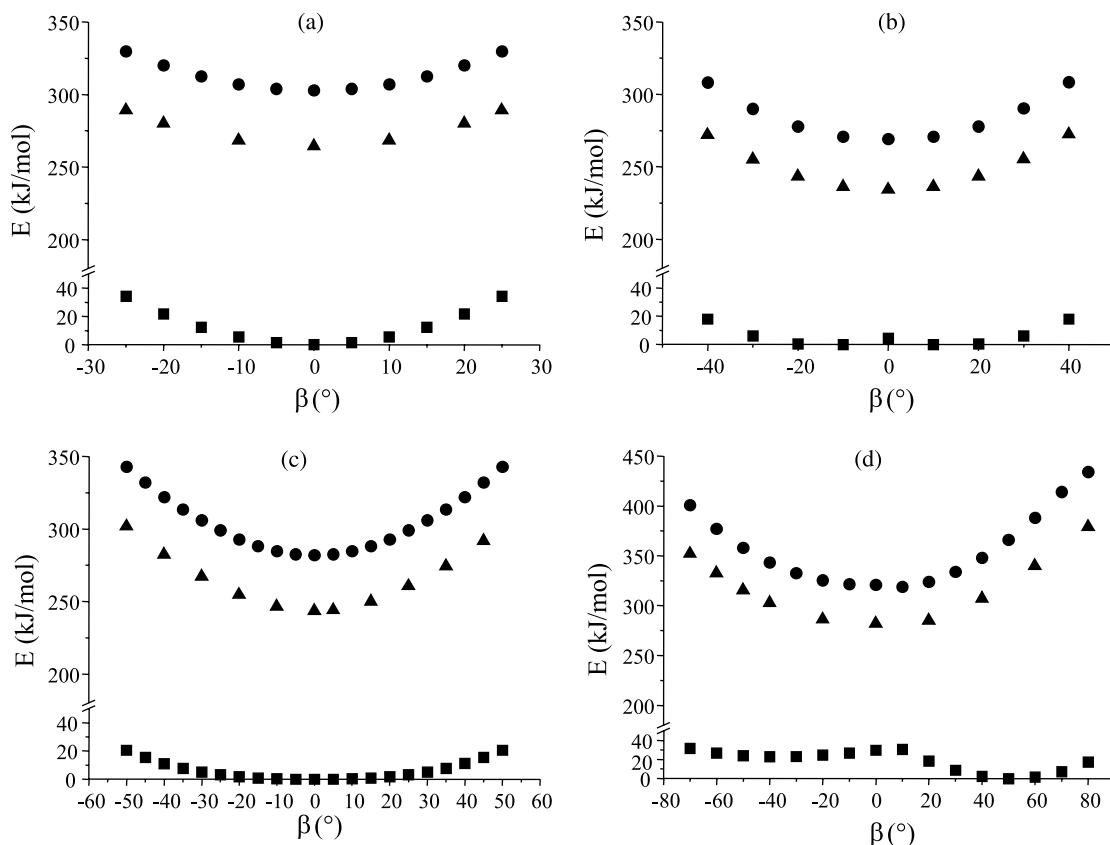


Fig. 5. Potential Energy Surfaces associated with the  $\beta$  dihedral angle: ground (■) and spectroscopic triplet states (▲: TDDFT; ●: DFT) for compound (a) I, (b) II, (c) III and (d) IV.

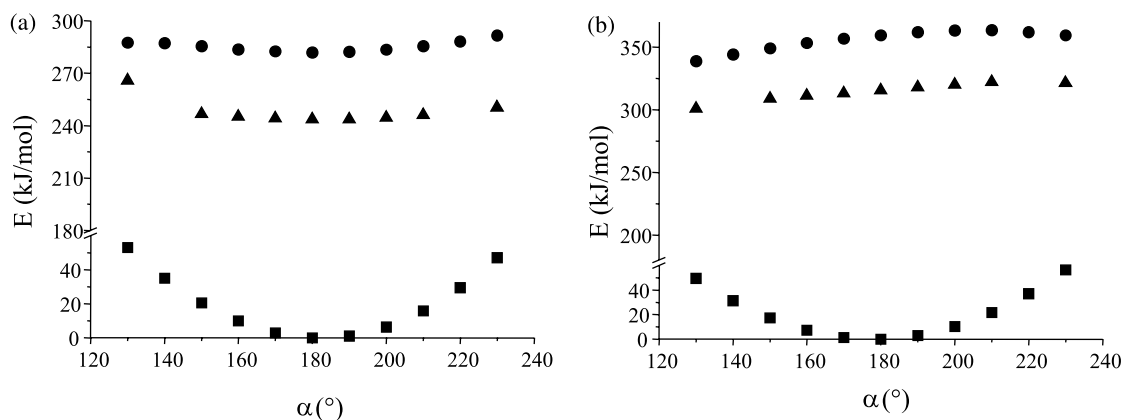


Fig. 6. Potential Energy Surfaces associated with the  $\alpha$  dihedral angle at the ground (■) and spectroscopic triplet states (▲: TDDFT; ●: DFT) for compounds (a) III and (b) IV.

obtained by the TDDFT method is about 40 kJ/mol below the value found at DFT level. This difference arises from the better prediction of spectroscopic parameters at TDDFT level. Very similar evolutions of the PESs calculated at the TDDFT or DFT levels give confidence to the trends observed. For sake of clarity, the results will be now discussed using the calculated TDDFT PESs for triplet states, the DFT triplet calculations leading to the same conclusions.

### 3.2.1. Influence of the single bond torsion

Fig. 5 shows that the PESs associated with the different dienes are very different from one molecule to another. For I, a thermal activation energy of about 5 kJ/mol along the ground state PES leads to a change of the energy required for the transition of about 2 kJ/mol. The energetic change corresponding to a similar activation energy is about 15 and 3 kJ/mol for II and V, respectively. The energy saved on the triplet transition is not strongly different than the thermal energy invested at the ground state. This fact explains the vertical character observed for compounds I, II and V.

For III, the PES associated with the ground state is more flat: a thermal activation of 5 kJ/mol allows a large distribution of molecules along  $\beta$  and leads to an energy change of the transition of about 19 kJ/mol. For this compound, a more important change of the spectroscopic triplet energy is related to the different populated structures

distributed along the ground state PES, in agreement with the non-vertical behavior experimentally observed.

For IV, the situation is more pronounced. From the ground state PES, a large distribution of molecules along  $\beta$  can be expected, and due to the asymmetric character of the PES, the required excitation energy to reach the triplet state is strongly affected by this parameter. For example, a thermal activation of 5 kJ/mol of the ground state molecule affects the calculated spectroscopic triplet energy by about 55 kJ/mol: 293 kJ/mol at  $\beta = 35^\circ$  and 348 kJ/mol at  $\beta = 65^\circ$ , respectively.

### 3.2.2. Influence of the double bond torsion

For I–III, the double bond is not affected by the transition between ground and triplet states, and therefore a thermal activation of this coordinate should have no effect on the energetic requirement of the transition. The PESs obtained along  $\alpha$  for compounds II and III clearly support this remark: one can calculate a difference of only 5 kJ/mol of the transition energy for a thermal activation of 5 kJ/mol (Fig. 6 for III).

For IV, the influence of the double bond torsion can be examined. From the PESs obtained (Fig. 6), it can be observed that a low thermal activation does not lead to a large exploration of the ground state structures. The energetic requirement for the torsion of a double bond is obviously higher than for a single bond. Assuming an activation energy



of 5 kJ/mol for the ground state PES, a maximum energy change (required for the transition) of 8 kJ/mol is calculated. This value is too small to account alone for the NVET behavior observed. For V, the PESs are not presented but similar conclusions are noted.

From these examples, it can be seen that the torsion of the single bond strongly affects the energetic requirement of the transition. This distribution of spectroscopic triplet energies along  $\beta$  has been observed mainly for III and IV in agreement with their experimentally observed NVET behaviors. Moreover, it seems that double bond torsion plays a minor role in this process even when this molecular coordinate corresponds to a structural change (see IV and V). These conclusions obtained on dienes are very similar to those found on oximes derivatives [20,21].

### 3.3. Data treatment through thermal activation mechanism

Many theoretical models have been proposed in the past to account for the triplet–triplet energy transfer reaction. Most of them are based on the Fermi's Golden Rule for non-radiative transitions [2,33–35]. Apart from an electronic term that describes the electronic coupling between the two partners, these models include a nuclear term by the way of Franck–Condon (FC) factors. Those factors are generally evaluated from the  $S_0 - T_1$  absorption spectra of the acceptor and the  $T_1 - S_0$  (in fact  $S_1 - S_0$ ) emission spectra of the donor [33–36]. Beyond the fact that these spectra are not available for all the compounds studied, the fitting of such data do not give useful information about the molecular coordinates involved with the transition: the remaining question is to unfold the role of the bonds that accommodate the differences between the  $S_0$  and  $T_1$  geometries, and that are responsible for the non-vertical behavior [7,37]. We proposed a totally different approach, assuming that FC factors are similar over the different thermally populated conformations experienced by the molecules prior the transition. Then, the rate constant can be described by an empirical law such as in Eq. (1), and the effects of the conformational distribution of acceptor molecules along the molecular

coordinates on the quenching rate constants can be introduced [21]. The PESs are assumed to be described by parabolic curves. At each  $\theta$  angle along the considered torsion mode, the energy  $E_T(\theta)$  required to reach the triplet curve is given by:

$$E_T(\theta) = E_{T \min} + \frac{1}{2} b_T \theta^2 - \frac{1}{2} b_G (\theta - \Delta\theta)^2, \quad (2)$$

where  $E_{T \min}$  corresponds to the difference between the minimum of the triplet PES and that of the ground state,  $\Delta\theta = \theta_{G \min} - \theta_{T \min}$  with  $\theta_{G \min}$  and  $\theta_{T \min}$  the values of the angles for the lowest energies of ground- and triplet-state PESs, respectively, and  $b_T$  and  $b_G$  are the corresponding coefficients of the parabolic PESs. The quenching rate constant,  $k_q(\theta)$ , at a given angle is assumed to obey the Sandros expression:

$$k_q(\theta) = \frac{k_d}{1 + \exp(\{E_T(\theta) - E_T^D\}/RT)}. \quad (3)$$

Introducing the thermal population of each geometry  $w(\theta)$ , given by the Boltzmann law, leads to the expression of the overall quenching rate constant  $k_q$ :

$$k_q = \sum_{\theta} w(\theta) \cdot k_q(\theta). \quad (4)$$

The results obtained are gathered in Table 3 together with the parameters obtained for the fit of PESs ( $\beta$ ) calculated above. It can be seen from Fig. 2 that this model fits fairly well all of the data for each diene and accounts for the observed NVET behaviors. For IV, the ground state PES exhibits a clear double-well behavior, and  $b_G$  has been determined for  $\beta \sim 50^\circ$ . Moreover, despite some small differences, the relatively good agreement between the results obtained by both methods assesses that the single bond torsion represents the major molecular coordinate responsible for the NVET behavior observed. For IV, the agreement between the two values is excellent. For I, II, III and V, the  $\Delta\theta$  values obtained by fitting the experimental data are higher than those found by calculations. A similar phenomenon was already observed for constrained oximes [21]. The deviation between these values can be due to thermal activations along other molecular coordinates that are actually neglected in the calculation of  $b_G$  and  $b_T$  from PESs.

Table 3  
Calculated parameters for the thermal activation model

	I		II		III		IV		V	
	PES <sup>a</sup>	TEn <sup>b</sup>	PES <sup>a</sup>	TEn <sup>b</sup>	PES <sup>a</sup>	TEn <sup>b</sup>	PES <sup>a</sup>	TEn <sup>b</sup>	PES <sup>a</sup>	TEn <sup>b</sup>
$b_G$ (kJ/mol deg <sup>2</sup> )	0.1	0.06	0.05	0.03	0.01	0.06	0.035	0.025	0.009	0.008
$b_T$ (kJ/mol deg <sup>2</sup> )	0.08	0.16	0.05	0.1	0.055	0.15	0.035	0.05	0.05	0.05
$\Delta\theta$ (°)	0	18.5	13.8	22.5	0	22.5	50.4	51	0	28
$E_T$ (kJ/mol)		242		221		222		232		226

<sup>a</sup> Obtained from a fit of the PESs at the DFT level for the ground state and TDDFT level for the triplet state.

<sup>b</sup> From a fit of the experimental data of Table 1 by using Eq. (4).

Concerning the triplet energies derived from the fit of the quenching plots by the thermal activation model, Table 3 shows that the deduced values are very close to those obtained experimentally (Table 1) or calculated at the DFT level (Table 2). The thermal activation model appears as very powerful not only for the prediction of the triplet energies, but also to bring about some useful information on the structural changes associated with the sensitized  $S_0 - T_1$  transition.

#### 4. Conclusion

The behavior of different dienes with controlled structures towards energy transfer in solution was studied with the aim to investigate the influence of the molecular structure on the reaction. In the series of compounds studied, an increase of the NVET character is found from I, II, V to III and IV. The trend observed is rationalized by a thermal activation mechanism based on the distribution of spectroscopic triplet energies. This approach appears to be general. The major molecular coordinate responsible for this behavior is identified and corresponds to the torsion of the single bond between the two double bonds. It clearly appears that this process is strongly influenced by the structural changes occurring between ground and excited states. Further works will deal with the effect of the reorganization energy in triplet energy transfer experiments involving various chemical structures.

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