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## Excited state charge separation in symmetrical alkenes

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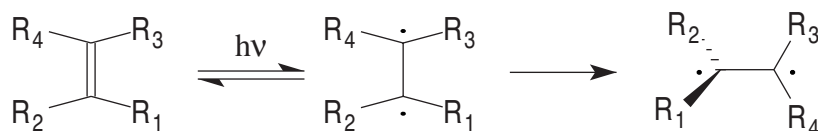


# **Introduction**

## 1.1. Background and Motivation

Apart from their versatile applicabilities as synthons, alkenes, i.e. organic compounds containing a carbon-carbon double bond, exhibit special dynamic behaviour as a result of this double bond. In their ground states, most alkenes resist rotation around these bonds under ambient conditions, and cis-trans isomerizations on the ground state potential energy surface (PES) prove to be processes associated with high activation barriers. Barriers around  $60 \text{ kcal.mole}^{-1}$  for thermal cis-trans isomerizations<sup>1</sup> are no exception, thus giving alkenes a high degree of conformational stability at ambient temperatures.

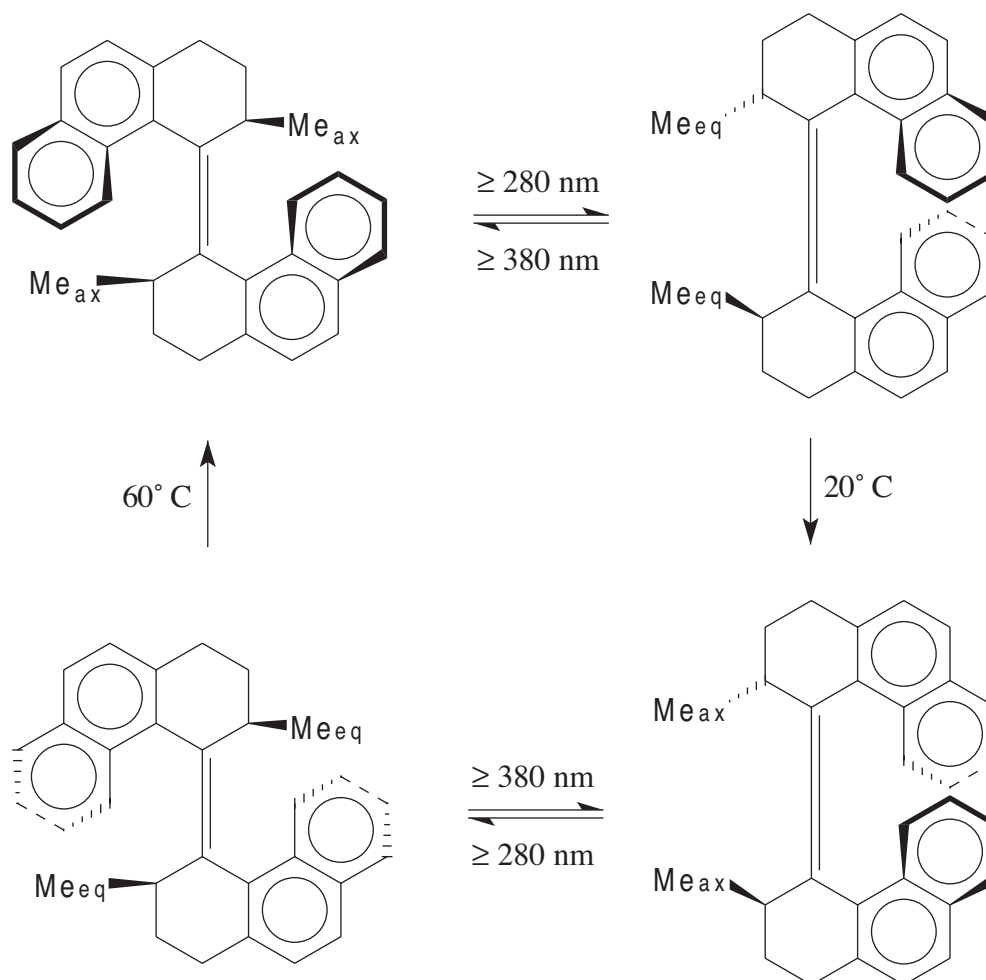
However, upon photo-excitation of an electron from the  $\pi$  molecular orbital (by means of a  $\pi^* \leftarrow \pi$  transition) of the alkene, this picture changes drastically. Because this excitation reduces the bond order of the olefinic bond<sup>2</sup>, rotation around this bond becomes more facile and exhibits only small or even non-existent activation barriers. In fact, once on their photoexcited potential energy surfaces, alkenes usually quickly depart their planar geometries around the double bond to undergo large conformational changes. This is caused by the aforementioned reduction of the bond order, which allows the release of steric repulsion present between vicinal functional groups attached to the double bond at the planar ground state geometries by rotation around this bond (figure 1.1). This conformational relaxation leads to a (near-) perpendicular orientation of the vicinal groups with respect to each other (orientation of  $R_1, R_2$  with respect to  $R_3, R_4$  in the right structure in figure 1.1).



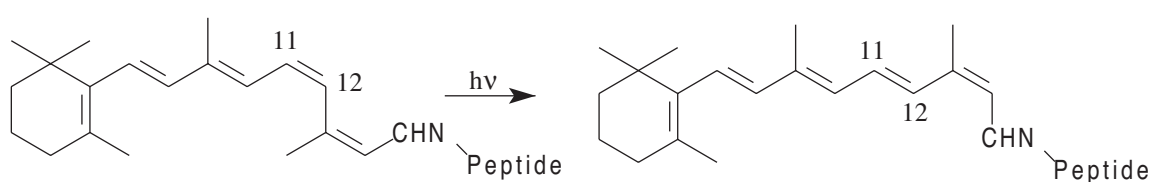
**Figure 1.1** Ground state geometry (left structure), vertically excited state geometry (middle structure) and relaxed excited state geometry (right structure) of alkenes.

The excited state dynamic behaviour of alkenes is widely studied, and in particular stilbene has often been used as a model compound to investigate the dynamics of photo-induced cis-trans isomerizations<sup>3,4</sup>.

The bistability of alkenes, i.e. their high conformational integrity on the ground state PES combined with the facile cis-trans (and trans-cis) rearrangements on the photo-excited PES makes them excellent building blocks for the development of molecular devices<sup>5</sup> such as molecular data storage elements, especially when the cis and trans form of the alkene have sufficiently different absorption spectra. A beautiful example of utilizing the alkene bistability can be found in figure 1.2, in which the dynamic behaviour of (3R,3R')-1,1',2,2',3,3',4,4'-octahydro-3,3'-dimethyl-4,4'-biphenanthrylidene on both ground and photo-excited PES is depicted<sup>6</sup>. In this case, the combination of alkene bistability with sterically demanding functional groups and chirality has led to a molecule exhibiting mono-directional relaxation behaviour under controlled conditions.



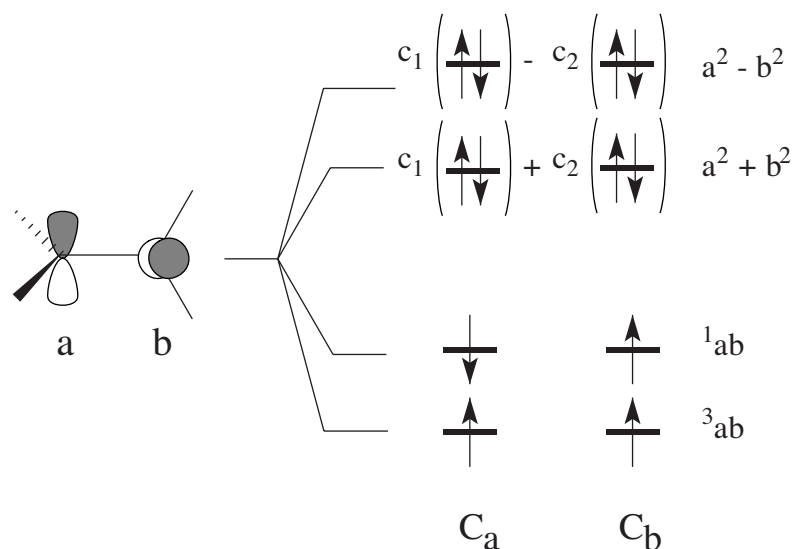
**Figure 1.2** Combination of thermally induced and light-induced dynamics of (3R,3R')-1,1',2,2',3,3',4,4'-octahydro-3,3'-dimethyl-4,4'-biphenanthrylidene.



**Figure 1.3** Photoinduced cis-trans isomerization of the retinal moiety in rhodopsin.

The bistability of alkenes has also found an important application in nature. By far the most famous example can be found in the process of vision in mammals. A crucial step in this process is the photoexcitation and subsequent cis-trans isomerization of the C<sub>11</sub>-C<sub>12</sub> bond in the retinal chromophore of the peptide rhodopsin<sup>7-9</sup> (figure 1.3), which is believed to trigger a series of events ultimately leading to vision.

An interesting feature of the photoinduced relaxation of alkenes is the occurrence of two near-degenerate excited state potential energy surfaces in the vicinity of the perpendicular geometry of alkenes<sup>10-12</sup>.



**Figure 1.4** Schematic representation (in terms of p-orbital occupation) of the four lowest lying electronic states of ethylene: the lowest energy triplet biradical ("<sup>3</sup>ab") state, the singlet ("<sup>1</sup>ab") biradical state and the two near degenerate singlet excited states ( $a^2 \pm b^2$ ). The two singlet excited states consist of two closed shell, ionic determinants (depicted by the doubly occupied p-orbitals) with coefficients  $c_1$  and  $c_2$  ( $c_1=c_2$  in symmetrical alkenes).

The main reason for making this an interesting feature lies enclosed in the antisymmetric electronic nature of the two states involved<sup>2, 13, 14</sup>. Figure 1.4 provides an intuitive picture of the shape of the electronic states of interest at the perpendicular geometry of ethylene.

As can be seen in figure 1.4, the two near-degenerate excited states both are linear combinations of two ionic determinants ( $a^2 \pm b^2$ ). In the case of  $C_2$ - or  $D_2$ -symmetrical alkenes like stilbene and ethylene, respectively, both ionic determinants will have equal weights in the wave function ( $c_1=c_2$ ) due to the molecular symmetry, thus leading to electronic states with zero dipole moments. However, according to quantum theory<sup>13, 15, 16</sup>, when these two states become degenerate, any linear combination of the two antisymmetric wave functions becomes equally acceptable. In other words, the symmetrical ( $a^2 + b^2$ ) versus ( $a^2 - b^2$ ) representation of figure 1.4 is as acceptable as the ( $a^2$ ) versus ( $b^2$ ) representation for these two respective states. Obviously, since the latter representations are purely ionic, this would provide excited states exhibiting large dipole moments even in intrinsically non-polar alkenes like ethylene, provided a symmetry-lowering perturbation of the wave function is present. This effect has been given the name 'sudden polarization', because it is predicted to occur in a confined region of the PES in the vicinity of the perpendicular geometry only<sup>17</sup>.

Theoretical studies on the parent alkene ethylene<sup>18, 19</sup> have suggested that the required symmetry lowering in symmetrical alkenes can be provided by a selective deformation of one half of the alkene, thus facilitating the necessary symmetry breaking of the molecule. However, spectroscopic investigations studying the sudden polarization

behaviour of tetraphenylethylenes in the condensed phase<sup>20-23</sup> show that the solvent has a distinct influence on the sudden polarization behaviour as well.

It has been suggested that the sudden polarization effect also plays a major role in the (cycloaddition) reactions involving non-polar cycloalkenes<sup>24-26</sup>, based on the obtained product ratios in these reactions. Less surprisingly, its occurrence has been reported in the photoexcited states of alkenes with intrinsically low symmetry, like push-pull polyenes<sup>27-31</sup>. More interestingly, it has been suggested that the effect may also play an important role in the triggering of the process of vision<sup>32</sup>. In addition, it is not unlikely that the excited state behaviour of chiroptical switches may be influenced by the occurrence of the sudden polarization phenomenon as well.

It must have become obvious to the interested reader that the sudden polarization effect is likely to play an important role in many photon driven processes. Therefore, the work presented in this thesis has focussed on the driving forces behind this effect. To prevent any form of bias caused by structural asymmetries (like in the case of push-pull stilbenes), the studies presented in this thesis have been limited to the investigation of the occurrence of charge separation in intrinsically non-polar  $D_2$ -symmetrical alkenes.

## 1.2 Outline of this Thesis

The content of this thesis is divided into a theoretical part (chapters 2-4) and an experimental part (chapters 5-6). In chapter 2, an extended description of the sudden polarization effect together with an overview of theoretical studies of this topic will be presented. As already mentioned in the previous section, these studies have led to the general assumption that the occurrence of the sudden polarization phenomenon in symmetrical alkenes is driven by an exothermic intramolecular symmetry-lowering perturbation (e.g. a selective pyramidalization of one of the olefinic carbon centers). In chapter 2, the outcome of a theoretical study investigating the correctness of this assumption will be given. In this study, the excited state PES of ethylene and tetramethylethylene at (near-)perpendicular geometries and various pyramidalization angles have been compared. It will be demonstrated that the concept of intramolecular symmetry breaking might not be as generally applicable as previously assumed.

The work reported in chapters 3 and 4 has been dedicated to investigate the possible role of the environment as the symmetry lowering element in the sudden polarization of ethylene. To model the solvent effects on the ethylenic excited states, the Direct Reaction Field (DRF) Model by Van Duijnen et al.<sup>33-35</sup> has been used.

In chapter 3, a general description of this model will be provided. In addition, the outcome of a preliminary study, in which the sudden polarization of the ethylene molecule in various non-symmetrical environments (i.e. a non-symmetrically polarized continuum with a number of different values of  $\epsilon$ ) has been investigated, will be presented. It will be shown that the environment is indeed capable of inducing the sudden polarization effect, but that the magnitude and stabilization of the polarized states depends on the applied values of  $\epsilon$ .

In chapter 4, the outcome of a DRF study in which the excited state behaviour of ethylene in various solvents has been modeled, will be presented. In this study, the

ethylene molecule has been enveloped by 50 discrete solvent molecules. The results of this study clearly suggest that only polar solvents are capable of effectively inducing and stabilizing the polar excited states, which raises the question whether the occurrence of charge separated states of symmetrical alkenes is largely solvent dependent.

Chapters 5 and 6 have been dedicated to finding an answer to this question by experiment. In chapter 5, the outcome of a study examining the excited state behaviour of tetraphenylethylene (TPE) by means of time-resolved pump-probe spectroscopy<sup>36</sup> will be presented, preceded by an extensive review of previous photoinduced experiments on TPE and a theoretical description of pump-probe spectroscopy. The TPE excited state behaviour has been investigated in various solvents at both femtosecond and picosecond time scales. It will be demonstrated that the TPE excited state twist dynamics are largely solvent dependent, and that the quantum yield of the sudden polarization of the TPE excited states critically depends on solvent polarity. This quantum yield is much smaller in the non-polar solvent cyclohexane than in a number of alcohols, thus providing a positive answer to the question posed on the basis of the results presented in chapter 4.

Finally, in chapter 6 the results of an extended pump-probe study will be presented. In this work, the excited state behaviour of several *p*-substituted TPEs in cyclohexane and ethanol has been investigated to establish the influence of electron directing functional groups on the sudden polarization effect and molecular dynamics of *p*-substituted-TPEs. It will be shown that large effects can be observed, although a clearcut correlation between the electron directing nature of the *p*-substituents and the sudden polarization effect could not be made.

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