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ARTICLES

Cooperating Rings in *cis*-Stilbene Lead to an S_0/S_1 Conical Intersection

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Photoexcited *cis*-stilbene decays to the ground state on the femtosecond time scale, so fast that fluorescence is not generally observed and vibrational relaxation is incomplete. Decay can be accompanied by cis-trans isomerization about the double bond linking the two benzene rings and by electronic rearrangement to yield 4a,4b-dihydrophenanthrene (DHP). MMVB calculations suggest that there are several geometries (in addition to the perpendicular minimum) at which efficient decay can take place. In particular, a conical intersection has been documented along photocyclization reaction coordinate to DHP which may be reached with almost no barrier from a quinoid minimum. This intersection arises from interaction between the two benzene rings. Such a crossing is suggested in the recent experimental work of Yoshihara et al. (Petek, H.; Yoshihara, K.; Fujiwara, Y.; Lin, Z.; Penn, J. H.; Frederick, J. H. *J. Phys. Chem.* **1990**, *94*, 7539−7543) and must form part of a new mechanism for the decay of this well-studied molecule.

Introduction

The photophysics of aryl olefins such as *cis*-stilbene[1−9] and styrene[10] has been studied using time-resolved spectroscopic techniques. Aspects of excited state behaviour have emerged which cannot be accounted for using the standard model of decay at a perpendicular funnel.[11] There is no intrinsic barrier to the radiationless decay of photoexcited *cis*-stilbene and the medium is controlling.[2k] Decay occurs to the ground state occurs on the femtosecond time scale in the gas phase, so fast[2k] that fluorescence is not generally observed[4a,c] and vibrational relaxation is incomplete.[2g−l]

Photoexcited *cis*-stilbene has two decay routes (see the review of experimental and theoretical literature given in ref 2k): (a) a geometrical cis−trans isomerization process (also seen in *trans*-stibene) and (b) an electronic rearrangement to yield 4a,4b-dihydrophenanthrene (DHP). As a result of jet experiments, Yoshihara and co-workers[5e] have suggested that the initial motion of a wavepacket on the S_1 surface is along the photocyclization reaction coordinate to DHP rather than along the cis−trans isomerization coordinate. In this work, our main purpose is to document the existence two structures that lie on the photocyclization reaction coordinate to DHP: (a) a quinoid structure (which correlates diabatically with S_3, the "ethylenic" state) in the Franck−Condon region and (b) a conical intersection that is very similar to the conical intersection in cZc-hexatriene. While we have also optimized the perpendicular minimum on the geometrical cis−trans isomerization path, because of the possible involvement of an ionic−covalent interaction (which cannot be computed using the modeling method used) we cannot draw firm conclusions regarding this pathway from our current results.

Early theoretical investigations of the *cis*-stilbene and styrene excited states (semiempirical[12,13] and ab initio[14a−c]) did not include full geometry optimisation of critical points on the potential energy surfaces. CASSCF and CAS-PT2 results[14d] for the vertical excitation region of *trans*-stilbene, indicate the presence of three covalent excited states with an interviening ionic state. Recent CASSCF calculations[15] have shown that decay funnels[16,17] often correspond not to pericyclic minima[19] but rather to unavoided surface crossings (conical intersections[18]) at which decay can be fully efficient.[18m] For styrene,[11] a recent CASSCF study[15j] showed that full geometry optimization is essential if such crossings are to be located. In particular, relaxation of the benzene ring following excitation must be considered.

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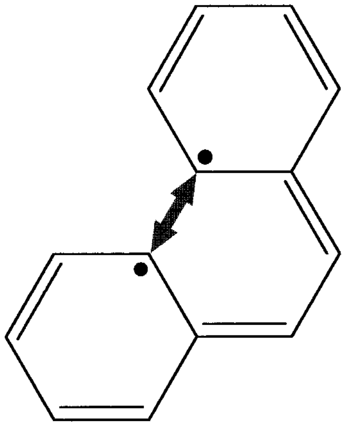
TABLE 1: Stilbene MMVB Energies Computed at the Optimized Geometries Illustrated in Figures 2−9

structure	S_0/E_h	S_1/E_h	$S_0 \rightarrow S_1$ gap/ kcal mol^{-1}	S_1 above $\mathbf{M}_{\mathbf{quin}}$/ kcal mol^{-1}	S_2/E_h	S_3/E_h
$\mathbf{M}_{\mathbf{ground}}$	−0.782 07	−0.628 95	96.08	13.01	−0.628 71	−0.612 47
$\mathbf{M}_{\mathbf{benz}}$	−0.777 97	−0.639 84	86.68	6.17		
$\mathbf{M}_{\mathbf{quin}}$	−0.759 34	−0.649 68	68.81	0.0	−0.620 63	−0.618 87
$\mathbf{M}_{\mathbf{perp}}$	−0.725 19	−0.638 59	54.34	6.96		
$\mathbf{X}_{\mathbf{coop}}$	−0.636 06	−0.636 00	0.04	8.58		
$\mathbf{X}_{\mathbf{benz}}$	−0.591 18	−0.591 03	0.09	36.80		
$\mathbf{X}_{\mathbf{buta}}$	−0.598 66	−0.598 51	0.09	32.11		
$\mathbf{X}_{\mathbf{trans}}$	−0.599 22	−0.599 09	0.19	30.24		

CASSCF geometry optimizations are not yet practical for aryl olefins with two or more aromatic rings because of the large number of electrons which must be correlated. However, we have recently demonstrated that the topology of the excited-state potential energy surfaces of styrene[15j] can be adequately reproduced[20] by a hybrid molecular mechanics−valence bond method−MMVB[21]−which is many orders of magnitude less expensive computationally than CASSCF. This suggests that MMVB may be used to understand the behaviour of the excited states of *cis*-stilbene.

For styrene and stilbene, MMVB calculations suggest that the energy gap is so large at the twisted intermediate on S_1[11] that internal conversion is unlikely to take place at this point. Further, the MMVB calculations presented here suggest that there are S_1/S_0 conical intersections in stilbene resembling those previously located in benzene[15i] and styrene[15j] which can be reached from the cis or trans side if sufficient vibrational excess energy is supplied. *However, what distinguishes cis-stilbene is the presence of an additional intersection, caused by an interaction between the two benzene rings, which terminates almost barrierless reaction coordinates.*



The existence of such a crossing is consistent with the lack of any detectable intermediate within 150 fs,[2j,k] and the recent suggestion[5e,f] that the cyclization motion is the key to understanding the *cis*-stilbene decay process. A conical intersection can also account for the existence of several reaction paths on the ground state[18o] which originate in the plane which lifts the degeneracy.[22] Cis−trans isomerization (35%), formation of dihydrophenanthrene (10%) and recovery of reactants (55%) can all take place in *cis*-stilbene[9] and, since the excited-state lifetime is so short, most of the coordinate leading to each of these products must lie on the ground state.

The geometry of the cooperating-ring conical intersection in *cis*-stilbene is very similar to a crossing previously located in cZc-hexatriene.[15g] Because there are well-defined double bonds within the benzene ring, it has been possible to confirm the existence of this crossing point ab initio using the CAS+GVB[23] approximation to CASSCF.

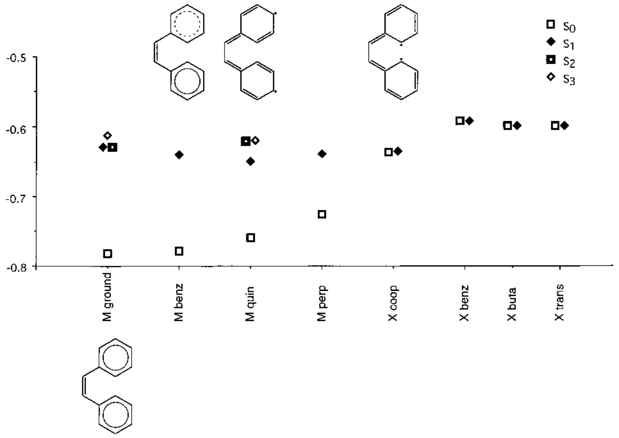


Figure 1. Relative energies of minima and conical intersections located for *cis*-stilbene with MMVB. The energy scale is in au.

Computational Details

MMVB[21] is a hybrid method, which uses the MM2 potential[24] to describe an inert molecular σ-framework. Active electrons−those involved in conjugation and new σ-bond formation−are represented by a Heisenberg Hamiltonian[25] in the space of neutral valence bond configurations. Because of this, MMVB can only describe covalent states.

A general set of molecular VB parameters (derived from CASSCF/4-31G calculations) are presently available for sp^2/sp^3 carbon atoms. Energies and analytical gradients can be calculated for the ground and valence excited states of systems with up to 24 carbon-active sites.[21b] Such computations take less than a minute for stilbene (with 14 active sites) on current RISC workstations. Minima on conical intersections[18] are optimized using the algorithm described in ref 26b.

The CASSCF/STO-3G optimization[27] was carried out using an approximation in which well-defined double bonds (four in this case) are treated as GVB pairs. This approximation, CAS+GVB,[23] reduces the total number of configurations substantially while preserving the important nondynamic correlation effects. (For a recent comparison of MMVB and CAS+GVB, see ref 15m). A single-point CAS+GVB/4-31G calculation was carried out at the optimized CAS+GVB/STO-3G geometry to confirm that the degeneracy still exists and that reoptimization at the higher level of theory would not alter the geometry significantly.

Results

MMVB energies for optimized minima and conical intersections are presented in Table 1 and Figure 1, with the corresponding geometries in Figures 2−9. As a “calibration”, the vertical excitation energies for *trans*-stibene are compared with ab initio results[14d] in Table 2.

There are three closely spaced singlet excited states in the Franck−Condon region of *cis*-stilbene. Using MMVB, we find that excitation is either localized in one of the benzene rings

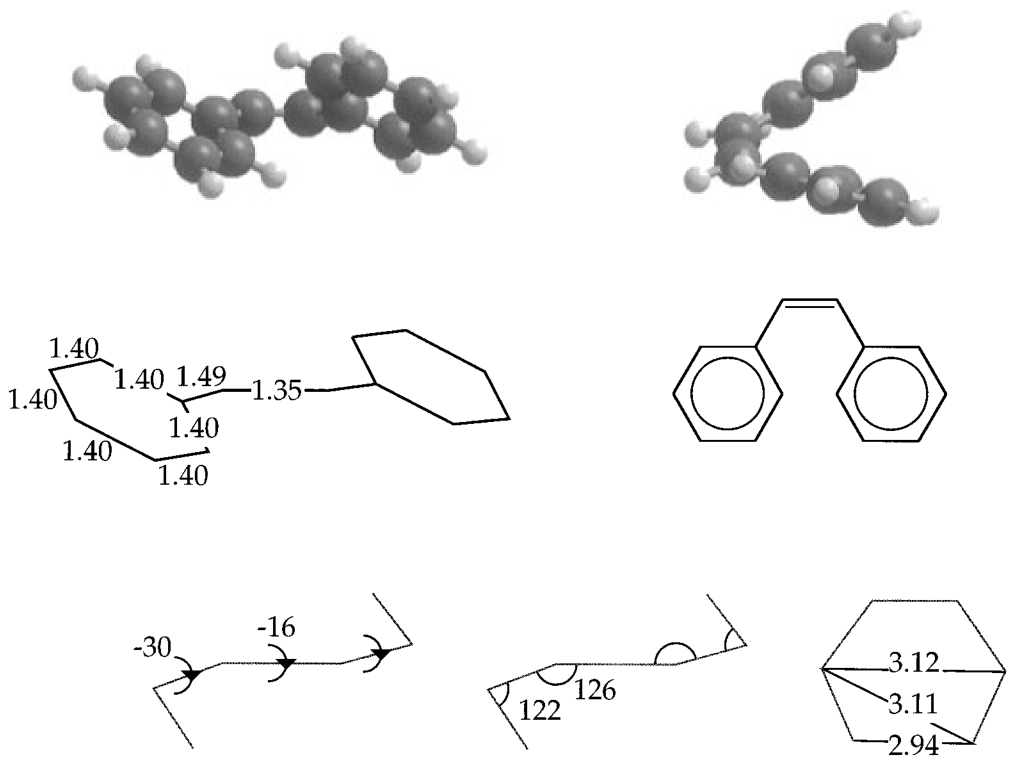
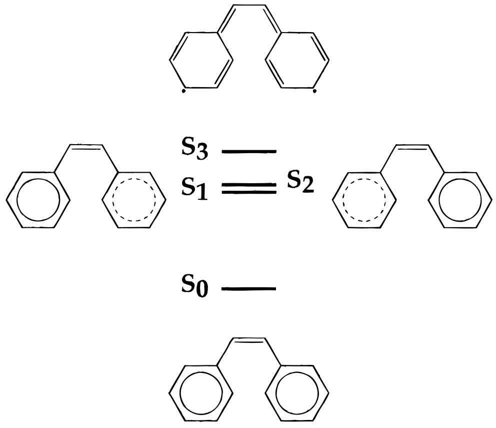


Figure 2. MMVB S$_0$ minimum $\mathbf{M_{ground}}$.

TABLE 2: *trans*-Stilbene MMVB and CASSCF Vertical Excitation Energies[14d] (in eV) Computed at Ground-State Optimized Geometries

state	MMVB (this work)	CASSCF (ref 14d)	CASPT2 (ref 14d)
1 ^1B_u	4.08	5.42	3.77
2 ^1B_u	(ionic state)	6.05	4.07
2 ^1A_g	4.09	5.41	4.13
3 ^1A_g	4.24	5.92	4.95
1 ^3B_u	1.89	3.02	2.56

(degenerate S$_1$ and S$_2$, the L_b states in benzene) or delocalized over the whole molecule (S$_3$, the ethylenic state) as shown by the following VB structures:



(This VB representation of the excited states is rather different from that used in other work[11c,12e,g,14a]). The S$_0$→S$_1$/S$_2$ energy separation in the Franck−Condon region is computed to be 96 kcal mol^{-1} (Table 1), in reasonable agreement[20] with the experimental absorption maximum at 266 nm (108 kcal mol^{-1}).[4b]

In Table 2 the MMVB results for *trans*-stilbene are compared with the results of Molina et al.[14d] computed with CASPT2. These results indicate that MMVB is capable of reproducing the most important electronic effects in the vertical excitation region. The CASSCF results predict the quasi-degeneracy of S$_1$ and S$_2$ ($^1B_u{}^1A_g$), although the energies are high because the orbitals have been state averaged. The ionic 2 ^1B_u state cannot be represented in MMVB.

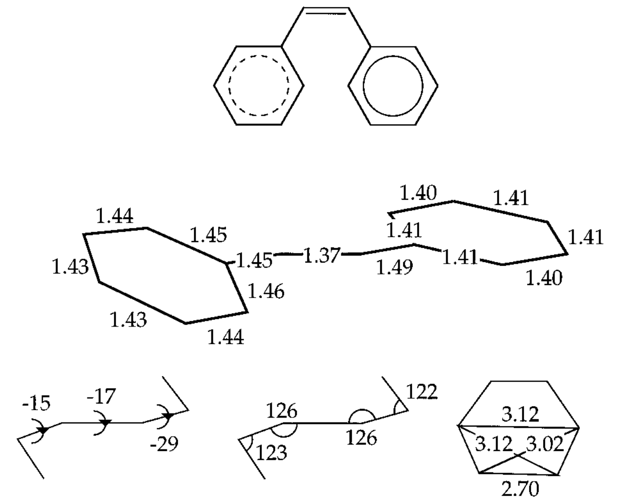


Figure 3. MMVB S$_1$ minimum $\mathbf{M_{benz}}$.

Each state in the Franck−Condon region is associated with a minimum on the S$_1$ surface of *cis*-stilbene: an $\mathbf{M_{benz}}$ for each ring (Figure 3) and $\mathbf{M_{quin}}$ (Figure 4). The lowest energy minimum (Table 1) is predicted to be the quinoid structure $\mathbf{M_{quin}}$ (Figure 4) which correlates diabatically with S$_3$ (the "ethylenic" state) in the Franck−Condon region. The S$_0$ → S$_1$ gap is computed to be 69 kcal mol^{-1} at this point, which is consistent with the observed fluorescence maximum[4b] at 405 nm (70 kcal mol^{-1}). Both components of S$_1$/S$_2$ are associated with equivalent minima $\mathbf{M_{benz}}$ (Figure 3) which are ~6 kcal mol^{-1} above $\mathbf{M_{quin}}$ (Table 1) and involve a relaxation of one ring matching that of benzene itself in S$_1$.[15i] All three quasi-planar S$_1$ minima ($\mathbf{M_{benz}} \leftrightarrow \mathbf{M_{quin}} \leftrightarrow \mathbf{M_{benz}}$) form a "pool" which permits excitation energy to be exchanged from one ring to the other.

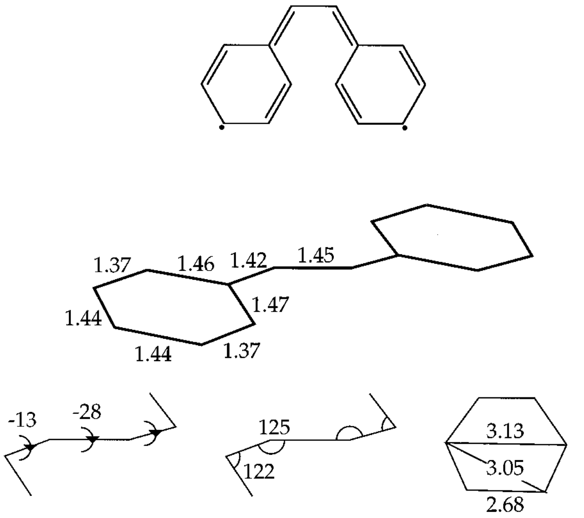


Figure 4. MMVB S_1 minimum $\mathbf{M_{quin}}$, which correlates with S_3 in the Franck−Condon region.

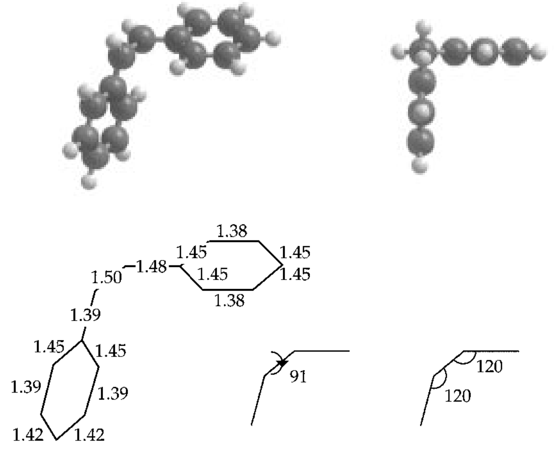


Figure 5. MMVB S_1 minimum $\mathbf{M_{perp}}$.

We have also located a perpendicular minimum ($\mathbf{M_{perp}}$, Figure 5) which is predicted to lie below S_1-S_3 in the Franck−Condon region (Figure 1). However, the $S_1 \rightarrow S_0$ energy gap at this structure is ∼50 kcal mol^{-1} (Table 1), which suggests that rapid internal conversion is unlikely to take place.[11] (Note that the computed gap is larger than the experimental value[4c] of ca. 40 kcal mol^{-1}). $\mathbf{M_{perp}}$ may also play a role in adiabatic isomerization from the trans side.[4] However, the role of $\mathbf{M_{perp}}$ on a cis−trans/trans−cis reaction path must remain an open question. There is the possibility of an ionic/covalent avoided crossing in this region which cannot be represented using MMVB so this problem requires high-level ab initio results.

Three types of S_1/S_0 conical intersection have been characterized, at which decay to the ground state can be fully efficient.[18m]

The structure $\mathbf{X_{benz}}$ (Figure 6) is a crossing point which originates in one ring only, and which is equivalent to the one previously located in benzene[15i] and styrene.[15j] The structure $\mathbf{X_{buta}}$ (Figure 7) is closely related to an S_0/S_1 crossing in butadiene[15d] and styrene:[15j] again, only one of the two benzene rings is involved, the central double bond is ∼90° twisted and hence this crossing could lead to cis−trans isomerization. (Another minimum on the $\mathbf{X_{buta}}$ crossing which was located from the trans side—$\mathbf{X_{trans}}$—is shown in Figure 8). Both $\mathbf{X_{benz}}$ and $\mathbf{X_{buta}}$ are predicted to lie above the Franck−Condon energies of S_1-S_3. MMVB has been shown to exaggerate the energy of structures with highly distorted rings, as was demonstrated with the styrene benchmark calculations.[15j,20] Nevertheless, some activation energy will be required for decay to take place at $\mathbf{X_{benz}}$ or $\mathbf{X_{buta}}$.

The lowest energy S_1/S_0 conical intersection in *cis*-stilbene—$\mathbf{X_{coop}}$ in Figure 9—lies along the photocyclization reaction coordinate to DHP rather than along the cis−trans isomerization coordinate. Very little activation energy is needed to reach this crossing (9 kcal mol^{-1} from $\mathbf{M_{quin}}$, Table 1) which lies below S_1-S_3 in the Franck−Condon region. The main geometric distortion is the close approach of the two benzene rings which are ∼1 Å closer than for the minima $\mathbf{M_{benz}}$ and $\mathbf{M_{quin}}$, although $\mathbf{X_{coop}}$ is closely related to $\mathbf{M_{quin}}$ electronically. Yoshihara has commented[5e,f] that the interaction between the two radical centres indicated in Figure 9 is attractive in S_1, suggesting that this crossing will be easily reached. In Figure 10 we show the energy profile along a linear interpolation from $\mathbf{M_{benz}}$ and $\mathbf{M_{quin}}$ to $\mathbf{X_{coop}}$. This profile provides upper bounds for barriers to decay at $\mathbf{X_{coop}}$, but the S_1 surface is so flat that we were not able to optimize transition structures.

We note that the conical intersection $\mathbf{X_{coop}}$ in *cis*-stilbene bears a remarkable resemblance to the conical intersection in cZc-hexatriene.[15g] Figure 11 shows the main geometrical parameters (calculated using MMVB) for the center of $\mathbf{X_{coop}}$ in *cis*-stilbene and the S_1/S_0 conical intersection in cZc-hexatriene.[15g] The crossing $\mathbf{X_{coop}}$ must exist even at the crudest level of ab initio theory. Accordingly, as a check of the MMVB result, we have optimised this structure using CAS+GVB.[23] The geometry is given in Figure 12 with the corresponding CASSCF geometry for the conical intersection in cZc-hexatriene from ref 15g shown in Figure 13. The simple C_2 symmetry of the MMVB structures has been lost but the essential feature—close approach of benzene rings—is retained. The origin of the intersection geometry can be understood using a simple valence bond model.[18h,29] There are three weakly interacting electrons in a triangular array, and a fourth distant radical center which takes the form of a ground-state allyl unit in cZc-hexatriene (Figure 13).

A dynamics treatment[13,28] is required to fully understand product formation. However, as we have discussed in previous work[15g] on cZc-hexatriene, the ground-state product formation

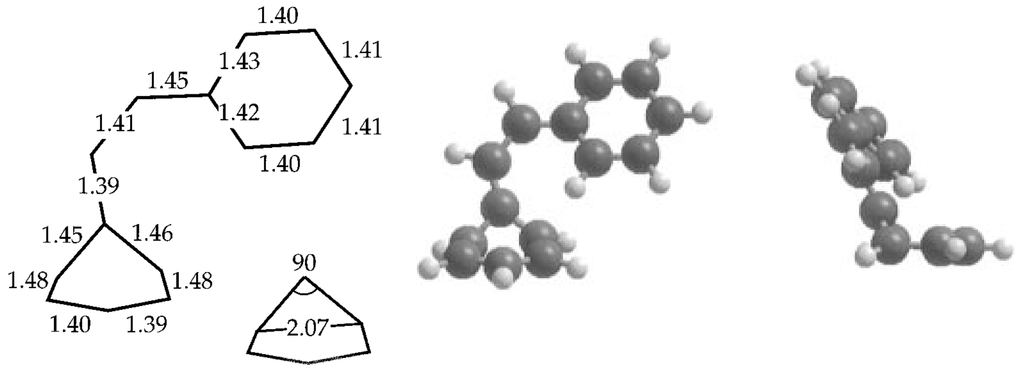


Figure 6. MMVB benzene-like S_1/S_0 conical intersection $\mathbf{X_{benz}}$.

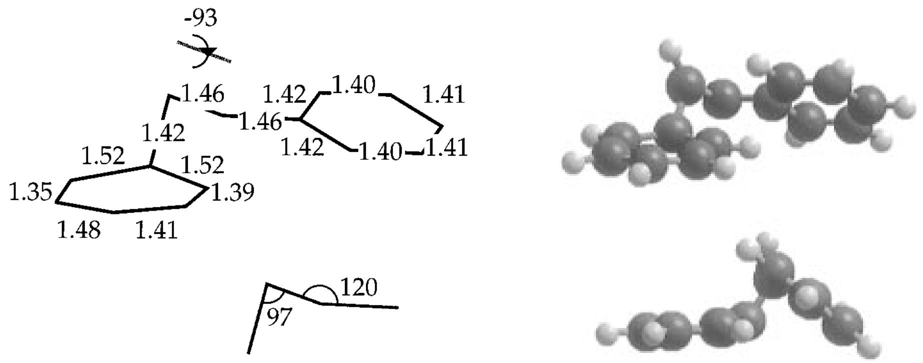


Figure 7. MMVB styrene-like S_1/S_0 conical intersection $\mathbf{X_{buta}}$.

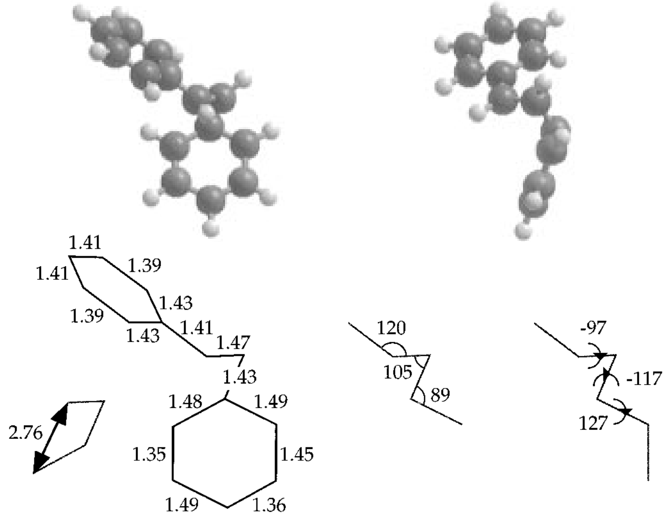


Figure 8. MMVB S_1/S_0 conical intersection $\mathbf{X_{trans}}$, which is another minimum on the $\mathbf{X_{buta}}$ intersection seam.

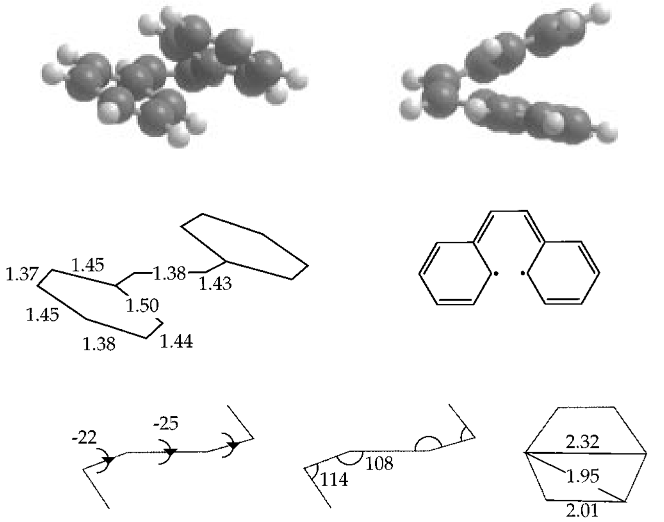


Figure 9. Low-lying MMVB S_1/S_0 conical intersection $\mathbf{X_{coop}}$.

can be rationalized in terms of the possible S_0 spin recoupling process. The three weakly interacting electrons in a triangular array can recouple along the coordinate which brings the radical centers together, and bond formation on S_0 may result, giving the cyclization product dihydrophenanthrene (DHP). Alternatively, the recoupling process can lead back to the reformation of S_0 *cis*-stilbene ($\mathbf{M_{ground}}$, Figure 2). The alternative pathway along the cis−trans isomerization coordinate results from recoupling involving the fourth radical center allyl unit as well.

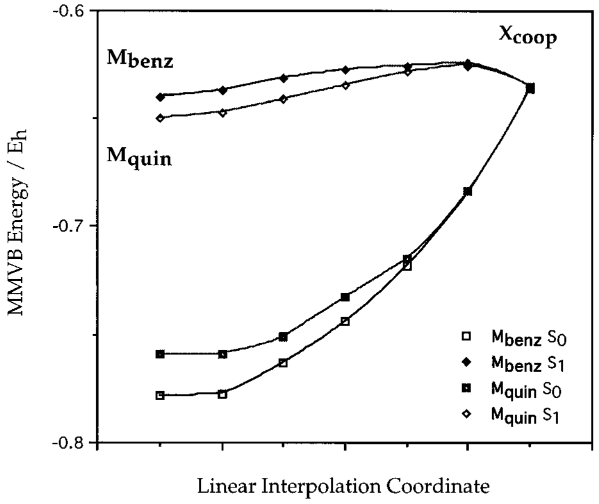


Figure 10. Linear interpolations from $\mathbf{M_{benz}}$ (Figure 3) and $\mathbf{M_{quin}}$ (Figure 4) to $\mathbf{X_{coop}}$ (Figure 9) which provides upper bounds to the barriers on the excited state.

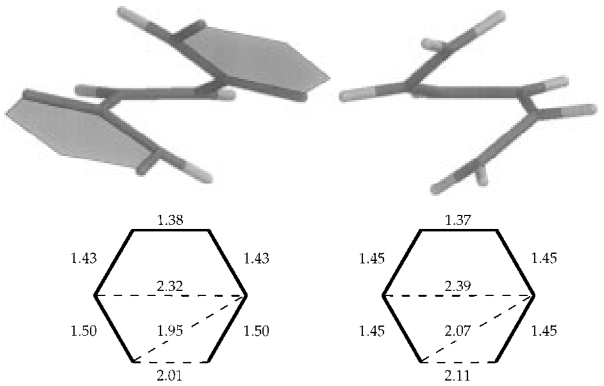


Figure 11. Comparision of $\mathbf{X_{coop}}$ (Figure 9) and the cZc-hexatriene conical intersection located with MMVB.

Conclusions

In this paper we have focused our attention on the decay mechanism of *cis*-stilbene along the photocyclization reaction coordinate to DHP rather than along the cis−trans isomerization coordinate. We have not addressed the competing cis−trans isomerization path in detail because of the possible role of an avoided crossing with the ionic state. The experiments which may be compared with our computations are gas-phase and free-jet expansion (e.g., ref 5e). However our energetics are not accurate enough to estimate the lifetimes (which involves the energy difference between $\mathbf{M_{quin}}$ and $\mathbf{X_{coop}}$). The central result of our computations is the surface topology in the region of $\mathbf{M_{quin}}$ and $\mathbf{X_{coop}}$ which is similar to the cZc-hexatriene and cyclohexadiene results obtained in ref 15g. Thus hexatriene

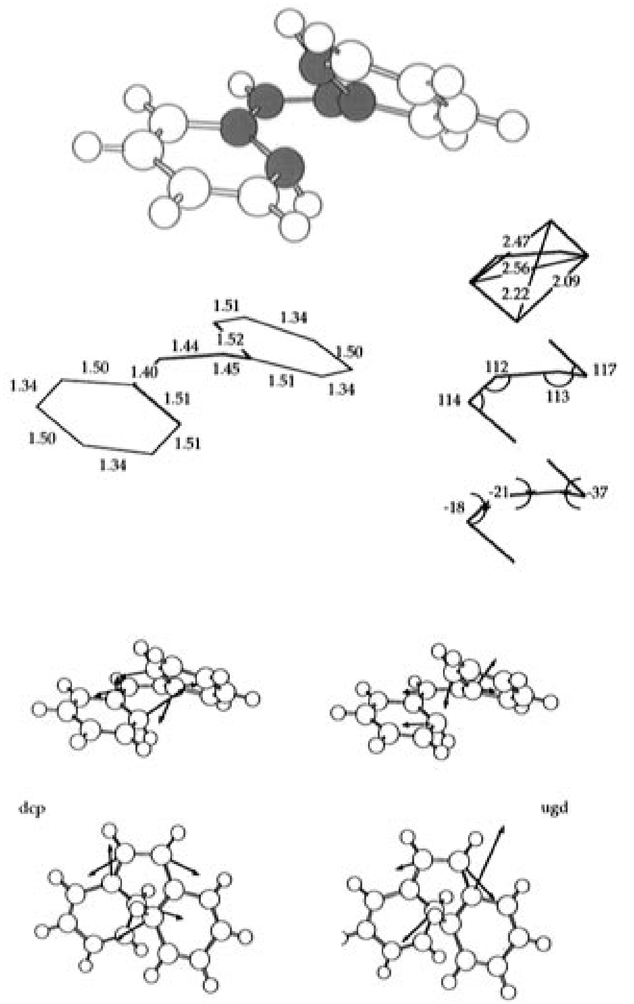


Figure 12. CASSCF/STO-3G S_1/S_0 conical intersection $\mathbf{X_{coop}}$. Two views of the gradient difference (ugd) and derivative coupling (dcp) vectors are shown, the directions which lift the degeneracy.

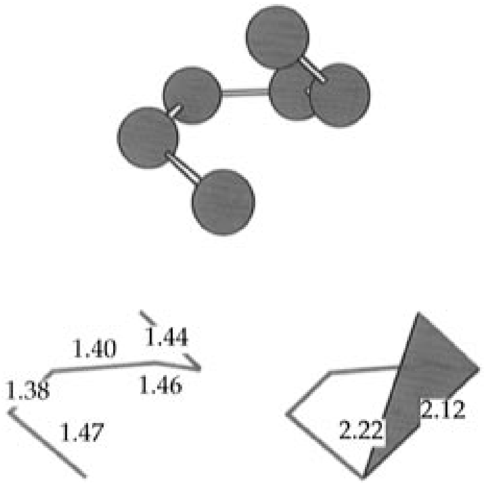


Figure 13. CASSCF/4-31G S_1/S_0 conical intersection of cZc-hexatriene, taken from ref 15g.

forms a good "model", and the conjecture of Yoshihara and co-workers,[5e] who have suggested that the initial motion of a wavepacket on the S_1 surface is along the photocyclization reaction coordinate to DHP rather than along the cis−trans isomerization coordinate, is supported by our theoretical results.

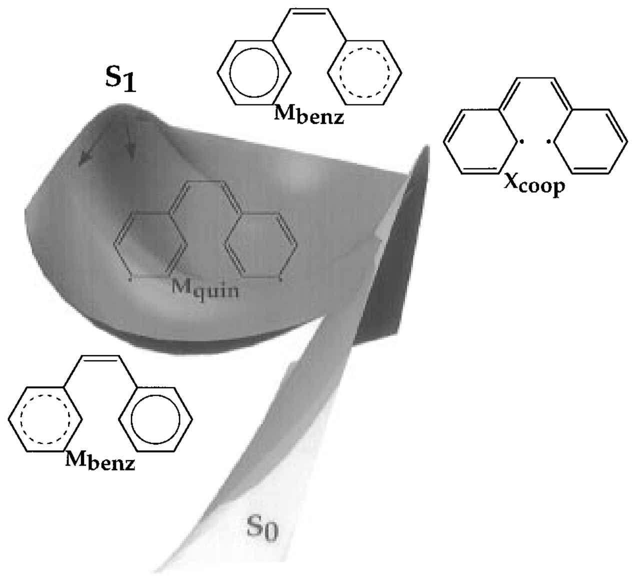


Figure 14. Illustrating the pool of minima on S_1, and the low-lying conical intersection.

MMVB calculations suggest that the potential energy surface of *cis*-stilbene can be represented schematically as shown in Figure 14. There are three quasi-planar S_1 minima, two of the form $\mathbf{M_{benz}}$ and one of the form $\mathbf{M_{quin}}$. The lowest energy surface crossing $\mathbf{X_{coop}}$—a conical intersection which arises from interaction between the two benzene rings—can be reached with almost no barrier. Such a crossing was anticipated in the experimental work of Yoshihara et al.[5e] Decay at this crossing is favored over the other surface crossings both energetically (low barrier) and entropically (because of the attraction between rings in S_1). The existence of such a crossing is consistent with the formation of several products on the ground state, and the difficulty in detecting fluorescence from *cis*-stilbene.

Adiabatic isomerization on S_1 is permitted energetically. However, the short timescale for the appearance of ground state stilbene (150 fs) suggests that cis−trans isomerization from the cis side is more likely to take place after decay. The possible S_0 spin recoupling process, after decay may open up S_0 valleys along the isomerization coordinate, a mechanism which may be relevant for the isomerization of the cis isomers of biological polyenes.[30] However, confirmation of this conjecture will require dynamics studies using a realistic potential energy surface.

Other possible mechanisms for cis−trans isomerization of *cis*-stilbene remain to be investigated. While we were able to rule out a zwitterionic ($CH2^{-}-CH_2^{+}-C_6H_5$) state in the photoisomerization of styrene,[15j] such structures cannot be treated with MMVB. The role of $\mathbf{X_{buta}}$ (Figure 7) in the cis−trans isomerization process needs to be investigated at a higher level of theory which can include the possible stabilization of such structures by ionic contributions.

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