

THE "PHANTOM" PHOTOCHEMICAL SINGLET STATE OF STILBENE AND ITS DIPHENYLPOLYENE RELATIVE

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Recently the conception on the cis-trans photoisomerization of stilbene has emerged that this process is governed by a higher excited 1A_g state which exhibits a minimum at the perpendicular conformation crossing the lowest excited 1B_u state upon bond rotation. An evaluation of the potential surfaces governing the photoisomerization process by a PPP SCF CI method revealed that there exists indeed such a photochemically active 1A_g state which in the planar molecule lies about 1 eV above the lowest absorption band and involves the excitations of two electrons from the SCF ground state. Extensions of the calculations to diphenylpolyenes demonstrate that this 1A_g state is related to the forbidden low-lying doubly excited 1A_g state observed earlier in these molecules.

1. Introduction

The finding of a low-lying optically forbidden 1A_g state in polyenes and diphenylpolyenes [1-4] has revived the study of polyene photochemistry. Because of their low energy these states should be responsible for much of the photochemical activity of these molecules. A testing ground for an understanding of polyene photochemistry is the well-known cis-trans photoisomerization of stilbene. During the last few years the 1A_g state mentioned above has emerged to play a cardinal role in this process. Saltiel et al. have postulated a "phantom" singlet state, not identical with the lowest optically allowed 1B_u state of the planar molecule, to be the lowest energy state at the perpendicular conformation of stilbene determining thereby the low barrier of photoisomerization [5]. Orlandi and Siebrand suggested that this "phantom" state connects with a doubly excited higher energy 1A_g state of the planar molecule [6]. Birch and Birks have presented experimental data supporting the idea that the photoisomerization of stilbene occurs via thermal activation of a higher excited state [7]. Recently, McClain and co-workers have observed a two-photon allowed electronic transition in stilbene above the lowest optical absorption band which has to be assign-

ed to a state of 1A_g symmetry [8].

In order to test the emerging picture of stilbene photoisomerization we have carried out PPP SCF CI calculations of the electronic potential surfaces of stilbene describing rotation around the central bond. The results presented below confirm the concept put forward in refs. [5-8]. We have also extended these calculations to diphenylpolyenes in order to link the findings on stilbene to the photoactivity of polyenes.

2. Theory

Only recently has it been realized that a complete spectrum of polyenes and their derivatives is obtained when double excitations are taken into account in a configuration interaction (CI) treatment [3,4]. We have therefore included in our description of the electronic states of stilbene and diphenylpolyenes all single and double excitations in a PPP SCF CI treatment. The calculations follow ref. [4] where it had been shown that such treatment yields a satisfactory description of benzene and polyenes. The PPP parameters employed are those of ref. [4] with the choice $\beta_0 = -2.60$ eV for the resonance integral at 1.397 Å bond length, and the Ohno formula for the Coulomb repulsion integrals.

3. Stilbene

In order to demonstrate the importance of double excitations for a complete description of the $\pi-\pi^*$ spectrum of stilbene we compare in fig. 1 the results of a CI calculation including only (all) single excitations (S-CI) with a CI calculation which includes all single as well as all double excitations with respect to the SCF ground state (S + D-CI). The S-CI states are grouped according to their covalent (${}^1A_g^-$, ${}^1B_u^-$) and ionic (${}^1A_g^+$, ${}^1B_u^+$) character. The +/- attributes to the symmetry character denote Pariser's alternancy symmetry of the electronic states which in the PPP approximation arises in addition to any spatial symmetry. Fig. 1 shows that the inclusion of double excitations in addition to single excitations in a CI treatment strongly lowers the covalent states relative to the ionic states resulting in a S + D-CI spectrum differing in its ordering from the S-CI spectrum. This had been observed previously by several authors [9, 10, 4]. Our calculations predict that there are three excitations contributing to the lowest absorption band of stilbene, the optically allowed ${}^1B_u^+$ state and two forbidden ${}^1B_u^-$ and ${}^1A_g^-$ excitations localized mainly in the benzene moieties (see below). At an energy of about 1 eV above these states is predicted a ${}^1A_g^-$ state of a strongly double excited character. As this state is two-photon allowed it has to be assigned to

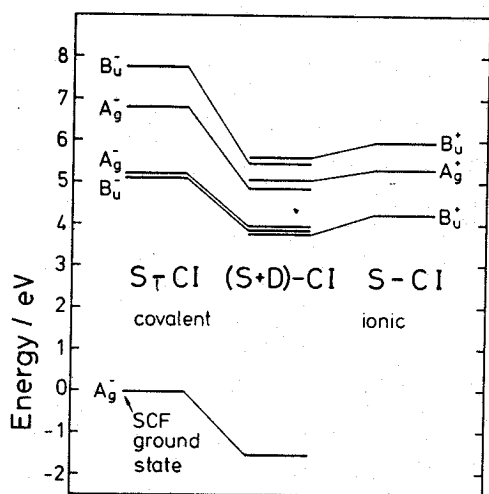


Fig. 1. Comparison of the energies of the conjugated π -electron system of stilbene resulting from a CI description including all single excitations from the SCF ground state (S-CI) and all single and double excitations (S + D-CI).

the two-photon transition detected by McClain and co-workers. Higher in energy are the allowed ${}^1A_g^+$ state (rigorously allowed only in the cis conformation) and the ${}^1B_u^+$ state which have to be assigned to the B and C bands of stilbene [11].

The energy spectrum presented in fig. 1 does not yield proper excitation energies. For this to be achieved triple and quadruple excitations have to be taken into account which induce an energy lowering of the excited states for ionic and covalent states approximately alike [12]. This lowering originates from a ground state type correlation involving those electrons not affected by the virtual excitations describing the excited states in the S + D-CI approximation. An estimate of the correct excited state energies accounting for this effect is given by the simple expression

$$E = E_{S+D} + [(N - n)/N] E_{0,S+D}, \quad (1)$$

where E_{S+D} stands for the CI energy (energy relative to the SCF ground state) resulting from a S + D-CI treatment, $E_{0,S+D}$ for the corresponding ground state energy and N for the number of π -electron pairs of the conjugated π -system (i.e. $N = 7$ for stilbene). n denotes the number of correlated electron pairs disrupted or disturbed by the electron excitation. An appropriate choice is $n = 1.5$. The excitation energies resulting from this estimate are listed in table 1. The excitation energies of the allowed transitions predicted by the S-CI and the S + D-CI calculations are in close agreement, reflecting the single excitation character of these transitions, and compare well with the experimental observations. The ${}^1A_g^-$ state predicted at 5.19 eV can be

Table 1
Excitation energies of stilbene (in eV) ^{a)}

State	S-CI	S + D-CI	Exp.
${}^1B_u^+$	4.22	4.17	4.21 [9]
${}^1B_u^-$	5.10	4.18	
${}^1A_g^-$	5.10	4.18	
${}^1A_g^+$	6.79	5.19	5.08 [8]
${}^1B_u^+$	5.29	5.35	5.43 [9]
${}^1B_u^-$	7.78	5.81	
${}^1B_u^+$	5.96	5.93	6.15 [9]
${}^1A_g^+$	6.83	6.11	

^{a)} Evaluated according to eq. (1).

identified with the two-photon absorption observed at $41\,000\text{ cm}^{-1}$ (5.08 eV).

In order to elucidate the role of this state in the photoisomerization of stilbene we have evaluated the potential surface for bond rotation around the central bond.

As our calculation restricts the electronic degrees of freedom to within the π -orbitals it solely yields the π -electron energy contribution to the bond rotation potential surface neglecting, for example, those contributions arising from σ - π coupling. Bruni et al. [13] have argued for the case of styrene that such coupling makes an important contribution, a result which has been refuted by minimum basis ab initio calculations [14]. In any case judging from the results of Bruni et al. [13] σ - π coupling should not affect the relative ordering of the ${}^1A_g^-$ and the ${}^1B_u^+$ excited states which is the feature of interest here. In the framework of the PPP method the bond rotation is simply accounted for by the weakening of the twisted bond resonance integral by means of the formula

$$\beta = \beta(0^\circ) \cos \alpha. \quad (2)$$

The results of S-CI and S + D-CI calculations [the latter corrected according to eq. (1)] are compared in fig. 2. The S-CI potential energies evaluated at 0° , 30° , 60° and 90° all exhibit a maximum for the perpendicular (90°) conformation. The S + D-CI calculations predict a maximum at 90° for the ${}^1A_g^-$ ground state and the ${}^1B_u^+$, ${}^1A_g^-$ and ${}^1B_u^-$ excited states corresponding to the 4.2 eV absorption band of stilbene but exhibits a minimum for the ${}^1A_g^-$ state at 5.19 eV. This state crosses the three lower excited states upon bond rotation to become the lowest excited singlet state at the perpendicular conformation, the "phantom" state postulated by Saltiel et al. [5].

Although our results agree qualitatively well with the conception of the photoisomerization process of stilbene propounded in refs. [5-8] the quantitative prediction concerning the barrier of photoisomerization is not at all satisfactory. The barrier predicted by our calculations, i.e. $E({}^1A_g^-, \approx 80^\circ) - E({}^1B_u^+, 0^\circ)$, is about 1 eV which differs from the values of 0.08 eV abstracted from experimental data [7] by an order of magnitude. This error is probably mainly due to the neglect of geometrical relaxation upon transition from the ground to the excited state (own unpublished results; refs. [14,15]).

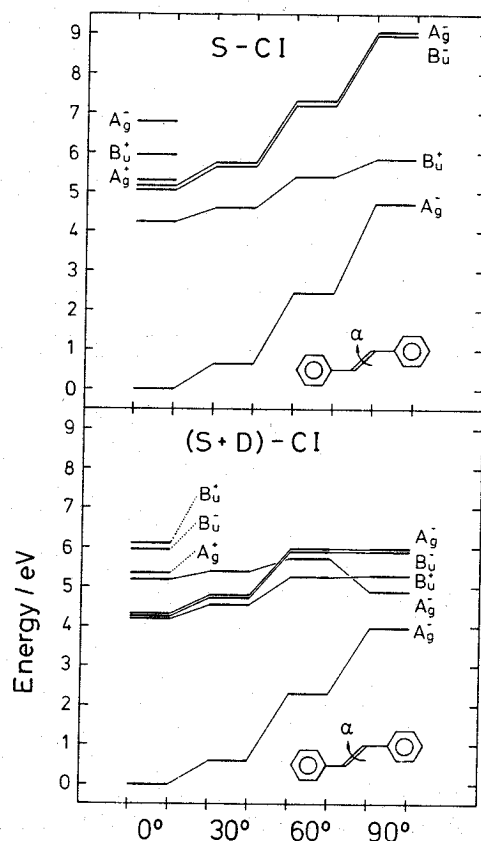


Fig. 2. Potential energies for isomerization around the central bond of stilbene predicted by a S-CI description and a S + D-CI description corrected according to eq. (1) — the ground state correlation energies at 0° and 90° are -1.533 eV and -2.259 eV , respectively.

The importance of photoisomerization in many photochemical and photobiological reactions call for more detailed quantum chemical studies as have been carried out recently [14,16,17].

4. Diphenylpolyenes

In order to link the mechanism of stilbene photoisomerization with the photobehaviour of diphenylpolyenes we have carried out S + D-CI calculations on diphenylpolyenes (diphenylbutadiene to diphenyldecapentaene) to determine which electronic excitation in these molecules is related to the photochemically active ${}^1A_g^-$ state of stilbene. For this purpose we have adopted, however, an artificial D_{2h} symmetry for the diphenylpolyenes, i.e. we assumed the angles

Table 2
S + D-CI energies ^{a)} of diphenylpolyenes $\phi-(C_2H_2)_n-\phi$
adopting D_{2h} symmetry (in eV)

State	n = 1	n = 2	n = 3	n = 4	n = 5
ground state					
$^1A_g^-$	-1.545	-1.777	-2.002	-2.220	-2.432
phenyl ring states					
$^1B_{2u}^-$	3.858	3.821	3.807	3.802	3.800
$^1B_{1g}^-$	3.862	3.821	3.807	3.802	3.800
$^1B_{1g}^+$	5.804	5.576	5.462	5.405	5.370
$^1B_{2u}^+$	5.870	5.594	5.468	5.408	5.370
ionic "polyene" states					
$^1B_{3u}^+$	3.896	3.455	3.110	2.847	2.646
$^1A_g^+$	5.035	4.805	4.540	4.247	3.958
$^1B_{3u}^+$	5.432	5.350	5.167	4.994	4.805
covalent "polyene" states					
$^1A_g^-$	4.835	4.035	3.495	3.156	2.942
$^1B_{3u}^-$	5.604	4.922	4.382	3.920	3.569
$^1A_g^-$		5.328	4.693	4.580	4.211
$^1B_{3u}^-$			5.309	5.044	4.724
$^1A_g^-$				5.232	4.833

a) Energies with respect to the SCF ground state.

between adjacent C-C bonds of the polyene moieties to have the value 180° rather than the real 120° value. This approximation increases the number of symmetry classes of the electronic transitions thereby decreasing greatly the computational effort and affects only slightly the predicted CI energy values and properties of the electronic states (e.g. the largest error in the CI energies is less than 0.17 eV). The D_{2h} symmetry has the additional advantage that it bears the characterization of its B_{1g}^- and B_{2u}^- states as excitations involving only the phenyl rings.

Table 2 lists the CI energies of the electronic states of the diphenylpolyenes. The excited states have been ordered in three groups, involving excitations in the phenyl rings, and involving ionic and covalent excitations affecting the polyene moieties. The phenyl ring excitations are found to depend only weakly on the polyene length. The $^1B_{3u}^+$ states constitute the polyene type $^1B_u^+$ states, the lowest state being responsible for the strong absorption band of the polyenes. The $^1A_g^+$ states become optically allowed upon cis-trans isomerization, i.e. these states constitute the so-called cis band. The low-lying covalent states ($^1B_u^-$, $^1A_g^-$) in-

crease in number as the polyene length increases. In the case of diphenyldecapentaene five covalent states are found in the same energy range as the three lowest ionic states none of which is being accounted for by a S-CI description. The covalent states are predicted, however, all to lie above the lowest $^1B_{3u}^+$ state. For example in the case of diphenyloctatetraene the calculated $^1A_g^-$ excited state lies 0.31 eV above the $^1B_{3u}^+$ state whereas experimental observation places it below this state [1].

In order to explain this deficiency of the S + D-CI description we compare in table 3 the CI-energies of the polyene-type states of diphenyldecapentaene with those of the polyene-decapentaene the latter being described by a S + D-CI calculation as well as by a CI calculation including also all triple and quadruple excitations (S + D + T + Q-CI). Table 3 links the $^1B_{3u}^-$ and $^1A_g^-$ transitions of diphenyldecapentaene to their counterparts in decapentaene. In the latter molecule the $^1A_g^-$ covalent excited state is predicted by the S + D-CI calculation to lie below the optically allowed $^1B_u^+$ state. However, the energy difference resulting from such calculation decreases for longer polyenes and, in fact, for $C_{18}H_{20}$ the $^1A_g^-$ state is placed above the $^1B_u^+$ state. This peculiar behaviour originates from the fact that the S + D-CI basis is too limited to describe the excited $^1A_g^-$ state properly. Table 3 shows that an S + D + T + Q-CI description of decapentaene lowers the energy of the $^1A_g^-$ state relative to the $^1B_u^+$

Table 3
Comparison of CI energies ^{a)} (in eV) of diphenyldecapentaene and decapentaene

D_{2h} -diphenyldecapentaene		Decapentaene		
state	S + D-CI	state	S + D-CI	S + D + T + Q-CI
$^1A_g^-$	-2.432	$^1A_g^-$	-1.250	-1.366
$^1B_{3u}^+$	2.646	$^1B_u^+$	3.452	2.913
$^1A_g^+$	3.958	$^1A_g^+$	5.242	4.409
$^1B_{3u}^+$	4.805	$^1B_u^+$	6.365	5.486
$^1A_g^-$	2.942	$^1A_g^-$	3.221	2.308
$^1B_{3u}^-$	3.569	$^1B_u^-$	4.008	3.200
$^1A_g^-$	4.211	$^1A_g^-$	4.785	3.968
$^1B_{3u}^-$	4.732	$^1B_u^-$	5.242	4.425
$^1A_g^-$	4.833	$^1A_g^-$	5.391	4.395

a) Energies with respect to SCF ground state.

state by 0.4 eV. This is due to the large contribution of open-shell triple and quadruple excitations to the wavefunction of the excited $^1A_g^-$ state. For a proper description of the $^1B_u^+ - ^1A_g^-$ level spacing which has been observed to place the $^1A_g^-$ state above the $^1B_u^+$ ($^1B_{3u}^+$) state for diphenylbutadiene and below this state from diphenyloctatetraene onward [18] one needs therefore to include triple and quadruple excitations in the expansion of the $^1A_g^-$ state. Another contribution to this level spacing comes from coordinate relaxation in the excited states (unpublished results; ref. [19]).

5. Conclusion

We have confirmed on the basis of a calculation of the potential surfaces governing the photoisomerization of stilbene that this process involves a crossing to a higher excited state of 1A_g symmetry and doubly excited character. In showing this we have demonstrated that the inclusion of double excitations in a CI treatment is necessary for a qualitatively correct description of the excited state potential surfaces. The photochemically active 1A_g state of stilbene corresponds to the low-lying 1A_g state in diphenylpolyenes observed by Hudson and Kohler suggesting a similarly important role of this state for the photochemistry of polyenes.

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