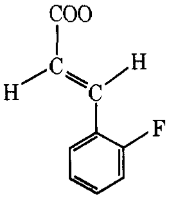
Deuterium substitution shows that a significant part of the fluorine relaxation in Ia must arise from dipolar interactions with the β-vinyl hydrogen. Taking the contribution of the β-hydrogen to relaxation ($R_1 \approx 0.062$) and the values for $D_\|$ and $D_\perp$ found for *o*-fluorocinnamate, we estimate that the average distance between this hydrogen and the *o*-fluorine must be about 2.2 Å. This is essentially the proton–fluorine distance which obtains when the molecule is in the conformation shown in III, and since any other orientation about the carbon–carbon bond which holds the acrylate group to the *o*-fluorophenyl ring *increases* this distance, we must conclude that structure III represents the only significantly populated conformation of *o*-fluorocinnamate. It may be recalled that *o*-fluorobenzaldehyde exists exclusively as the rotamer analogous to III.[12b] Description of the molecular tumbling of the fluorocinnamates in terms of two diffusion coefficients is reasonably successful, although possibly a more complete model is needed to account for the relaxation data of Ia. The anisotropy of motion ($D_\|/D_\perp = 4–6$) is greater with these compounds than with more simply monosubstituted benzenes[1] ($D_\|/D_\perp \sim 1.3–1.8$) as would be expected given the relative molecular dimensions or the likely association of the anions with solvent. Although it is clear that solvent molecules can influence the relaxation of nuclei on the periphery of the fluorocinnamates, more data are needed to define the role of solvent effects in the molecular dynamics of these species.



III

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A Theoretical Study of the Structure of Cyclobutadiene

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Abstract: Ab initio calculations both on the SCF level and with electronic correlation have been performed for the square singlet and triplet and the rectangular singlet states of planar cyclobutadiene. In the square geometry the singlet turns out to be more stable than the triplet by about 7 kcal/mol. This violation of Hund's rule is explained as an effect of "dynamic spin polarization". Distortion of the square geometry to a rectangular structure stabilizes the singlet state further. The equilibrium structure of cyclobutadiene shows long C–C single bonds of 1.57 Å and normal double bonds, similar to the bond lengths observed experimentally for substituted cyclobutadienes. The energy difference between the rectangular and the square structure of singlet cyclobutadiene is estimated to be 14 kcal/mol.

I. Introduction

The structure of cyclobutadiene is still a vividly discussed subject.[1,2] Most experiments seem to be in favor of a square structure of the unsubstituted cyclobutadiene in its ground state.[1] For an alkyl-substituted cyclobutadiene, however, the rectangular singlet structure is well established by x-ray structural analysis.[3] In a recent paper Borden[2] presented theoretical arguments favoring a square singlet to be the ground state of cyclobutadiene.

Previous ab initio calculations,[4-6] on the other hand, do not support a square structure to be a minimum of the singlet

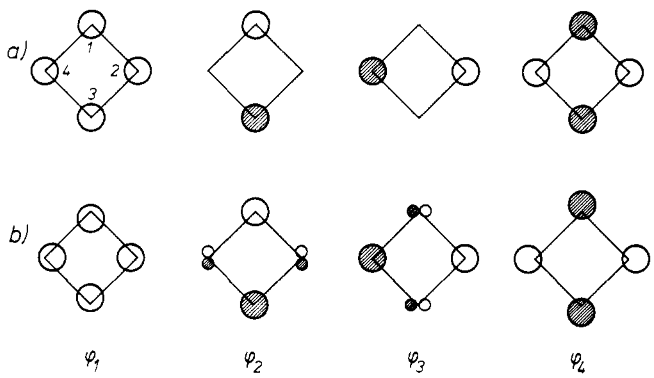

Figure 1. The π orbitals of cyclobutadiene (a) without and (b) with inclusion of d functions.

surface of the unsubstituted cyclobutadiene, but indicate that the rectangular singlet would be considerably more stable than the square singlet (11 kcal/mol as given by Buenker and Peyerimhoff[4]). Since those calculations did not include correlation or included only a part of the correlation of the π system within a minimal basis treatment (ref 4), we performed a series of refined ab initio calculations in order to determine the ground-state multiplicity of square cyclobutadiene and the minimum of its singlet potential surface.

II. The Multiplicity of the Square Structure and Hund's Rule

In the SCF approximation the square singlet and triplet states ($M_S = 0$) of cyclobutadiene have to be represented by two-determinantal wave functions:

$$\Phi_{T,S} = \frac{1}{\sqrt{2}}(\Phi_1 \pm \Phi_2)$$

$$\Phi_1 = |\varphi_1\alpha\varphi_1\beta\varphi_2\alpha\varphi_3\beta| \equiv |1\bar{1}2\bar{3}|$$

$$\Phi_2 = |\varphi_1\alpha\varphi_1\beta\varphi_2\beta\varphi_3\alpha| \equiv |1\overline{12}3|$$

(in which for the sake of simplicity only the π orbitals were denoted). While Φ_T is invariant with respect to arbitrary unitary transformations among φ_2 and φ_3, the lowest singlet is given by Φ_S only if φ_2 and φ_3 have a nodal structure as represented in Figure 1a (minimum of the exchange integral (23|23)).

An arbitrary unitary transformation between φ_2 and φ_3 is equivalent to the mixing of Φ_S with the two other singlet configurations $|1\bar{1}2\bar{2}|$ and $|1\bar{1}3\bar{3}|$, thus changing the form of the wave function of the lowest singlet state.

If the energies of the singlet and triplet are computed separately by open-shell SCF calculations,[7,8] their difference will be

$$\Delta E_{SCF} = E_{SCF}(\Phi_S) - E_{SCF}(\Phi_T) \approx (23|23)^S + (23|23)^T$$

as long as the exchange integrals (23|23) calculated with the singlet and triplet SCF orbitals (upper index S and T, respectively) are not too different and small (thus obtaining the same doubly occupied MO's for both states).

As a first step we performed open-shell SCF calculations for the two states of square cyclobutadiene ($R_{CC} = 1.44$, $R_{CH} = 1.10$ Å) using different basis sets. In a minimal basis set (contracted from 5s,2p on C/2s on H) we obtained for ΔE_{SCF} a value of 4.1 kcal/mol. The use of a double ζ basis (contracted from 7.3/3 Huzinaga[9]) increased this value slightly to 4.7 kcal/mol. However, the addition of d functions at the carbon atoms led to a higher ΔE_{SCF} of 6.4 kcal/mol. The increase in the exchange integral is due to the fact that the d functions allow φ_2 to spread over the C atoms 2 and 4 and φ_1 over 1 and 3, maintaining the nodal structure as indicated in Figure 1.

However, as the calculations of Buenker and Peyerimhoff[4] have shown, electron correlation within the π system lowers the energy of the singlet more than that of the triplet. The reason for this extra stabilization of the singlet is what we like to call a "dynamic spin polarization". It has been partly discussed by Borden.[2] Here we will give only a short account of this effect on the two states of cyclobutadiene, postponing a complete discussion of spin polarization to a forthcoming paper.[10]

In a CI-type treatment for the singlet and the triplet one has to include those singly substituted configurations describing the excitation of one electron from a doubly occupied orbital into a virtual orbital which have nonvanishing matrix elements with the Hartree–Fock wave function. For the excitation of an electron from φ_1 to a virtual orbital φ_k these singly excited configurations are

$$\Phi_S{}^1 = \frac{\sqrt{3}}{6}(|1\bar{k}2\bar{3}| + |\bar{1}k2\bar{3}| + |1\overline{k2}3| + |\bar{1}k\bar{2}3| - 2|\overline{1k}23| - 2|1k\overline{23}|)$$

$$\Phi_T{}^1 = \frac{1}{2}(|1\bar{k}2\bar{3}| + |\bar{1}k2\bar{3}| - |1\overline{k2}3| - |\bar{1}k\bar{2}3|)$$

$$\Phi_T{}^2 = \frac{1}{\sqrt{2}}(|\overline{1k}23| - |1k\overline{23}|)$$

their matrix elements with Φ_S and Φ_T being, respectively,

$$\langle\Phi_S|H|\Phi_S{}^1\rangle = \sqrt{\frac{3}{2}}(1|K_2 - K_3|k)$$

$$\langle\Phi_T|H|\Phi_T{}^1\rangle = \frac{1}{\sqrt{2}}(1|K_2 - K_3|k)$$

$$\langle\Phi_T|H|\Phi_T{}^2\rangle = (1|K_2 + K_3|k)$$

The other singly excited configurations fulfill the Brillouin theorem and do not contribute to the correlation energy in first-order perturbation theory.

Obviously, the matrix element of Φ_S with $\Phi_S{}^1$ is $\sqrt{3}$ times larger than that of Φ_T with $\Phi_T{}^1$. This leads to a stabilization which is three times larger for the singlet than for the triplet, provided that the energy denominators are equal. In cyclobutadiene the exchange integral $(1|K_2 - K_3|4)$ is rather large for the bonding π orbital φ_1 and the antibonding π orbital φ_4. $(1|K_2 + K_3|4) = 0$ from symmetry reasons, and both exchange integrals are rather small if φ_k is a σ-type virtual orbital. Thus, there is essentially one single configuration responsible for the strong correlation stabilization of the singlet.

For the physical interpretation the well-known basic principles of spin polarization[11] in systems with one unpaired electron are shortly repeated. An unpaired electron interacts differently with the two electrons of any doubly occupied orbital depending on their relative spin orientations. There is less repulsion for parallel spins than for antiparallel spins. Thus, it is energetically favorable for the two electrons of a doubly occupied orbital to correlate their spins with the spin of the single electron, such that in a region of space where the single electron is found with α spin an electron of the doubly occupied orbital will have α spin at that time with higher probability than β spin. This spin polarization can be taken into account by taking different MO's for different spins or by adding singly excited configurations to the restricted SCF wave function as we have done in this work.

In our case we have to deal with two singly occupied MO's. The spin polarization scheme now depends on the relative spin orientations of the two single electrons. Thus, two situations can occur which result in two different types of spin polarization:

(i) The spins of the singly occupied MO's are antiparallel. The spin polarization of the doubly occupied π MO φ_1 (which gives the largest contribution to the energy lowering) is accomplished by mixing the antibonding π^* MO into φ_1, as indicated in Figure 2. Since the spin states of the two electrons may as well be interchanged, no net spin density results anywhere. In this case we speak of a dynamical spin polarization.

(ii) The spins of the two electrons are parallel. In this case the spin polarization of the lowest π orbital φ_1 is obtained by mixing into φ_1 a virtual π^* orbital which is symmetric with respect to the C_4 axis and built up by essentially 3p type AO's (cf. Figure 2). This leads to a radial spin separation and nonzero spin densities are to be expected. It is the static type of spin polarization as it is observed in radicals.

Energetically, the second type of spin polarization is less important in our example, since the necessary virtual orbitals are fairly high in energy.

In the triplet the spins are antiparallel with respect to one quantization axis and parallel with respect to the other two ($\langle S^2 \rangle = 2$). Thus we get one contribution of type I and two contributions of type II (the factor of $\sqrt{2}$ in the matrix element). It should be added that the quantization axis can be chosen in an arbitrary way. The decisive point is that in the triplet the spins of the two single electrons are parallel with a probability of two-thirds and antiparallel with a probability of one-third.

In the singlet, on the other hand, the spins are antiparallel with respect to all three quantization axis. We get only a spin polarization of type I, which is therefore energetically almost three times as large as in the case of the triplet (the factor of $\sqrt{3}$ in the matrix element).

The arguments presented above correspond to the following mathematical derivation. One describes the spin polarization of φ_1 by replacing φ_1 by $\varphi_1 \pm \varphi_k$ for all three quantization axis, develops the determinants into a series (neglecting the terms with λ^2), and transforms to one quantization axis, thus obtaining exactly $\Phi_S - \lambda\Phi_S{}^1$ as given in the CI treatment (For more detailed discussion see ref 10).

We calculated the different contributions of the spin polarization by a perturbation approach in which for each occupied orbital the virtual orbitals were optimized in order to give maximum interaction matrix elements with the SCF wave functions. The results of these calculations are given in Table I for the three different basis sets described before. The stabilization of the singlet by spin polarization is indeed considerably larger than that of the triplet, leading to a singlet ground state for planar square cyclobutadiene, in violation of Hund's rule. Nearly 90% of this difference in stabilization is due to the polarization of the π orbital φ_1.

The total energy difference of 13.9 kcal/mol which we obtained with our minimal basis is in very good agreement with the corresponding value of 13.6 kcal/mol reported by Buenker and Peyerimhoff[4] for their minimal basis CI calculations. However, as Table I shows, the energy difference is considerably reduced by improvement of the basis set: The increase in the flexibility of the s,p basis reduces the effect of spin polarization, while the addition of d functions increases the SCF singlet-triplet splitting by increasing the exchange integral. Thus, the energy difference in the largest basis set employed is only 7 kcal/mol. A similar effect has been observed by Silver and Stevens in their CI calculations on square planar H_4.[12]

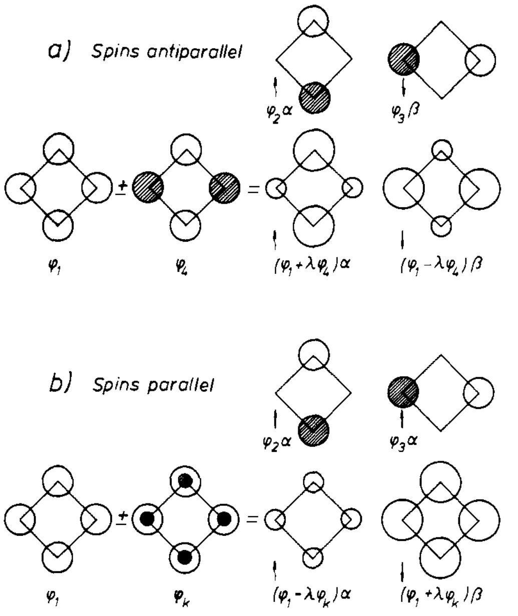

Figure 2. A schematic representation of the spin polarization of the doubly occupied π MO φ_1 of cyclobutadiene by two unpaired electrons in φ_2 and φ_3 with (a) antiparallel and (b) parallel spins.

Table I. Contributions of the Spin Polarization to the Energy of Square Planar Cyclobutadiene ($R_{CC} = 1.44$, $R_{CH} = 1.10$ Å; all energies in atomic units)

Basis set	5.2/2 minimal	7.3/3 double ζ	7.3/3 + d(c) double ζ
$(23/23)^S$	0.0033	0.0037	0.0049
$(23/23)^T$	0.0033	0.0038	0.0053
ΔE_{SCF}	0.0066	0.0076	0.0102
Spin-polarization T (Φ_{T_2})	0.0455	0.0354	0.0329
(Φ_T)	0.0028	0.0069	0.0079
(total)	0.0482	0.0423	0.0409
S	0.0769	0.0655	0.0628
ΔE_{SP}	−0.0287	−0.0232	−0.0219
$\Delta E = \Delta E_{SCF} + \Delta E_{SP}$	−0.0221	−0.0156	−0.0117
ΔE, kcal/mol	13.9	9.8	7.3

Table II. SCF and Correlation Energies of Square and Rectangular Singlet Cyclobutadiene (energies in atomic units, basis 7.3/3)

	Square	Rectangular	ΔE
C–C bond lengths, Å	1.44	1.54/1.34	
E_{SCF}	−153.4172	−153.4205	0.0033
	(2)[a]	(1)[a]	
E_{corr} (IEPA, π)	0.0629[b]	0.0810	0.0181
$E_{SCF} + E_{corr}$ (IEPA, π)	−153.4801	−153.5014	0.0214

[a] Number of determinants given in parentheses. [b] Estimated as described in text.

III. Square vs. Rectangular Singlet Cyclobutadiene

In order to determine whether planar singlet cyclobutadiene has a square or a rectangular structure as its energy minimum, we performed a series of SCF and correlation calculations for the rectangular geometry ($R_{CC} = 1.54$ and 1.34 Å, $R_{CH} = 1.10$ Å, ∢CCH = 135°) as well as for the square structure ($R_{CC} = 1.44$, $R_{CH} = 1.10$ Å, ∢CCH = 135°). The correlation calculations for the rectangular singlet and the square triplet were performed within the IEPA scheme.[15,16] The correlation energy of the square singlet was estimated by taking the IEPA correlation energy of the triplet and adding the difference in the spin polarization energies of the two states.

In the IEPA calculations we included all pairs belonging to the π system and in addition all the interpairs between the π system and the other localized valence orbital MO's. As the calculations have shown, the difference in the correlation energy of the two structures is almost entirely due to the difference in correlation energy of the π system. In the case of the triplet the single excitations discussed before account for al-

Table III. SCF and Correlation Energy for Cyclobutadiene for Different CC Bond Lengths[a]

$R_{C=C}$, Å	R_{C-C}, Å	$-E_{SCF}$, au	Correlation energy of the carbon skeleton, in au		
			IEPA	PNOCI	CEPA
1.34	1.48	153.4083	−0.2674	−0.2073	−0.2318
1.34	1.54	153.4205[b]	−0.2701	−0.2086	−0.2333
1.34	1.60	153.4245[c]	−0.2732	−0.2101	−0.2353
1.34	1.66	153.4220	−0.2768	−0.2118	−0.2378
1.31	1.60	153.4250	−0.2664	−0.2069	−0.2306
1.37	1.60	153.4199	−0.2805	−0.2135	−0.2404
1.30	1.58	153.4236	−0.2631	−0.2053	−0.2283
1.40	1.48	153.3961	−0.2828	−0.2145	−0.2430

[a] In order to save computer time in the correlation calculations, the basis functions at the hydrogens were contracted to one group. The contraction coefficients were taken from the MO of the H_2 molecule. For two structures the SCF energies without this contraction are given as well. [b] 153.4345 without the contraction of the H basis. [c] 153.4385 without the contraction of the H basis.

most 75% of the π correlation energy. These calculations were performed with the 7.3/3 basis. The results are given in Table II.

For the π correlation energy of the square triplet we obtained 0.0416 au, while that of the rectangular singlet turned out to be 0.0810 au. The difference in spin polarization energy confined to the polarization of φ_1 is 0.0569 au (S) − 0.0356 au (T) = 0.0213 au, such that the total π correlation energy of the square singlet is estimated to be 0.0629 au. Together with the SCF contribution of 0.0033 au in favor of the rectangular geometry we expect the rectangular singlet to be about 0.0214 au = 13 kcal/mol lower in energy than the square singlet.

The energy difference between the rectangular and the square structure can be estimated in quite a different approach. Taking the concerted asymmetric stretching as the coordinate for the distortion of the square singlet, one calculates the force constant for that stretching mode near the energy minimum where the CEPA scheme is fully applicable. The CEPA calculations yield 1.55–1.33 Å as the minimum and 25.8 mdyn/Å as the force constant. Assuming a cosine potential for the distortion one obtains 0.015 au = 9.4 kcal/mol for the energy difference between the two structures.

IV. The Equilibrium Structure of Cyclobutadiene

As a last step we determined the optimum structure of the rectangular singlet state, particularly to check whether the very long C–C single bond of 1.60 Å as observed in the x-ray analysis of substituted cyclobutadiene[3] is due to substituent or crystal structure effects or is a property of cyclobutadiene itself.

First, in SCF approximation and with the 7.3/3 double ζ basis set we got long C–C single bonds of 1.605 Å (for ethane 1.548 Å with the same basis) and normal C–C double bonds of 1.321 Å (1.310 Å in ethylene). In addition, the single bond lengths were optimized after adding d functions to the basis. Then, the optimum was computed to be 1.572 Å (1.532 Å for ethane). This reoptimization of the C–C bond lengths lowers the energy of the rectangular singlet further by 0.0012 au, such that it is now expected to be 0.0226 au = 14 kcal/mol below the square singlet. The optimum of the C–C bond length in the square singlet is 1.444 Å (1.441 Å for the triplet) within the 7.3/3 basis. When the spin polarization effects are included the equilibrium bond lengths change only slightly. They are 1.455 Å for the square singlet and 1.453 Å for the triplet. This optimization of the bond lengths has virtually no influence on the singlet–triplet energy separation.

The effect of correlation on C–C single bond lengths in saturated hydrocarbons such as ethane is very small.[17] However, cyclobutadiene is a special case because of a low-lying π^* orbital which becomes degenerate with the highest occupied MO for the square structure. Therefore we had to check whether correlation tends to shorten the CC single and to lengthen the CC double bonds in cyclobutadiene. For this purpose we calculated the CEPA correlation energy[13,14] within the carbon skeleton for different CC bond lengths. The results are given in Table III. The correlation energy shows the normal behavior of an increase with increasing bond length for the single as well as for the double bonds. Thus, the optimal structure contains 0.022 Å longer single bonds and 0.037 Å longer double bonds than the optimal SCF structure. The corresponding values for ethane and ethylene are 0.018 and 0.029 Å, respectively. In order to get correct bond lengths one has to include the interbond correlation of the CH with the CC and the CH bond orbitals as well.[17] Thus, we do not give a CEPA equilibrium structure of cyclobutadiene. The results, however, prove that there is no tendency for the correlation to shorten the long single bonds or to favor a less rectangular structure. A more detailed analysis shows that π correlation alone would in fact give a structure with shorter single and longer double bonds.

We should emphasize that at equilibrium the distortion from the square geometry is large enough to remove the degeneracy between $|1\bar{1}2\bar{2}|$ and $|1\bar{1}3\bar{3}|$ completely and to guarantee that our closed-shell CEPA scheme is applicable (2 and 3 denote here the symmetry adapted π orbitals of the rectangular structure). This is not true for the square geometry with the degeneracy between the two determinants.

V. Conclusion

We conclude that cyclobutadiene should have a rectangular singlet ground state with very long C–C single bonds. Even for the square structure the singlet is lower in energy than the triplet due to spin polarization effects and in violation to Hund's rule. Thus, if a square cyclobutadiene is really observed experimentally, it could only be a metastable triplet which might be separated by a barrier from the singlet.[18]

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On the Extent of Charge Separation in Suddenly Polarized Twisted Excited States of Linear Polyenes

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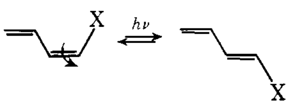
Abstract: The lowest $^1\pi\pi^*$ singlet excited states of butadiene are stabilized when twisted to 90° around one double bond and become strongly ionic. These zwitterionic excited states, which occur in cis-trans photoisomerizations of polyenes, are rather difficult to treat in a correct manner. It is shown that an open shell SCF calculation for the diradical ground state, followed by a *limited* CI, *overestimates* the charge separation and dipole moment in the ionic excited states. By allowing a larger flexibility to the wave functions, one demonstrates that (i) the positive and negative net charges attract each other and tend to concentrate on either side of the twisted double bond and (ii) the σ polarization effect stabilizes these localized structures and diminishes the net charges. Both phenomena diminish the excited state dipole moment and charge separation. These conclusions do not hold for the *protonated* Schiff bases, for which the excited state bears a single charge without the counterpart of opposite sign and where an important charge migration may occur.

Several semiempirical studies have shown that in its lowest singlet $^1\pi\pi^*$ excited state, the butadiene molecule might undergo a rotation around *one* of its double bonds[2] losing its center of symmetry. The first ab-initio study of the excited state geometry[3a] kept the center of symmetry of the molecule, and only allowed two simultaneous and equal rotations ($\theta_1 = \theta_2$) around the C_1C_2 and C_3C_4 double bonds. An analytic approach to the problem also suggests a full rotation (θ_1 or $\theta_2 = 90°$) around one double bond.[3b] This is a likely phenomenon if one remembers that in ethylene the $\theta = 90°$ rotation diminishes the energy of the V^1 $\pi\pi^*$ singlet state from 7.6 to 4.9 eV according to the simplest experimental considerations (energy stabilization of 2.7 eV) and from 8.2 to 6.2 eV according to the most recent and refined quantum mechanical calculations[4] (energy stabilization of 2.0 eV). The vertical S_0-S_1 transition of butadiene occurs at about 5.9 to 5.7 eV,[6] i.e., 1 eV above the lowest estimate of the (0–0) transition of ethylene; one may therefore guess that a twisted butadiene, where the excitation is located on one double bond, is already more stable than the planar excited singlet state. The residual delocalization which may occur in a twisted butadiene should give a supplementary stabilization of the 90° structure and bring its energy below 4.9 eV. A recent ab-initio study[5] actually confirms that the perpendicular structures are more stable than the planar one. Moreover the twisted conformations of the lowest excited singlets appear to be very likely intermediate in direct cis-trans photoisomerizations of C–C bonds.



These photoisomerizations are a basic photochemical reaction of conjugated chains and concern, for instance, besides ethylene and butadiene, styrene, stilbene, and retinene. (For recent theoretical studies of these molecules, see for instance ref 7–9.) It may be important therefore to analyze the electronic structure of these twisted intermediates.

From elementary considerations of valence bond theory one may divide the four lowest excited states of ethylene into covalent and ionic states. The ground state is essentially covalent since in the π part of the wave function, described from the two $2p_\pi$ AO's a and b, the radical components $|a\bar{b}|$ and $|b\bar{a}|$ have a larger weight than the ionic structures $|a\bar{a}|$ and $|b\bar{b}|$; the ionic component disappears for $\theta = 90°$ ($\phi_0{}^\pi = 1/2^{1/2}\,|a\bar{b} + b\bar{a}|$). For all values of θ, the $\pi\pi^*$ triplet state is purely covalent, $\phi_T{}^\pi = 1/2^{1/2}\,|a\bar{b} - b\bar{a}|$. The lowest singlet V state, represented by the $\pi\pi^*$ single excitation, is purely ionic, $\phi_V{}^\pi = 1/2^{1/2}|a\bar{a} - b\bar{b}|$. Another singlet state may be introduced in the π minimal basis set; for the planar configuration it is essentially a doubly excited configuration $\pi^*\bar{\pi}^*$ in the MO representation, but for the perpendicular conformation this state becomes purely ionic $\phi_Z{}^\pi = 1/2^{1/2}|a\bar{a} + b\bar{b}|$. The two ionic states are close in energy, and if the symmetry is broken by a chemical substitution or a deformation on one CH_2 group, ϕ_V and ϕ_Z may interact and strongly mix. Bonacic-Koutecky et al.[10] have shown that for $\theta = 90°$, a slight perturbation on one carbon gives two very polar, excited states with a net charge of about ±0.9 e on each carbon. The full charge displacement, $\Delta g = 1.0$ e, is represented by the limit wave functions $\phi_{Z_1}{}^\pi = |a\bar{a}|$ (−e ,+e structure) and $\phi_{Z_2}{}^\pi = |b\bar{b}|$ (+e,−e structure). $\phi_{Z_1}{}^\pi$ and $\phi_{Z_2}{}^\pi$ are weakly mixed in the calculated wave functions. The same authors[10] analyzed the charge distribution of the excited *s-cis,s-trans*-1,3,5-hexatriene when rotated around the central double bond (which is most likely to undergo a rotation[2c]).

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