CI Study of Geometrical Relaxation in the Excited States of Butadiene. Energy Surfaces and Properties for Simultaneous Torsion and Elongation of One Double Bond

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Abstract: The energy surfaces of the four lowest-lying singlets and the two lowest-lying triplet states of butadiene for the simultaneous twist and elongation of one double bond have been determined by employing large-scale CI treatments. The singlet ground state and the second triplet state exhibit a barrier to rotation and elongation. In contrast, this geometrical relaxation is energetically favorable for the lowest triplet and the lowest three excited singlet states. For intermediate and large twist angles the singlet energy surfaces approach each other closely and the corresponding wave functions contain a mixture of covalent and ionic contributions. At the 90° twist the excited covalent singlet state lies most likely in between two zwitterionic polar states with the dipole moments in opposite directions. The polarity of zwitterionic states develops gradually over a large interval of the twist angle. There is an indication that the lowest singlet excited state energy surface exhibits a minimum at an intermediate twist angle in addition to the one at the 90° twist. The relative position of two minima can be easily influenced by chemical substitution.

A theoretical investigation of the geometrical relaxation in the excited states of polyenes with respect to the simultaneous twist and elongation of one double bond is of great interest in the study of photochemical reactions. The proposed mechanisms of photoisomerizations of polyenes or of bicyclization first require careful determination of the energy surfaces of the low-lying excited states and an understanding of the characteristic changes in the corresponding electronic structures along the important parts of the reaction path. After initial light absorption and during its rapid thermalization the molecule seeks a minimum on the excited state energy hypersurface which can easily occur for biradical geometries. The torsion of one of the double bonds in butadiene which produces a nonsymmetrical biradical may represent such a situation. Butadiene has been chosen as the smallest polyene for which the simultaneous study of geometrical relaxation in several close-lying excited states is still feasible in the framework of ab initio large-scale CI treatments.

In connection with cis–trans isomerization the twisting of different polyenic bonds has been investigated by employing different semiempirical[1-4] and ab initio[5,6] treatments. These studies include the triplet states of butadiene.

The studies of the singlet excited states of planar polyenes employing semiempirical CI treatments resulted in an interesting prediction that the lowest-lying singlet excited state is of the same symmetry as the ground state. Therefore, this excited state might be spectroscopically accessible only by two-photon excitations. In other words, the second ^1A_g state lies below or close to the ^1B_u state.[7] This prediction seemed to be confirmed by experimental finding[8] which stimulated further theoretical[9] and experimental work[10] on polyenes. The singlet states of butadiene, which admittedly might not yet acquire the properties of longer polyenes completely, have been investigated in their planar geometry by employing ab initio large-scale CI treatments.[11-13] The spectroscopical assignments for the vertical transitions are still not completely settled. In addition, the low-lying singlet states of a zwitterionic nature for the pronounced biradical geomergy, i.e., the 90° terminally twisted butadiene[14-16] have been studied in connection with the sudden polarization effect.[17-19] The simple CI treatments employed have followed the idea of the four-state

model for biradicals which arises from a two-center, two-orbital VB picture yielding a pair of close-lying singlet–triplet states and a pair of close-lying excited singlet states.[20]

The purpose of this paper is to determine the potential energy surfaces of the four lowest singlet states for the twisting of one double bond and to characterize the change in the electronic wave function along the geometrical path. Although the emphasis is on finding and characterizing the energy minima, which certainly occur for nonplanar geometries, an attempt has been made to correlate the corresponding wave functions with the low-lying singlet excited states of the planar butadiene. For example, it is important to know if the wave functions at the minima contain features of a zwitterionic polar nature or some characteristics of the covalent second 2^1A_g state.

An adequate description of close-lying energy hypersurfaces including regions of the avoided crossings offers a challenge for theoretical treatments. Due to the fact that the molecule does

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Excited States of Butadiene

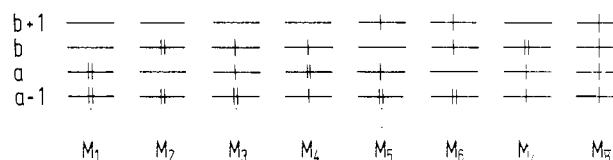*J. Am. Chem. Soc., Vol. 104, No. 25, 1982* 6901

not have any elements of point group symmetry in the twist interval except for the planar and 90° twisted geometries, the simultaneous description of four singlet states is required. Consequently, a multireference four-roots treatment in the framework of very large-scale CI is inevitable. The applicable large-scale CI method at present is the MRD-CI approach.[21] The treatments of the electron correlation problem by means of the graphical unitary group approach might be capable of handling the multireference CI problem in the near future.[22] MCSCF procedures adequate for the simultaneous description of several excited states of the same symmetry are still under development.

I. Method

The description of the close-lying excited states of relaxed butadiene is strongly dependent on the size and details of the CI treatment employed, but not substantially on the AO basis set. Therefore, a small AO basis set (4-31G) has been chosen which yields reasonable results in the large part of the twisting interval. In fact, an AO basis set of double-ζ quality even when augmented by polarization functions does not substantially influence the shape of the energy surfaces obtained from the treatment with 4-31G AO basis. Of course, for the proper description of the excited states of planar butadiene the use of basis sets of better quality is necessary. Nevertheless, the energy ordering of the two valence excited states of planar butadiene 2^1A_g (mixture of valence excited configurations) and ^1B_u (HOMO–LUMO excitation) in which we are particularly interested is not changed when an AO basis set of better quality than the 4-31G or double-ζ basis is employed if the appropriate CI treatment is applied (cf. ref 13). It is worth mentioning that a geometrical change such as the twisting of one double bond is extremely energetically unfavorable for any excited state containing Rydberg character.

The choice of the one-electron functions which are employed for building up the CI spaces is much more of a problem because the large but incomplete CI does not necessarily overcome the inadequacy of the single set of MO's which is available due to the lack of symmetry and which are employed for the simultaneous description of several singlet states. The most important requirement is that the Hartree–Fock MO's do not introduce an unbalanced description of close-lying states.[23-25] In other words, an optimal description of one of the states and a relatively poor description of another one due to the inadequate one-electron functions employed might not only invert the energy ordering but also change the physical picture of the problem. As has been shown in previous papers,[23-25] the triplet SCF MO's seem to be the most adequate choice of one-electron functions for CI treatments of the several singlet states of biradical geometries because no preference is given to one radical site over the other. Another possible choice is, of course, the four different sets of natural orbitals produced from CI multireference four-roots procedure based on the triplet orbitals. Each set of NO's employed in separate four-roots CI treatments yields a good description of only one corresponding state.[24] If the electronic states of the same symmetry lie very close to each other or exhibit weakly avoided crossing, it is difficult to judge if the separate NO-CI treatment of each state has accidently favored one state over the other due to an incomplete CI treatment.[24,26] One could also consider using the averaged natural orbitals from the density matrix of the four singlet states as the one-electron functions in the new CI treatment of these states. Nevertheless, we employ the lowest triplet SCF

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Scheme I

MO's to span singlet and triplet CI spaces throughout this paper (T-MO-CI). In addition, the CI treatments for each root with the natural orbitals of the corresponding root (NO-CI) have been carried out for the 90° terminally twisted butadiene in C_s symmetry.

For an adequate description of the four lowest-lying singlet states of terminally twisted butadiene in the whole twisting interval θ = 0–90 the reference CI space contains eight configurations which differ from each other in the occupation numbers of the two highest occupied and two lowest unoccupied MO's. They are basically built up from π carbon orbitals: The reference space for the two lowest-lying triplet states contains six configurations M_3–M_8 except that the doubly excited configuration M_6 is replaced by the singly excited configuration a − 1 → b + 1. These reference configurations turned out to be most important from the preliminary calculations of the energy surfaces.

Variational energies for four singlet states have been determined in such a manner that single and double excitations with respect to the reference space (a) from the π MO's to all virtual orbitals except to the two highest ones and (b) from π MO's and 5 doubly occupied MO's lying below them to 25 virtual orbitals are allowed. In the former case "full single and double π" CI with respect to the eight reference configurations has been carried out (T = 0). In the latter case only the eight lowest occupied molecular orbitals and their virtual counterparts have been excluded from the correlation treatment. The highest occupied MO excluded from the treatment and the lowest one taken as a one-electron function to build up the CI spaces exhibit a fairly large energy gap. Among eight occupied MO's which are not employed in the CI treatment the lowest four consist of 1s AO's located at carbon atoms. The remaining four MO's either contain outer s orbitals of carbon atoms or represent primarily C–H bonding. The CI space generated for the 14 electrons using 32 MO's contains ~200 000 spin-adapted functions among which up to 9000 configurations are selected if the energy selection threshold is chosen to be T = 12 μhartree. In this case an extrapolation technique for obtaining energies for $T \rightarrow 0$ had to be applied.

For the determination of two triplet states the extended CI treatment analogous to treatment b for the singlet states has been employed. (The reference space consisted of six instead of eight configurations as already described.)

II. Averaged Extrapolation Technique

The customary extrapolation technique[27] sometimes runs into difficulty resulting in an improper assignment of the lowerings of discarded configurations to the proper roots. We therefore introduce a procedure which keeps track of the proper root with the help of the overlap with the corresponding vector of the reference space.

The reference CI space yields eigenvalues ϵ_I with eigenvectors $|M_I\rangle$, where I labels the root. The energy lowering $l_I(T)$ due to the discarded configurations $|d_L\rangle$ for each root I at the given energy selection threshold T can be approximated as

$$l_I \approx \sum_L \frac{\langle d_L|\hat{H}|M_I\rangle^2}{E_L - \epsilon_I} \qquad (1)$$

The diagonalization of the selected space for the given threshold yields eigenvalues $E_K^{(v)}$ with eigenvectors $|v_K\rangle$. If the reference space has been adequately chosen, one can expand the selected vectors approximately in terms of reference vectors:

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$$|v_K\rangle = \sum_{I=1}^{N} |M_I\rangle\langle M_I|v_K\rangle = \sum_{I=1}^{N} s_{IK}|M_I\rangle \qquad (2)$$

where the coefficients are overlaps between the eigenvectors of the reference and selected space. Then, the second-order corrections in energy can be written as

$$E_K^{(2)} = \sum_L \frac{\langle d_L|\hat{H}|v_K\rangle^2}{E_L - E_K^{(v)}}$$

$$\simeq \sum_L \sum_{IJ} s_{IK}s_{JK} \frac{\langle d_L|\hat{H}|M_I\rangle\langle M_J|\hat{H}|d_L\rangle}{E_L - E_K^{(v)}}$$

$$= \sum_I s_{IK}^2 \sum_L \frac{\langle d_L|\hat{H}|M_I\rangle^2}{E_L - E_K^{(v)}} + \text{cross terms } (I,J) \quad (3)$$

The cross term has been neglected under the assumption that the multiplication and addition of matrix elements with random phases probably leads to a relatively small overall contribution. Furthermore, replacing $E_K^{(v)}$ by ϵ_I one obtains

$$E_K^{(2)} \approx \sum_{I=1}^{N} s_{IK}^2 \left(\sum_L \frac{\langle d_L|\hat{H}|M_I\rangle^2}{E_L - \epsilon_I} \right) = \sum_{I=1}^{N} s_{IK}^2 l_I \qquad (4)$$

As the $\epsilon_I > E_K^{(v)}$ at least for the lowest state of each symmetry, the replacement of $E_K^{(v)}$ by ϵ_I leads to an overestimate of $E_K^{(2)}$. The correction in energy due to the discarded configurations is the sum of the lowerings for all roots weighted by an overlap between the vector in the selected space and vectors of the corresponding roots in the reference space. The lowerings of the discarded configurations are averaged in this manner if there is more than one reference vector with which the overlap is large. Such a situation might easily occur if the two or more states of the same symmetry undergo avoided crossings and the corresponding wave functions are strongly mixed.

After the second-order correction in energy is determined, the extrapolation to $T = 0$ is carried out as described elsewhere[27]

$$E_K^{(D)} = E_K^{(v)}(T_1) + \lambda E_K^{(2)}(T_1) = E_K^{(v)}(T_2) + \lambda E_K^{(2)}(T_2) \quad (5)$$

where T_1 and T_2 are the two lowest thresholds chosen and the parameter λ is determined by eq 5 itself.

Finally, in order to determine Davidson's[28] or Siegbahn's[29] energy correction to the double CI space we define an averaged zero-order energy as

$$E_K^{(0)} = \frac{(\sum_I s_{IK}\langle M_I|)\hat{H}(\sum_J s_{JK}|M_J\rangle)}{\sum_I s_{IK}^2} = \frac{\sum_I s_{IK}^2\epsilon_I}{\sum_I s_{IK}^2} \qquad (6)$$

The Siegbahn full CI estimate takes the form

$$E_K = E_K^{(0)} + \frac{1 - \sum_{I=1}^{N} s_{IK}^2}{\sum_{I=1}^{N} s_{IK}^2}(E_K^{(D)} - E_K^{(0)}) \qquad (7)$$

The averaged extrapolation technique described has been implemented in the Wuppertal–Bonn CI package which we employ throughout the paper.
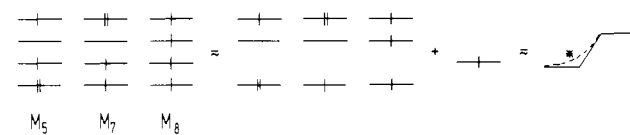
III. Energy Surfaces and Dipole Moments

The 4π-electrons CI treatment for the twist and prolongation of one double bond in butadiene yields a very oversimplified picture of the four singlet states considered (Figure 1). At the planar geometry the lowest excited state of 2^1A_g character lies substantially below the ^1B_u state.[30] (Notice that only valence and not Rydberg states are considered because of our main interest on relaxation effects in excited states.) As expected the expansion
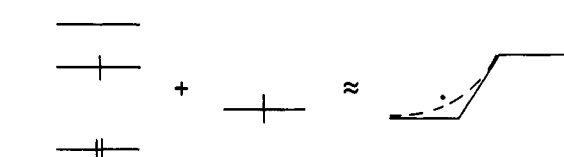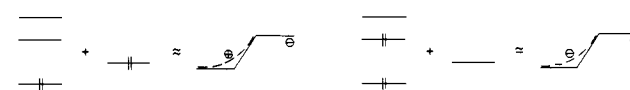
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Scheme II

Scheme III

M_5 M_7 M_8

Scheme IV

Scheme V

of the wave functions for the second 2^1A_g state contains predominantly contributions of one doubly excited configuration (a → b, a → b) and of two complementary singly excited configurations (a − 1 → b) and (a → b + 1)[13] (configurations M_2, M_4, and M_5 from Scheme I).

At the 90° twist there is the lowest-lying singlet excited state $C = S_1$ of "covalent" nature in addition to the three singlet states usually found in biradical geometries (a diradical $D = S_0$ and two zwitterionic states $Z_1 = S_2$, $Z_2 = S_3$). The correlated wave function of the covalent lowest singlet excited state (C) contains three predominant contributions (M_5, M_7, M_8; cf. Scheme I) with almost equal weights. For the 90° twisted geometry the four important molecular orbitals which are used to build up the reference configurations exhibit almost completely localized allylic and methylenic features: Consequently the predominant configurations in the first excited singlet state can be characterized as belonging to the "excited allyl + methylene" structure: The lowest diradical state (D) can, of course, be characterized by "ground state allylic + methylene" structure while Z_1 and Z_2 are polar states with extra charge on the methylene group and extra charge in the allylic triad, respectively: As shown in Figure 1, the ionic states lie 40 kcal/mol above the lowest-lying excited state C at 90° twisted geometry. The twisting is energetically favorable for all three excited singlet states while the ground state exhibits a barrier to rotation of 60 kcal/mol. The minima on the energy surfaces of both polar states Z_1 and Z_2 are located around 90° twist. The energy surface of the lowest excited state C is very shallow in the geometrical interval $\theta = 60$–90°, indicating the possibility of a minimum away from the 90° terminally twisted geometry.

The dipole moment curves for all four states given in Figure 2 clearly reflect the gradual change in the features of electronic wave functions. The polarity of the Z_1 and Z_2 states already develops at low twisting angles reaching maximum values for dipole moments of opposite sign at 90° twist. Neither of the covalent states D and C exhibits a sizable dipole moment throughout the interval. The Z_1 and Z_2 surfaces do not approach the C surface in the intermediate twisting interval which would reflect the mixed character of the respective wave functions due to lack of symmetry.
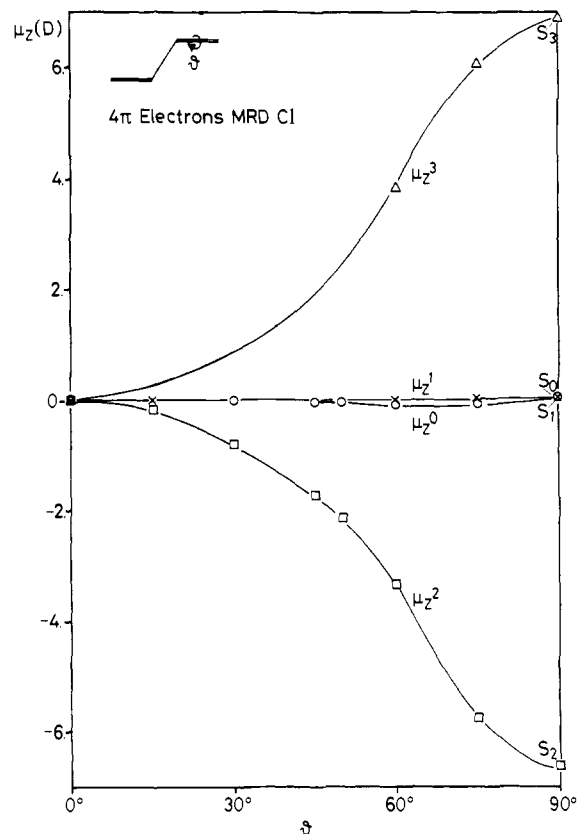
Such a simple picture disappears if the inclusion of correlation effects is extended to other than "π electrons". Obviously extension of correlation, explicitly included, affects zwitterionic states differently than the covalent ones leading to a changed shape of the energy surfaces and even changed ordering of the three singlet excited states with respect to the 4π-CI results.

The variational energy surfaces obtained from 8M/4R ($T = 12$ μhartree) CI treatment for 14 electrons "distributed" among
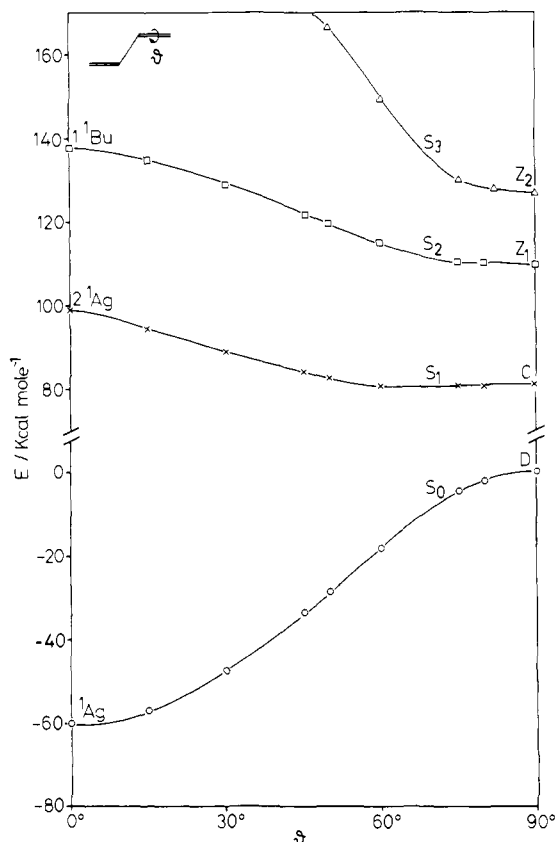
Figure 1. Potential curves for the lowest four singlet states S_0 (O), S_1 (×), S_2 (□), and S_3 (△) or butadiene as functions of simultaneous twist and elongation of one double C=C bond. (The elongation from 1.337 to 1.416 Å has been interpolated for the twist interval θ = 0–90°.) The 8M/4R (cf. Scheme I for reference configurations) "full" single and double CI treatment (T = 0) for 4π electrons has been employed. The MO's obtained from the triplet SCF procedure for the lowest triplet state are utilized to build up the CI spaces of 6068 dimension. For the AO basis set 4-31G basis has been employed. For the large twist angles S_0 ≡ D, S_1 ≡ C, S_2 ≡ Z_1, S_3 ≡ Z_3.

32 MO's are shown in Figure 3. Even when energy surfaces and corresponding wave functions are far away from the realistic ones because the number of selected configurations (~10 000) represents only a small part of the full 8 MRD-CI space (~200 000), they show some interesting features. The energy gap between second 2^1A_g and ^1B_u states of planar butadiene is much smaller than in the case of 4π-electrons CI treatment. In this paper no attempt has been made to determine exactly the relative position of 2^1A_g and ^1B_u states. Previous generalized valence bond and CI calculations[31,32] gave rise to the ^1B_u state lying substantially below the 2^1A_g state. This is most likely due to the leading role of the double excited configuration in the expansion of the wave function for the 2^1A_g state in both mentioned treatments. In our MRD-CI treatment in addition to the double excited configuration two singly excited configurations play equally important roles. Moreover, the energy ordering of the 2^1A_g and ^1B_u states depends also on the choice of the one-electron functions used to build up CI spaces if the CI is not complete. For example, if the MO's from the closed-shell SCF are employed instead of the triplet SCF MO's, the energy gap between the 2^1A_g and ^1B_u states is extremely small (for variational energies, ~3 kcal/mol; for extrapolated energies, ~13 kcal/mol). In summary, for planar butadiene 2^1A_g and ^1B_u states most likely lie very close to each other.

At the 90° twist the second covalent state C lies close to but above both polar states Z_1 and Z_2. This indicates that there is a substantial mixing among the wave functions of all three excited

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Figure 2. μ_z^0 (O), μ_z^1 (×), μ_z^2 (□), and μ_z^3 (△) components of the dipole moment (in the direction of the C=C double bond) of S_0, S_1, S_2, and S_3 states of butadiene as a function of twist and prolongation of one C=C bond for the same treatment as in Figure 1. Negative and positive values of dipole moments mean extra charge on the methylene group and on the allylic triad, respectively.

states in the intermediate twist interval giving rise to several avoided crossings in this geometrical region. The dipole moment curves given in Figure 4 also reflect such a behavior. Around θ = 60° all three singlet excited states have almost the same absolute value of the dipole moment component $|\mu_z|$. For twist angles larger than 60° a pronounced polar character of $Z_1 = S_1$ and $Z_2 = S_2$ states develops and at θ = 90° the highest singlet excited state $S_3 = C$ finally becomes completely covalent in character. The analysis of the correlated wave functions in terms of localized structures given in Figure 5 demonstrates exactly the described features.

For this purpose it is extremely useful to express the correlated wave functions in the terms of localized VB-like structures. In order to characterize the states we use the square of the coefficients of the Slater determinants which are grouped into four contributions assigned to four structures in the localized representation. The procedure which transforms the CI expansion based on delocalized orbitals into the CI expansion based on localized orbitals is given in the Appendix. In short, four π localized MO's a − 1, a, b, and b + 1 (cf. Scheme II) are taken as the reference point. The localization of the corresponding MO's for $\theta \neq 90°$ is carried out by using a unitary transformation (cf. eq A1 and A2) so that the 20 Slater determinants for singlet states (4 π electrons, 4 MO's) can be transformed into the localized basis (cf. eq A5). Finally, the most important part of the calculated correlated wave functions for each state which consists of the coefficients of the reference configurations
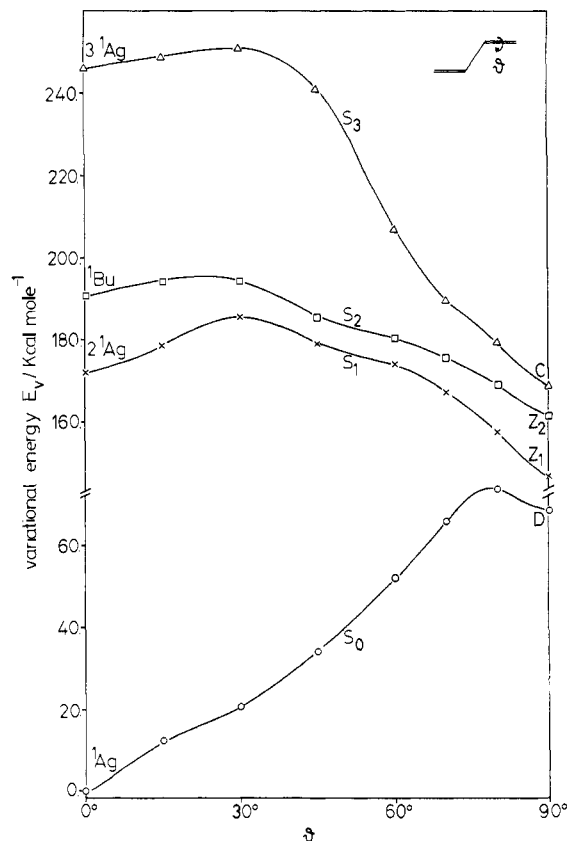
$$\Psi = \sum_{K=1}^{8} c_K \phi_K \qquad (8)$$

is transformed into the localized representation

$$\Psi = \sum_{J=1}^{20} \sum_{K=1}^{8} c_K \langle \phi_K | \phi_{J}' \rangle \phi_{J}' \qquad (9)$$

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Figure 3. Variational energies of the lowest four singlet states S_0 (O), S_1 (X), S_2 (□), and S_3 (△) of butadiene as function of simultaneous twist and elongation of one double bond obtained from the 8M/4R CI treatment with energy selection threshold $T = 12$ μhartree. From 198 092 spin-adapted functions up to 8650 configurations are selected (8 lowest occupied MO's and their virtual counterpart are not included in the CI). Triplet MO's are employed to build up the CI space.

Scheme VI

The ϕ_J' are then grouped into four contributions: (I) Slater determinant with allylic localized MO's occupied as in the ground state of allyl + singly occupied localized methylene MO's; (II) all Slater determinants with singly or doubly occupied virtual MO's of localized allylic character + singly occupied methylene localized MO; (III) all Slater determinants with doubly occupied methylene localized MO; (IV) all Slater determinants with two doubly occupied localized allylic MO's. They are labeled respectively as "ground state allyl + methylene", "excited allyl + methylene", "charge transfer to methylene", and "charge transfer to allyl". These four different kinds of contributions can be schematically represented by four structures: The analysis of all four wave functions in the twist interval in terms of the weighting factors α, β, γ, and δ of these four structures is given in Figure 5. The weight α of structure I increases with twisting for the ground states S_0. The first excited state contains an equal mixture of β and γ weights (structures II and III) at $\theta \approx 50°$ and resumes a completely polar nature with charge transfer to methylene at $\theta = 90°$ (large weight γ of structure III). The second excited state S_2, in the intermediate twisting interval, is a mixture of covalent structure II (large β) and of both charge transfer structures III and IV (γ and δ). At $\theta = 90°$ S_2 has a pronounced polar character with charge transfer to allylic triad (δ). The third excited state has contributions from all four structures at low twist angles and becomes covalent at $\theta = 90°$ with large contribution β of excited allyl + methylene structure (II).

In order to find out how the neglected portion of the electronic correlation affects the shapes of excited state energy surfaces we
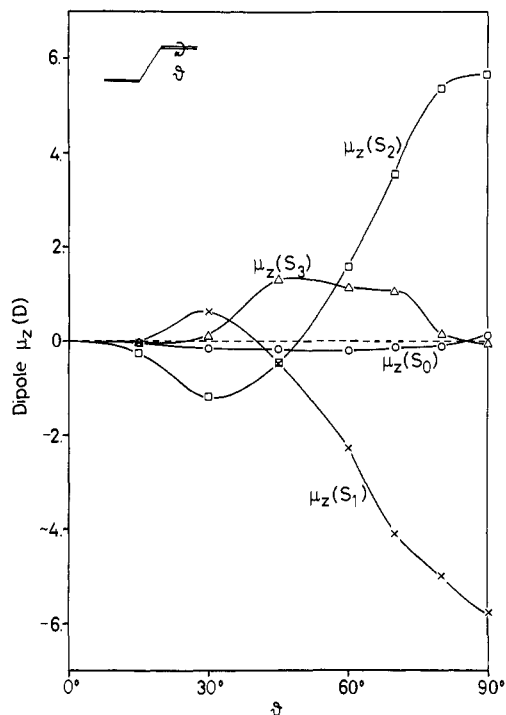

Figure 4. $\mu_z{}^0$ (O), $\mu_z{}^1$ (X), $\mu_z{}^2$ (□), and $\mu_z{}^3$ (△) components of dipole moment (in the direction of the C=C double bond) of S_0, S_1, S_2, and S_3 states of butadiene as a function of twist and prolongation of one C=C bond for the same treatment as in Figure 3.
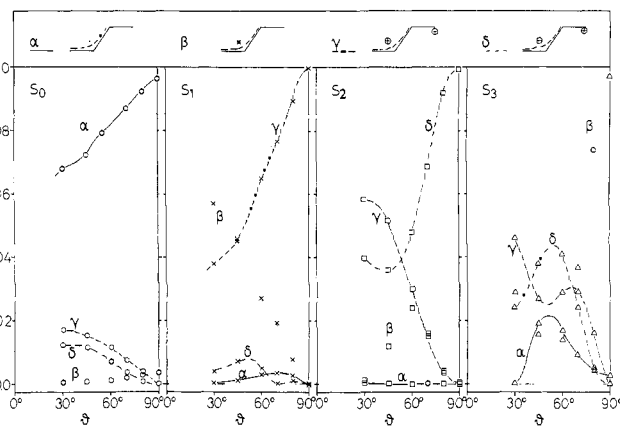
Figure 5. Weights α of ground state allyl + methylene, β of excited allyl + methylene, γ of charge transfer to methylene, δ of charge transfer to allyl VB-like structures (see eq 9 and Appendix) in the singlet states S_0, S_1, S_2, and S_3 of butadiene as a function of the twist and elongation of one double bond. Wave functions from a 8M/4R, $T = 12$ μhartree triplet-MO-CI treatment as in Figure 3. The analysis of the wave functions in the twist interval $0 < \theta < 30$ has not been carried out because localization necessary for the consideration of VB-like structures is not yet even approximatively reached.

have applied the averaged extrapolation technique described in section II and Siegbahn's correction (eq 7) for the "full" CI and the resulting energy surfaces are shown in Figures 6 and 7, respectively.

Both energy surfaces of the two lowest singlet excited states S_1 and S_2 approach each other closely for the intermediate twisting angles, while for $60° < \theta < 90°$ all three singlet excited states lie very close to each other. Moreover, there is an indication of two minima on the energy surface of the first excited state. Even when the identity of states loses its meaning in the region of large mixing, the variational wave functions are used to characterize the states corresponding to the extrapolated or full CI estimated energies. The first excited state in the interesting region of the twist interval $30° < \theta < 70°$ is of mixed covalent and ionic nature. At $\theta = 90°$ the extrapolation technique yields an excited covalent
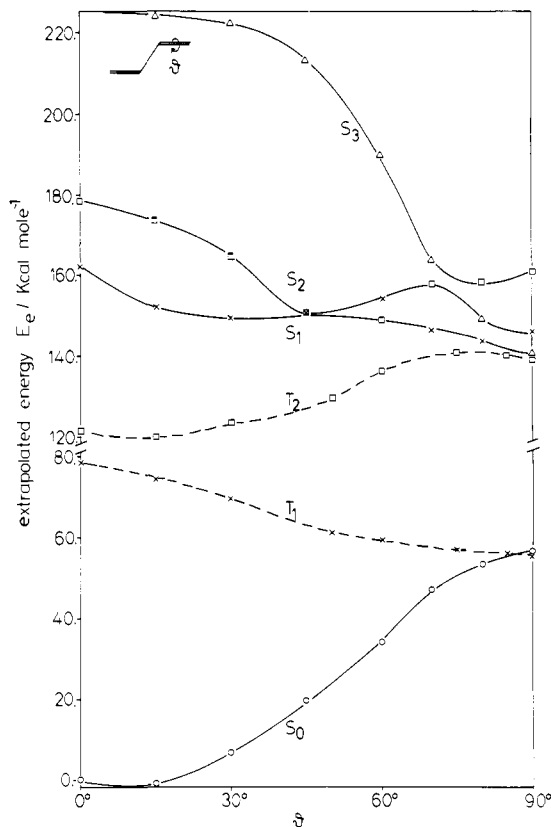
Figure 6. Averaged extrapolated energies ($T \rightarrow 0$) toward "full" single and double multireference CI (cf. eq 4 and 5) of the four lowest singlet states S_0, S_1, S_2, and S_3 and the two lowest triplet states T_1 and T_2 of butadiene as a function of twist and elongation of one double bond. For singlet states the extrapolation has been carried out for the energies obtained from 8M/4R, $T = 12$ μhartree triplet-MO-CI treatment as in Figure 3. For triplet states the extrapolation has been made for energies obtained from the 6M/2R, $T = 10$ μhartree CI treatment with triplet SCF MO's from the lowest triplet. For the choice of reference configurations see section II. (For singlet excited states ×, □, and △ label the first, second, and third excited states according to energy ordering obtained from variational treatment.)

state as the lowest excited state while the full CI estimate places the covalent state between two polar states. This is by no means a definitive determination of the relative position of excited states (covalent vs. polar) but it is a definite indication that the role of the excited covalent state might be as important as the role of zwitterionic states for the photochemical processes involving such biradical geometries.

Taking advantage of the C_s symmetry at the 90° twist we have carried out larger CI treatments for two covalent states (5M/2R, $T = 6$ μhartree) and for two zwitterionic states (4M/2R, $T = 5$ μhartree) separately using NO orbitals of each state as one-electron functions for building up the CI spaces. In this case, variational, extrapolated and full CI estimated procedures yield the same energy ordering of the states; i.e., the excited covalent state C lies in between the two zwitterionic states Z_1 and Z_2 (Table I).

In order to find out if the exclusion of eight occupied and eight virtual orbitals from the CI treatment influences the ordering of the states, we have employed additional CI treatments in which only four occupied and four virtual counterparts are deleted. The NO-CI treatments analogous to those of Table I have been carried out. Only the energy selection threshold T has been increased to 20 μhartree because of larger CI spaces due to the smaller number of one-electron functions excluded from the CI. Again the covalent excited state C lies in between two zwitterionic states Z_1 and Z_2 ($\Delta E(Z_1-Z_2) = -13$ kcal/mol, $\Delta E(Z_1-C) = -9$ kcal/mol). In other words, more extended CI treatment involving 22 electrons yields the same ordering of covalent vs. ionic excited states at the 90° twist as the CI applied on 14 electrons.
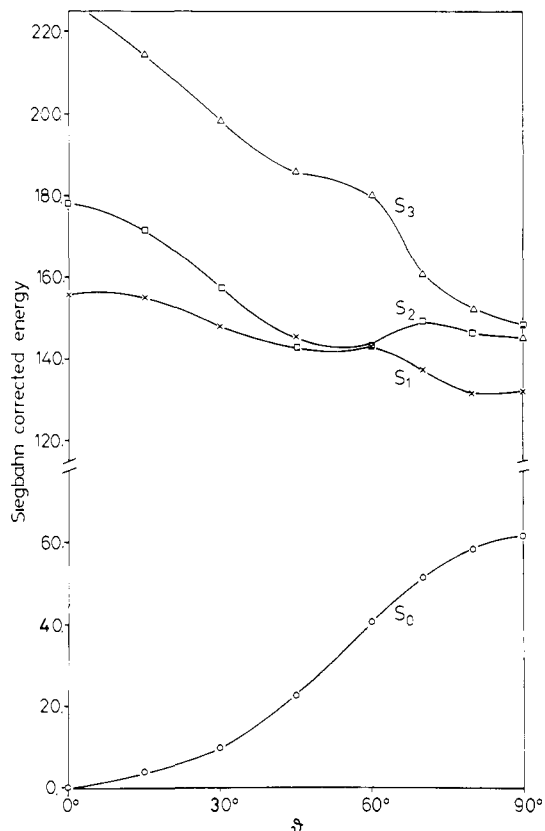
Figure 7. Siegbahn's "full" CI estimated energies (cf. eq 7) of four lowest singlet excited states of butadiene as a function of twist and elongation of one double bond. The correction has been introduced for the energies obtained from the CI treatment described in Figures 3 and 6.

Table I. CI Energies (in au) for the 90° Terminally Twisted Butadiene in C_s Symmetry Employing Natural Orbitals as One-Electron Functions

one-electron basis	covalent states[a]		ionic states[b]	
	D, NO(1^1A'')	C, NO(2^1A'')	Z_1, NO(1^1A')	Z_2, NO(2^1A')
$E_v{}^c$	−154.7523	−154.6070	−154.6318	−154.6091
$E_{ex}{}^d$	−154.7617	−154.6297	−154.6355	−154.6130
$E_{FCI}{}^e$	−154.7708	−154.6388	−154.6491	−154.6272

[a] 4M/2R, $T = 5$ μhartree treatments with NO(1A'') and NO(2A'') as one-electron functions obtained from the corresponding triplet-MO-CI treatment for two A'' states. [b] 4M/2R, $T = 5$ μhartree treatments with NO(1A') and NO(2A') as one-electron functions obtained from the corresponding triplet-MO-CI treatment for two A' states. [c] Variational energies. [d] Extrapolated energies. [e] Davidson's "full" CI estimate for energies.

Furthermore, the pyramidalization of the methylene group lowers only the zwitterionic polar state with extra charge on the methylene group Z_1. In contrast, this geometrical change is unfavorable for all of the other three states: for both covalent states and for the polar state with extra charge in an allylic triad (Table II). Therefore, it is to be expected that at $\theta = 90°$ the covalent excited state lies between the two polar states. This ordering might be very easily influenced by any chemical substitution.

The two energy hypersurfaces for the two lowest triplet states have been determined for the whole twist interval as shown in Figure 6. The twisting and simultaneous prolongation of one double bond in butadiene is energetically favorable for the lowest triplet state, while the second triplet exhibits a barrier to rotation. At the 90° twist the energies of the lowest triplet and singlet states almost coincide and the second triplet lies slightly below the first excited singlet state.

The wave function of the lowest triplet state can be characterized by the localized diradical triplet structure (ground state

Table II. Energies (in au) for the 90° Terminally Twisted Butadiene with Pyramidalization at the CH_2 Group in C_s Symmetry

$\phi,^c$ deg		covalent states^a		ionic states^b	
		$1^1A''$	$2^1A''$	$1^1A'$	$2^1A'$
0	$E_V{}^d$	-154.7487	-154.5962	-154.6154	-154.5922
	$E_{ex}{}^e$	-154.7614	-154.6309	-154.6205	-154.5973
	$E_{FCI}{}^f$	-154.7714	-154.6400	-154.6548	-154.6292
20	$E_V{}^d$	-154.7455	-154.5910	-154.6194	-154.5843
	$E_{ex}{}^e$	-154.7610	-154.6308	-154.6304	-154.5967
	$E_{FCI}{}^f$	-154.7707	-154.6397	-154.6543	-154.6208
40	$E_V{}^d$	-154.7408	-154.5874	-154.6246	-154.5581
	$E_{ex}{}^e$	-154.7566	-154.6266	-154.6367	-154.5709
	$E_{FCI}{}^f$	-154.7541	-154.6355	-154.6612	-154.5951
60	$E_V{}^d$	-154.7278	-154.5743	-154.6275	-154.5201
	$E_{ex}{}^e$	-154.7442	-154.6150	-154.6393	-154.5600
	$E_{FCI}{}^f$	-154.7541	-154.6242	-154.6651	-154.6242

^{a} 4M/2R, $T = 6$ μhartree CI treatment employing triplet MO's as one-electron functions to build up CI spaces for two singlet A'' states. ^{b} 6M/2R, $T = 6$ μhartree CI treatment employing triplet MO's as one-electron functions to build up CI spaces for two singlet A' states. ^{c} Pyramidalization angle. ^{d} Variational. ^{e} Extrapolated. ^{f} Davidson "full" CI estimated energies.

allyl + methylene) through a large part of the twist interval. At the 90° twist one singly occupied MO is of pronounced methylenic nature and in the other singly occupied MO prevails a nonbonding allylic orbital with a larger AO coefficient at the carbon atom attached to the twisted bond. Therefore, the lowest triplet is fairly localized in the twisted double bond. In the expansion of the wave function of the second triplet state for the planar geometry three configurations a – 1 → b, a → b + 1, and b – 1 → b + 1 play a leading role. At the 90° twist three leading configurations are triplet analogues to the three dominant configurations of the singlet covalent excited state C (M_5, M_7, M_8; cf. Scheme I). Therefore, the second triplet at $\theta \simeq 90$ can be characterized by the localized excited covalent triplet structure (excited allyl + methylene).

IV. Discussion

The influence of simultaneous twist and elongation of one double bond in butadiene on its low-lying singlet excited states can be qualitatively discussed with the help of estimated energies of three VB-like structures as shown in Scheme VII. The energy of the excited allyl + methylene structure remains almost constant while the energies of both charge transfer structures to methylene and to allyl decrease as the twisting and elongation of the C=C bond advances. At the 90° twist, due to the C_s symmetry of the nuclei, the excited allyl + methylene contribution to the wave function cannot mix with charge transfer contributions, so that excited states can be easily characterized as covalent C and charge transfer $Z_1(-)$ and $Z_2(+)$ with opposite dipole moments, respectively. In the neighborhood of $\theta = 90°$ contributions from all three structures basically enter the correlated wave functions of all three singlet excited states. For the intermediate twisting angles the interaction between the covalent structure and the charge transfer to methylene is likely to occur. Consequently, one can expect that, if the lowest excited singlet state exhibits a minimum for 30 < θ < 60, the corresponding wave function should be of mixed covalent and ionic nature. Whether the covalent or ionic character prevails depends on the region where the minimum occurs. The wave functions of the singlet excited states corresponding to the minima at the 90° twist are either purely polar or purely covalent in nature.

Our largest CI treatments predict the polar state with charge transfer to the methylene group to be the lowest singlet excited state at the 90° twist, although the covalent state and another polar state with an opposite μ_z component of the dipole moment lie very close to it.

There is also a strong indication that another minimum on the lowest singlet energy surface might occur at an intermediate twist angle. The exact location of this minimum and quantitative determination of its relative position with respect to the minimum at the 90° twist are beyond the scope of the present investigation. It is necessary to emphasize that even for a qualitative discussion

Scheme VII
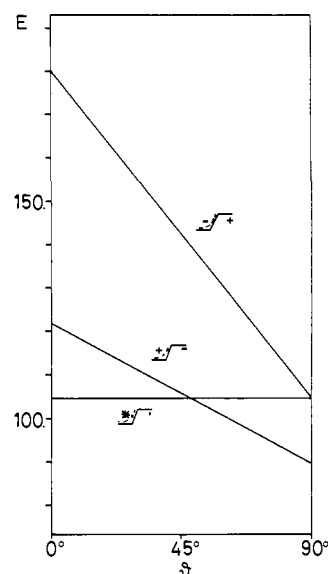
of the low-lying singlet excited states, state-of-the-art large-scale CI treatments are necessary. The correlation effects introduced only among π electrons or configuration selection based on chemical intuition[33] might easily lead to a wrong qualitative description of the states under consideration. In treatments of this type the covalent states are usually better described than the zwitterionic ones during the geometrical relaxation so that an overall unbalanced picture might arise.

A possible existence of a minimum away from the 90° twist in the lowest singlet excited state (a prediction which should be taken with caution) implies that the return to the ground state singlet energy surfaces from such a minimum has only one downhill direction. In contrast, the return from a minimum at the 90° twist to the ground state singlet has two equivalent downhill directions. The funneling from such different minima[3] with a very different electronic nature might easily be responsible for very different photochemical yields in the cis–trans isomerization of different polyenes. Certainly, the notion that a nearly 50:50 partitioning between the two ground state geometrical isomers is the only possibility is untenable.[34] The energy surface of S_1 between 20° and 160° twist is so flat that further perturbation of substituents, steric constraints, etc., can easily result in a minimum anywhere in that region depending on the detailed molecular structure of the diene.

The theoretical understanding of the electronic structure of the corresponding wave functions (covalent vs. ionic or mixed) is important for a mechanistic view of the reactions involving such intermediates.[35,36]

It is worth mentioning that the polarity of the two zwitterionic states develops gradually and is large over a large interval of the twist angle, so that the zwitterionic states do not acquire their polarity suddenly. As there is substantial mixture of covalent and ionic nature in a large part of the twist interval, it is difficult to separate chemistry resulting from covalent or polar excited states. Moreover, in this region the vibronic coupling between covalent and ionic Born–Oppenheimer states might certainly play an important role.

(33) The energy surfaces for the four singlet states obtained by one of the authors (A.S.) employing a CI treatment with 100 configurations intuitively chosen are very similar to those obtained with the "4π-CI" treatment (cf. Figure 1). This investigation has been started at the CECAM Workshop "On Sudden Polarization Effects", 1979.

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Appendix

Expansion of the CI Wave Functions in the Basis of Localized Orbitals of Butadiene. The two highest occupied and two lowest unoccupied MO's of 90° terminally twisted butadiene are taken as localized reference orbitals $|R_J\rangle$ (cf. Scheme II, a − 1, ..., b + 1). Small AO coefficients at hydrogen atoms or the contribution of σ orbitals to four MO's are neglected so that entire localization at the CH_2 and at the allylic fragments is introduced.

For any twist angle $\theta \neq 90$ a rotation around the z axis is applied to HOMO yielding perpendicular conformation with respect to the CH_2 fragment. The localized orbitals $|R_J\rangle$ are then renormalized.

In order to obtain localized orthonormal orbitals $|L_1\rangle...|L_4\rangle$, we apply a unitary transformation U to the set of MO's $|M_1\rangle...|M_4\rangle$ for any twist angle θ:

$$\{...|L_J\rangle...\} = \{...|M_I\rangle...\}U \qquad (A1)$$

with

$$u_{IJ} = \langle M_I|L_J\rangle \qquad (A2)$$

The U matrix is determined through an iterative procedure according to the maximum-overlap criterium between the resulting $|L_J\rangle$'s with the reference orbitals $|R_J\rangle$:

$$\sum_J \langle R_J|L_J\rangle^2 = \text{max} \qquad (A3)$$

The transformation of Slater determinants ϕ_K built from the SCF MO's

$$\phi_K = \frac{1}{(4!)^{1/2}}\hat{\mathcal{A}}[|M_{K_1}\alpha\rangle|M_{K_2}\alpha\rangle|M_{K_3}\beta\rangle|M_{K_4}\beta\rangle] \qquad (A4)$$

into the Slater determinants ϕ_L' built from the localized orbitals

$$\phi_J' = \frac{1}{(4!)^{1/2}}\hat{\mathcal{A}}[|L_{J_1}\alpha\rangle|L_{J_2}\alpha\rangle|L_{J_3}\beta\rangle|L_{J_4}\beta\rangle] \qquad (A5)$$

is where the $u_{K_iL_j}$ are defined by eq A2. The expansion of the

$$\langle\phi_K|\phi_J'\rangle = \det\begin{pmatrix} u_{K_1L_1} & u_{K_1L_2} \\ u_{K_2L_1} & u_{K_2L_2} \end{pmatrix} \det\begin{pmatrix} u_{K_3L_3} & u_{K_3L_4} \\ u_{K_4L_3} & u_{K_4L_4} \end{pmatrix} \qquad (A6)$$

correlated wave function for each state considered is

$$\Psi = \sum_{J=1}^{20}\sum_{K=1}^{8} c_K\langle\phi_K|\phi_J'\rangle\phi_J' \qquad (A7)$$

Optical Studies of a Simple Polyene Schiff Base: Low-Lying Electronic Levels in the Free, Hydrogen-Bonded, and Protonated Species

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Abstract: Fluorescence and fluorescence excitation spectra of a model polyene Schiff base, *N*-(2,4,6,8,10-dodecapentaenylidene)butylamine, have been obtained in 77 K hydrocarbon glasses. The low-energy electronic transitions of this polyene Schiff base have been studied in a variety of hydrogen-bonding and protonating environments. All spectra are well resolved and allow the accurate location of electronic origins. For all three species, i.e., free Schiff base, hydrogen-bonded Schiff base, and protonated Schiff base, the fluorescence origins are substantially red shifted (3108, 2774, and 2238 cm^{-1}) from the origins of the strongly allowed absorptions. These experiments show that the lowest excited singlet in each of these Schiff base species correlates with the forbidden A_g^- states observed in analogous polyene hydrocarbons. These findings are compared with current theoretical predictions and discussed with regard to their implications for the photochemistries of other polyene Schiff bases, including rhodopsin.

Linearly conjugated π-electron systems have received considerable experimental and theoretical attention in recent years. This in large part stems from the involvement of polyenes (retinylidene Schiff bases) as chromophores in vision and certain photosynthetic processes.[2–4] The investigation of the *initial* photochemical events in these important biological processes has been an area of active interest.[5] Many studies have tried to develop a better description of polyene electronic states in order to consider possible mechanisms by which these chromophores funnel electronic excitations into specific chemical events, e.g., isomerizations and proton transfers.

A large share of the recent spectroscopic and theoretical work on polyenes has centered on simple hydrocarbons.[6–9] These systems offer several critical advantages. Their symmetries (C_{2h} point group for all-trans isomers) relieve computational burdens

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