ON AVOIDED CROSSING BETWEEN MOLECULAR EXCITED STATES;

PHOTOCHEMICAL IMPLICATIONS

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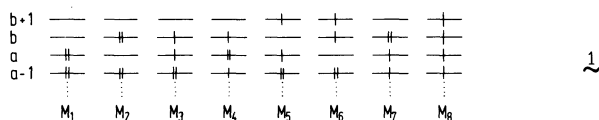Institut für Physikalische Chemie, Freie Universität Berlin, Takustr. 3, 1000 Berlin 33, BRD

Abstract - Consequences of geometrical relaxation in butadiene and in un-protonated Schiff base-allylideneimine (torsion around C=C, C=N and C-C bonds) for low lying singlet and triplet states have been investigated employing large scale CI treatments. The analysis of the correlated wavefunctions in terms of the VB-like ionic and covalent structures has been carried out. Importance of zwitterionic highly polar states of dienes as well as of the low lying covalent excited state has been discussed. Photochemical implications of different minima on the energy surfaces of excited states with contrasting features of the wavefunctions have been proposed.

INTRODUCTION

After the light absorption and during usually rapid thermalization a molecule seeks after a minimum on the energy surface of the excited state. Finding such minima through which the funneling to the ground state might occur and characterization of the corresponding wavefunctions is of great importance for proposing mechanisms of photochemical reactions which involve such geometrically relaxed species as intermediates. An important geometrical variation which can take place in photoisomerization of polyenes and their analogs (unprotonated Schiff bases) is the twisting motion of one C=C double bond or of one hetero C=N double bond (1-7). It has been found several years ago (8), and since intensively investigated (9-22), that the twisting around one olefinic double bond giving rise to an asymmetrical biradical invokes new features in low lying zwitterionic singlet states (sudden polarization effect). It is possible to expect that besides these zwitterionic polar states also low lying covalent excited states might play an important role in photochemistry of polyenes and Schiff bases. Therefore, we have studied the consequences of geometrical relaxations on low lying singlet and triplet states of two dienes (butadiene and allylideneimine) employing ab initio large scale configuration interaction (CI) treatments. The leading terms of the large correlated wavefunctions have been transformed into the ionic and covalent VB-like structures so that the nature of excited states can be discussed in more chemical terms. The assignment of ionic, covalent or mixed features to the wavefunctions at the found minima has been made. With this tool the regions of avoided crossings and therefore the calculated shapes of energy surfaces in different twisting intervals are easily comprehended. Comparison between the geometrical relaxation in butadiene and in allylideneimine is particularily important for an understanding of the qualitative difference between the nature of intermediates with partly broken homoatomic and heteroatomic double bond.
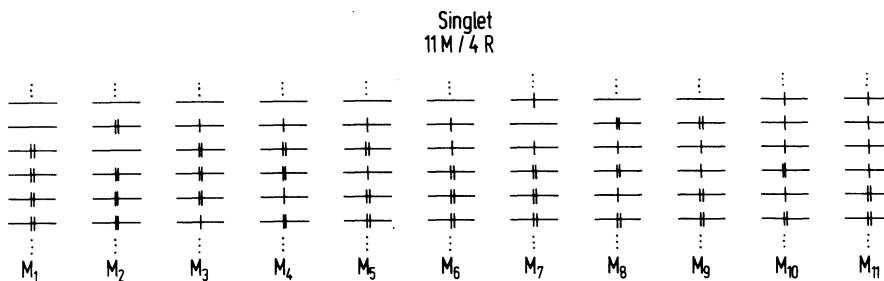
METHOD

For simultaneous description of four singlets and three triplets in different twist intervals multireference double CI treatment MRD-CI (23) has been employed. Because the emphasis is put on the relaxed geometries and not on planar ones, relatively small AO basis sets of double zeta quality (24) when utilized yield reliable results (18). Therefore, the 4-31G basis (25) has been employed for consideration of valence states. For Rydberg states of planar butadiene compare ref. (26-28). The triplet SCF MO's have been used as one-electron functions to span the singlet and triplet CI spaces because this one-electron basis yields a balanced description of both diradical centers (10,14,15). For a description of four singlet states of butadiene in the twist interval $\Theta=[0,90^{\circ}]$ 8 reference configurations given in Scheme $\underset{\sim}{1}$ are neces-
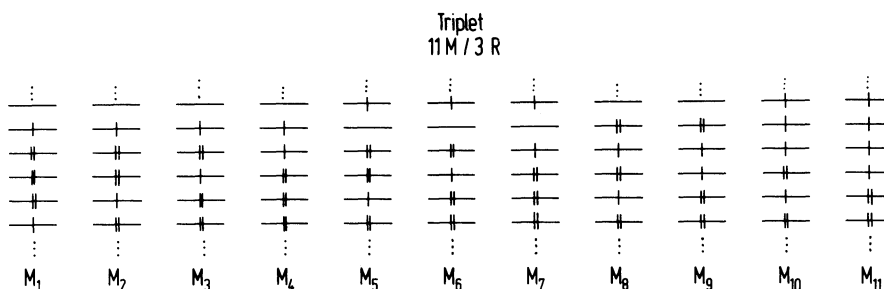


sary (eight mains/four roots (8M/4R) treatment). They differ in occupation numbers of four π

MO's. For two triplets the reference space consist of 6 configurations $M_3$ to $M_8$ of $1$ except that $M_6$ is replaced by the singly excited configuration (a-1)→(b+1) (6M/3R treatment). The configurations which span the reference spaces in the CI treatments of four singlets and three triplets of allylideneimine in both twist intervals (for C=C, and C=N bonds) are given in Scheme $2$ and $3$, respectively.

**Singlet**
**11 M / 4 R**



$M_1 \quad M_2 \quad M_3 \quad M_4 \quad M_5 \quad M_6 \quad M_7 \quad M_8 \quad M_9 \quad M_{10} \quad M_{11}$

$2$

**Triplet**
**11 M / 3 R**



$M_1 \quad M_2 \quad M_3 \quad M_4 \quad M_5 \quad M_6 \quad M_7 \quad M_8 \quad M_9 \quad M_{10} \quad M_{11}$

$3$

Obviously, leading configurations involve excitations from MO's containing nitrogen lone pair AO's in addition to the excitations among four π MO's. In both cases, for butadiene and for allylideneimine the 8 lowest occupied MO's and their virtual counterparts are excluded from the CI treatments. Although the correlation is taken into account only for 14 electrons, dimensions of the CI spaces for multireference-multi roots treatments range from ∼200 000 to ∼600 000. Employing the energy selection threshold T (23) we select up to ∼10 000 configurations. In order to determine the energies for T→0 (full MRD-CI) the averaged extrapolation technique (29) has been employed and the full CI estimated energies according Siegbahn (30) have been calculated. Use of the energy selection procedure is less critical for determination of singlet excited states for allylideneimine than for butadiene. In the latter case the singlet excited states undergo weakly avoided crossings so that the detail of the CI treatment is important for their description.

### GEOMETRICAL RELAXATION IN LOW LYING SINGLET AND TRIPLET STATES OF BUTADIENE.

Although the main emphasis has been put on determination of properties of excited states and on characterization of their main features for non equilibrium geometries, the excited states for the planar geometry have been also considered. The described large scale 8M/4R CI treatment yields $2^1A_g$ state below the $^1B_u$ state (cf. References 31-35). As expected one doubly excited and two complementary singly excited configurations ($M_2$, $M_4$ and $M_5$ from Scheme $1$) contribute mostly to the expansion of the $2^1A_g$ wavefunction with almost equal weights. The energy gap between the two lowest valence excited states $2^1A_g$ and $^1B_u$ is relatively small and depends on details of the CI treatment employed (cf. Reference 29).
For the 90° terminally twisted butadiene four important MO's which are differently occupied in the reference configurations are fairly localized at allylic or at methylenic part of the molecule (Scheme $4$). Therefore, the correlated wavefunctions of four singlet states can be analyzed in terms of four localized VB-like structures (Scheme $5$): I "ground state allyl +



$a-1 \qquad\qquad a \qquad\qquad b \qquad\qquad b+1 \qquad\qquad 4$
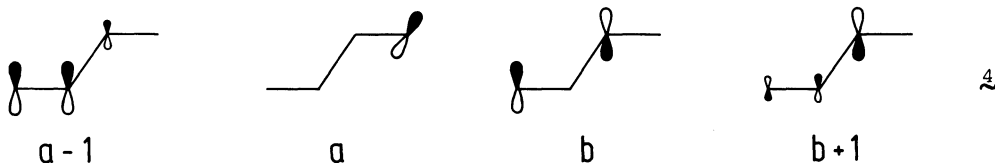
methylene", II "excited allyl + methylene", III "charge transfer to methylene" and IV "charge transfer to allyl".

$$\underset{I}{\phantom{x}} \qquad \underset{II}{\phantom{x}} \qquad \underset{III}{\phantom{x}} \qquad \underset{IV}{\phantom{x}}$$

$$\underset{\sim}{5}$$
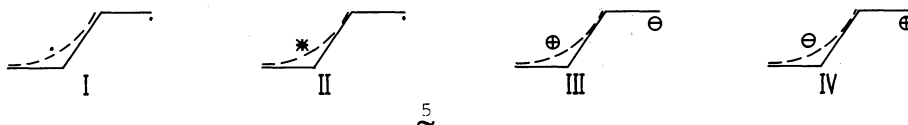
The procedure employed to transform the correlated wavefunctions (obtained by the large CI treatments) from the delocalized to the localized representation described in Reference (29) can be applied for large part of the twist interval in which the four MO's are localized to some extent. At the $90^{\circ}$ twist the lowest singlet state D is of covalent diradical nature (Scheme 6) while the second covalent state C contains three equally dominant configurations which are represented by an "excited allyl + methylene" VB-like structure (Scheme 7).

$$\underset{\sim}{6} \qquad D$$

$$M_5 \qquad M_7 \qquad M_8 \qquad \qquad C$$

$$\underset{\sim}{7}$$
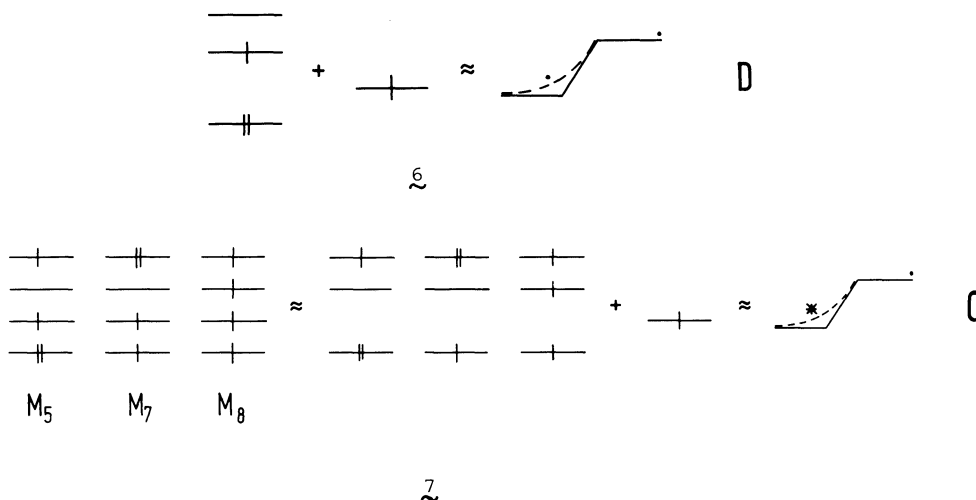
Two zwitterionic states $Z_1$ and $Z_2$ are of polar nature because of dominant contribution with charge transfer to methylene and to allyl, respectively (Scheme 8).

$$Z_1 \qquad\qquad\qquad Z_2$$

$$\underset{\sim}{8}$$
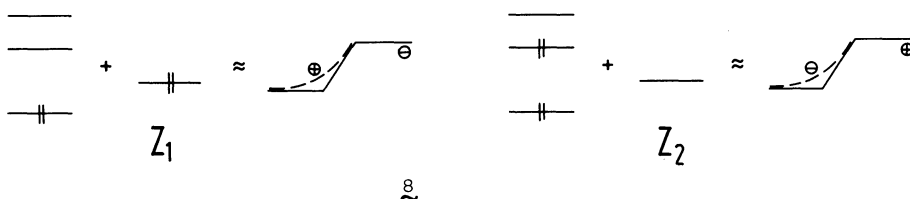
The variational energies of four singlet states for the planar and the $90^{\circ}$ twisted geometries are given in Figure 1. The avoided crossing between covalent excited state and both polar zwitterionic states indicated in Figure 1 have been found employing the analysis of the wavefunctions in terms of the VB-like structures. Curves of dipole moment component $\mu_z$ given in Figure 2 demonstrate also a large mixing between covalent and zwitterionic states in the intermediate twist interval. The complete energy surfaces for twist and elongation of one C=C bond obtained by the averaged extrapolation technique and full CI estimated energies (cf. Ref. 29) are given in Figures 3 and 4, respectively. The ordering of the singlet excited states at the $90^{\circ}$ twist depends on details of the CI procedure employed. It seems most likely that the covalent excited state C lies in between two zwitterionic polar states $Z_1$ and $Z_2$ (with dipole moment components oriented in opposite direction). Fairly flat shape of the energy surface of the first singlet excited state $S_1$ indicates that besides a minimum at $\Theta = 90^{\circ}$ another minimum might occur at an intermediate twist angle. The corresponding wavefunctions differ substantially in nature. At the $90^{\circ}$ twist the $S_1 = Z_1$ is of pronounced polar nature with extra charge on methylene group while at intermediate twist angles the $S_1$ state is a mixture of covalent and ionic contributions with prevailing covalent features. Which of the two minima is lower depends on the detailed molecular structure of the diene. The funneling through such two minima of $S_1$ to the ground state $S_0$ which exhibits a maximum in energy at $\Theta = 90^{\circ}$ should give rise to different photochemical yields of two ground state isomers. Moreover, the photochemistry in solution should distinguish processes involving excited states of covalent, ionic or mixed nature.
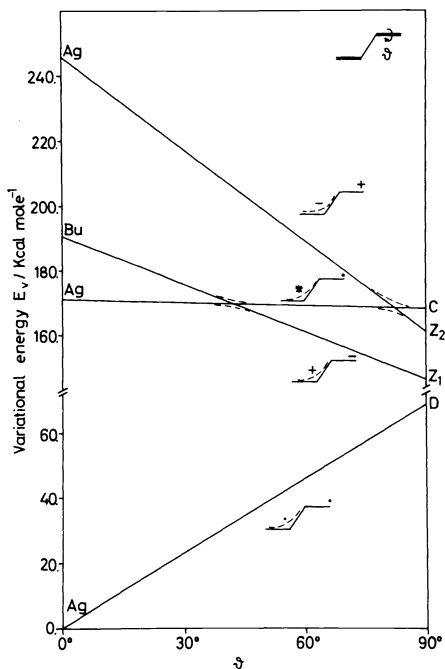
Fig. 1 Variational energies of $S_0$, $S_1$, $S_2$, $S_3$ of butadiene at $\Theta = 0°$ and $90°$ obtained from the 8M/4R,T=12μh CI treatment. The end points are connected with straight lines according to the main features of the wavefunctions expressed in terms of VB-like structures I-IV.
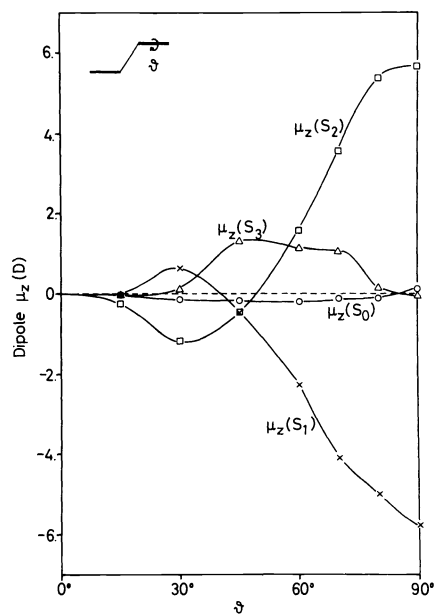


Fig. 2 The $\mu_z^0$(-o-), $\mu_z^1$(-x-), $\mu_z^2$(-□-), $\mu_z^3$(-Δ-) components of dipole moment (in the direction of the C=C bond) of $S_0$, $S_1$, $S_2$ and $S_3$ states of butadiene as a function of torsion and elongation of one C=C bond for the same treatment as in Fig. 1.
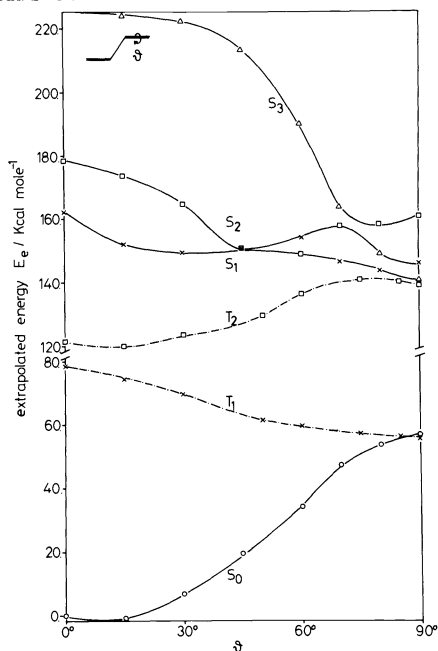


Fig. 3 Averaged extrapolated energies T→O for 4 singlet states and 2 triplet states of butadiene as a function of twist and elongation of one C=C bond (from 1.337 to 1.416 Å). The extrapolation is carried out for the energies obtained from 8M/4R,T=12μh and 6M/3R,T=10μh CI treatments for singlets and triplet, respectively. (x, □ and Δ label $S_1$, $S_2$ and $S_3$ according to energy ordering obtained from variational treatments.
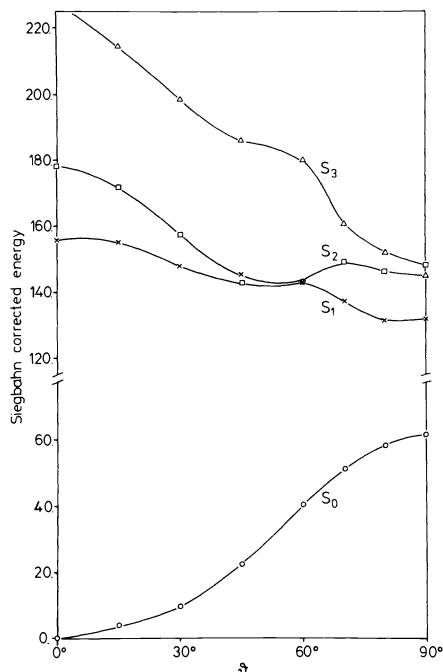


Fig. 4 Siegbahn's full CI estimated energies of $S_0$, $S_1$, $S_2$ and $S_3$ states of butadiene as a function of twist and elongation of one C=C bond. The correction has been introduced for the energies obtained from the CI treatment described in Figures 1 and 3.

The twist and elongation of one C=C bond is energetically favorable for the lowest triplet state $T_1$ while the second triplet $T_2$ exhibits a barrier (cf. Figure 3). The lowest triplet state can be qualitatively characterized by localized triplet diradical structure I. At the $\theta=90^{\circ}$ HOMO has methylenic features and LUMO is of allylic nonbonding nature but with larger coefficient at the carbon atom attached to the twisted bond so that the localization in the twisted bond is apparent. At planar geometry three configurations (a-1)→b,(a→b+1) and (b-1)→(b+1) dominate the expansion of the wavefunction of the second triplet. At the $90^{\circ}$ twist second triplet can be characterized by the triplet, "excited allyl + methylene" structure. The wavefunction is dominated by triplet analogs to three leading configurations of the co-valent excited singlet state C. For the twisted geometries there are two pairs of very close lying triplet and singlet states $S_0$, $T_1$ and $S_1$, $T_2$ (cf. Figure 3).

GEOMETRICAL RELAXATION IN LOW LYING SINGLET AND TRIPLET STATES OF UNPROTONATED SCHIFF BASE (ALLYLIDENEIMINE)

Most important MO's for planar and the terminally twisted ($\theta_1$=90 and $\theta_3$=90) geometries of allylideneimine are given in Scheme 9



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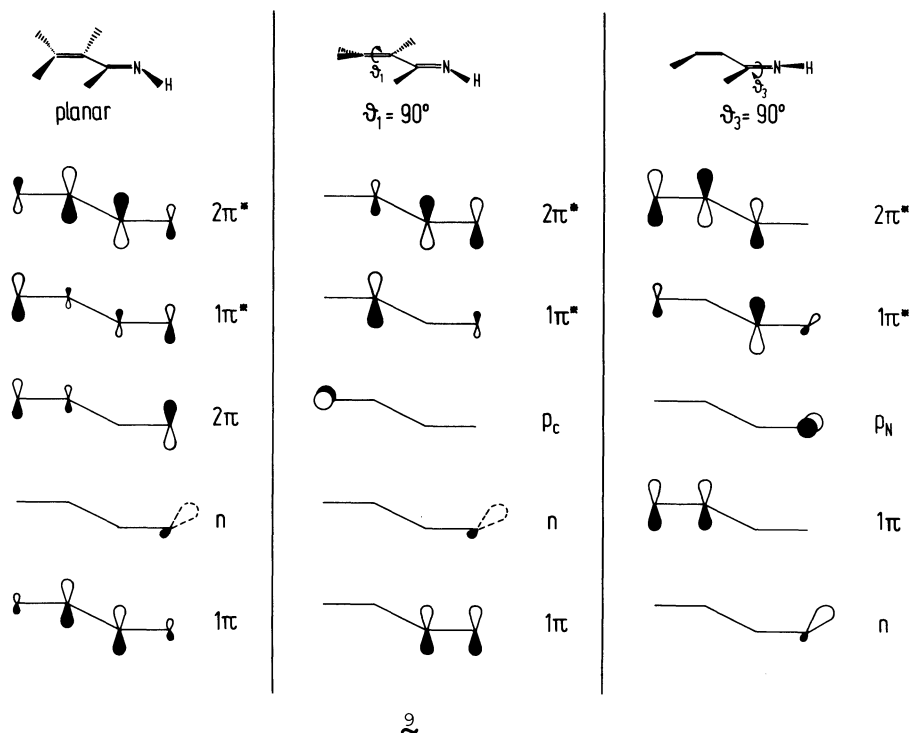
The leading configurations in the wavefunctions of singlet and triplet states considered in both twisting intervals (around C=C and C=N bonds) differ in occupation numbers of these five MO's (cf. Scheme 2 and 3). In addition to excitations from two bonding to two antibonding π MO's as in the case of butadiene, the excitations from the MO with primarily nitrogen lone pair character is important for the low lying excited states. In a fact for the planar geome-try the first valence excited singlet state is n→1π* state while $S_2$ and $S_3$ are analogous to the $2^1A_1$ and $^1B_u$ state of planar butadiene.
Again the analysis of the correlated wavefunctions can be easily carried out in terms of lo-calized VB-like structures due to localized nature of MO's at $\theta_1$=90$^{\circ}$ and of $\theta_3$=90$^{\circ}$. For the 90$^{\circ}$ twist around C=C bond the main features of the correlated wavefunctions together with the localized structures are given in Scheme 10. The lowest singlet state $S_0$ is of diradical nature, while the first excited state $S_1$ is a mixture of ionic structure with charge trans-fer to the CCN triad and of covalent structure with excitations within the CCN triad. Two highest lying considered singlet excited states are zwitterionic polar states $S_2$ and $S_3$ with charge transfer to the methylene and charge transfer to the CCN triad, respectively. In com-paring the main features of these states with those of four singlet states for the 90$^{\circ}$ twist-ed butadiene there is a striking difference in the nature of the $S_1$ state due to the asymme-try introduced through the nitrogen atom in allylideneimine. Namely the mixture of covalent and ionic structures is now possible even at $\theta_1$=90$^{\circ}$. Therefore, the energy of $S_1$ is consi-derably lower than the energies of two zwitterionic very close lying polar states $S_2$ and $S_3$ as shown in Figure 5. The acceptor effects of methylene and nitrogen atom at different ends of the molecule are in competition with each other. Consequently there are no three very close lying singlet excited states at $\theta_1$=90$^{\circ}$ as in the case of butadiene.
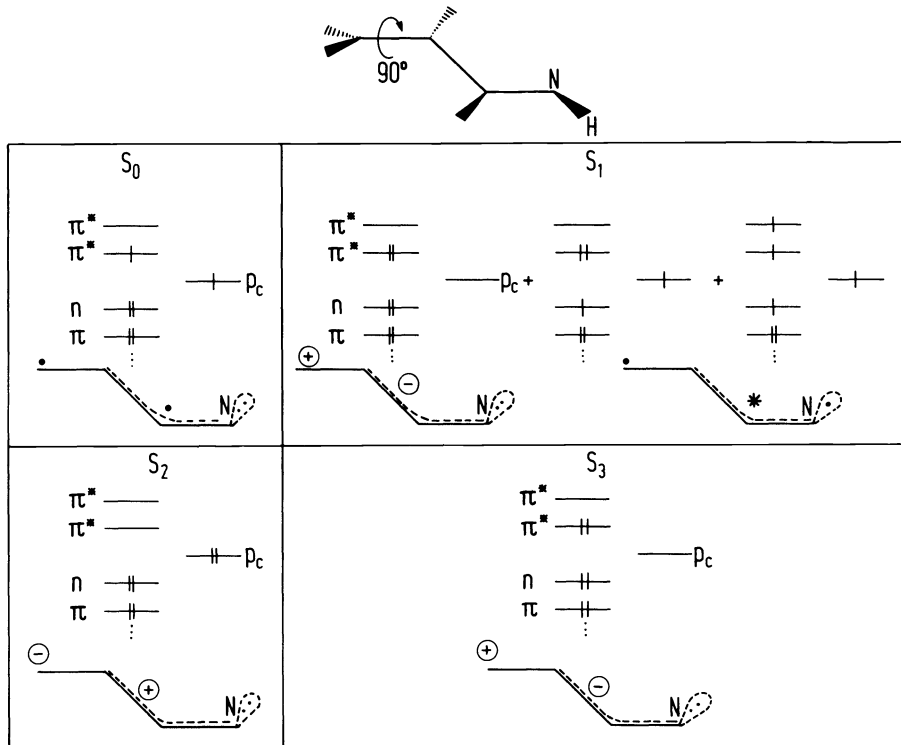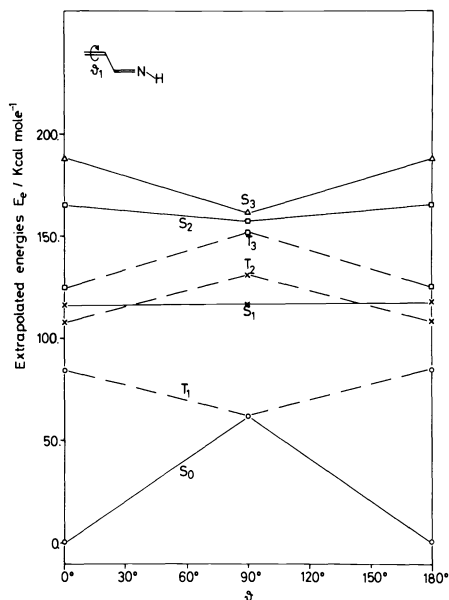
Fig. 5 The averaged extrapolated energies of four singlet and three triplet states for the planar allylideneimine and the 90° twisted around C=C bond obtained from 11M/4R and 11M/3R,T=15μh CI treatments (cf. Scheme 2 and 3). The end points are connected with straight lines. The C=C bond is elongated from 1.345 at $\theta_i$=0° to 1.416 Å at $\theta_1$=90°.
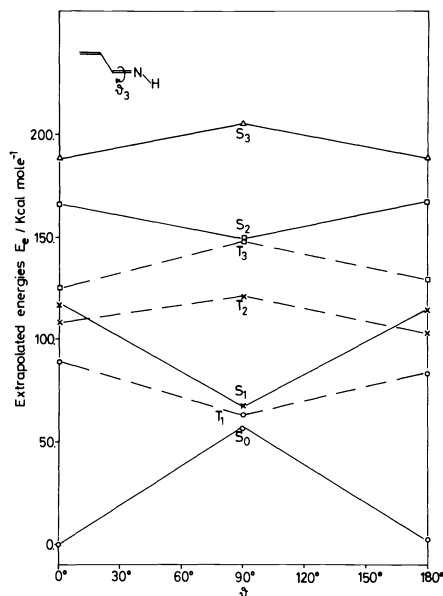
Fig. 6 The averaged extrapolated energies of four singlet and three triplet states for planar allylideneimine and the 90° twisted around C=N bond obtained from the analogous CI treatments as in Fig. 5. The end points are connected with straight lines. The C=N bond is elongated from 1.30 at $\theta_3$=0° to 1.37 at $\theta_3$=90°.

Nevertheless, the twist around the C=C bond in allylideneimine is not energetically favorable for the first singlet excited state $S_1$. There is a barrier to rotation in $S_1$ indicating an avoided crossing between $S_1$ and $S_2$ states (cf. Reference 36). Namely the $S_1$ looses n→π* nature for twist angles $\Theta_1 > 60°$. The important changes in the leading features of the wavefunctions along the twist interval $\Theta_1 = [0,90°]$ are also mirrored in the values of dipole moment component $\mu_z$ for four singlet states (see Table I). The $\mu_z(S_0)$ of the ground state remains almost unchanged through the $\Theta_1$ twist. Dipole moment in $S_1$ changes drastically as soon as the state looses n-π* features resuming at the $\Theta_1 = 90°$ almost the same value as $\mu_z(S_0)$. Large positive value of $\mu_z(S_2)$ and negative value of $\mu_z(S_3)$ at $\Theta_1 = 90$ means extra charge on methylene group and extra charge in CCN triad, respectively. At the $\Theta_1 = 90°$ the $S_1$ state lies lower than the $S_1 = Z_1$ state of the 90° terminally twisted butadiene with respect to the ground state $S_0$ of the planar geometries. In this connection it is worth of mentioning that the n→π* state of planar allylideneimine is ~55 kcal/mol below the second excited state $S_2$. The excitation energies of $S_2$ and $S_3$ states are very similar to the excitation energies of the $2^1A_g$ and $^1B_u$ states for the planar butadiene. (Notice that no attempt has been made to determine precisely the excitation energies (cf. Figures 3 and 5)). The twist of the C=C bond in allylideneimine is favorable for the first triplet state $T_1$ (π→π*) which lies slightly below the $S_0$ state

Table I: The $\mu_z$ Component of Dipole Moment (in Debyes) of the $S_0$, $S_1$, $S_2$ and $S_3$ States of Allylideneimine for Twist Around C=C and C=N Bond $\Theta_1$ and $\Theta_3$, Respectively Obtained from the 11M/4R, T=15μh CI treatments.

| $\Theta_1^{(o)}$ | $\mu_z(S_0)$ | $\mu_z(S_1)$ | $\mu_z(S_2)$ | $\mu_z(S_3)$ |
|---|---|---|---|---|
| 0 | -1.80 | 0.86 | -1.81 | -2.60 |
| 30 | -1.71 | 0.92 | -1.46 | -2.60 |
| 60 | -1.69 | 0.65 | -1.87 | -1.79 |
| 90 | -1.78 | -1.62 | 2.64 | -4.20 |
| $\Theta_3^{(o)}$ | | | | |
| 30 | -2.09 | 0.08 | -1.19 | -3.63 |
| 60 | -2.15 | -0.77 | -0.76 | -4.28 |
| 90 | -2.72 | -0.82 | -0.69 | -3.66 |

at $\Theta_1 = 90°$ (only 0.3 kcal/mol). For the large twist angles the excitation is localized in the C=C bond (cf. MO's for $\Theta_1 = 90°$ of Scheme 9). Second triplet $T_2$ is of n→π* nature for planar geometry and at $\Theta_1 = 90°$ resumes the features of localized structure with excitations within the CCN triad. The twist is unfavorable for $T_2$ and $T_3$ states.
Completely new features are introduced in the low lying singlet states of allylideneimine through the twist around the C=N bond (Fig. 6 and Scheme 1). There is an avoided crossing between the two lowest singlet states $S_0$ and $S_1$ for $\Theta_3 > 80$ so that at $\Theta_3 = 90°$ $S_0$ resumes polar features with extra charge at the NH group. The diradical state $S_1$ lies only ~10 kcal above the $S_0$. The $S_2$ is of covalent excited nature and the other polar state with extra charge in allylic triad does not lie among four lowest singlet states. The leading features of the four wavefunctions and corresponding localized structure are given in Scheme 11. The values of the



90°

$S_0$    $S_1$

$S_2$    $S_3$
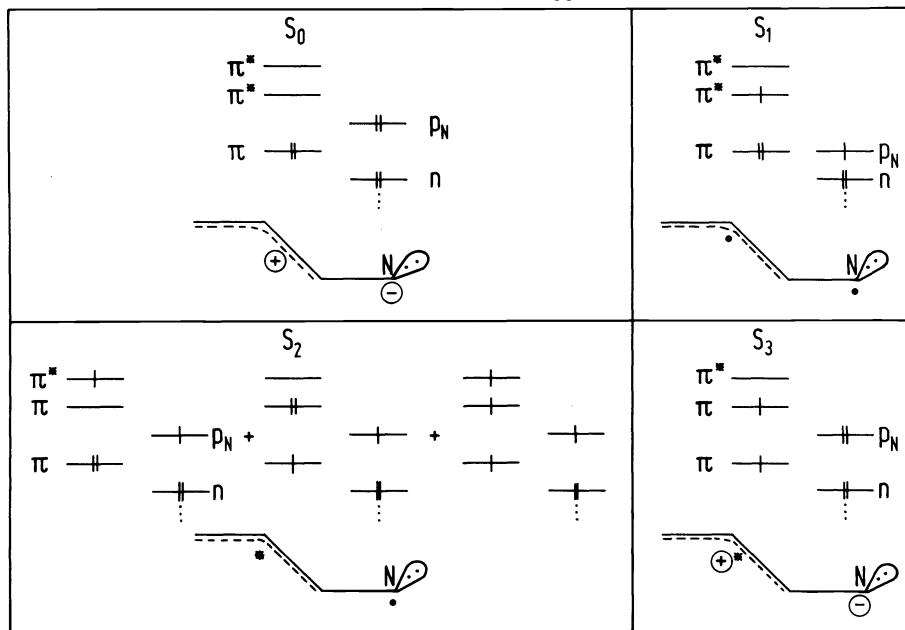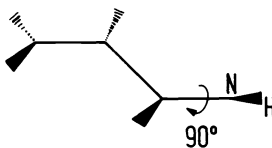
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dipole moment component $\mu_z$ for all four singlet states in the twist interval $\Theta_3 = [0,90^\circ]$ are given in Table 1. Notice, that the $\mu_z(S_o)$ has the largest negative value at $\Theta_3 = 90^\circ$ indicating extra charge at nitrogen atom. The twist around C=N bond is extremely favorable for the first excited state so that at $\Theta_3 = 90^\circ$ there are only two close lying singlet states ($S_o$ and $S_1$). In between these two singlet states there is the lowest triplet state $T_1$ of diradical nature with excitation localized primarily in the C=N bond. The twist is unfavorable for other two triplet states $T_2$ and $T_3$.

Finally, it is worth of mentioning the results of relaxation in the C-C single bond as well as of the simultaneous torsion around two double bonds or around one single and one double bond. For all four singlet excited states the torsion around C-C single bond is unfavorable even when the barrier hight in the ground state is only $\sim$11 kcal/mol. Also simultaneous twist around C=C and C=N, or around C=C and C-C or around C=N and C-C bonds costs more energy than the relaxation in the individual double bonds C=C or C=N.

SUMMARY

The importance of covalent excited state for geometrically relaxed species should not be underestimated although one of the polar zwitterionic states might be substantially stabilized or destabilized by the adequate chemical substitution. It is not excluded that a minimum on $S_1$ energy surface with covalent or mixed (covalent and ionic) features of the wavefunction occurs for the intermediate twist around the C=C bond of polyenes. In this case the assumption that nearly 50:50 yield between the two groundstate geometrical isomers (37) is the only possible outcome is not longer valid. Comparing the consequences of the twist around C=N and C=C bonds in allylideneimine the former geometrical relaxation is much more favorable in $S_1$ state. The situation might easily change by substitution or by increase of a polyenic size.

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