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Critically heterosymmetric biradicaloid geometries of of protonated Schiff bases*

Possible consequences for photochemistry and photobiology

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Ab initio large scale calculations confirm the existence of an $S_0 - S_1$ conical intersection at orthogonally twisted double bond geometries in the protonated Schiff bases, methaniminium and propeniminium, originally predicted from the simple two-electron, two-orbital model. In the vicinity of these geometries, the S_0 and S_1 wavefunctions differ by a translocation of a positive charge. Several conjectures are formulated for the consequence of these results for photochemical cis-trans isomerization around double bonds in protonated Schiff bases and a possible relation to the primary step in the vision process is pointed out.

Key words: S_0-S_1 conical intersection — Photoisomerization — Protonated Schiff bases — Vision

I. Introduction

S_0-S_1 *surface touching*

The outcome of photochemical organic reactions in solution is largely dictated by the geometries at which the excited molecules return to the electronic ground state. An understanding of organic photochemical paths therefore requires a knowledge of the geometries at which the S_1 or T_1 state hypersurface has a minimum or at which it touches the S_0 surface or at least approaches it very

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

closely ("funnel"), and of the probabilities that one or another of these minima or funnels is actually reached upon excitation [1].

Among the various possible molecular geometries, particularly likely candidates for minima in S_1 or T_1 and for regions of S_0-S_1 touching are those which are of biradicaloid character, i.e. those at which a molecule has two approximately non-bonding orbitals occupied by a total of only two electrons in low-energy electronic states. Strongly twisted double bonds represent an important example of biradicaloid geometries and are believed to be the S_1-S_0 return points in photochemically induced geometrical isomerization, one of the most important organic photochemical processes.

Perfect biradicals, in which the two non-bonding orbitals have equal energies and do not interact, often have quite large S_0-S_1 gaps, considering that the excitation is between degenerate orbitals. For instance, in 90° twisted ethylene the gap is 85 kcal/mol [2]. Imperfect biradicals, or biradicaloids, in which the two maximally localized non-bonding orbitals differ in energy but do not interact (heterosymmetric biradicaloids) are predicted [3, 4] by a simple two-orbital two-electron model [5, 6] to have smaller S_0-S_1 gaps. For a particular orbital energy difference, the gap should vanish altogether and the S_0-S_1 states should be degenerate (critically heterosymmetric biradicaloid [4]). This is of particular interest for the theory of organic photochemistry, as it could lead to high quantum yields and to dynamic memory effects.

According to the simple model, the relatively large S_0-S_1 exitation energy in most perfect biradicals, such as twisted ethylene, is due to the zwitterionic nature of the excited state. Small S_0-S_1 gaps should result in twisted charged double bonds such as a protonated Schiff base, whose two termini have quite different electronegativities, since their electronic structures in S_0-S_1 differ by charge translocation rather than charge separation [3, 4].

Since the photochemistry of protonated Schiff bases has been of considerable interest in view of its relation to the primary event in vision, and since photochemically induced charge translocation is of considerable interest in its own right, we feel that the predictions of the simple model are sufficiently intriguing to be worthy of testing by a good-quality *ab initio* calculation. We have selected the methaniminium and propeniminium cations as simple candidates for critically heterosymmetric biradicals and have used a large-scale CI calculation to obtain information on the S_0-S_1 gap at their orthogonally twisted geometries. In the following, we first briefly summarize the relevant parts of the simple model before presenting a comparison with the *ab initio* results. In comparison with our preliminary results on protonated Schiff bases published previously [3, 4], in this work the geometry has been optimized at the SCF level in the S_0, S_1 and T_1 states for planar and orthogonally twisted double bonds. Also S_0-S_1 energy gaps were determined more reliably through the use of a more extensive CI. Finally, we consider the possible implications for photochemistry and for the primary process in vision.

2. Critically heterosymmetric biradicaloids in the two-electron two-orbital model

In this simple model, two electrons in two approximately non-bonding orbitals (active space [5, 6]) are treated explicitly and all others are represented by a fixed core.

For two electrons placed in two orthogonal ($S_{\mathcal{A}\mathcal{B}}=0$) but otherwise general orbitals $\mathcal{A}$ and $\mathcal{B}$, the Hamiltonian matrix for the three singlet spin adapted configurations has the form [4]

$$\begin{array}{c} {}^1|\mathcal{A}^2-\mathcal{B}^2\rangle \\ {}^1|\mathcal{A}^2+\mathcal{B}^2\rangle \\ {}^1|\mathcal{A}\mathcal{B}\rangle \end{array} \begin{pmatrix} E(T)+2K'_{\mathcal{A}\mathcal{B}} & \delta_{\mathcal{A}\mathcal{B}} & \gamma^-_{\mathcal{A}\mathcal{B}} \\ \delta_{\mathcal{A}\mathcal{B}} & E(T)+2(K'_{\mathcal{A}\mathcal{B}}+K_{\mathcal{A}\mathcal{B}}) & \gamma_{\mathcal{A}\mathcal{B}} \\ \gamma^-_{\mathcal{A}\mathcal{B}} & \gamma_{\mathcal{A}\mathcal{B}} & E(T)+2K_{\mathcal{A}\mathcal{B}} \end{pmatrix}. \qquad (1)$$

The diagonal elements are expressed in terms of the triplet energy $E(T)$, the exchange integral $K_{\mathcal{A}\mathcal{B}}$ and a combination of integrals of the Coulomb type, $K'_{\mathcal{A}\mathcal{B}}$:

$$E(T)=h_{\mathcal{A}\mathcal{A}}+h_{\mathcal{B}\mathcal{B}}+(J_{\mathcal{A}\mathcal{A}}+J_{\mathcal{B}\mathcal{B}})/4+J_{\mathcal{A}\mathcal{B}}/2-K'_{\mathcal{A}\mathcal{B}}-K_{\mathcal{A}\mathcal{B}} \qquad (2)$$

$$K'_{\mathcal{A}\mathcal{B}}=[(J_{\mathcal{A}\mathcal{A}}+J_{\mathcal{B}\mathcal{B}})/2-J_{\mathcal{A}\mathcal{B}}]/2, \qquad (3)$$

where $h_{\mathcal{A}\mathcal{A}}$ and $h_{\mathcal{B}\mathcal{B}}$ are one-electron integrals.

The interaction among singlet configurations is given by the quantities $\gamma_{\mathcal{A}\mathcal{B}}$, $\gamma^-_{\mathcal{A}\mathcal{B}}$ and $\delta_{\mathcal{A}\mathcal{B}}$:

$$\gamma_{\mathcal{A}\mathcal{B}}=2h_{\mathcal{A}\mathcal{B}}+(\mathcal{A}\mathcal{A}\,|\,\mathcal{A}\mathcal{B})^*+(\mathcal{B}\mathcal{B}\,|\,\mathcal{B}\mathcal{A}) \qquad (4)$$

$$\gamma^-_{\mathcal{A}\mathcal{B}}=(\mathcal{A}\mathcal{A}\,|\,\mathcal{A}\mathcal{B})^*-(\mathcal{B}\mathcal{B}\,|\,\mathcal{B}\mathcal{A}) \qquad (5)$$

$$\delta_{\mathcal{A}\mathcal{B}}=h_{\mathcal{A}\mathcal{A}}-h_{\mathcal{B}\mathcal{B}}+(J_{\mathcal{A}\mathcal{A}}-J_{\mathcal{B}\mathcal{B}})/2. \qquad (6)$$

Here, $\gamma_{\mathcal{A}\mathcal{B}}$ can be interpreted as a measure of the interaction between orbitals $\mathcal{A}$ and $\mathcal{B}$, $\gamma^-_{\mathcal{A}\mathcal{B}}$ is connected with the degree of localization of the two orbitals, and $\delta_{\mathcal{A}\mathcal{B}}$ measures their electronegativity difference. We will choose $\delta_{\mathcal{A}\mathcal{B}}\geq 0$, and therefore label $\mathcal{B}$ as HOMO and $\mathcal{A}$ as LUMO. For a perfect biradical, $\gamma_{\mathcal{A}\mathcal{B}}$ and $\delta_{\mathcal{A}\mathcal{B}}$ vanish.

The choice of the orbitals $\mathcal{A}$ and $\mathcal{B}$ is not important in principle, since we shall deal with exact solutions of the model. For the localized orbitals, $\mathcal{A}=A$ and $\mathcal{B}=B$, and for the most delocalized orbitals, $\mathcal{A}=a$ and $\mathcal{B}=b$, the quantity $\gamma^-_{\mathcal{A}\mathcal{B}}$ vanishes and the Hamiltonian matrix simplifies. For either choice, only two quantities, $\gamma_{AB}(\gamma_{ab})$ and $\delta_{AB}(\delta_{ab})$, will determine the deviation from the perfect biradical and the degree of mixing of the individual configurations, ${}^1|\mathcal{A}^2-\mathcal{B}^2\rangle$, ${}^1|\mathcal{A}^2+\mathcal{B}^2\rangle$ and ${}^1|\mathcal{A}\mathcal{B}\rangle$, as they produce the final three singlet states.

We adopt the name "biradicaloid" for "imperfect" biradicals in which the two real orthogonal orbitals either interact, or have different energies, or both. The following classification is useful [4]: (i) homosymmetric biradicaloids ($\gamma_{AB}=\delta_{ab}\neq 0$, $\delta_{AB}=\gamma_{ab}=0$); (ii) heterosymmetric biradicaloids ($\delta_{AB}=\gamma_{ab}\neq 0$; $\gamma_{AB}=\delta_{ab}=0$) and (iii) nonsymmetric biradicaloids ($\delta_{AB}=\gamma_{ab}\neq 0$; $\gamma_{AB}=\delta_{ab}\neq 0$). In the present context of S_0-S_1 surface touching in a protonated Schiff base heterosymmetric biradicaloids are of central interest.

For the choice of the most localized orbitals $\mathscr{A} = A$ and $\mathscr{B} = B$ ($\gamma_{AB} = 0$) the Hamiltonian matrix (1) for heterosymmetric biradicaloids ($\delta_{AB} \neq 0$, $\gamma_{AB} = 0$) takes a block diagonal form. The configurations ${}^1|A^2+B^2\rangle$ and ${}^1|A^2-B^2\rangle$ mix, giving rise to two states:

$$|2\rangle = \cos\beta\,{}^1|A^2+B^2\rangle + \sin\beta\,{}^1|A^2-B^2\rangle \tag{7}$$

$$|1\rangle = -\sin\beta\,{}^1|A^2+B^2\rangle + \cos\beta\,{}^1|A^2-B^2\rangle, \tag{8}$$

where the mixing parameter

$$\beta = \frac{1}{2}\tan^{-1}\frac{\delta_{AB}}{K_{AB}} \tag{9}$$

is related to the perturbation of the systems away from a perfect biradical, as determined by the ratio of the electronegativity difference between orbitals A and B and the exchange integral.

The corresponding energies are

$$E(|2\rangle) = E(T) + 2K'_{AB} + K_{AB} + \sqrt{K_{AB}^2 + \delta_{AB}^2} \tag{10}$$

$$E(|1\rangle) = E(T) + 2K'_{AB} + K_{AB} - \sqrt{K_{AB}^2 + \delta_{AB}^2}. \tag{11}$$

The configuration ${}^1|AB\rangle$ which does not mix has the energy

$$E({}^1|AB\rangle) = E(T) + 2K_{AB}. \tag{12}$$

The wavefunction of the state $|1\rangle$ is the out-of-phase linear combination of the "hole-pair" configurations ${}^1|A^2+B^2\rangle$ and ${}^1|A^2-B^2\rangle$. For infinitely large δ_{AB}, i.e. $\beta = \pi/4$, it simplifies to

$$|1\rangle = {}^1|B^2\rangle.$$

The wavefunction of the ${}^1|AB\rangle$ state is of "dot-dot" nature, with one electron in each localized orbital.

It is clear that $E(|2\rangle)$ has the highest energy and corresponds to S_2. The energy ordering of $E(|1\rangle)$ and $E({}^1|AB\rangle)$ depends on the size of K_{AB} and K'_{AB} and on the magnitude of the perturbation δ_{AB}. The condition for S_0-S_1 degeneracy is $\delta_{AB} = \delta_c$, where

$$\delta_c = 2\sqrt{K'_{AB}(K'_{AB} - K_{AB})}. \tag{13}$$

Clearly, those special perfect biradicals in which K_{AB} and K'_{AB} are equal ("axial biradicals") have degenerate S_0 and S_1 states, but these are not of interest in the present investigation. For most perfect biradicals, $K_{AB} \neq K'_{AB}$ and S_0 is not degenerate with S_1. Equation (13) then determines the size of the perturbation δ_{AB} that is required to produce S_0-S_1 degeneracy in a perturbed biradicaloid, and thus defines a critically heterosymmetric biradicaloid within the simple model. Then, of course, the ionization potential of each component of these degenerate states is the same. Condition (13) is most easily met in charged biradicaloids in which ${}^1|B^2\rangle$ and ${}^1|AB\rangle$ differ in charge location but neither of these configurations involves charge separation. According to the simple model, protonated Schiff bases with one double bond broken by an orthogonal twist thus represent good candidates for critically heterosymmetric biradicaloids.

We introduce the additional terms, weakly and strongly heterosymmetric biradicaloids. In the former, $\delta \ll \delta_c$, S_0 is of dot-dot nature ($^1|AB\rangle$) and S_1 of hole-pair nature ($^1|B^2\rangle$) (e.g. twisted propene [7], cf. sudden polarization [8]). In strongly heterosymmetric biradicaloids, $\delta \gg \delta_c$, S_0 is given by $^1|B^2\rangle$ and S_1 by $^1|AB\rangle$ (e.g. orthogonally twisted aminoborane). These are typical examples in that S_0 is represented by a configuration that involves no formal charge separation and S_1 by a configuration that does.

Caution is warranted concerning the energy ordering predicted by the two-electron two-orbital model for states which do not differ much in energy, (e.g. by $2K_{AB}$). At better approximations, some weakly heterosymmetric biradicaloids actually have T_1 above S_0 [9] and an inverted energy ordering of the out-of-phase and in-phase linear combinations of the hole-pair configurations in the S_1 and S_2 states [10]. This does not significantly affect the condition (13) for critically homosymmetric biradicaloids. Although no longer exact, it can still serve as an useful guide in the search for this type of biradicaloids.

3. *Ab initio*-CI calculations for methaniminium and propeniminium

In order to test the predictions of the simple two-electron, two-orbital model concerning the occurrence of $S_0 - S_1$ touching and the nature of the wavefunctions of a critically heterosymmetric biradicaloid, we have carried out calculations for methaniminium, $H_2C{=}NH_2^+$, and propeniminium, $H_2C{=}CH\text{-}CH{=}NH_2^+$, as a function of the twist angles, using an *ab initio* large scale CI procedure [7]. For the planar and the 90° twisted structures the geometry was optimized at the SCF level with the 4-31G AO basis for the S_0, S_1 and T_1 states. This simplification is acceptable, since for heterosymmetric biradicaloid geometries the SCF configurations dominate the expansion of the large CI wavefunctions of the S_0, S_1 and T_1 states. Both the direct CI [11] and MRD-CI [12] calculations have been carried out for the geometries corresponding to the SCF minima, in order to test the reliability of the CI results for the determination of the $S_0 - S_1$ energy gap. All single and double excitations with respect to a chosen set of selected reference configurations were included in the direct CI. For the same CI spaces in the MRD-CI procedure configurations were selected according to the energy threshold criterion; and the energies, extrapolated for the full MRD-CI space, were compared with the direct CI energies.

The potential curves for singlet and triplet states as functions of the twisting angle and other geometrical parameters were determined by the MRD-CI procedure, since for most of these geometries no symmetry is present. Therefore, S_0 and S_1 both belong to the same irreducible representation. The required multi-reference multi-root procedure is available in the framework of the MRD-CI method. Since in this case a simultaneous balanced description of the S_0 and S_1 states at the truncated CI level is needed for a large range of geometries, the choice of the one-electron functions for the construction of the CI spaces is important. We use triplet SCF MO's in the MRD-CI calculations for the two lowest roots, but these are not optimal for either S_0 or S_1. In order to correct for this deficiency, for some geometries of special interest the natural orbitals of each state were used as its own one-electron functions in the successive two-root CI calculation. For methaniminium additional calculations with the 6-31G** AO basis set have been carried out.

3.1. *Methaniminium*

The energy surfaces of several singlet and triplet states of methaniminium as a function of simultaneous twist and elongation of the C=N bond, calculated with the 6-31G** AO basis set, are given in Fig. 1. At 90° twist and the C–N bond length of the 1.37 Å a near S_0-S_1 touching has been found. At this geometry the HOMO and LUMO are of localized nature and correspond to *p* orbitals localized at N and C, respectively. The wavefunctions of the S_0 and T_1 states are of the "dot-dot" nature, with positive charge mainly on the nitrogen atom, and the wavefunction of the S_1 state of the "hole-pair" nature, with positive charge mostly on the carbon atom. The charge translocation from the N to the C atom occurs as expected from the simple theory. The two-electron, two-orbital description of this critically symmetrical biradicaloid is thus suitable for characterizing the leading features of the correlated S_0 and S_1 wavefunctions. The 4-31G closed-shell SCF geometry optimization, constrained to 90° twist structure yields 1.349 Å for the C–N bond length. The open-shell SCF procedure yields 1.436 Å (Fig. 2). The CI energies calculated at the optimized SCF geometries and S_0-S_1 energy gaps are given in Table 1. For the same geometrical structures the direct-CI procedure with the 6-31G** AO basis again yields a near S_0-S_1 touching (cf. Table 1).

3.2. *Propeniminium*

In this case, the search for critically heterosymmetric biradicaloids involves a twist around both the C=N and the C=C double bonds. Closed and open shell SCF geometry optimization has been carried out for the 90° twisted C=C and the 90° twisted C=N bonds (Fig. 3). The S_0 and S_1 energy gaps obtained from direct CI and MRD-CI are in good agreement (Table 2). The vertical $S_0^{\dagger}-S_1$ energy gaps for the SCF-optimized structures of the S_1 state are of comparable size for the C=C and C=N 90° orthogonal twists. ($S_0^{\dagger}$ labels ground state calculated at the SCF optimized geometry for the S_1 state.) The difference is in the character of the S_0 and S_1 wavefunctions. For the 90° twisted C=C bond the ground state S_0 is characterized by the dot-dot structure $^1|AB\rangle$, with the positive charge located at the methylene group and the S_1 state is dominated by the hole-pair structure $^1|B^2\rangle$. In contrast, for the 90° twisted C=N bond S_0 is dominantly described by the hole-pair structure $^1|B^2\rangle$, with positive charge translocated into the allylic triad, and S_1 is of the "dot-dot" nature $^1|AB\rangle$ (Fig. 4). In terms of the simple model, the SCF-optimized biradicaloid geometries for the

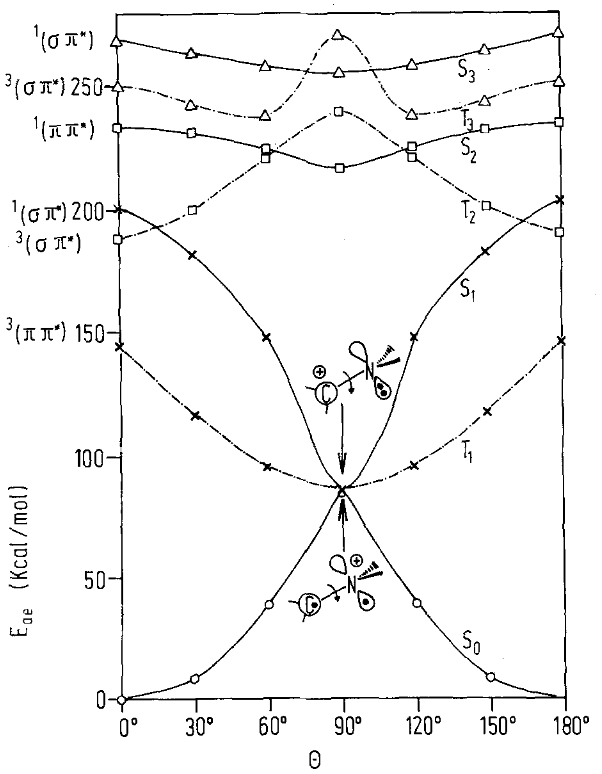

Fig. 1. Averaged extrapolated energies [13] of the four singlet states S_0, S_1, S_2, S_3 and three triplet states T_1, T_2, T_3 of methaniminium as a function of the twist angle θ with simultaneous elongation of the C=N bond from 1.263 Å at $\theta = 0°$ to 1.37 Å for $\theta = 90°$, using $l(\theta) = l(90°)\sin^2\theta + l(0°)\cos^2\theta$. Other bond lengths (CH = 1.09 Å, NH = 1.02 Å) and bond angles (HCN=CNH = 120°) were kept constant. Correlation has been included for 12 electrons among 58 MO's in the 6-31G** AO basis set. For the singlet states the extrapolation has been carried out for the variational energies obtained from the 8M/3R and 5M/1R treatments for ^1A and ^1B states with energy selection threshold $T = 35$ μh. For three ^1A states and one ^1B state up to 5600 and 1800 SAF's were selected from the 31 740 and 209 100 possible, respectively. The MO's of the triplet SCF ^3A state were employed to build the CI spaces for the ^1A states. The triplet states ^3A and ^3B were obtained from 4M/2R and 3M/1R treatments selecting up to 3400 and 1800 configurations from 244 400 and 208 950 SAF's, respectively

C=C and C=N 90° twist give rise to approximately equal and opposite electronegativity differences $\delta_{C=C} - \delta_c$ and $\delta_{C=N} - \delta_c$, so that the energy difference between the "dot-dot" and "hole-pair" structures is approximately the same (Fig. 5). For both twists the $\delta_{C=C}$ and $\delta_{C=N}$ values are not far from δ_c. It is to be expected that changes in geometrical parameters other than the twist angle might easily bring either $\delta_{C=C}$ or $\delta_{C=N}$ to equality with δ_c.

In addition, two cuts through the three energy surfaces S_0, S_1 and T_1 are shown in Figs. 6 and 7 for the C=C and C=N twist. In order to approximate the steepest descent path from the S_1 state, all C-C and C-N bond lengths l_i were varied simultaneously with the twist θ towards the 90° twisted structures. Starting

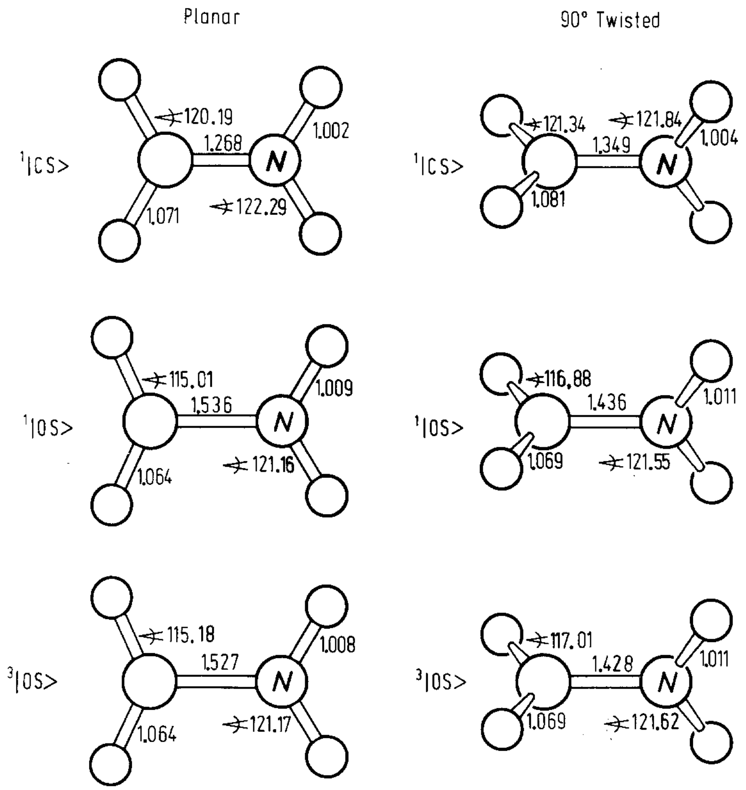

Fig. 2. Optimized geometries for planar and 90° twisted structures of methaniminium $^{1,3}|OS\rangle$ and $^{1}|CS\rangle$ label results obtained from the open shell singlet, triplet and closed shell single HF procedure, respectively

from the vertically excited planar S_1 state (structure optimized for the S_0 state) and changing the geometry towards the S_1 optimized structure at 90° twist around the C=C or the C=N bond, one reaches the orthogonal minimum on the S_1 energy surfaces without encountering a barrier. From this minimum return to the S_0 state should occur readily due to the small S_0-S_1 gap and the molecules should then follow the fate dictated by the shape of the S_0 state and yield the ground states of the two geometrical isomers. The barriers to rotation in the ground states are lower than shown in Figs. 6 and 7 by about 5 kcal/mol due to geometrical relaxation in the S_0 states at the orthogonal C=C or C=N twist, as is clear from comparison of the vertical and non-vertical S_0-S_1 energy gaps (Table 2).

The other representative cut shown in Figs. 6 and 7, less likely to be followed in the actual photochemical reaction starts at optimized planar geometry of the S_1 state and ends again with the optimal geometries for the S_1 state of the 90° twisted C=C and C=N bonds, respectively.

Both examples, twisted methaniminium and propeniminium, illustrate clearly

Table 1. Direct-CI energies of S_0, S_1 and T_1 states for the 90° twisted SCF optimized geometries of methaniminium, $S_0 - S_1$ energy gaps and type of wavefunctions (WF)

	E (a.u.)	WF	$S_0^\dagger - S_1$ (kcal/mol)	$S_0 - S_1$ (kcal/mol)
S_0	−94.3306[a]	$^1\|AB\rangle$		−8.1[a]
	−94.5645[c]	$^1\|AB\rangle$		
$S_0^\dagger$	−94.3264[a]	$^1\|AB\rangle$	−5.5[c]	
	−94.5625[b]	$^1\|AB\rangle$	1.5[b]	
S_1	−94.3177[a]	$^1\|AB\rangle$		
	−94.5649[b]	$^1\|B^2\rangle$		
	−94.5642[c]	$^1\|B^2\rangle$	−0.2[c]	
T_1	−94.3273[a]	$^3\|AB\rangle$		

[a] 4-31G AO basis set

[b] 6-31G** AO basis set. Energies and $S_0 - S_1$ gap for the optimized 4-31G structures (cf. Fig. 2)

[c] 6-31G** AO basis set energies of $S_0 - S_1$ for the geometry given in Fig. 1 at 90° twist (C—N bond length is 1.37 Å). $S_0^\dagger$ refers to the ground state calculated at the geometry optimized for the excited S_1 state

that the conditions for the $S_0 - S_1$ surface touching or near touching obtained from the simplest possible model for heterosymmetric biradicaloids are roughly valid even at the *ab initio* CI model of these prototype systems, and that the wavefunctions are indeed approximately those expected.

4. Cis-trans isomerization: proton translocation and vision

Since the conclusions concerning $S_0 - S_1$ surface touching in twisted protonated Schiff bases that were deduced from the simple model have received such strong support from these *ab initio* calculations on methaniminium and propeniminium, it is of interest to consider their possible implications in photochemistry. As the outcome of photochemical reactions is apt to depend strongly on dynamical properties of the system, about which little is known, it is only possible to formulate reasonable conjectures. Three such conjectures come to mind, to be further tested by theory or, more likely, experiment.

(i) We have not actually spent much effort attempting to locate the exact geometries at which $S_0 - S_1$ touching and conical intersections occur in our model two systems. Still, the fact that the wavefunctions for S_0 and S_1 differ in symmetry at orthogonal twist, are nearly degenerate, and are well described as $^1|AB\rangle$ and $^1|B^2\rangle$ (in either order), depending on geometry, leaves no doubt that a suitable geometrical variation actually produces the sought $S_0 - S_1$ touching in orthogonally twisted protonated Schiff bases. In solution, it is possible that a suitable arrangement of the solvent environment needs to be combined with the intramolecular geometrical distortions.

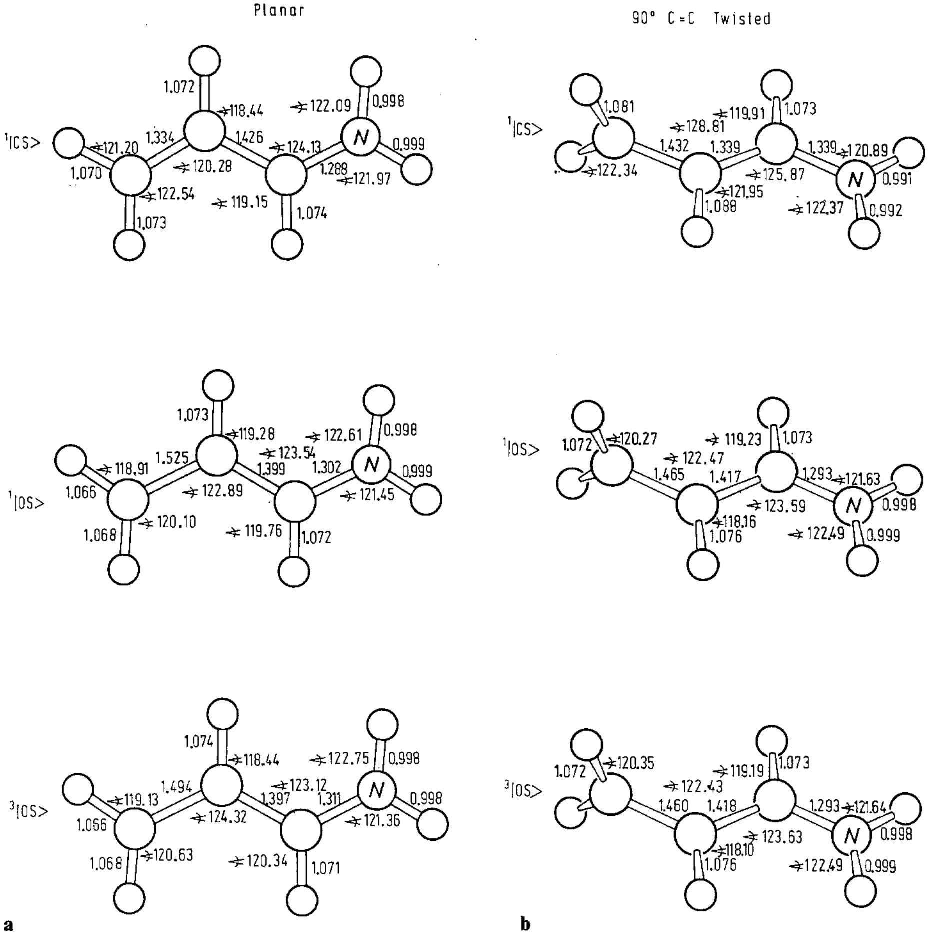

Fig. 3a–c. Optimized geometries of the planar (**a**), 90° C=C twisted (**b**) and 90° C=N (**c**) twisted structure of propeniminium at the 4-31G SCF level. $^{1,3}|OS\rangle$ and $^{1}|CS\rangle$ label results obtained from the open shell singlet, triplet and closed shell singlet HF procedure, respectively

Return from S_1 to S_0 through a conical intersection is highly likely to occur the first time the molecule reaches the requisite geometry and leads one to expect momentum effects, i.e. dynamical memory in a sense that has been discussed in photochemistry repeatedly [1, 4, 14]. Then, the sum of the quantum yields of the cis to trans and the trans to cis photoisomerizations could deviate substantially from unity even in the absence of competing processes and could be as large as two or as small as zero, even if both photoisomerizations occur through the same conical intersection. We are not aware of any experimental evidence for such behaviour at this time, except possibly in the case of rhodopsin [15]; and further experimental investigations would clearly be worthwhile. In retrospect, it should perhaps not be surprising that nature has apparently opted for the use of a dynamic memory effect to increase the quantum yield of the primary step in vision.

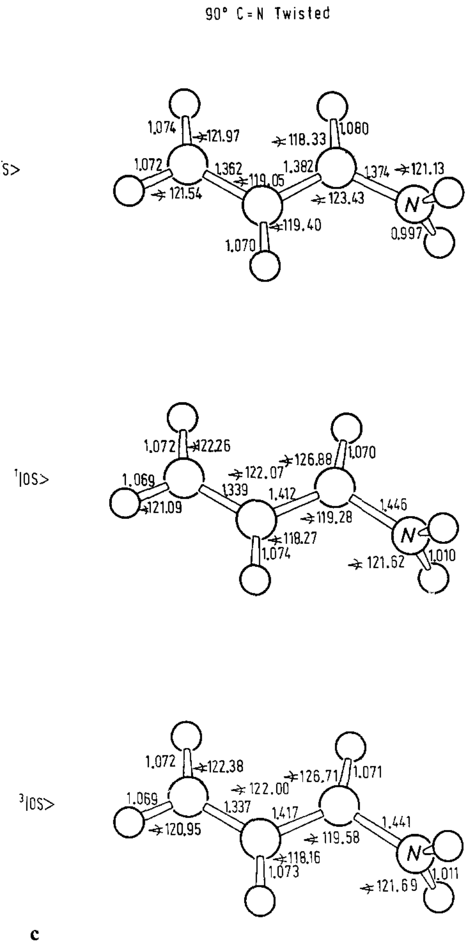

Fig. 3 (continued)

(ii) In protonated Schiff bases containing several conjugated double bonds, a choice is possible among two or more bonds around which geometrical isomerization could occur. The probabilities with which the local minima in S_1 that correspond to these individual twists are reached are complicated functions of the shape of the S_1 surface, but it is perhaps reasonable to suggest that all else being the same, the deepest minima will be surrounded by the smallest barriers, and will therefore tend to be reached preferentially. Then, conical intersections, in which S_1 actually touches S_0 should be particularly favourable. Predictions of relative reactivity with respect to twisting around the various double bonds could than be based on an evaluation of the relative energies of the $^1|AB\rangle$ and $^1|B^2\rangle$ configurations.

In propeniminium, the two choices were a C=N twist and a C=C twist and both appear to have the potential of producing a conical intersection: the $CH_2{=}CH{-}CH^{+}{-}+{-}NH_2$ combination is a bit more stable than

Table 2. CI Energies of S_0, S_1 and T_1 states for the SCF-optimized structures of propeniminium, S_0-S_1 energy gaps and type of wavefunction (WF)

	90° twisted C=C E(a.u.)			90° twisted C=N E(a.u.)		
	Direct CI	MRD-CI	WF	Direct CI	MRD-CI	WF
S_0	−171.3237[a]	−171.3196[a]	$^1\|AB\rangle$	−171.3274[d]	−171.3274[d]	$^1\|B^2\rangle$
$S_0^\dagger$	−171.3158[a]	−171.3100[a]	$^1\|AB\rangle$	−171.3236[d]	−171.3208[d]	$^1\|B^2\rangle$
S_1	−171.2871[b]	−171.2831[b]	$^1\|B^2\rangle$	−171.2881[e]	−171.2860[e]	$^1\|AB\rangle$
T_1	−171.3226[c]	−171.3241[c]	$^3\|AB\rangle$	−171.2858[f]	−171.2857[f]	$^3\|AB\rangle$
$S_0^\dagger-S_1$ (kcal/mol)	−18.02	−16.88		−22.30	−21.87	
S_0-S_1 (kcal/mol)	−22.99	−22.92		−26.10	−25.97	

$S_0^\dagger$ labels energies of the S_0 state calculated for the optimal structure of the S_1 state. The dimension of the CI space for all single and double excitations with respect to X reference configurations (XM) is

[a] 420 958 (4M)
[b] 104 278 (3M)
[c] 647 171 (3M)
[d] 108 444 (3M)
[e] 352 580 (3M)
[f] 647 171 (3M)

In the MRD-CI procedure up to 10 000 configurations have been selected. The extrapolated energies are listed

$CH_2{=}CH{-}\dot{C}H{-}+{-}\dot{N}H_2^+$, and the $CH_2^+{-}+{-}CH{=}CH{-}NH_2$ less than $\dot{C}H_2{-}+{-}CH{=}CH{-}\dot{N}H_2^+$. However, suitable geometrical distortions and solvent effects will probably make up for the difference, permitting both processes to proceed via a conical intersection. A prediction of preferential reactivity is therefore not possible at the present level of knowledge (our previous calculations [4] were less exhaustive and suggested that the C=N twist will be preferred in the S_1 state since the C=C twist cannot produce a conical intersection; we no longer believe this to be correct).

The choices will be more clear-cut as the number of double bonds in conjugation increases and the energy differences between $^1|AB\rangle$ and $^1|B^2\rangle$ as a function of the choice of the bond for twisting become more pronounced. It is possible that this is one of the factors that account for the remarkable specificity of the isomerization around one double bond in rhodopsin and bacteriorhodopsin. In this regard, the steric demands of the pocket in which the chromophore is located need not be the only important consideration.

(iii) In the ground state of those strongly twisted protonated Schiff bases in which return to planarity is prevented, say by suitable steric constraints, and more generally in the ground state of charged critically heterosymmetric biradicaloids, one can expect bistability. One stable ground-state form would be produced from the "critical geometry" by a geometrical distortion in the molecule, or perhaps more readily in its environment, that removes the S_0-S_1 degeneracy by stabilizing $^1|AB\rangle$ over $^1|B^2\rangle$. This form will have the positive charge located

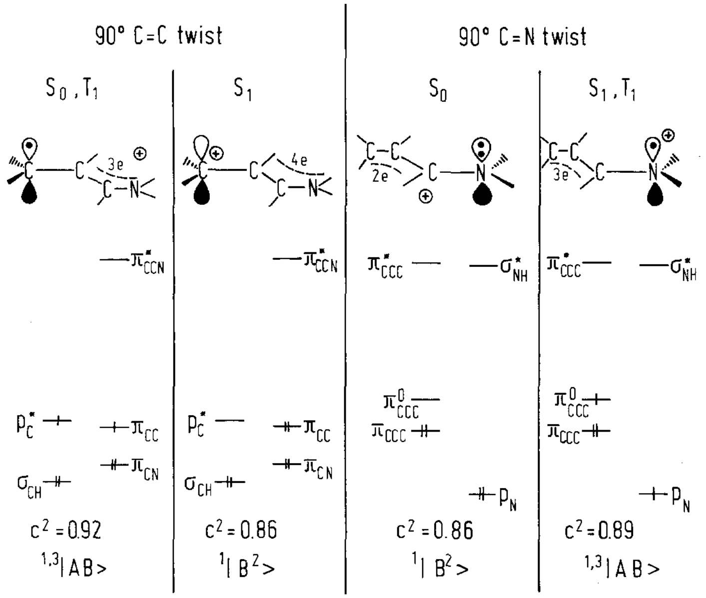

Fig. 4. Characterization of the S_0, S_1 and T_1 wavefunctions for the 90° C=C and the 90° C=N twisted geometries of propeniminium in terms of "hole pair" and $^1|B^2\rangle$ and $^{1,3}|AB\rangle$ structures. The occupation of important localized MO's in the leading configuration of the wavefunction is indicated as well as the weight (C^2) of this configuration in the CI expansion

on the fragment B. In the other stable ground-state form, $S_0 - S_1$ degeneracy will be removed by stabilizing $^1|B^2\rangle$ over $^1|AB\rangle$, and here, the positive charge will be located on fragment A. The two forms will thus differ by charge translocation and by an interchange of positions of single and double bonds.

Electronic excitation from S_0 and S_1 should result in the conversion from one to the other form by reversal of the geometrical distortion that produced the starting form from the "critical" geometry. Because the A and B orbitals avoid each other in space nearly perfectly, the transition density for the $S_0 - S_1$ transition

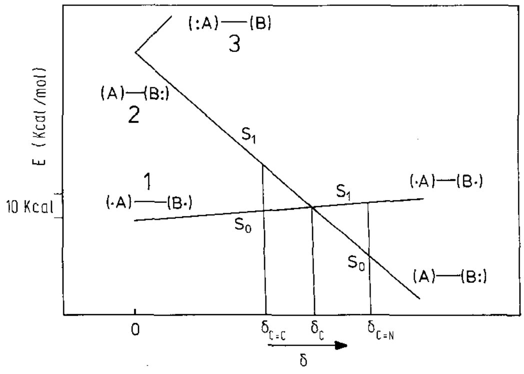

Fig. 5. Schematic energy diagram of the "hole-pair" and "dot-dot" configurations as a function of the electronegativity difference δ between two radical centers. From the calculated $S_0 - S_1$ energy gap for the 90° twisted C=C and the 90° twisted C=N geometries of propeniminium estimated values of δ for both heterosymmetric biradicaloids are indicated

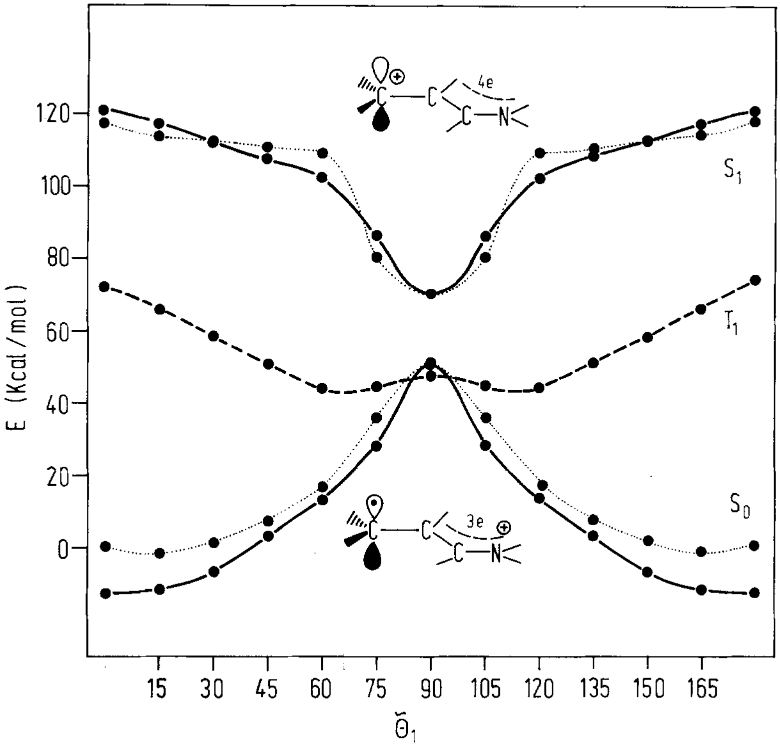

Fig. 6. 4-31G MRD-CI S_0, S_1, and T_1 surfaces of propeniminium for a simultaneous twist around the C=C bond by angle θ and variation of all three C—C and C—N bond lengths according to $l_i(\theta) = l_i(90°) \sin^2 \theta + l_i(0°) \cos^2 \theta$ where l_1, l_2 and l_3 label the C=C, C—C and C=N bond. The values of $l_i(90°)$ and $l_i(0°)$ are those of Fig. 3a from the SCF-optimized S_1 geometry at 90° twist to the SCF optimized planar S_1 geometry (· · ·) and Fig. 3b from the SCF optimized S_1 geometry at 90° twist to the SCF optimized S_0 geometry at the planar geometry (——). Other geometrical parameters than l_i and θ are kept constant and are those of the optimized S_1 geometry at 90° twist (cf. Fig. 3). 10M/2R was used for S_0 and S_1 and 3M/1R for T_1, correlating all except 1*s* core electrons of C and N atoms

will be small and its intensity low. If such a system were to be used as a bistable photochemical charge translocating element, excitation into higher singlets followed by internal conversion would probably have to be used in order to use photons efficiently.

If the protonated Schiff base is not forced to be twisted exactly to orthogonality, each of the two forms might exist in a cis and a trans form, so that up to four stable ground state isomers appear possible.

Finally, as discussed in more detail elsewhere [4], it is possible that the charge translocation and bistability that we have just discussed play a role in the energy storage that occurs in the primary steps in vision in which rhodopsin is transformed into bathorhodopsin. The large deuteration effect on the rate and the tunneling mechanism at low temperatures apparently have nothing to do with the proton carried by the nitrogen of the Schiff base since this proton is not lost in the

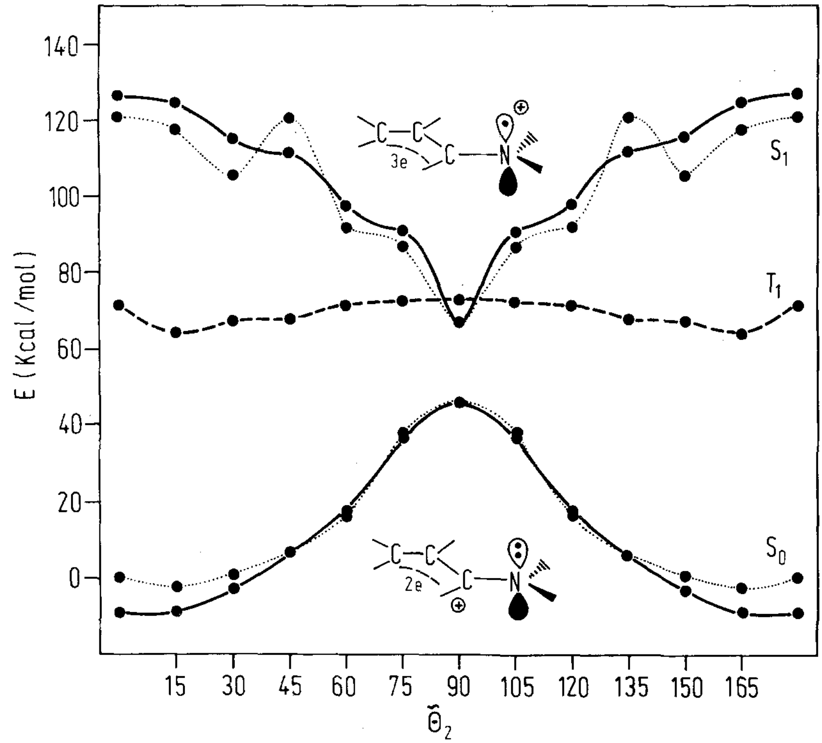

Fig. 7. The MRD-CI (13M/2R) S_0, S_1, and T_1 energy surfaces of propeniminium for the simultaneous twist around C=N bond and variation of all C—C and C=N bond lengths in analogous manner as described for Fig. 6

isomerization. Rather, they could well reflect the motion in the environment referred to above. This could take the specific form of deprotonation of a site near the ionone ring that acquires the positive charge upon excitation and protonation of a site near the Schiff base nitrogen which loses this positive charge. Such motion would then be responsible for an interchange of the relative stability of the $^1|AB\rangle$ and $^1|B^2\rangle$ forms of the orthogonally twisted chromophore and thus for return form S_1 to S_0 via a conical intersection. It is possible that a similar mechanism with coupled twisting and proton translocation applies in the case of bacteriorhodopsin even though the deuteration effect there is much smaller.

In conclusion, it appears likely that the confirmation of the results of the simple model by a more reliable *ab initio* calculation will stimulate further work in the photochemistry of protonated Schiff bases and may have relevance for the primary event in vision.

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