Theor Chim Acta (1985) 68: 45-55

THEORETICA CHIMICA ACTA

Photochemical *syn–anti* isomerization of a Schiff base: A two-dimensional description of a conical intersection in formaldimine

Vlasta Bonačić-Koutecký

Institut für Physikalische Chemie, Freie Universität Berlin, 1000 Berlin 33, Federal Republic of Germany

Josef Michl

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, USA

(Received May 17, 1985)

The shape of the S_0, S_1, and T_1 potential energy surfaces of formaldimine, $CH_2{=}NH$, is explored in the two-dimensional subspace defined by the twisting and linear inversion motions which correspond to the geometrical *syn-anti* isomerization, using an *ab initio* large-scale CI method. Minima in the S_1 and T_1 surfaces as well as a S_0-S_1 conical intersection are identified and the photoisomerization mechanism is discussed.

Key words: Photochemistry — *syn-anti* isomerization — Formaldimine — Conical intersection

1. Introduction

Geometrical isomerization about a double bond is one of the much studied classical processes in organic photochemistry. Its presumed involvement in the visual process [1, 2] provides its investigations with a particularly general appeal.

The progress of a *cis-trans* isomerization about a double bond with four ligands, such as C=C, can be followed using a single coordinate which describes a generalized twisting motion. The *syn-anti* isomerization about a double bond with three ligands, such as C=N, is intrinsically more complicated in that it can be effected by either of two linearly independent kinds of motion, or by their linear combination: twisting and in-plane inversion at the nitrogen atom (Fig. 1).

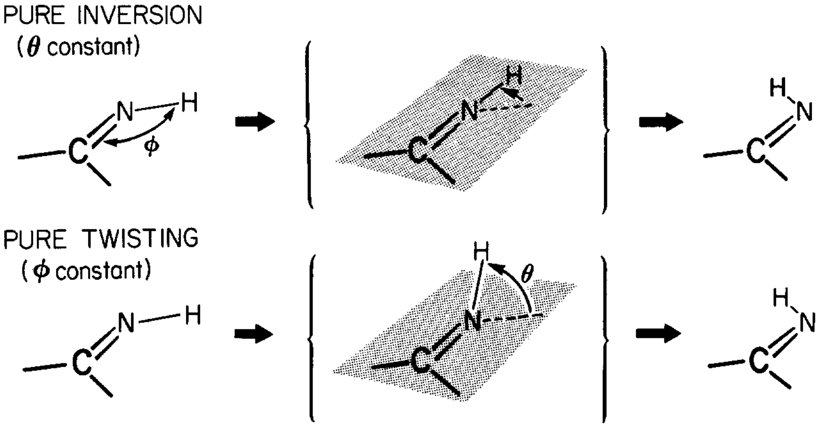

Fig. 1. The inversion and twisting paths for formaldimine *syn-anti* isomerization. The CNH valence angle is ϕ and the twist angle is θ

An experimental determination of the isomerization path preferred in a particular electronic state is difficult. The current belief [3-7] that in simple imines thermal isomerization chooses the inversion path, while photochemical isomerization proceeds along a twisting path, is based primarily on calculations [8-13]. In spite of the intrinsically two-dimensional nature of the problem, previous calculations did not explore in sufficient detail a two dimensional subspace of the nuclear coordinate space in the lowest singlet state S_0, relevant for the thermal process, and the next higher singlet (S_1) and the lowest triplet (T_1) states, relevant for photochemical processes.

In particular, it is not known at what geometry the minima in the S_1 and T_1 surfaces are located. In solution or solid phase photochemistry, and under other conditions where vibrational deactivation is rapid, these are presumably the geometries at which the molecules reenter the S_0 ground state after initial excitation, subsequently relaxing to thermalized ground state products.

We have used an *ab initio* large-scale CI procedure to map out the relevant two-dimensional subspaces for the twisting and inversion in the S_0, S_1, and T_1 electronic states of the simplest imine, $CH_2{=}NH$. We find that the S_0 and S_1 surfaces actually touch, thus providing an extremely efficient "funnel" for the return of electronically excited singlet molecules to the ground state, possibly even competing with vibrational thermalization.

In addition, this investigation also provided information on the trends in the lowest excitation energy of the C=N chromophore as a function of the two geometrical variables, and these are useful in our experimental investigations of bridgehead imines with variously distorted C=N bonds [8, 14-16].

2. Method of calculation

Multireference double CI treatments [17, 18] with extrapolation and of quality described in detail elsewhere [9] were employed for the simultaneous descriptions of the three lowest singlet and of the two lowest triplet states. For reference configurations, we used all eleven singlet and all nine triplet configurations which had weights in excess of 0.05 in the expansion of the correlated wavefunctions anywhere in the whole twist (θ) and valence (ϕ) angle interval $\theta = [0, 90]$, $\phi = [90, 180]$. This resulted in the use of several thousand configurations in the CI treatment.

Triplet SCF MO's were used as one-electron functions to span both the triplet and the singlet CI spaces because they yield the most balanced description of two close-lying singlet states for biradicaloid geometries [9]. They are less suitable for S_0 at planar geometries, but these are the least important for our purposes. Both the 4-31G and 6-31G** AO basis sets were used at a fair number of geometries and yielded very similar surface shapes. The final calculations were done for a grid of 36 geometries using the 4-31G basis.

3. Results

3.1. Qualitative analysis

Before presenting numerical results, we shall consider some qualitative correlation diagrams pertinent to the isomerization problem [14].

At orthogonal twist ($\theta = \pm 90°$), formaldimine has C_s symmetry and can be expected to have two low-energy singlet states (Fig. 2):

(i) A "closed-shell" A′ state with a lone pair in a $2p_N$ orbital and with polar σ as well as "π" bonds between C and N (**1**). The "π" interaction will be due to an overlap between a $2p_C$ orbital on carbon and a hybrid sp_N^x orbital on N, and will become less pronounced as ϕ, the valence angle CNH, decreases. Thus for $\phi > 90°$, the orthogonally twisted formaldimine still is a doubly bonded species,

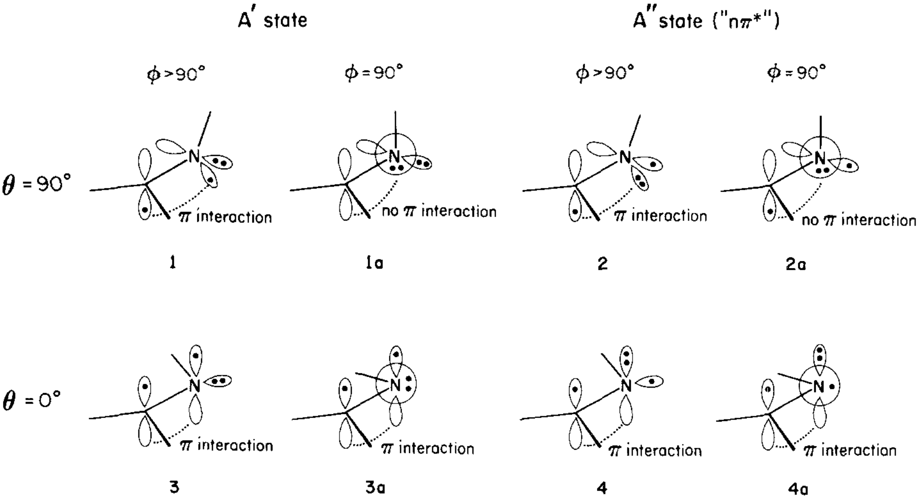

Fig. 2. Valence-bond representations of the A' and the A'' singlet states of orthogonally twisted ($\theta = 90°$) and planar ($\theta = 0°$) formaldimine for sp^x hybridization ($\phi > 90°$) and no hybridization ($\phi = 90°$) on nitrogen

analogous to a partially twisted singly pyramidalized ethylene. At $\phi = 90°$, the "π" interaction will vanish as the hybrid orbital becomes a pure $2s_N$ orbital (1a). The "π" orbital will then be localized on $2s_N$ and the "π^*" orbital on $2p_C$ in the first approximation, so that the orthogonally twisted formaldimine is a singly bonded biradicaloid, analogous to orthogonally twisted and singly pyramidalized ethylene.

(ii) An "open-shell", or "$n\pi^*$", A'' state with a single electron in the lone $2p_N$ orbital, two electrons in the "π" and one in the corresponding "π^*" orbital (2). Up to a point, the energy of this state can be expected to decrease as the valence angle ϕ decreases from 180° and a $2s_N$ lone pair develops (2a).

The numerical results described below show that the two states actually cross as the valence angle ϕ is varied from 180° to 90°. Since they are of different symmetries, the crossing is not avoided and a $S_0 - S_1$ surface touching results. The anticipated correlation diagram is shown in Fig. 3A.

At planarity ($\theta = 0°$ or 180°), formaldimine again has C_s symmetry and its lowest two singlet states can again be expected to be related by an $n\pi^*$ excitation (Fig. 2):

(i) A "closed shell" ground state singlet A' with a lone pair in an sp^x hybrid orbital and with polar σ as well as π bonds between C and N (3, 3a). The π interaction will be between a $2p_C$ and a $2p_N$ orbital regardless of the valence angle ϕ, and planar formaldimine clearly is a doubly bonded species. The lone-pair orbital energy as well as the σ bond energy will depend on ϕ and an energy minimum can be expected somewhere near a CNH angle $\phi = 120°$.

(ii) A higher-energy $n\pi^*$ "open-shell" singlet A" with a single electron in the lone orbital, two electrons in the π orbital, and one electron in the π^* orbital state (4, 4a). As a function of the twist angle θ, the singlet state energies must

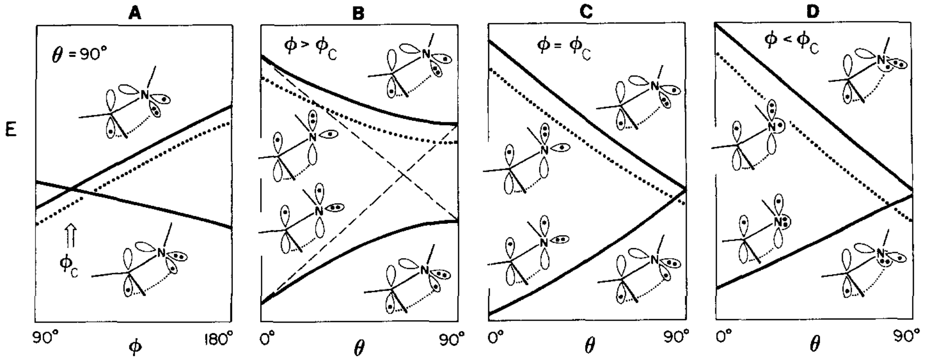

Fig. 3. Correlation diagrams for formaldimine: (A) change in the CNH valence angle ϕ at orthogonal twist ($\theta = 90°$), (B) change in the twist angle θ at a large fixed valence angle ϕ, (C) change in the twist angle θ at the critical value of the valence angle ϕ, (D) change in the twist angle θ at a small fixed valence angle ϕ. Singlet states: before configuration mixing (dashed line), and after configuration mixing (full line). Triplet state: dotted line

connect smoothly. Molecular symmetry at values of θ other than 0°, ±90°, and 180° is C_1, so that state crossings may be avoided. It is already known from calculations [9] at valence angle $\phi = 115°$ that such an avoided crossing indeed occurs: at $\theta = 0°$ the energy of the VB structure 3 lies below that of 4 but at $\theta = \pm 90°$ the energy of 2, obtained from 3 by an orthogonal twist, lies above that of 1, obtained from 4 by the same twist. Such an avoided crossing is expected in correlation diagrams drawn for CNH valence angles ϕ larger than that at which the $S_0 - S_1$ touching occurs but not at smaller values of ϕ. Examples of these correlation diagrams are shown in Figs. 3B-3D.

The open-shell singlet state has a companion triplet state. It can be anticipated to run approximately parallel to the singlet, at somewhat lower energies. At the biradicaloid geometries near $\theta = \pm 90°$, $\phi = 90°$, it can be expected to represent the lowest electronic state of the system.

3.2. Computational results

Figure 4 provides an illustration of the statement that the 6-31G** and 4-31G basis sets yield qualitatively similar results at a more or less arbitrarily chosen series of geometries. The following discussion is based on extrapolated [9 17, 18] large-scale CI results obtained using the 4-31G basis set.

The results of the numerical calculations for the S_0, S_1, and T_1 states are shown as contour plots in Figs. 5-7, and along three selected cuts in Figure 8. They agree with the qualitative analysis, both with respect to surface shapes and

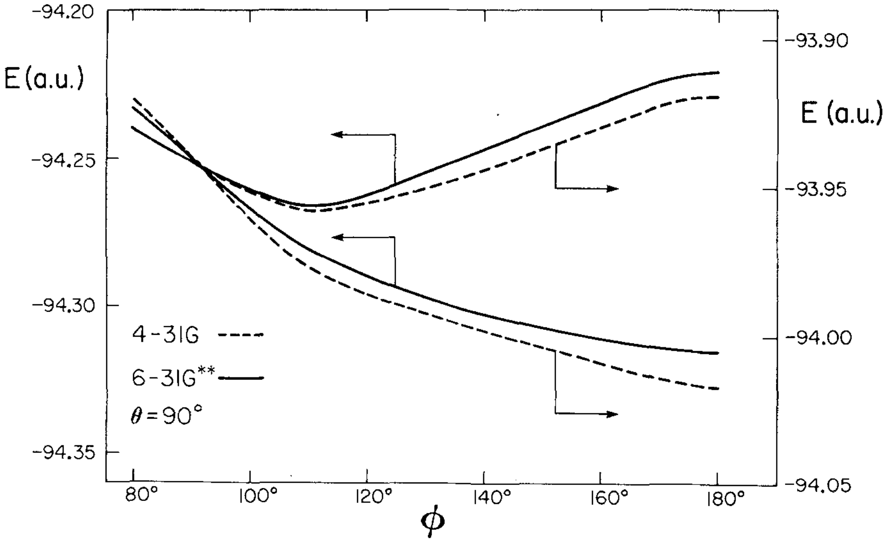

Fig. 4. An example of the qualitative agreement of S_0 and S_1 state energies of formaldimine obtained using 4-31G (dashed line) and using 6-31G** (full line). Orthogonal twist ($\theta = 90°$), $r_{CN} = 1.37$ Å, $r_{CH} = 1.069$ Å, $r_{NH} = 1.01$ Å, valence angle HCN, 119.2°

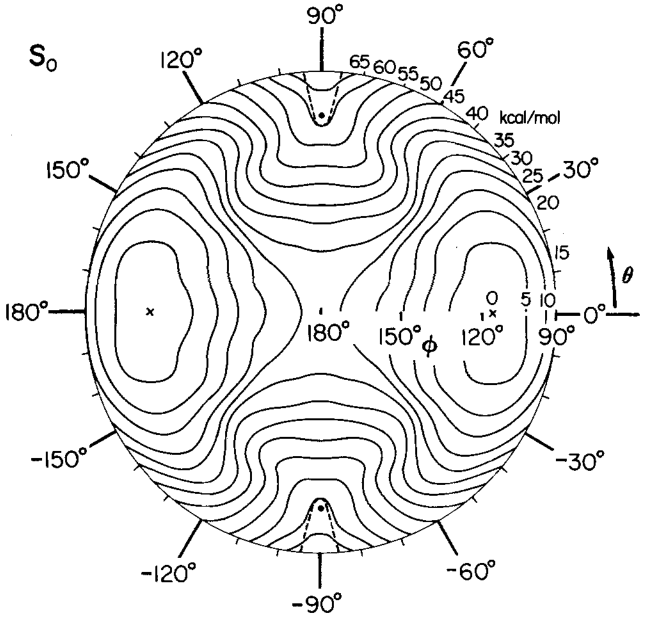

Fig. 5. An energy contour map for the S_0 state of formaldimine. The radial variable is the CNH valence angle ϕ, the angular variable is the twist angle θ. For other geometrical parameters, see text. Energies in kcal/mol are given relative to that at the two equilibrium geometries, indicated by crosses at $\theta = 0°$, 180°, and $\phi = 115°$. The dots at $\theta = \pm 90°$, $\phi = 106.5°$ represent the $S_0 - S_1$ touching points. The dashed lines indicate the $S_0 - T_1$ intersection

the nature of the wavefunctions. The S_2 and T_2 states are at distinctly higher energies at all geometries investigated presently and are not shown.

The choice of the geometrical parameters which define the two-dimensional subspace mapped in Figs. 5-7 requires comment. Since we are primarily interested in photochemical processes, the S_1 and T_1 surfaces are of key importance, particularly in the region near their minima. The T_1 state has the open-shell electronic structure described above at all geometries of interest, S_1 has this structure at almost all geometries of interest. We have optimized the geometry of the open-shell singlet state at the SCF level under the constraint of orthogonal twist ($\theta = 90°$), and that of the triplet state with no constraint, using the gradient minimization technique. The resulting geometrical parameters are collected in Table 1. Calculations for S_1 at a few geometries distorted away from orthogonality all gave higher energies and showed that both surfaces have minima at orthogonally twisted geometries, as expected. In the S_1 state, the optimum CNH valence angle ϕ is somewhat smaller than the ~115° characteristic of the equilibrium geometry in the S_0 ground state.

Since the optimized geometries of the S_1 and T_1 states were quite similar, we have decided to map the two surfaces in a common two-dimensional subspace. In order to optimize this subspace, we have used the gradient technique to carry

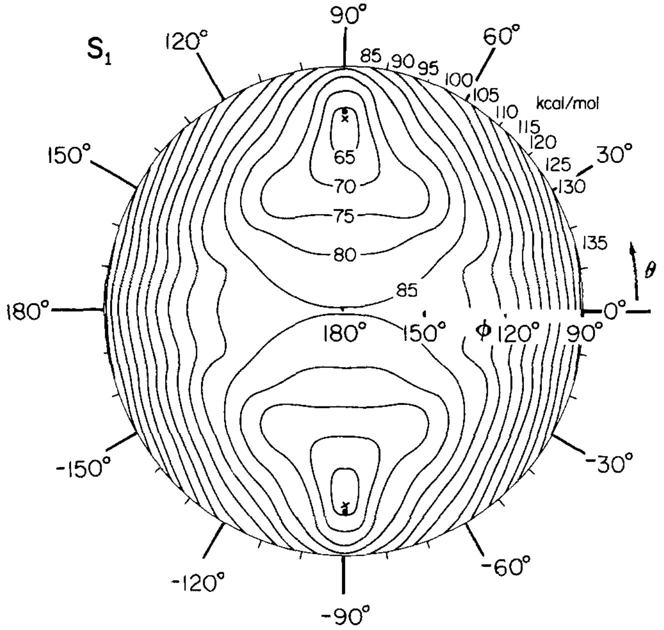

Fig. 6. An energy contour map for the S_1 state of formaldimine. The radial variable is the CNH valence angle ϕ, the angular variable is the twist angle θ. For other geometrical parameters, see text. Energies in kcal/mol are given relative to that of the S_0 state at its equilibrium geometry. The dots at $\theta = \pm 90°$, $\phi = 106.5°$, represent the $S_0 - S_1$ touching points, the crosses at $\theta = \pm 90°$, $\phi = 109°$ represent the positions of the minima in S_1: −93.9656 a.u. (extrapolated), −93.9587 a.u. (variational)

out a series of SCF geometry optimizations for the open-shell singlet state under the constraint of orthogonal twist at a series of constrained CNH valence angles ϕ. Each of these geometries was then used for a series of CI calculations for singlet and triplet states in which only the twist angle θ was varied from 0° to 90° and bond lengths as well as all other bond angles were kept constant.

This procedure is expected to give essentially the optimal shapes for the S_1 and T_1 surfaces computed at the CI level, particularly near orthogonal geometries. It should be noted that the open-shell SCF configuration is by far the leading configuration in the CI expansion (weight 93% for S_1 and 94% for T_1 at the respective minima), justifying the use of geometries optimized at the SCF instead of the much more expensive CI level. This optimism is supported by the close agreement between the positions of minima in the S_0, S_1 and T_1 surfaces shown in Figs. 5–7 and those obtained at the SCF level (Table 1).

The two-dimensional subspace of the nuclear configuration space thus defined for the photoisomerization reaction is clearly far from optimal for a discussion of ground-state chemistry, although the S_0 surface still shows all the already known important qualitative features: two minima for the equivalent *syn* and *anti* isomers of planar formaldimine with a CNH valence angle of 115°, communicating through a saddlepoint located about 25 kcal/mol higher at a linear

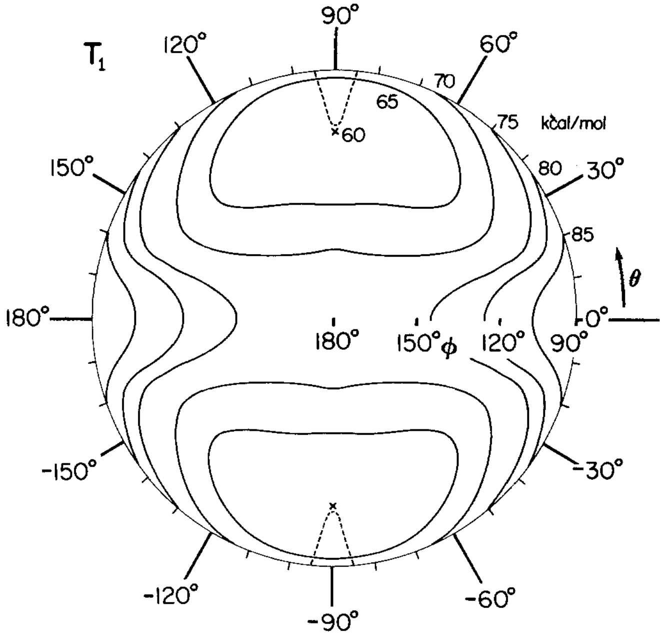

Fig. 7. An energy contour map for the T_1 state of formaldimine. The radial variable is the CNH valence angle ϕ, the angular variable is the twist angle θ. For other geometrical parameters, see text. Energies in kcal/mol are given relative to that of the S_0 state at its equilibrium geometry. The crosses at $\theta = \pm 90°$, $\phi = 112°$ represent the positions of the minima in T_1. The dashed lines indicate the $S_0 - T_1$ intersection

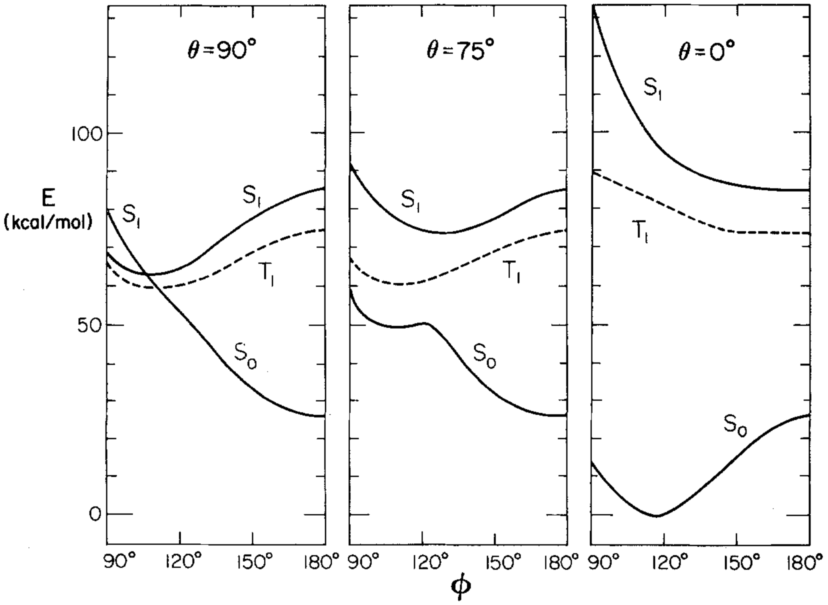

Fig. 8. Selected cuts through the potential energy surfaces displayed in Figs. 5-7

Table 1. SCF optimized geometries of formaldimine in S_0, S_1 and T_1 states[a]

	r(C—N)	r(N—H)	r(C—H)	ψ(CNH)	α(HCN)	θ(twist)
S_0	1.256	1.006	1.076	115.7°	122.0°	0°
S_1	1.422	1.017	1.069	112.6°	119.2°	90°
T_1	1.402	1.014	1.069	115.1°	119.2°	90°

[a] 4-31G, open-shell SCF for S_1 and T_1, closed-shell SCF for S_0.

CNH geometry, with out-of-plane twisting paths higher in energy (Fig. 5). For our purposes, the primary significance of the S_0 surface consists in defining the S_0-S_1 and S_0-T_1 gaps, important for the understanding of radiationless transitions, and for the nature of the ultimate photoproducts.

As shown in Figs. 6 and 7, the shapes of the S_1 surface and the considerably flatter T_1 surface resemble each other and are very different from that of the S_0 surface: orthogonal geometries rather than planar ones are preferred, and among them, valence angles near 115° rather than 180° are preferred. The very small S_0-S_1 gap at orthogonal geometries in the region $100° < \phi < 120°$ can be viewed as a consequence of the conical intersection located at the orthogonal geometry at a CNH angle of $\phi \simeq 106.5°$. The touching point is located on a weakly sloping part of the surfaces, a fraction of a kcal/mol above the minimum in S_1. In the region of the touching point and at smaller ϕ values, the system has the features expected for a biradicaloid species; in particular, it has a triplet as the lowest electronic state.

4. Discussion

Conical intersections of S_0 with S_1 have not been invoked much in mechanistic proposals concerning geometrical isomerization about double bonds. In the absence of lone pairs and low-energy $n\pi^*$ states, the S_1 and S_0 surfaces of a twisted isolated double bond remain separated by a large gap unless the atoms or groups of atoms at the two termini differ very considerably in electronegativity, as in the orthogonally twisted formaldiminium ion $CH_2{=}NH_2^+$, where the "covalent" VB structure ($\dot{C}H_2{-}\dot{N}H_2^+$) is approximately of the same energy as the "polarized" VB structure ($CH_2^+{-}\ddot{N}H_2$) [19-22].

The present results show that in this regard formaldimine, and presumably simple unprotonated Schiff bases in general, are quite different. The small S_0-S_1 gap found in several prior calculations for twisted formaldimine [9] was thus clearly not accidental but rather, is a consequence of a weakly avoided crossing related to a nearby S_0-S_1 conical intersection.

Similar considerations apply to systems of conjugated double bonds. Here again, in the absence of $n\pi^*$ states S_0-S_1 conical intersections are to be expected only for those twists around C=C or C=N double bonds which produce two (usually delocalized) radical centers A· and B· in such a way that the energies of the VB structures $\dot{A}$-$\dot{B}$ and A-$\ddot{B}$ are comparable [9, 19-22]. The $n\pi^*$ states of unprotonated Schiff bases again offer additional opportunities in this regard and we believe that the small S_0-S_1 gap calculated for twisted allylidene imine [9] also is a consequence of a nearby S_0-S_1 conical intersection.

Figures 5-7 suggest that a vertical excitation of a simple imine to the S_1 state should be followed by vibrational relaxation to an orthogonally twisted geometry and to the funnel in S_1, followed by a very rapid radiationless relaxation to S_0. This should leave little opportunity for fluorescence or intersystem crossing. Even if some of the S_1 molecules fluoresce or proceed to T_1 (or if they were initially excited into T_1), they should still rapidly land on the same ridge in the S_0 surface as those that followed the $S_1 \rightarrow S_0$ internal conversion path. Since in the region of its minimum the T_1 surface is nearly degenerate with S_0, $T_1 \rightarrow S_0$ intersystem crossing should be rapid. Once a molecule is back in the S_0 electronic state, it should vibrationally relax rapidly to one of the two symmetry-equivalent planar forms of the imine, "*syn*" and "*anti*", with equal likelihood. The direct and sensitized *syn* → *anti* as well as *anti* → *syn* photoisomerization yields should then both be equal to 0.5. In less symmetrical simple imines, the two quantum yields need no longer be equal but they should still add up to unity.

Two factors which have not been considered so far might invalidate the above conclusions. First, excursions from the S_1 (or T_1) minimum in directions other than those leading towards the funnel (or S_0-T_1 intersection line), either induced thermally or occurring during the initial period of vibrational cooling after the primary light absorption and/or intersystem crossing events, could take the molecules to saddlepoints in the S_1 (or T_1) surfaces from which motion in directions not explored here would be possible, thus opening new photochemical channels. Experimentally, it is known at least in some cases that long-wavelength excitation of an imine causes a rapid *syn-anti* isomerization and no other detectable photochemical product formation [14].

The second possible reason for a deviation of the quantum yields from 0.5 is intrinsically more interesting. In the immediate vicinity of the conical intersection radiationless jumps from S_1 to S_0 should have a particularly high probability, so that trajectories which take the molecules into this region, either from the originally reached vertical excited geometry, or by thermally induced excursions from the region near the S_1 minimum, are likely to be responsible for the bulk of the radiationless return from S_1 to S_0. If a significant fraction of the excited molecules reaches the region of the conical intersection without having lost dynamical memory of their original geometry, *syn* or *anti*, quantum yields of the photochemical *syn* → *anti* and *anti* → *syn* isomerizations, which are equal by symmetry, may both deviate from 0.5 even in the absence of other competing processes.

Such a hypothetical possibility has been considered previously in an abstract fashion [23] and also on the concrete example of an olefin *cis-trans* isomerization [24], inspiration being provided by the photochemical behavior of the visual pigment, rhodopsin. However, as pointed out above, in the absence of lone pairs and $n\pi^*$ states only charged ordinary double bonds, such as a protonated Schiff base, $CH_2{=}NH_2^+$, are likely to have very small S_0-S_1 gaps or perhaps even a S_0-S_1 conical intersection and thus an opportunity to exhibit this type of behavior [25]. In this sense, it is perhaps not purely accidental that the chromophore of rhodopsin is a protonated Schiff base. However, so far we are not aware of definitive experimental evidence for this type of dynamic behavior, either in a free or a protonated Schiff base. The present results suggest that simple Schiff bases are promising candidates in the search for this type of behavior.

Acknowledgement. This work was supported by the Deutsche Forschungsgemeinschaft (Bo 627/5-1), by the National Science Foundation (CHE-81-21122), and by a John S. Guggenheim Fellowship to J.M.

References

1. Kropf, A., Hubbard, R.: Ann. N. Y. Acad. Sci. **74**, 266 (1958); Yoshizawa, T., Wald, G.: Nature **197**, 1279 (1963).
2. For a recent photochemical investigation of a Schiff base of 11-*cis*-retinal, see Becker, R. S., Freedman, K.: J. Am. Chem. Soc. **107**, 1477 (1985).
3. Patai, S.: The Chemistry of the Carbon-Nitrogen Double Bond, New York: Interscience Publishers 1970
4. Padwa, A.: Chem. Revs. **77**, 37 (1977).
5. Pratt, A. C.: Chem. Soc. Rev. **6**, 63 (1977)
6. Sandorfy, C.: Top. Curr. Chem. **86**, 91 (1979)
7. Paetzold, R., Reichenbächer, M., Appenroth, K.: Z. Chem. **21**, 421 (1981).
8. Michl, J., Radziszewski, G. J., Downing, J. W., Wiberg, K. B., Walker, F. H., Miller, R. D., Kovacic, P., Jawdosiuk, M., Bonačić-Koutecký, V.: Pure Appl. Chem. **55**, 315 (1983).
9. Bonačić-Koutecký, V., Persico, M.: J. Am. Chem. Soc. **105**, 3388 (1983)
10. Howell, J. M.: J. Am. Chem. Soc. **98**, 886 (1976).
11. Macaulay, R., Burnelle, L. A., Sandorfy, C.: Theor. Chim. Acta **29**, 1 (1973)
12. Osamura, Y., Kitaura, K., Nishimoto, K., Yamabe, S.: Chem. Phys. Lett. **63**, 406 (1979)
13. Russegger, P.: Chem. Phys. **34**, 329 (1978)
14. Radziszewski, J. G., Downing, J. W., Jawdosiuk, M., Kovacic, P., Michl, J.: J. Am. Chem. Soc. **107**, 594 (1985)
15. Radziszewski, J. G., Downing, J. W., Wentrup, C., Kaszynski, P., Jawdosiuk, M., Kovacic, P., Michl, J.: J. Am. Chem. Soc. **106**, 7996 (1984)
16. Radziszewski, J. G., Downing, J. W., Wentrup, C., Kaszynski, P., Jawdosiuk, M., Kovacic, P., Michl, J.: J. Am. Chem. Soc. **107**, 2799 (1985)
17. Buenker, R. J., Peyerimhoff, S. D.: Theor. Chim. Acta **35**, 33 (1974)
18. Buenker, R. J., Peyerimhoff, S. D. Butscher, W.: Mol. Phys. **35**, 771 (1978)
19. Bonačić-Koutecký, V., Michl, J., Köhler, J.: Chem. Phys. Lett. **104**, 440 (1984).
20. Bonačić-Koutecký, V., Michl, J.: J. Am. Chem. Soc. **107**, 1765 (1985)
21. Bonačić-Koutecký, V., Koutecký, J., Michl, J., unpublished results
22. Bonačić-Koutecký, V., Köhler, J., unpublished results
23. Michl, J.: Mol. Photochem. **4**, 243 (1972): Top. Curr. Chem. **46**, 1 (1974)
24. Weiss, R. M., Warshel, A.: *J. Am. Chem. Soc.* **101**, 6131 (1979)
25. The implication in ref. 24 that this type of behavior is general for olefins was based on a simple Hückel approximation and is incorrect. In ethylene and propene a fairly high-level calculation [26] showed large S_1-S_0 gaps and only very small S_1-S_0 jump probabilities at orthogonal geometries
26. Persico, M., Bonačić-Koutecký, V.: J. Chem. Phys. **76**, 6018 (1982).