

MNDO CI STUDY OF THE PHOTOISOMERIZATION OF PENTADIENIMINIUM

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Photoisomerization mechanism in model retinal-like protonated Schiff base pentadieniminium was investigated by using MNDO method with configuration interaction. Isomerizations around various double bonds were studied and twisted biradical geometries in S_0 and S_1 states were optimized. Photoisomerization proceeds exclusively around the central double bond where the twisted S_1 state is strongly stabilized and the $S_0 - S_1$ gap is minimal.

Protonated Schiff base (PSB) of retinal plays the important role in many bio-optical devices created by the nature. It is a chromophore of the visual pigment rhodopsin, whose photoisomerization from 11-*cis* to all-*trans* form is the first step in the complex process of transformation of light into a nerve impulse. During the last few years still other related mechanisms of PSBs bio-optical activity have been discovered and other can be expected¹.

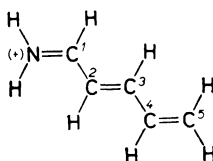
Photoisomerization of PSB of retinal is regioselective and proceeds with a high quantum yield. This phenomenon was an object of intensive research, both experimental and theoretical (for an excellent review see ref.¹).

Most authors agree that the absorbing state of PSBs is ${}^1B_u^+$ one, followed by ${}^1A_g^-$ state (although PSBs have only C_s symmetry the notation for polyenes (C_{2h})) is commonly used and the superscripts + and - reflect the in-phase and out-of-phase combinations of configurations in CI wave function, respectively). On the basis of INDO CI calculations² it was stated that photoisomerization proceeds in the ${}^1A_g^-$ state. This was confirmed also by recent MNDO study³. *Ab initio* large scale CI calculations⁴ on methaniminium and propeniminium confirmed the existence of an $S_0 - S_1$ conical intersection in twisted double bond geometries of these molecules.

The goal of present work was to contribute to better understanding of geometry and electronic structure of PSBs in excited states and mechanism of their photoisomerization.

CALCULATIONS

As a model system for retinal we have chosen the pentadieniminium (PDI).



This molecule, although relatively small, has all structural elements relevant for the study of retinal photoisomerization.

The calculations have been performed using the semiempirical MNDO method⁵. Although this method was designed primarily for the study of reactions in the ground state, it has proved very useful also for the study of excited states. MNDO was shown to yield energies of excited states too negative but ordering of states, their relative distances, and effects of substituents are reproduced well⁶⁻⁸. Optimized excited state geometries, especially having biradical character, are also described satisfactorily⁹. We have calculated MNDO CI torsion potential curves for photoisomerizations around various double bonds of different polarity¹⁰. Calculated curves practically mimic the *ab initio* ones.

Cis and *trans* ground state geometries of PDI were fully optimized on the SCF level. Geometries twisted around particular double bonds were partially optimized (bond lengths between heavy atoms) with 3×3 configuration interaction (CI) based on the half-electron molecular orbitals¹¹. Dependence of energies of particular states on the twist angle was calculated for geometries obtained by linear variation between optimized ground state and excited state geometries. These curves were calculated by CI with 16 monoexcited configurations from the reference open shell half-electron singlet (i.e. also some biexcited configurations from the closed shell ground state were used).

RESULTS AND DISCUSSION

PDI is an isoelectronic molecule with hexatriene (HT). They differ only in strongly withdrawing protonated nitrogen. The influence of this atom on electronic distribution can be clearly seen from Table I, where calculated net atomic charges in both PDI and HT are compared.

MNDO CI calculations give for the lowest vertical absorption in PDI value of 2.51 eV. This transition is of ${}^1B_u^+$ character (using the C_{2h} symmetry labelling) and the excited state is of HOMO \rightarrow LUMO nature. The second transition is ${}^1A_g^-$ one at 3.73 eV. Its wave function is composed of HOMO-1 \rightarrow LUMO and HOMO² \rightarrow LUMO² configurations with about the same weight. *Ab initio* excitation energies (idealized geometry, MR SDCI)¹² are 4.6, and 6.4 eV for ${}^1B_u^+$, and ${}^1A_g^-$ states, respectively. Experiment also gives this ordering of states for PSBs (ref.¹³). For comparison we have also calculated absorption spectrum for HT. The ordering of

$^1B_u^+$ and $^1A_g^-$ transitions in this system is still an open problem for organic photochemistry. The former lies at about 5 eV (ref.¹⁴), the latter, because of its forbidden nature, was not observed, yet. MNDO gives as the lowest the $^1A_g^-$ transition at 3.82 eV followed by the $^1B_u^+$ transition at 4.36 eV. Most theoretical works support this ordering of states (for a recent review see ref.¹⁵) but some calculations yield the $^1B_u^+$ state as the lowest¹⁶.

Calculation of vertical excitation energies was of course not the main objective of our work. The method we have used is not even suitable for such study. We focused mainly on the relaxed geometries. In PSB containing several double bonds a choice is possible among particular bonds around which photoisomerization could occur. The most preferred will be the twisted conformation in which S_1 touches S_0 , i.e. these two surfaces exhibit conical intersection.

As a result of twist the molecule divides into two orthogonal subsystems. A biradical is created with three closely lying singlet states¹⁷, a covalent one (D) and two zwitterions (Z_1 and Z_2). In the case of twisted symmetrical polyenes, like ethylene or hexatriene, D state is the lowest and two zwitterionic states formed by in-phase and out-of-phase combinations of Z_1 and Z_2 configurations lie higher in energy. In perturbed systems one zwitterionic state is considerably stabilized and may fall even under the D state. For a particular polarity of the twisted double bond these two states are degenerate (such systems are called critical biradicaloids^{17,18}) and exhibit conical intersection with resulting very efficient photoisomerization.

In PDI there are three double bonds of different polarity. For terminally twisted C=C bond the lowest excited singlet will be of covalent nature represented by $\dot{C}H_2- + -CH=CH-CH=CH-\dot{N}H_2^+$ combination. For C=N twisted geometry the Z_1 state represented by $CH_2=CH-CH=CH-CH_2^+ + -NH_2$ combination will be the lowest. For geometry twisted around the central C=C bond energies of D and Z_1 states represented by $CH_2=CH-\dot{C}H- + -CH=CH-\dot{N}H_2^+$, and $CH_2=CH-CH^+ + -CH=CH-NH_2$ combinations, respectively, would be about the same.

These qualitative conclusions were fully justified by results of MNDO calculations. In Fig. 1 calculated torsion potential curves for twist around all three double bonds

TABLE I
Calculated net atomic charges for pentadieniminium (PDI) and hexatriene (HT)

Molecule	N/C	C(1)	C(2)	C(3)	C(4)	C(5)
PDI	-0.192	0.075	0.116	-0.149	0.042	0.112
HT	-0.049	-0.079	-0.049	-0.049	-0.079	-0.049

are shown, and in Table II the most important structural and electronic parameters for planar ground state and twisted biradical states of PDI are summarized. For N=C twisted geometry the S_0 state has Z character and the $S_0 - S_1$ gap is 1.65 eV. For the terminally twisted C=C geometry S_0 has, on the other hand, covalent character and the $S_0 - S_1$ gap is also quite large (1.11 eV). During the rotation around the central C=C bond (in this case the curves are not symmetrical with respect to twist angle 90° because they represent isomerization from *trans* to *cis* isomer) the S_0 and S_1 states approach each other and the energy difference between them in twisted geometry is only of 0.17 eV. Moreover, even small changes in geometry reverse ordering of these states. As a result of this near-touching a very efficient return to the ground state in this point is possible.

For comparison we have also calculated torsion curves for the photoisomerization around both terminal and central C=C bonds in HT. Results differ considerably from those presented in this article. The $S_0 - S_1$ gaps in both twisted conformations of HT are much greater, about 2 eV, what is consistent with previous *ab initio* calculations¹⁹.

On the conclusion it can be said that MNDO calculations presented here have proved that conjugated PSB photoisomerize most effectively around the central double bond because the S_1 state is strongly stabilized here and the $S_0 - S_1$ gap

TABLE II

Relevant geometry parameters and atomic charges of planar ground state and twisted biradical states of PDI and their relative energies (in eV)

Parameter	S_0	S_0	S_0	S_1	S_0	S_1	S_0	S_1
	<i>trans</i>	<i>cis</i>	N=C(1) tw.		C(2)=C(3) tw.		C(4)=C(5) tw.	
$r_{N=C(1)}$	1.334	1.334	1.389	1.402	1.338	1.354	1.339	1.355
$r_{C(2)-C(3)}$	1.430	1.429	1.410	1.343	1.427	1.376	1.425	1.391
$r_{C(3)=C(4)}$	1.383	1.382	1.414	1.451	1.453	1.438	1.410	1.423
$r_{C(4)-C(5)}$	1.447	1.446	1.421	1.442	1.400	1.439	1.387	1.370
$r_{C(5)=C(6)}$	1.357	1.358	1.379	1.323	1.378	1.357	1.448	1.410
N	-0.192	-0.188	-0.522	0.269	-0.275	-0.148	-0.214	-0.263
C(1)	0.075	0.000	0.410	-0.207	0.187	0.178	0.234	0.233
C(2)	0.116	0.128	-0.142	0.032	-0.591	0.132	-0.060	-0.290
C(3)	-0.149	-0.141	0.207	-0.048	0.532	-0.149	-0.034	0.040
C(4)	0.042	0.031	-0.154	-0.071	-0.091	-0.084	0.141	-0.554
C(5)	0.112	0.116	0.186	-0.013	0.224	0.049	-0.112	0.778
ΔE	0.00	0.05	1.34	2.99	1.60	1.77	1.24	2.35

is minimal. Photoisomerization proceeds via a biradical which correlates with the doubly excited vertical state.

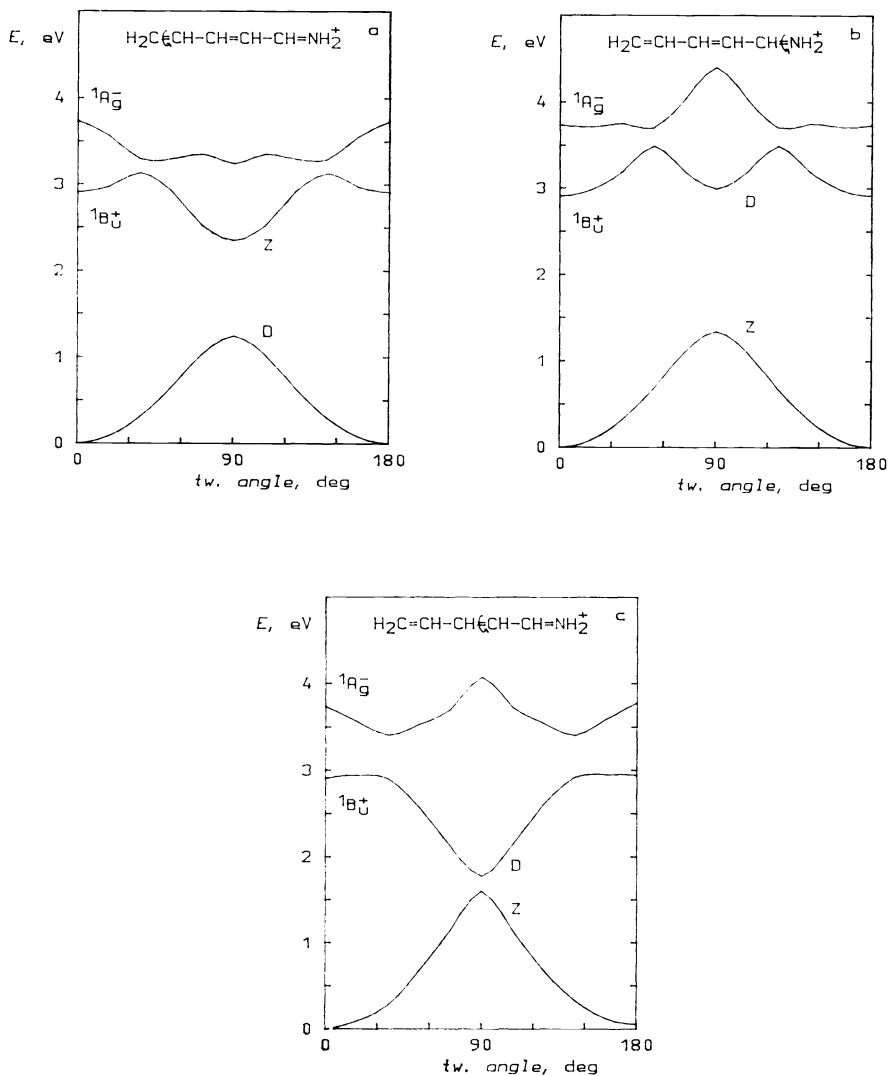


FIG. 1
Potential energy curves for the rotation around a terminal $C=C$ bond, b $C=N$ bond, and c central $C=C$ bond in pentadieniminium

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