Table III. Measurement of the Equilibrium Constant for **10** + **21** ⇌ **20** + **19**. $K_{eq} = (20)(19)/(10)(21)$

	equilibrium concentrations, mmol	
compound	procedure A[a]	procedure B[a]
10	1.01×10^{-3}	2.00×10^{-3}
21	0.77×10^{-3}	0.66×10^{-3}
20	2.58×10^{-3}	2.79×10^{-3}
19	2.77×10^{-3}	4.19×10^{-3}
K_{eq}	9.2 ± 2.0	8.9 ± 2.0

[a] See text.

65 h. The reaction was monitored by ^{1}H NMR analysis to determine the relative concentrations of each component. No change was evident after 65 h.

Procedure B. To a solution of 2.1 mg (3.69×10^{-3} mmol) of **2** in 2 mL of deuteriochloroform was added 1.5 mg (3.85×10^{-3} mmol) of **10**; the solution was stirred in the dark at room temperature for 65 h. The relative concentrations of the components were monitored by ^{1}H NMR analysis and showed no change after 65 h.

10 + **21**. **Procedure A.** To a solution of 2.3 mg (3.54×10^{-3} mmol) of **21** in 3 mL of deuteriochloroform was added 1.4 mg (3.59×10^{-3} mmol) of **10**; the solution was stirred for 50 h in the dark at room temperature. The reaction was monitored by ^{1}H NMR analysis to determine the relative concentrations of each component. No change was evident after 50 h.

Procedure B. To a solution of 3.1 mg (4.79×10^{-3} mmol) of **20** in 3 mL of deuteriochloroform was added 1.9 mg (4.85×10^{-3} mmol) of

19; the solution was stirred at room temperature in the dark for 50 h. The reaction was monitored by ^{1}H NMR analysis to determine the relative concentrations of each of the components. No change was evident after 50 h.

Variable-Temperature C^{13} NMR Studies of 20. The C^{13} NMR spectrum of the silver complex of **20** was measured using a 2.5×10^{-2} M solution in deuteriochloroform with a Nicolet NT 360 spectrometer. At 20 °C, the spectrum showed a sharp singlet at 31.3 ppm (sp^3 carbons), a sharp singlet at 138.7 ppm (sp^2 carbons), and a broad singlet at 125.5 ppm (sp^2 carbons bound to Ag$^+$). When the solution was cooled, the signals broadened and showed coalescence at near −10 °C. In the range of −50 to −65 °C, the solution showed six sharp singlets at 31.5 and 31.2 (sp^3 carbons), 139.3, 138.1, and 133.8 (sp^2 carbons), and 117.1 ppm (sp^2 carbon bound to Ag$^+$). When these measurements were repeated using a lower concentration (1.89×10^{-2} M), coalescence occurred at approximately 0 °C.

Spectroscopy and Photochemistry of Conjugated Nonprotonated Schiff Bases: Application of an ab Initio Derived Heisenberg Effective Hamiltonian

J. Sanchez-Marin[1] and J. P. Malrieu*

Contribution from the Laboratoire de Physique Quantique (E.R.A 821 du C.N.R.S), Université Paul Sabatier, 31062 Toulouse Cedex, France. Received July 16, 1984

Abstract: A Heisenberg effective Hamiltonian, previously derived for conjugated hydrocarbons and imines, is extended to treat nπ* excited states as well as ground and ππ* states; this Hamiltonian is applied to the conjugated (nonprotonated) Schiff bases series up to five double bonds. The vertical excitation energies to the neutral excited states are calculated as a function of the chain length and extrapolated to larger systems; the excited-state geometries are optimized by showing the extreme importance and diversity of geometrical relaxations: this problem is illustrated in details for 2-propen-1-imine (allylidenimine) for which accurate MO-CI calculations are available. The 90° twisting of CC double bonds has been investigated in both ground and neutral excited states; the perturbation due to the heteroatom is larger in the excited states than in the ground state. It seems undoubtly that for large enough polyenimines, the "^1A_g" excited state is lower than the "^1B_u" allowed state and that cis–trans isomerization around internal double bonds is possible on the ^1A_g surface.

1. Introduction

The absorption and photochemical properties of polyenes is an important topic in visible and UV spectroscopy[2] and a sort-of permanent test field for theoretical models.[3-9] Recently, a new approach based on the use of a Heisenberg effective Hamiltonian (HEH) has been successfully applied to the study of the photochemistry of linear polyenes, permitting an easy prediction of conformational and energetic properties of some important excited states,[10] a study of rotational barriers in both ground[11] and excited states,[10] and an analysis of the photochemical role of the ^1A_g lower

(1) On leave from the Department de Quimica-Fisica, Facultat de Quimica, Universitat de València, Dr. Moliner 50, Burjassot (Valencia) Spain.

(2) See, e.g.: (a) Jaffe, H. H.; Orchin, M. "Theory and Applications of Ultraviolet Spectroscopy"; Wiley: New York, 1962. (b) Murrell, J. N. "The Theory of the Electronic Spectra of Organic Molecules"; Wiley: New York, 1963.

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neutral excited state.[10] The relatively low computational cost of the HEH approach made it possible to extrapolate some energetic and structural properties of a linear polyene as functions of the number n of conjugated carbon atoms.[10,11] In spite of the experimental difficulties, the spectroscopy of the conjugated imines has been extensively studied in the last few years,[12-14] due to the importance that these compounds (conjugated Schiff bases and their protonated analogues) seem to play in the vision photochemistry.

A Heisenberg effective Hamiltonian has been proposed to treat compounds containing conjugated π double bonds of both C=C and C=N types.[15] The reliability of this Hamiltonian has been successfully tested on the properties of small polyenimines and azines.

The present work is devoted to the study of some photochemical and structural properties of the neutral (in a VB sense) states of conjugated Schiff bases involving larger conjugated systems, such as the retinal Schiff base; the cis–trans photoisomerization of its protonated species could play an important role in the vision mechanism.[16]

As for linear polyenes, the nature of the lowest singlet state of these large systems remains controversial, since it may have either ionic (^1B_u) or neutral (the ^1A_g* "hidden" state) character.[14] The HEH model seems able to predict the energetic location and structure of the neutral ^1A_g* singlet excited state, which is rather difficult to treat correctly in MO-CI schemes.

However, the >C=N— chromophore introduces a nonbonding electronic pair whose role in the spectroscopy of Schiff bases cannot be ignored.[2] To answer this problem, the HEH model has been extended to treat the $n\pi$* neutral excited states. This model shows that the $n\pi$* states are only weakly stabilized by the extension of conjugation; they, therefore, should play a minor role in the photochemistry of long conjugated chains, as also suggested by the available experimental evidences.[13]

In section 3, the ground-state conformations and the thermal rotational barriers around double C=C bonds are considered. The analysis of perpendicularly twisted systems suggests the study of the conformations of linear conjugated Schiff bases with an odd total number of conjugated atoms (even number of C atoms). Finally, in sections 4 and 5, the vertical transition energies, the relaxed geometries of excited states, and the twisting behavior of $^3B_1$ and ^1A_g $\pi\pi$* states as well as the lowest $n\pi$* triplet and singlet ($^3A'$ and $^1A'$)[17] properties are treated. General extrapolation fittings allow us to treat the evolution of transition energies as a function of n, the number of conjugated atoms.

2. Heisenberg Effective Hamiltonian for $n\pi$* States

This section will not repeat in details the structure of the Heisenberg Hamiltonian, which is bielectronic in nature and only deals with the neutral situations, introducing effective exchange operators between adjacent atoms, nor the precise parametrization for the ground and $\pi\pi$* states which are given in detail in ref 11 and 15.

2.1. Structure of the Hamiltonian. Nitrogen and oxygen heteroatoms involve nonbonding lone pairs n, and the conjugated heteroatom containing molecules exhibit low lying $n\pi$* excited states. The crudest description of such $n\pi$* excited states of a >C=N— bond from the ground state MO's n, π, and π* gives nearly equal weights on neutral C·N:·

$$(p_C)^1(p_N)^2(n)^1 \text{ and ionic C·· N: } (C-N^*)(p_C)^2(p_N)^1(n)^2$$

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(17) As it is usual in the study of photochemical properties of polyenimines, the excited states are noted with the symbols of the correlated states in all-trans polyenes that belong to C_{2h} symmetry. The A′ notation of the $n\pi$* states refer to the C_s planar symmetry of the imine.
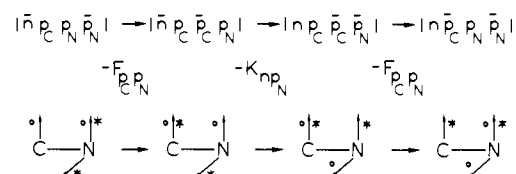
Scheme I

Table I. Coefficients a_n for the Polynomial Expansions of R_{CN}' and g_{CN}' as $\sum a_n (r_{CN})^n$ (au)

parameter	a_0	a_1	a_2	a_3	a_4	a_5
R_{CN}'	7.7786	−40.2964	26.6035	−8.9533	1.5379	−0.1076
g_{CN}'	0.0805	−0.0792	0.0117	0.0196	−0.0095	0.0012

structures, where p_C and p_N refer to the π ($2p_z$) AO's of C and N, respectively. The major effect of further CI is to enhance the weight of the neutral structure with respect to the ionic one. In view of this essentially neutral character, the $n\pi$* states may be treated in a HEH formalism, i.e., an effective Hamiltonian built on $|np_C(p_N)^2|$ and $|\bar{n}p_C(p_N)^2|$ neutral determinants. Such a two-by-two matrix, having the symmetrical form, may be written

$$
\begin{array}{cc}
n\bar{p}_C(p_N)^2 & \bar{n}p_C(p_N)^2
\end{array}
$$
$$
\begin{bmatrix}
R' - g' & g' \\
g' & R' - g'
\end{bmatrix}
\tag{1}
$$

for symmetry reasons, and the eigenvectors are necessarily a triplet

$$^3(n\pi^*) = (n\bar{p}_C + \bar{n}p_C)(p_N)^2/(2)^{1/2} \tag{2}$$

of energy $E(^3n\pi^*) = R'$ and a singlet state

$$^1(n\pi^*) = (n\bar{p}_C - \bar{n}p_C)(p_N)^2/(2)^{1/2} \tag{3}$$

of energy $E(^1n\pi^*) = R' - 2g'$.

For $n\pi$* states, the ordering is necessarily $E(^3n\pi^*) < E(^1n\pi^*)$ and g' is now negative (ferromagnetic coupling).

The origin of the effective spin coupling g' between np_C and $\bar{n}p_C$ is no longer the delocalization into ionic structures nn̄ or $p_C\bar{p}_C$ since these are of another overall symmetry. The mechanism is thus different from that given by Anderson[18] to explain the effective antiferromagnetic coupling in Mott insulators through ionic structures ("super-exchange" mechanism). The coupling occurs from a third-order contribution, with a monocentric spin exchange K_{np_N} occurring on the N atom when in the ionic C^+N^- configuration (see Scheme I).

If the ionic configurations are supposed to lie at any energy ΔE above the neutral ones, $F_{p_Cp_N}$ being the π hopping (Fock) integral between the two π orbitals, the resulting coupling

$$g' = -(F_{p_Cp_N})^2 K_N / (\Delta E)^2 \tag{4}$$

is negative and much smaller in amplitude than the second-order effective coupling between adjacent $2p_z$ AO's. The Heisenberg Hamiltonian deals with half-filled bands, i.e., where each atom brings one active electron (and eventually lone pairs). This model shows a strong opposition between two types of Heisenberg Hamiltonians. When the active (lonely) electrons on adjacent atoms belong to the same symmetry, the left–right hopping integral results in a charge fluctuation and the ionic structures lead to an antiferromagnetic coupling. When the active electrons are located in two AO's of different symmetries, this direct hopping is prohibited and the antiferromagnetic coupling results from direct σ–π exchange in the instantaneous ionic structures.

2.2. Nonempirical Extraction of R' and g'. From the eigenvalues of matrix 1, the r_{CN}-dependent R' and g' parameters can be extracted (as was done for the $\pi\pi$* states of C=N[11,15]) from the accurately calculated potentials of the $^3(n\pi^*)$ and $^1(n\pi^*)$ states of methylimine.

(18) Anderson, P. W. *Phys. Rev.* **1959**, *115*, 1, *Solid State Phys.* **1963**, *14*, 99.

Table II. Linear Conjugated Imines. Planar Ground-State (S_0 or D_0) Optimized Bond Lengths (Å)

n^a	N_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C_5-C_6	C_6-C_7	C_7-C_8	C_8-C_9	C_9-C_{10}
4	1.299	1.448	1.350						
		$(1.445)^b$	(1.351)						
6	1.300	1.446	1.358	1.443	1.353				
			(1.360)	(1.442)	(1.353)				
8	1.300	1.445	1.361	1.439	1.362	1.442	1.353		
				(1.438)	(1.362)	(1.441)	(1.353)		
10	1.300	1.445	1.361	1.438	1.364	1.437	1.358	1.441	1.353
					(1.365)	(1.438)	(1.363)	(1.441)	(1.353)
3	1.362	1.402							
		(1.389)							
5	1.311	1.425	1.408	1.375					
			(1.411)	(1.371)					
7	1.307	1.434	1.389	1.400	1.421	1.366			
				(1.395)	(1.424)	(1.364)			
9	1.305	1.437	1.380	1.411	1.404	1.387	1.428	1.361	
					(1.407)	(1.382)	(1.430)	(1.360)	

$^a n$ = number of conjugated atoms (π electrons). ^{b} Values in parentheses refer to same state of polyenes calculated with the same model.[11]

The lowest excited $n\pi^*$ states of CH_2=NH, methylimine, had been calculated at a multireference CI-MO level (DZD basis set), using the CIPSI method[19] up to a degree of accuracy comparable to that used in the ground and first π triplet[15] and with the same geometry taken from Eades et al.,[20] except for the variable CN bond length. Figure 1 shows the resulting potentials. The π states, already reported elsewhere,[15] are included to clarify the ordering of the lowest excited states of methylimine.

The values of R' and g' are expressed in Table I as polynomial expansions in r (bond distance C–N in au).

As seen in Figure 1, the equilibrium distances are calculated to be 1.354 Å for the $^3(n\pi^*)$ ($^3A'$) and 1.373 Å for the $^1(n\pi^*)$ ($^1A'$) states. It must be recalled that the potentials pictured in Figure 1 concern the C_s symmetry. The relaxation of other geometrical parameters such as the pyramidalization angle of C atom or the C–N twisting dihedral angle could be treated in an identical way, but it has not been taken into account in this paper.

The vertical transition energies to $n\pi^*$ states (corresponding to the ground state conformation) are calculated to be 4.38 eV for the triplet $^3A'$ and 5.05 eV for the singlet $^1A'$, which compares very well with the MRD-CI results of Bonačić-Koutecký and Persico[21] for a similar geometry (4.67 eV for the triplet state, 4.97–5.12 eV for the singlet as estimated from Figure 7 of ref 21) and with the experimental $n\pi^*$ band of nonconjugated C=N compounds (nonconjugated imines) which appears in the far-UV spectra in the region of 230–250 nm (5.39–4.96 eV).[22]

The $n\pi^*$ HEH so obtained can be easily applied to the $n\pi^*$ states of larger systems by using the functional dependence of the $n\pi^*$ HEH on the geometrical parameters summarized in Table 1.

The method was firstly applied to the 2-propen-1-imine (allylidenimine) in its equilibrium ground-state geometry (r(C=N) = 1.299, r(C—C) = 1.448, r(C=C) = 1.350 Å).[15] The $^1(n\pi^*)$ is calculated to be at 4.45 eV; this value compares fairly well with the experimental $n\pi^*$ transition in singly conjugated imines which appears at 4.59 eV.[12,14] The MRD-CI method with a 4-31G AO basis set predicts the same state to be at 5.03 eV,[21] wilst the $^3(n\pi^*)$ lowest state vertical transition energy is calculated to be 4.63 eV. Our HEH calculation gives 3.96 eV. That result has encouraged us to apply the method to more extensively conjugated Schiff basis.

3. Ground-State Conformation and C–C Rotational Barriers of Conjugated Schiff Bases

Due to its projected nature, the HEH model can only deliver the states whose wave function is mainly built on V-B neutral
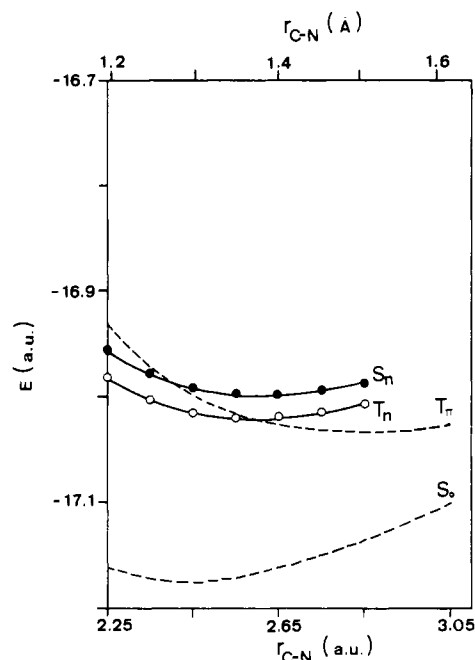

Figure 1. MO-CI potentials of the ground and lowest excited states of methylimine.

configurations. Unfortunately, the neutral ground-state wave function of the planar C=N system becomes essentially ionic when the double bond is twisted to 90°.[21,23] This work is, therefore, restricted to the study of planar and C=C twisted conformations. However, it must be recalled that the thermodynamically most favorable process of isomerization involving a double bond in the ground state of a conjugated Schiff base is, by far, the syn–anti inversion via a linear C=H—H transition state (hydrogen flipping) whose barrier energy is calculated to be about 30 kcal mol^{-1}.[21] The ground-state twist barriers for C=C and C=N double bonds are very similar (55–60 kcal mol^{-1}). however, the extensive conjugation seems to have little influence on the hydrogen flipping and the C=N twist energy barriers as has been evidenced by Osamura et al.[24] For these reasons, and due to the major photochemical interest of C=C twisting for the vision problem, we have focused our effort on the influence of the dimension of the conjugated system on the C=C torsional barrier.

3.1. Even Linear Conjugated Imines. The optimized C–C and C–N bond lengths calculated up to the 2,4,6,8-nonatetraen-1-imine

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Table III. Even Linear Conjugated Imines. Vertical (ΔE^V) and Relaxed (ΔE^R) Absorption Energies and Vertical Emission Energies (ΔE^V_{em}) for the Lowest $\pi\pi^*$ and $n\pi^*$ Neutral Excited States[a] (in eV)

	ΔE^V				ΔE^R				ΔE^V_{em}			
	$\pi\pi^*$		$n\pi^*$		$\pi\pi^*$		$n\pi^*$		$\pi\pi^*$		$n\pi^*$	
n[b]	T	S	T	S	T	S	T	S	T	S	T	S
2[a]	4.96		4.38	5.05	3.85		4.17	4.79	2.87		3.95	4.57
4	3.33	7.82	3.96	4.45	2.72	6.36	3.76	4.14	2.11	5.15		3.80
6	2.59	6.16	3.85	4.27	2.08	5.06	3.59	3.86	1.57	4.15		3.42
8	2.18	5.09	3.81	4.19	1.69	4.15	3.51	3.71	1.23	3.41		3.20
10	1.91	4.37	3.78	4.14	1.43	3.50	3.46	3.61	0.98	2.85		3.05

[a] The MO-CI values for methylimine are included. [b] n is the number of conjugated atoms.
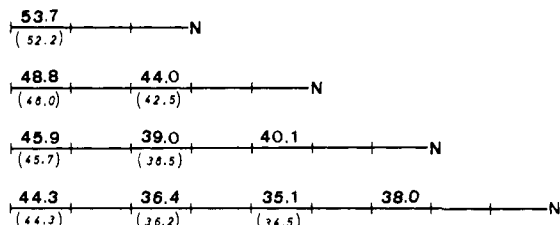

Figure 2. Barriers to rotation (in kcal/mol^{-1}) around C=C double bonds in linear polyenimines. Values in parentheses correspond to equivalent barriers in linear polyenes. The carbon atoms are represented by the + symbol.

(number of conjugated atoms $n = 10$) are shown in Table II. The same values calculated for the respective polyenes have been referenced elsewhere[11] but are included here for clarity. It is evident that the substitution of =CH$_2$ into =NH as the terminal group of the polyene can be considered as a local perturbation, whose effect in the bond lengths never extends besides the C$_3$–C$_4$ bond and is independent on the chain dimension for $n > 8$; the bond alternation of ground-state polyenes is clearly maintained.

The torsional barriers about C=C bonds are calculated from the energy of the relaxed 90° twisted conformation and are summarized in Figure 2. The barriers for polyenes are included too. In both series the lowest barriers concern internal bonds, and this barrier decreases with the conjugated chain length; the C=N group breaks the symmetry, and the C=C bonds near the C=N group have slightly larger rotational barriers than the corresponding C=C bonds on the opposite side of the molecule (cf. 38 kcal/mol for the C$_3$=C$_4$ bond vs. 36 kcal/mol for the C$_7$=C$_8$ bond in C$_9$NH$_{11}$).

The 90° twisted conformation of a polyene can be properly thought of as the sum of two odd conjugate chains linked through a twisted C–C bond. The twisting breaks the conjugation, and the two subsystems are only slightly coupled.[11] From the optimized structures and energies of small odd polyenes and polyenimines (see below), the rotational barriers of longer chains ($n > 10$) can be easily estimated. For $n = 12$, if E_{θ_2} (respectively θ_3) represents the energy of the C$_4$–C$_5$ (respectively C$_6$–C$_7$) 90° twisted conformation and assuming that the twisted bonds contributes with a constant energy, it can be written

$$E_{\theta_2} - E_{\theta_3} = (E_{n=5} - E_{n=7})^{imine} + (E_{n=7} - E_{n=5})^{polyene} = 0.46 \text{ kcal/mol}$$

The positive value of $E_{\theta_2} - E_{\theta_3}$ confirms the tendence to favorize the twisting about the central double bond further from the N atom.

However the local perturbation nature that can be attributed to the substitution of =CH$_2$ for =NH is now evidenced by the little differences in the torsional barriers introduced by such substitution.

The rotation around an internal double bond in a $4n + 2$ linear polyene has been stimated to be 18.2 kcal/mol as n tends toward infinite.[11] So, and provided that both the terminal H flapping and the rotation about C=N double bond barriers would not be strongly affected by conjugation, as it seems to be the case,[24] for a large enough value of n, the central C=C torsion must become the most favorable thermal rotation about a double bond. Actually, the energetic barrier to twist the central double bond of

a $4m + 2$ polyene has an estimated value of 34.8 kcal/mol for $m = 3$ and of 27.5 for kcal/mol $m = 4$ (i.e., $n = 4m + 2 = 18$ conjugated atoms).[25] As long as the imine barriers do not differ from polyene ones in more than 1 kcal/mol, we can estimate that thermal cis–trans isomerization about the most central C=C double bond will become the most favorable process for conjugated chains containing 18 atoms (including the N atom).

3.2. Odd Linear Conjugated Imines. Besides the above mentioned interest for the study of long even chain twisting, the ground doublet states of odd polyenimines deserve some attention for the soliton problem[26] which has been widely studied for polyenic chains. The soliton is a radicalar deformation which tends to localize in the center of an odd polyene, restoring opposite bond alternations on both of its sides The soliton is rather mobile (it

does not cost much energy to move), and its versatility might be sensible to the presence of a C=N bond at the chain end. The ground-state conformations have been optimized up to $n = 9$ (see Table II). In a polyenic odd chain, the presence of a soliton is evidenced, in our approach, by two symmetrically equal bond lengths in adjacent bonds, their values ranging about 1.40 Å (i.e., the typtical value of allyl bond lengths). In the conjugated imines, a slight but clearly appreciable dissymmetry is induced by the presence of the terminal N atom, and it can be said that the perturbative effect of the imino group is propagated further for odd than for even polyene ground states and remains evident even in the largest systems considered here ($n = 9$).

4. Excitation Energies and Planar Excited-State Conformations

4.1. Even Linear Conjugated Imines. Table III summarizes the calculated transition energies to the excited states in the minimum energy conformation of the ground state, ΔE^V (vertical absorption), in its relaxed geometry, ΔE^R (0–0 transition energies) together with the vertical emission energy from the relaxed excited geometry to the ground state, ΔE^V_{em}; both lowest available $\pi\pi^*$ and $n\pi^*$ neutral excited states are reported. Comparison has already been achieved[15] between our vertical transition energies and those obtained by ab initio MO-CI calculations.[21] When the geometries for 2-propen-1-imine reported in ref 21 for a more relevant comparison are used, the agreement between our transition energies and these is excellent for the lowest $^3(\pi\pi^*)$ state (3.41 eV for 3.66 eV), good for the $n\pi^*$ states as mentioned in section 2 (3.99 eV instead of 4.68 eV for the triplet, 4.50 eV instead of 5.08 eV for the singlet), and poorer for the $^1A_g^-$ neutral excited state (7.88 eV instead of 7.20 eV).

The dependence of these transition energies on the number, n, of conjugated atoms is best visualized in Figure 3. The values of Table III have been fitted to polynomial expressions in n^{-1} and n^{-2}. The resulting n-independent coefficients represent the limit of transition energy as n tends to infinity and have been used in Figure 3 as the zero abscisa values. When known,[12,13,27] the band

(25) Values calculated by using the general expressions reported in ref 11.
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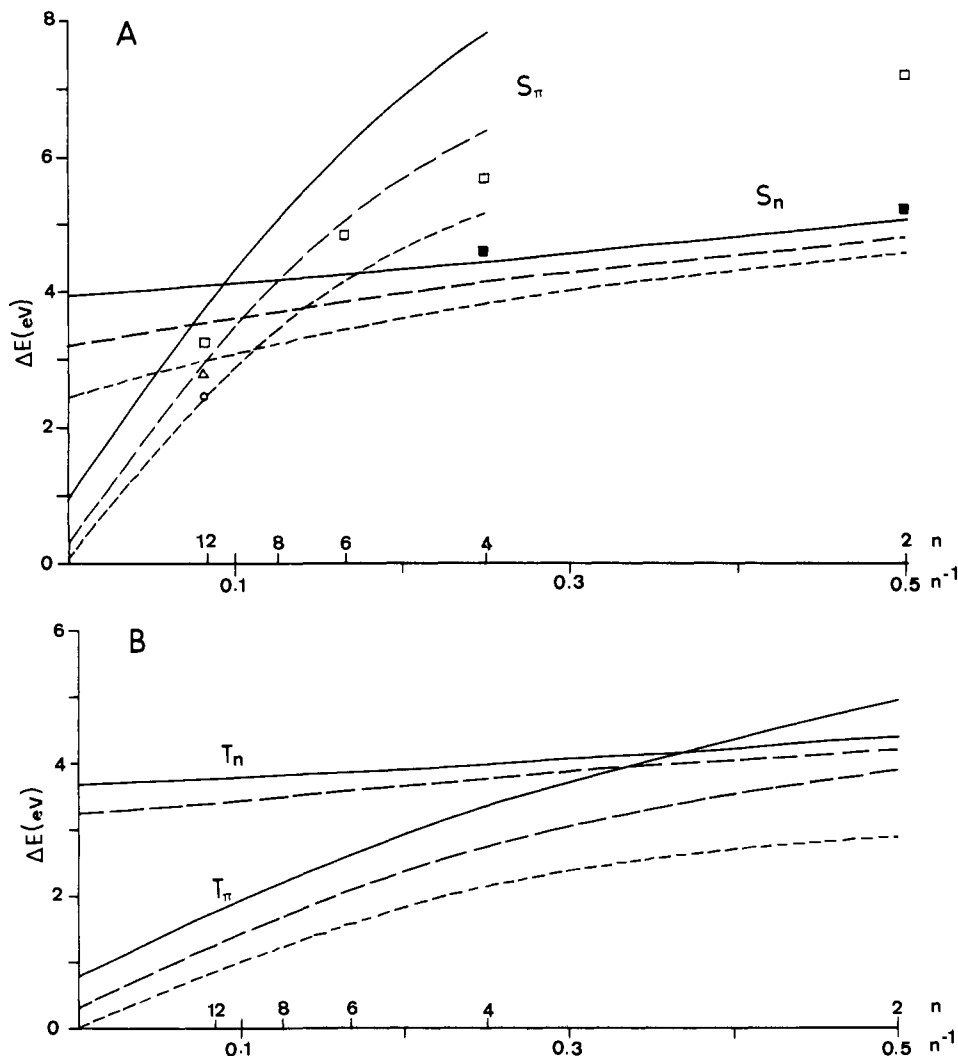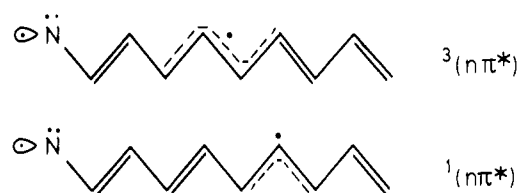
Figure 3. Electronic transition energy as a function of the number (n) of conjugated atoms in linear conjugated Schiff bases. (A) Lowest neutral singlets. (B) Lowest neutral triplets. (—) Vertical absorption energies. (———) 0–0 transitions. (- - -) Vertical emission energies. Some experimental values are shown. (□) V ← N mean band maxima.[12,13,27] (△) 0–0 emission from the ^1A_g excited state for $n = 12$.[27] (○) ^1A_g fluorescence emission band maxima for $n = 12$.[27] (■) $^1(n\pi^*)$ band maxima.[13]

maxima of the V ← N $\pi\pi^*$ large band are indicated in Figure 3 too.

Experimental information concerning the $^1(n\pi^*)$ band maximum can be obtained for nonconjugated and singly conjugated imines but not for larger conjugated ones.[13] A similar behavior is known for polyenic ketones and aldehydes even though $(n\pi^*)$ band maxima have been reported for up to four conjugated double bonds.[28] For polyenals and polyenones, the $n\pi^*$ band maxima is extrapolated to lie below the $\pi\pi^*$ large N ← N band maximum for seven or eight conjugated double bonds.[28] If one considers that the separation between the $n\pi^*$ and $\pi\pi^*$ band maxima is much larger for polyenals than for polyenimines (e.g., for two conjugated double bonds, about $14\,100$ cm^{-1} in β-cyclocitral,[28] $10\,340$ cm^{-1} in N-ethylcrotonaldehydimine),[14] our prediction that the $(n\pi^*)$ singlet will cross the ^1B_u dipole allowed state for four or five conjugated bonds seems to be reasonable.

The nature of the lowest singlet excited state for the nonprotonated Schiff base of retinal seems to be now clearly established as correlating with the forbidden $^1A_g^-$ states of polyene hydrocarbons.[27,29] The fluorescence and fluorescence excitation spectra of a extensively conjugated Schiff base model (number of conjugated atoms $n = 12$) measured by Palmer et al.[27] provided excellent ΔE^R and ΔE^V_{em} values to test the validity of our ex-

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Scheme II

trapolated values concerning the ^1A_g state. From the polynomial fitting of values in Table III, a 0–0 transition energy of 3.04 eV is obtained, to compare with the experimental value 2.76 eV.[27] Also, the maximum of the emission band is calculated to be 2.46 eV (experimental: 2.43 eV).[27] So, the agreement between these theoretical and measured values as well as the fact that both of them lie under the corresponding experimental ΔE^{0-0} and ΔE^V_{cm} energies for the ^1B_u state (3.15 and 3.31 eV, respectively) support the lowest singlet excited state of the free nonprotonated Schiff base of retinal to be of $^1A_g^-$ character.

As compared with the optimized geometries of the ground state, the perturbation introduced by the imine =NH group in the $\pi\pi^*$ excited states bond lengths of polyenes is important and more localized in triplet ^3B_u that in singlet ^1A_g (see Table IV). However, the qualitative description proposed elsewhere[10] for these states (especially the asymptotic behavior of the lowest triplet state as a soliton pair) is completely valid for imines and will not be repeated here.

Table IV. Even Linear Conjugated Imines. Planar Lowest Neutral $\pi\pi^*$ and $n\pi^*$ States Optimized Bond Lengths (Å)

state	n^a	N_1–C_2	C_2–C_3	C_3–C_4	C_4–C_5	C_5–C_6	C_6–C_7	C_7–C_8	C_8–C_9	C_9–C_{10}
^1A_g ($\pi\pi^*$)	4	1.469	1.442 (1.444)^b	1.512 (1.511)						
	6	1.420	1.391	1.438 (1.434)	1.404 (1.398)	1.484 (1.478)				
	8	1.376	1.381	1.449	1.410 (1.390)	1.436 (1.439)	1.382 (1.380)	1.454 (1.445)		
	10	1.350	1.391	1.449	1.392	1.422 (1.419)	1.401 (1.397)	1.442 (1.443)	1.380 (1.381)	1.429 (1.422)
^3B_u $^3(\pi\pi^*)$	4	1.382	1.369 (1.364)	1.469 (1.452)						
	6	1.342	1.392	1.462 (1.460)	1.371 (1.377)	1.422 (1.413)				
	8	1.325	1.409	1.438	1.366 (1.365)	1.449 (1.443)	1.388 (1.393)	1.398 (1.392)		
	10	1.317	1.419	1.419	1.375	1.446 (1.445)	1.369 (1.371)	1.431 (1.427)	1.401 (1.405)	1.383 (1.380)
$^1A'$ ($n\pi^*$)	4	1.408	1.373	1.374						
	6	1.372	1.358	1.433	1.402	1.381				
	8	1.371	1.354	1.440	1.381	1.409	1.416	1.370		
	10	1.370	1.353	1.442	1.372	1.422	1.396	1.396	1.424	1.364
$^3A'$ ($n\pi^*$)	4	1.367	1.394	1.384						
	6	1.368	1.376	1.408	1.417	1.369				
	8	1.368	1.369	1.418	1.400	1.390	1.427	1.362		
	10	1.368	1.365	1.425	1.389	1.402	1.411	1.383	1.431	1.360

^{a,b} See Table II.

Table V. Odd Linear Conjugated Imines. Planar Lowest Neutral $\pi\pi^*$ and $n\pi^*$ Doublets Optimized Bond Lengths (Å)

state	n^a	N_1–C_2	C_2–C_3	C_3–C_4	C_4–C_5	C_5–C_6	C_6–C_7	C_7–C_8	C_8–C_9
$^2(\pi\pi^*)$	3	1.439	1.476 (1.481)^b						
	5	1.389	1.394	1.412 (1.400)	1.457 (1.452)				
	7	1.351	1.393	1.437	1.420 (1.425)	1.388 (1.387)	1.428 (1.421)		
	9	1.332	1.405	1.433	1.393	1.406 (1.399)	1.431 (1.431)	1.390 (1.392)	1.406 (1.401)
$^2(n\pi^*)$	3	1.369	1.344						
	5	1.369	1.352	1.445	1.352				
	7	1.369	1.354	1.442	1.361	1.442	1.353		
	9	1.369	1.354	1.440	1.363	1.438	1.362	1.441	1.353

^{a,b} See Table II.

Table VI. Odd Linear Conjugated Imines. Vertical (ΔE^V) and Relaxed (ΔE^R) Absorption Energies and Vertical Emission Energies (ΔE^V_{em}) for the Lowest ($\pi\pi^*$) and ($n\pi^*$) Neutral Doublets^a (in eV)

	ΔE^V			ΔE^R			ΔE^V_{em}	
	$^2(\pi\pi^*)$			$^2(\pi\pi^*)$				
n^b	imines	polyenes^a	$^2(n\pi^*)$	imines	polyenes^a	$^2(n\pi^*)$	$^2(\pi\pi^*)$	$^2(n\pi^*)$
3	4.12	3.82	2.31	3.66	3.44	2.17	3.22	2.07
5	3.14	2.89	2.67	2.83	2.62	2.42	2.51	2.24
7	2.48	2.32	2.88	2.25	2.10	2.54	2.00	2.30
9	2.06	1.95	3.01	1.86	1.75	2.62	1.65	2.33

^{a} Values for polyenes are from ref 10. ^{b} See Table III.

The $n\pi^*$ state geometries are very different from those of the $\pi\pi^*$ states (Table IV). A solitonic perturbation appears that tends to affect the most central bonds both in triplet and in singlet states. Schematically, the $n\pi^*$ states for the $n = 10$ polyenimine can be represented as in Scheme II.

The solitonic perturbation seems to be slightly displaced from the center toward the terminal HN= group in $n\pi^*$ triplet, and slightly moved off it in the $^1(n\pi^*)$ singlet. This effect is due to the weak $K_{n\pi}$ exchange between the localized σ electron and the π unpaired electron, which stabilizes the triplet state and destabilizes the singlet state.

4.2. Odd Linear Conjugated Imines. The study of excited-state relaxed geometries and electronic excitation energies in odd linear conjugated systems provides indirect information about these properties in electronically excited polyenes when 90° twisted around a C=C double bond, in the same way as it was discussed

for the ground state. The $^2(\pi\pi^*)$ and $^2(n\pi^*)$ lowest doublet geometries are shown in Table V for conjugated systems up to $n = 9$. The vertical and relaxed 0–0 calculated transition energies are summarized in Table VI.

The excited doublet $\pi\pi^*$ state dependence in n^{-1} parallels that of odd polyenes, and its relaxed geometry is quite close to that of the similar $^2(\pi\pi^*)$ excited doublet state in even polyenes.[10] However, the symmetry breaking introduced by the imino HN= group is a long-range effect and perturbs significantly the two central solitonic bonds even in the longest systems ($n = 9$).
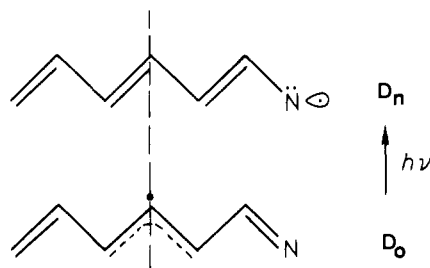
The $n\pi^*$ doublet exhibits a paradoxical behavior as its excitation energy grows as n increase. This increase is large for ΔE^V and ΔE^R and little but clear for ΔE^V_{em}. A qualitative explanation of this behavior can be obtained from structural arguments. It can be noticed from Table V that the $n\pi^*$ doublet presents a regular even ground-state-like structure, with single and double alternating

Conjugated Nonprotonated Schiff Bases

J. Am. Chem. Soc., Vol. 107, No. 7, 1985 1991

Table VII. 90° Twisted Conformation (Å) and Energies (eV) of Excited States of 2-Propen-1-imine at Different Geometries

conformations	b	assumed in ref 21	C·(CCN)·[a]	C·(CCN)·*[a]	twisted $n\pi^*$ states[a]
C_4–C_3 (twisted)		1.416	1.464	1.464	1.464
C_3–C_2		1.470	1.402	1.475	1.344
C_2–N_1		1.300	1.326	1.440	1.369
		Energies for Each Conformation			
C·(CCN)·					
singlet $^1A''$	(2.64)	2.45	2.33[a]	2.77	2.43
triplet $^3A''$	(2.64)	2.50	2.37[a]	2.81	2.46
C·(CCN)·*					
triplet $^3A''$	(6.51)	6.67	6.48	6.01[a]	6.57
singlet $^1A''$	c	6.68	6.49	6.02[a]	6.57
C·(CCN)· $n\pi^*$					
triplet $^3A'$	(5.76)	5.07	4.66	5.02	4.53[a]
singlet $^1A'$	(5.08)[d]	5.07	4.67	5.02	4.53[a]

[a] Conformations optimized with HEH method and corresponding energies (this work). [b] Values between parentheses are from ref 21. [c] Apparently unfound in ref 21. [d] Strong mixture with ionic structure.

Scheme III

bond lengths; on the other hand, the ground state presents a solitonic deformation in the center of the chain, and that generates a reversing in the single–double–single bond lengths ordering on the =N— containing half-chain. So, the larger the polyene, the larger will be the structural reordering that excitation $D_0 \rightarrow D_n$ introduces and the larger the required excitation energy (see Scheme III).

5. Cis–Trans Photoisomerizations around C=C Bonds

The exact theoretical treatment of the set of lowest excited states in polyenic Schiff bases would be a very difficult task. The difficulties met in such a study can be evidenced by considering the 2-propen-1-imine (allylidenimine) molecule, the lower excited states of which have been the subject of a careful theoretical study.[21]

The lowest excited states of this molecule, when 90° twisted around the C=C bond, may be classified according to their symmetry with respect to the C_3C_2N plane and according to their physical (neutral or ionic) content in the V-B approach (Scheme IV).

The lowest states (i.e., the ground state and the lowest triplet) are both diradicalar C_4·(C_3C_2N)· and antisymmetric $^1A''$ and $^3A''$. They correlate with the $S_0(X^1A_g)$ ground state and lowest ^3B_u triplet state in the planar conformation (cf. Figure 4). The $n\pi^*$ excited states are both neutral and symmetrical, and they correlate with the $n\pi^*$ excited states of the planar conformation. The last class of neutral states is built from C_4·(C_3C_2N)·* diradicalar states where the allylic C_3C_2N fragment is excited and they are antisymmetrical and correlate, from their physical content, with the second triplet (^3A_g) and "hidden" ^1A_g state of the planar conformation. The zwitterionic states are of $C_4^-(C_3C_2N)^+$ and $C_4^+(C_3C_2N)^-$ character, they are symmetric singlet states, and the former correlates with the ^1B_u ionic excited state of the planar conformation. This classification being a zeroth order approach, some interaction may occur in the twisted conformation between the $^1n\pi^*$ and ionic $C-(CCN)^+$ states, which are of the same symmetry.[21]

For intermediate twisting angles the symmetry disappear, and the various surfaces may cross through (weakly) avoided crossings. A major problem comes from the fact that of the various states having different physical content, for a given value of the twist
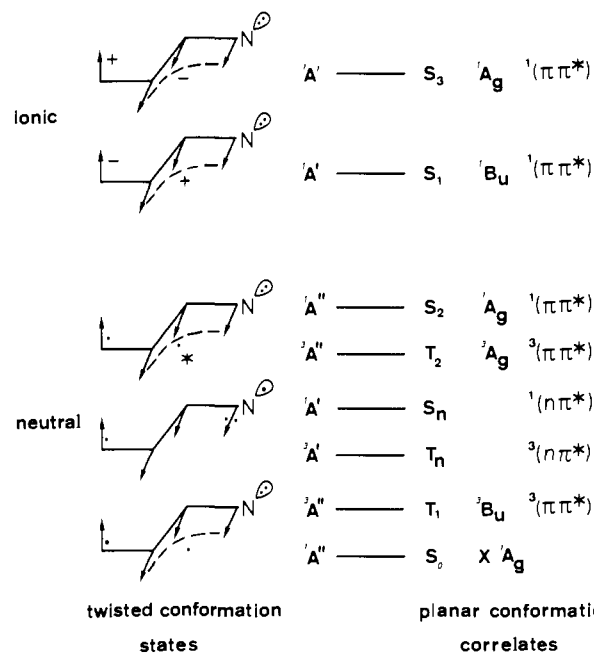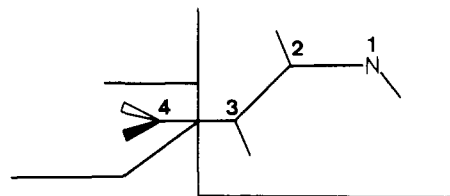

Figure 4. Lowest excited states in 2-propen-1-imine. The correlation between the twisted and planar conformations is shown.

Scheme IV

angle θ, the bond lengths may be quite different in the various states and the understanding of the relative position of the excited surfaces and of their crossings should take into account the geometry relaxation.
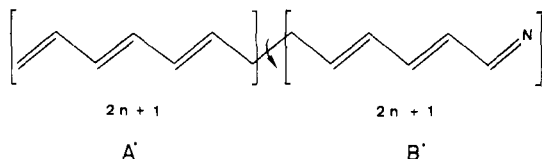
The amplitude and the influence of the proper geometry relaxations appear clearly on 2-propen-1-imine from Table VII; the central C_2C_3 bond is 1.344 Å in the $n\pi^*$ state, while 1.476 Å in the neutral singlet C·(CCN)·* state. The geometry used in ref 21 cannot handle these differential events and seems rather inappropriate for any of the competing states. The geometry changes induce large variations (0.5 eV) in the energies of the nonoptimized states.

Since the ionic states have not been treated in this work, the strong mixing observed in ref 21 between the $n\pi^*$ and ionic $C^+(CCN^-)$ configuration cannot be treated in our model. This coupling stabilizes the lowest excited singlet to 5.0 eV from a value

Table VIII. Energies of Neutral Excited States in Polyenimines when 90° Twisted around Double C=C Bonds. All Energies Are in eV

n^a	4^c	6^c		8^d			10^d			
twisted angle[b]	θ_1	θ_1	θ_2	θ_1	θ_2	θ_3	θ_1	θ_2	θ_3	θ_4
$S_n^{\perp\,e}$	6.02	5.37	4.95	4.36	4.52	4.24	3.75	4.14	3.83	3.98
$T_n^{\perp\,e}$	4.53	4.10	4.55	3.91	4.11	4.53	3.82	3.94	4.12	4.93

^{a} n is the total number of conjugated atoms. ^{b} θ_i is the dihedral angle about the ith C=C double bond away from C=N bond. ^{c} For $n = 4$ and $n = 6$, all values are calculated in a direct way. ^{d} For $n = 8$ and $n = 10$, values are estimated from odd conjugated fragment energies. ^{e} $S_n^{\perp}$: excited singlet ^1A_g 90° twisted around the C=C bond. $T_n^{\perp}$: $^3(n\pi^*)$ excited state in the same conditions.

Scheme V

for the diabatic $^1n\pi^*$ state which would be nearly degenerate with the $^3n\pi^*$ state calculated at 5.76 eV. For the same geometry, we already have the $n\pi^*$ configuration at significantly lower energies (5.06 eV), and the proper geometry relaxation, leading to a C·$\overset{|}{\smile}$C=C—N· structure (quite different from a $C^+(CCN)^-$ geometry) brings down the $n\pi^*$ configuration to 4.53 eV. In this geometry the coupling with the ionic structure $C^+(CCN)^-$ would be very weak. Another discrepancy concerns the disappearance of the neutral excited singlet C·(CCN)·* in ref 21. The optimized geometry energy of this state in the twisted conformation is 6.02 eV in our model, which seems to the slightly higher than the observed vertical $\pi\pi^*$ absorption (5.9 eV), which indicates that a C$\overset{|}{\smile}$C photoisomerization would not involve the $^1A_g^-$ neutral singlet excited surface.

Despite the difficulty of a correct treatment of these excited-state surfaces, as evidenced by the preceding discussion, we think that a systematic search of the twisted conformations and energies of the neutral states might be useful to enlighten their possible implication in cis–trans photochemical processes. The approach may be considered as "diabatic" in the sense where the possible crossings with ionic states do not appear explicitly, but these crossings should occur for intermediate values of θ; moreover, our model allows for a systematic geometrical relaxation of the neutral-state conformations.

Table VIII summarizes the energies of twisted $^1A''$ (twisted "hidden" ^1A_g) and $^3(n\pi^*)$ states of the lower polyenimines obtained with our HEH model.[30]

For the lowest members of the series, the most favorable twisted conformation concerns the C=C most external bond, as occurred in the polyenic series.[10] For longer systems, a tendency for internal double bond rotation appears, as occurred also for linear polyenes, and it is sure that for very large imines, the twisting in the neutral excited singlet surface would involve the most internal C=C bond. For intermediate values of n, the situation is even more intricate than for polyenes, due to the perturbation by the =NH substitution, as appears for $n = 12$; for this molecule, the relative ordering of excited singlet energies corresponding to conformations 90° twisted around the first, second, etc. double C=C bond (θ_1, θ_2, etc.) up to θ_4 can be estimated from the odd linear fragments

as was done for the ground state (see above). In this way, the relative order for the energies of twisted neutral singlet results to be $E_{\theta_1} > E_{\theta_3} > E_{\theta_2} > E_{\theta_4}$ with $E_{\theta_1} - E_{\theta_3} = 0.03$ eV, $E_{\theta_3} - E_{\theta_2} = 0.13$ eV, and $E_{\theta_2} - E_{\theta_4} = 0.16$ eV, to be compared with $E_{\theta_2} > E_{\theta_4} > E_{\theta_3} > E_{\theta_1}$ for $n = 10$ (cf. Table III). However, it is interesting to analyze the physical content of the excited wave function when the rotation around an internal double bond defines two subsystems of equal lengths (Scheme V). In such a system the excitation tends to locate on the polyenic fragment (A·*B·) since the $D_0 \rightarrow D_1$ excitation energy is lower in polyenes than in polyenimines (see Table VI). However, when the rotation defines two subsystems of different lengths, the longer fragment will be excited irrespective of what fragment bears the =NH group.[31]

Due to the local character of the =NH perturbation, one may expect that the asymptotic behaviors (as $n \rightarrow \infty$) of polyenimine transition energies and photochemical cis–trans isomerization should be the same as for polyenes. Further studies on larger systems would be relevant to check the convergence between the two isoelectronic series. A similar previous work on polyenes has lead to the major conclusion that the cis–trans isomerizations around internal double bonds were possible on the neutral singlet surface while it should not be possible on the ionic (dipole-allowed) surface. The same conclusion seems to be valid for the polyenimines, the neutral excited singlet in the 90° twisted conformation remaining at lower energies than the vertical excitation to the allowed "^1B_u" excited state and than the vertical excitation to the "^1A_g" neutral excited state; from the values obtained in the present work up to $n = 10$, it seems that one may predict that for $n > 12$, the following inequalities should be valid

$$\Delta E^V(^1B_u) > \Delta E^V(^1A_g) >$$
$$\Delta E^V_{90°} \text{ (twisted around internal C=C) } (^1A_g)$$

indicating that the cis–trans isomerization might proceed through the neutral excited singlet potential surface.

One should remember that the above conclusions have no reason to be valid for protonated Schiff bases for which both the ground and lower excited states are intrinsically ionic.[8]

(30) Triplet $^3A''$ and singlet $^1(n\pi^*)$ are quasi-degenerate with the $^1A'$ and $^3(n\pi^*)$ states respectively in its 90° twisted conformation and will not be explicitly discussed here.

(31) Of course, the $(n\pi^*)$ excitation takes place only in the N-carrying fragment, and the regularity of $D_0 \rightarrow D_n$ excitation energies as reported in Table VI ensures a regular behavior of photoisomerization barriers. The effect of chain length in the rising of excitation energies has been discussed above and it brings out, as a consequence, that photoisomerization is always predicted to be favorable about $\theta_1(\beta-\gamma$ C=C double bond).