

Although these calculations have not been able to describe quantitatively the enthalpies of these biologically important hydrolysis reactions, for most of the charged molecules they do give more precise estimates of the ΔH values than have been heretofore available. Thus, they provide an interesting testing ground for theoretical models which include more sophisticated treatments of solvation effects: to calculate correctly ΔH (hydrolysis) in solution for charged forms of both pyrophosphate and phosphocreatine.

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References and Notes

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- (30) Phosphoenolpyruvate was an exception; for it we use the average distance from the phosphoryl oxygen to the five ($3\text{P}\cdots\text{O}^{2-}$ and $2\text{C}\cdots\text{O}^{2-}$) oxygens.
- (31) Note that a reaction field model correctly models the heat of vaporization of H_2O ($\Delta H \sim 10$ kcal/mol)²⁷ but not that of acetic acid ($\Delta H \sim 10$ kcal/mol).²⁷
- (32) For acetyl phosphate, we are quoting the free energy and enthalpy of hydrolysis of the anion $\text{CH}_3\text{COOPO}_3\text{H}^-$, since no experimental values of $\text{CH}_3\text{COOPO}_3\text{H}_2$ were reported. However, by analogy with $\text{H}_4\text{P}_2\text{O}_7$ vs. $\text{H}_3\text{P}_2\text{O}_7^-$, whose enthalpies of hydrolysis are -7.6 and -7.3 kcal/mol, respectively, we expect this difference to be small.

Theoretical Model for the Conversion of an Even π Orbital to an Odd π Orbital System and Its Implication to Vision

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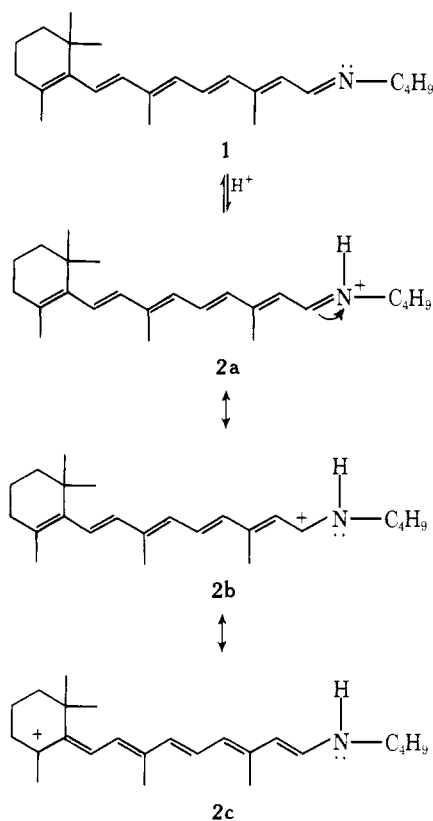
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Abstract: A computer program based on PPP molecular orbital approximations is used to calculate the conversion of an even π orbital system to an odd π orbital system. The model is based on an even system of 12 atoms that goes to an odd system of 11 and is selected to represent the conversion of *N*-retinylidene-*n*-butylamine to the *N*-retinylidene-*n*-butylammonium cation. The conversion is brought about by gradually increasing the charge on nitrogen (Z_p) that is used to polarize the π electrons. In the calculations, the increase in Z_p is accounted for by continuously adjusting orbital occupancy and the coulomb integral α_N . As Z_p changes, the following output parameters are examined: excitation energy, wave function geometry, eigenvalues of wave functions, bond orders, electron density, and resonance energy. The output parameters are completely consistent with conversion from even to odd as the value of Z_p goes to unity. The eigenvectors reveal that the first π orbital is transformed from a molecular orbital to an atomic orbital centered over nitrogen. Also the first unoccupied MO is transformed from antibonding to nonbonding. The overall changes in the π system are related to the chromophoric molecule in visual pigments.

Retinal in its 11-cis configuration is the chromophore molecule that condenses with visual proteins in a Schiff base linkage to form visual pigments. Retinal absorbs at approximately 380 nm, yet it condenses with specific visual proteins to form pigments with λ_{max} values from 440 to 575 nm. Ren-

dering a satisfactory explanation of this so-called bathochromic shift has been a problem of considerable difficulty. Most recently explanations are based on the effect of the counter negative charge on the positively charged organic cation and also on the effect of twisting about essential single bonds. At-

Scheme I



tention was first focused on the possibility that the counteranion plays a major role in wavelength regulation by Kropf and Hubbard,¹ and theoretical calculations were first made on this model by Wiesenfeld and Abrahamson.² Erickson and Blatz³ in their work with model visual pigment chromophore molecules reported experimental evidence which showed that the counteranion does indeed control the wavelength of the chromophore. The postulate of Kropf and Hubbard and the calculations of Wiesenfeld and Abrahamson pertained solely to retinal and its Schiff base as an even π orbital system.

Blatz first focused attention on the possibility that the even π orbital system in visual chromophores may be converted into an odd π orbital system.⁴ Odd π orbital systems of approximately the same length as even π orbital systems exhibit a λ_{\max} value that is considerably red shifted. A good example of the spectroscopic difference between an even and odd system is furnished by retinol, an even system with ten atoms in the π system, which absorbs at about 325 nm and by the retinyl cation, an odd system with 11 atoms in the π system, which absorbs at 588.5 nm.⁵ The absorption λ_{\max} values of two series of even and odd polyenes have been determined and reported.^{5,6}

Blatz⁷ has employed a qualitative valence bond treatment to show that under appropriate conditions the protonated Schiff base may undergo conversion from an even to an odd π system. This is visualized as shown in Scheme I. Structure **1** represents the unprotonated Schiff base which would be expected to be virtually a pure even π system. The protonated species is represented by structures **2a**, **2b**, and **2c**. When the anion is close, the positive charge is localized on nitrogen and structure **2a** makes a major contribution to the ground state. Clearly, structure **2a**, as written, may be considered to be even. When the anion is removed, the positive charge is no longer localized on nitrogen, and consequently it is free to delocalize over the carbon π system. This is represented by structures **2b** and **2c**, the two isoenergetic limiting resonance structures. Both of these structures are odd. Thus as the contribution of **2a**

decreases, the π system becomes progressively more odd. It should be noted that the limit of the delocalization process, as expressed by **2b** and **2c**, is equivalent to the retinyl cation, and the expected limiting wavelength of the protonated Schiff base should be that of the retinyl cation, 588.5 nm.

An empirical relationship was derived between excitation energy of the π system, ΔE , and the sum of the interionic distances, d , expressed as:

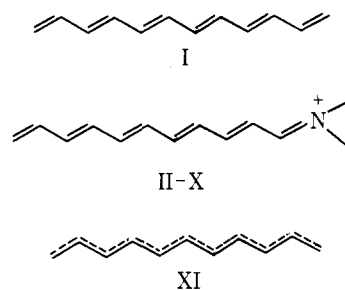
$$\Delta E = \Delta E^\circ + d_0 e^2 / \epsilon d^2 \quad (I)$$

Other quantities are: d_0 , a constant; e , the electron charge; and ϵ , the dielectric constant. In the derivation, it was recognized that the charge on the cation is one, $Z_c = 1$. At the same time it was recognized that the positive charge was engaged in two separate work functions: coulombic work in the form of ionic bond formation, Z_i , and π electron polarization or electron redistribution, Z_p , so that $Z_c = Z_p + Z_i = 1$. The interdependence of Z_i and Z_p is of primary importance to the work reported here. However, to return to eq I, if ΔE is plotted against $1/d^2$ the intercept of the ordinate is ΔE° . For four solvents, the average value for ΔE° was found to be 584 nm, a value in good agreement with the experimental value of the retinyl cation.

A number of theoretical calculations have been made on charged even systems;^{9,10} calculations have also been reported on charged odd systems.^{10,11} These studies were concerned primarily with calculation of excitation energies. In the work described here, we are interested in fundamental molecular properties in addition to excitation energies. Inspired by results of the valence bond treatment described earlier, this study was undertaken to see what LCAO-MO-SCF methods could contribute to understanding the changes taking place as the charge on nitrogen, that is Z_p , is increased. As the charge on nitrogen is increased the effect on such properties as orbital geometry, orbital energy, electron distribution, bond order, and excitation energy is studied. These properties will be compared with those from application of simple organic resonance theory.

Method of Calculation

Physical Model. The procedure was to first calculate the all-carbon, even π orbital system dodecahexaene exemplified by case I. Next the all-carbon, odd π orbital system, the un-



decapentaenylic cation, case XI, was calculated. These two cases form the limits between which the protonated Schiff base will change as the π electron polarization charge, Z_p , increases from zero to unity. The changing charge is represented by cases II to X. These nine cases give rise to nine calculations of the protonated Schiff base. These various calculations represent ground states resulting from increasing participation of resonance structures **2b** and **2c** accompanied by decreasing contribution of structure **2a**.

In case II, $Z_c = 1$, $Z_i = 1$, and $Z_p = 0$. In this case nitrogen bears a formal +1 charge, but it is completely engaged in ionic interaction with the counter negative charge. The resulting structure is equivalent to the unprotonated Schiff base and can be calculated with those input parameters. In case X, $Z_c = 1$,

Table I. Values of Parameters^a in Calculations of Even π Systems with Increasing Charge on Terminal Atom Compared with Pure Even and Odd π Systems

case	input parameters				output parameters				
	electron occupancy		Z_p^b	α_N	$\Delta E, \text{eV}$	$\lambda_{\text{max}}, \text{nm}$	electron density		P_{11-12}^c
	N	C					q_{11}	q_{12}	
I		1.000			3.464	358	0.989	1.014	0.942
II	1.000	1.000	0	-9.240	3.299	376	0.961	1.053	0.921
III	1.078	0.993	0.078	-10.250	3.231	384	0.903	1.147	0.910
IV	1.134	0.988	0.134	-10.973	3.143	394	0.864	1.207	0.896
V	1.250	0.977	0.250	-12.474	2.908	426	0.789	1.348	0.850
VI	1.368	0.967	0.368	-14.000	2.664	465	0.729	1.484	0.783
VII	1.500	0.955	0.500	-15.708	2.433	508	0.687	1.622	0.684
VIII	1.613	0.944	0.613	-17.170	2.321	534	0.675	1.721	0.589
IX	1.750	0.932	0.750	-18.942	2.247	552	0.689	1.819	0.476
X	2.000	0.909	1.000	-22.176	2.215	560	0.771	1.918	0.312
XI		0.909			2.271	546	0.803		

^a Other parameters $\beta_0 = -2.40 \text{ eV}$, $\beta_{C=C} = -2.16 \text{ eV}$, $\beta_{C=N} = -1.80 \text{ eV}$, $\alpha_0 = 9.00 \text{ eV}$. ^b π polarization charge on nitrogen. ^c Bond order.

$Z_i = 0$, and $Z_p = 1$. The negative charge is at infinity and the electrostatic interaction is zero. Therefore the entire positive charge on nitrogen is engaged in π electron polarization. Cases III to IX have fractional values of Z_i and Z_p . For example, case V represents the species resulting when the negative charge engages $3/4$ of the positive charge, $Z_i = 0.75$, and $1/4$ of the positive charge is used to polarize the π system.

Selection of Input Parameters. The computer program used here is the same as the one used in earlier work,^{8,11} and it was written to take into account the LCAO-MO-SCF approximations of Pariser-Parr-Pople.^{12,13} The program takes into consideration the effect of configurational interaction arising from mixing all singly excited configurations. Excited states can be improved by similar techniques, but our program assumes the same molecular geometry for the ground and excited states and is not able to achieve self-consistency in eigenvalues with respect to molecular geometry.

It was assumed that the coulomb integral, α_N , should be sized to reflect the change of Z_p on nitrogen. Thus it should vary between the value for an unprotonated Schiff base and a limiting value consistent with $Z_p = +1$. Previous investigators chose various values for α_N including the value for pyrrole and pyridinium salts. Neither of these values represent the value when $Z_p = +1$. Nitrogen is neutral in pyrrole, and the value of Z_p in pyridinium is judged to be 0.5 or less. In previous work⁸ we successfully used values of McWeeney and Peacock¹⁴ and Brown and Penfold.¹⁵ The limiting value of the coulomb parameter h_0 was therefore set to be 5.39, and h_N , the value of the coulomb parameter in each specific charge case, is a fraction of h_0 ; $h_N = Z_p h_0 = Z_p 5.39$. The value of $\alpha_N = \alpha_{N_0} + h_N \beta_0$ where $\alpha_{N_0} = -9.240 \text{ eV}$ and $\beta_0 = -2.40 \text{ eV}$. Thus for case V (see Table I) where $Z_p = 0.25$, $\alpha_N = -12.474 \text{ eV}$.

The assigned occupancy of each p orbital was also made a function of Z_p . For cases II-X there are 12 orbitals and 12 electrons. In case II the occupancy of each orbital including nitrogen is 1. In case V, when $Z_p = 0.25$, the occupancy of nitrogen was assigned to be 1.25 and the remaining electrons were assigned to the 11 carbon atoms which results in an occupancy of 0.977 electron per orbital. The occupancy values and α_N values assigned as a function of Z_p are given in Table I. Additional parameter values used in the calculations are: $\alpha_0 = -9.00 \text{ eV}$, $\beta_{C=C} = -2.64 \text{ eV}$, $\beta_{C=C} = 2.16 \text{ eV}$. The value of $\beta_{C=N}$ will be discussed under Results.

Results

Calculation of Excitation Energies. Once parameterization had been completed, preliminary calculations were made. When $\beta_{C=N}$ was adjusted to -1.800 eV , excitation energies of 3.299 eV, $\lambda_{\text{max}} 376 \text{ nm}$, and 2.215 eV, $\lambda_{\text{max}} 560 \text{ nm}$, were

calculated when Z_p was set at 0 and 1, respectively. The corresponding experimental values of 3.42 eV, $\lambda_{\text{max}} 363 \text{ nm}$ and 2.11 eV, $\lambda_{\text{max}} 588.5 \text{ nm}$ for the Schiff base are: 375 nm by Wiesenfeld and Abrahamson;² 366 nm by Schaffer et al.;¹⁶ and 384 nm by Suzuki et al.¹⁷ Theoretical calculations on the protonated Schiff base gave 579¹⁷ and 524 nm.⁹ The values calculated in this work are in agreement with experimental values and previously calculated experimental values. Thus for the calculation of cases II to X, $\beta_{C=N}$ was set at -1.800 eV and Table I gives the resulting values of ΔE , λ_{max} , electron density at atoms 11 and 12 (q_{11} and q_{12}), and the bond order, P , for the carbon-nitrogen bond for all 11 cases.

The calculated values of ΔE decrease smoothly as Z_p increases, but the decrease is not linear. From eq 1 the excitation energy for any salt of a protonated Schiff base can be calculated as:

$$\Delta E = \Delta E^\circ - \frac{Z_i Z_a e^2}{\epsilon d} \quad (2)$$

The value of ΔE when $Z_p = 0$ can be given as

$$\Delta E_{\text{SB}} = \Delta E^\circ - \frac{Z_a e^2}{\epsilon d_0} \quad (3)$$

It will be recalled that when $Z_p = 0$, $Z_i = 1$ and $d = d_0$. If (2) is divided by (3)

$$\frac{\Delta E - \Delta E^\circ}{\Delta E_{\text{SB}} - \Delta E^\circ} = Z_i d_0 / d \quad (4)$$

But $d_0/d = Z_i$, and eq 4 can be rearranged:

$$\Delta E = (\Delta E_{\text{SB}} - \Delta E^\circ) Z_i^2 + \Delta E^\circ \quad (5)$$

Thus the excitation energy of the protonated Schiff base should vary with the square of the ionic interaction charge, and the intercept should be the excitation energy of the retinyl cation. Furthermore, when $Z_i = 1$, eq 5 reduces to $\Delta E = \Delta E_{\text{SB}}$.

In the accordance with eq 5, the calculated excitation energies for cases II to X are plotted vs. Z_i^2 in Figure 1. The plot, open circles, has good straight line correspondence over a wide range of Z_i^2 ; however, the curve is S shaped at the extremities. The experimental excitation energies of the Schiff base ($Z_p = 0$) and retinyl cation ($Z_p = 1$) are shown as triangles, and for ease of comparison with experimental values, they are joined by a straight line. The calculated values give a reasonable approximation of this line. A linear regression of all 11 points gives a straight line equation of $\Delta E = 1.199 Z_i^2 + 2.183$ with a coefficient of determination of 0.988. If the points at both extremities are neglected, $\Delta E = 1.312 Z_i^2 + 2.141$ with a coefficient of determination of 0.997. The equation for the line joining the two experimental points is: $\Delta E =$

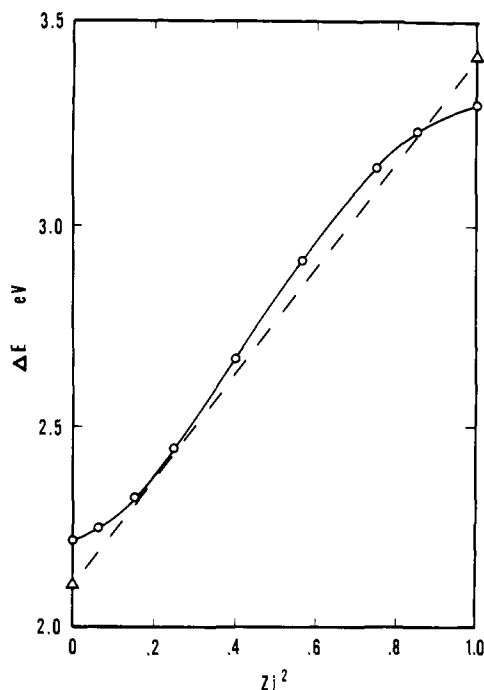


Figure 1. The calculated excitation energy ΔE (open circle) is plotted against the square of the fractional positive charge engaged in ion bond formation. The experimental values of the excitation energy of the retinyl cation, 2.107 eV, $Z_p^2 = 0$, and *N*-retinylidene-*n*-butylamine 3.415 eV, $Z_p^2 = 1$, are plotted as triangles and joined by a broken straight line.

$1.308Z_p^2 + 2.107$. It is concluded that the calculated values of ΔE can be approximated as a linear function of Z_p^2 , although the calculated values show departure when Z_p approaches either 0 or 1.

Change in Orbital Geometry with Charge. Resonance predicts that as the positive charge on nitrogen is increased more π electron density will be drawn toward nitrogen. Thus as Z_p increases, resonance structure **2a** will contribute less and structures **2b** and **2c** will contribute more to the composition of the ground state. Both resonance structures **2b** and **2c** are drawn with the π electrons, which were originally located between the C and N, now centered or localized on nitrogen. Of course the limit of this process is complete localization of electrons on nitrogen and this implies accommodation through sp^3 hybridization. Application of resonance theory also shows that in the limit the even orbital system becomes odd. As the contribution of resonance structure **2a** goes to zero, the ground state is made up entirely of contributions from **2b** and **2c**, and structures **2b** and **2c** are both odd in p orbital composition.

In Figure 2 selected molecular orbitals are formed from calculated eigenvectors. The first three molecular orbitals, ψ_1 , ψ_2 , and ψ_3 of case II ($Z_p = 0$), are represented; these orbitals have the completely regular geometry anticipated from a typical even system. ψ_1 has no node, ψ_2 has one node, and ψ_3 has two nodes. The wave functions are almost symmetrical. The first antibonding orbital of case II is also shown as ψ_7 . Once again the calculated results are as expected; six nodes appear, all centered between carbon atoms. All of the MO's calculated for case II are almost identical to those calculated for the all-carbon dodecahexaene. Dramatic changes in molecular geometry begin to occur in case VII where the input parameters have been adjusted to allow $Z_p = 0.5$. Inspection of VII, ψ_1 , shows considerable electron density drawn toward the nitrogen end of the π system. In ψ_2 , the node has undergone considerable displacement toward the right as the orbital begins to approach the shape of orbital II, ψ_1 . The same outcome is noticed for case VII, ψ_3 ; both nodes are displaced toward the right so that the shape of VII, ψ_3 , approaches that of II, ψ_2 .

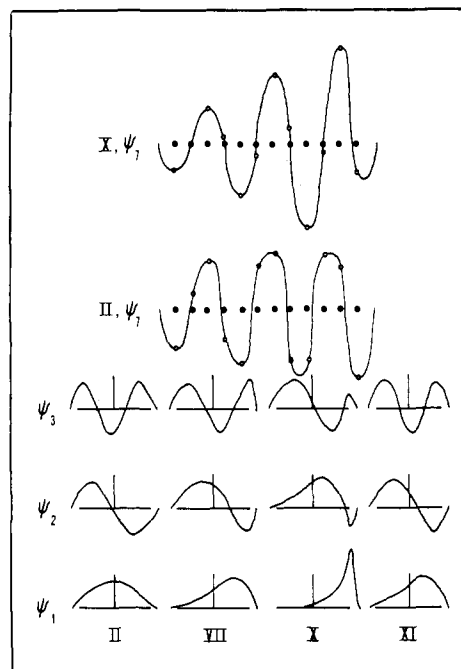


Figure 2. The calculated eigenvectors of the first three wave functions ψ_1 , ψ_2 , and ψ_3 are plotted for dodecahexaene I, the undecapentaenylic cation XI, and the protonated Schiff base when $Z_p = 0, 0.5$, and 1.0 , respectively. ψ_1 is seen to change from a MO to an atomic orbital. The wave function for the first antibonding MO ($Z_p = 0$) II, ψ_7 is seen to convert to a nonbonding MO ($Z_p = 1$) X, ψ_7 .

The results are even more dramatic in case X where Z_p has reached its maximum value of +1; the geometry indicates that ψ_1 has been converted from a molecular orbital to an atomic orbital centered on atom 12, the nitrogen atom. Of course this outcome is consistent with predictions of resonance theory. At the same time X, ψ_2 has assumed the appearance of II, ψ_1 ; instead of a node between atoms 6 and 7, the MO now extends over 11 atoms before going to 0. A node now appears between 11 and 12. Case X, ψ_3 is equivalent of II, ψ_2 , and thus a clear pattern emerges. As Z_p increases, ψ_1 of the even system is converted into an atomic orbital and the system goes odd in terms of remaining MO's. The ψ_2 of the even system is converted into ψ_1 of the odd system, and each bonding orbital of the even system, ψ_n , is converted into ψ_{n-1} of the odd system.

Odd π systems have a number of bonding π orbitals equal to the number of antibonding orbitals, but additionally odd systems also have one nonbonding orbital. The even system under consideration here with its 12 orbitals has been converted into an odd system with 11 orbitals. Of the 11, five would be expected to be bonding and five would be expected to be antibonding. Thus ψ_7 would be the former antibonding orbital converted into a nonbonding orbital. The wave function of a nonbonding orbital passes through the even atoms of the π system. Examination of case X, ψ_7 shows that the wave function does indeed pass through the even atoms. The atoms are shown as full circles and the eigenvectors are shown as open circles. Also shown in Figure 1 are the first three MO's of the odd system, the undecapentaenylic cation, XI, ψ_1 , XI, ψ_2 , and XI, ψ_3 . Note how closely X, ψ_2 resembles XI, ψ_1 and X, ψ_3 resembles XI, ψ_2 . Thus we conclude from examination of wave functions that as Z_p goes to 1 the even π system goes odd.

Change in Bond Order with Charge. Resonance theory predicts that as the 12 p orbital even Schiff base goes to the 11 orbital odd system, bond orders should change, particularly the carbon-nitrogen bond order. In structure **2a** the C-N bonding is double, whereas in structures **2b** and **2c** the bonding is single. As the value of Z_p approaches one, structure **2a** will

Table II. Calculated Bond Orders for Even π Systems with Increasing Positive Charge on Nitrogen Compared with Pure Even and Odd π Systems

case	bond order										
	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	9-10	10-11	11-12 ^a
I	0.942	0.333	0.885	0.355	0.877	0.358	0.878	0.352	0.887	0.332	0.942
II	0.941	0.333	0.855	0.356	0.876	0.360	0.875	0.360	0.868	0.383	0.921
V	0.941	0.334	0.883	0.359	0.870	0.370	0.861	0.383	0.838	0.437	0.850
VII	0.940	0.337	0.877	0.371	0.852	0.400	0.823	0.444	0.766	0.550	0.684
IX	0.937	0.343	0.864	0.394	0.820	0.449	0.766	0.525	0.677	0.673	0.476
X	0.932	0.351	0.846	0.422	0.783	0.500	0.709	0.595	0.602	0.762	0.312
XI	0.929	0.356	0.837	0.435	0.765	0.523	0.682	0.627	0.559	0.816	
XIa	0.917	0.380	0.787	0.521	0.662	0.660	0.526	0.784	0.383	0.916	
XIb	0.882	0.454	0.743	0.559	0.651	0.651	0.559	0.743	0.454	0.882	

^a Case I, carbon-carbon bond; case II \rightarrow X, carbon-nitrogen bond; case XI, no 12th atom.

Table III. Calculated Electron Densities for Even π Systems with Increasing Positive Charge on Nitrogen Compared with Pure Even and Odd π Systems

case	electron density per atom											
	1	2	3	4	5	6	7	8	9	10	11	12 ^a
I	1.014	0.989	1.001	0.997	1.001	0.999	0.999	1.000	0.997	1.000	0.987	1.014
II	1.013	0.989	1.000	0.998	0.998	1.000	0.996	1.001	0.992	1.000	0.961	1.053
V	1.010	0.985	0.982	1.001	0.966	1.012	0.943	1.024	0.902	1.037	0.789	1.348
VII	1.003	0.984	0.959	1.005	0.927	1.021	0.885	1.037	0.824	1.051	0.678	1.662
IX	0.990	0.982	0.928	1.007	0.882	1.022	0.834	1.031	0.780	1.038	0.689	1.819
X	0.976	0.979	0.896	1.006	0.843	1.014	0.801	1.013	0.774	1.010	0.771	1.918
XI	0.966	0.981	0.882	1.006	0.827	1.009	0.789	1.000	0.769	0.970	0.803	
XIa	0.913	0.992	0.822	1.003	0.771	1.005	0.770	1.001	0.819	0.991	0.911	
XIb	0.900	0.977	0.822	1.993	0.794	1.010	0.794	1.993	0.822	0.977	0.900	

^a Case I, charge on carbon; case II \rightarrow X, charge on nitrogen of Schiff base; case XI, odd system, no 12th atom.

continue to make a continually smaller contribution and structures **2b** and **2c** will make an ever larger contribution to the ground state so that the C-N bond will go from double to single. The same findings emerge from results presented here. Table I shows all of the values for the C-N bond order that were calculated. Table II shows bond orders for all atoms in the π system for the following species: dodecahexaene, the undecapentaenylic cation, and cases II, V, VII, IX, and X, where Z_p is assigned to be 0.00, 0.25, 0.50, 0.75, and 1.00, respectively. Of course the single most important result with respect to bond order is to see the C-N bond order go from that of a double to a single bond. This result is consistent with resonance theory and with the conclusion of the previous section concerning orbital geometry. Both the change in orbital geometry of ψ_1 and the C-N bond distance imply rehybridization of the nitrogen from sp^2 to sp^3 .

The bond orders for case I, dodecahexaene, and case XI, the undecapentaenylic cation, are included for comparison with the protonated Schiff base. Values of 0.942 and 0.333 are typical values from our program for terminal double and single bonds, respectively. This strong bond alternation tends to decrease somewhat as the center of the chain is approached; here values of 0.877 and 0.358 are found. Values for the protonated Schiff base are in good agreement with these values. The undecapentaenylic cation also shows strong bond alternation at its extremities; however, bond alternation is considerably diminished at the center. The bond orders for C_{1-2} and C_{2-3} are 0.929 and 0.356, respectively, close to the values already noted for double-single bond alternation. However, for C_{5-6} , C_{6-7} , and C_{7-8} the bond orders are 0.765, 0.523 and 0.682, respectively, which compare favorably with the value of 0.638 for the ideal aromatic bond. Clearly the bond order near the center is considerably less alternating and assumes values near that of the aromatic bond. Case X, the Schiff base with $Z_p = 1$, quantitatively follows the same pattern, the pattern for an odd orbital system. Attention must also be called to the behavior of the bond order at C_{10-11} . In case II it is quantitatively a

single bond $P_{10-11} = 0.383$. As Z_p is increased, the bond order of C_{10-11} goes toward and beyond the value of 0.638 for the aromatic bond. A final value of 0.762 is achieved. All of these results are consistent with resonance theory and indicative of changing from an even to odd system.

The undecapentaenylic cation deserves special consideration. The species would be expected to have mirror image symmetry about carbon atom six, giving rise to an identical value of electron density and bond order on either side of this atom. The bond order values shown for XI are not completely symmetrical. Using our computer program, self-consistency in bond order is achieved through the use of constant values of $\beta_{C=C}$ and β_{C-C} that were used in cases I to X. However, the cation can be calculated as being initially a symmetrical species; i.e., the bond lengths and the β values can be made equal at the outset. With bond lengths set at 1.40 Å and $\beta = 2.40$ eV, the calculated bond orders are shown as XIb. The species is symmetrical.

It is also possible to start the calculation with alternating bond lengths and alternating β values and approach convergence to a symmetrical species. This was done by changing the molecular coordinates and β values as a function of the newly calculated bond lengths. The end result of four successive calculations of XI is shown as XIa. Inspection of the bond orders (Table II) and electron densities (Table III) clearly shows that these properties are approaching the desired symmetry.

Change in Orbital Energy with Charge. In Figure 3, the calculated energies of molecular orbitals of selected compounds are displayed for comparison. Case I, dodecahexaene, and case XI, the undecapentaenylic cation, are included for comparison with the limiting cases of the protonated Schiff base, cases II and X. Cases V, VII, and IX are given to facilitate internal comparison of the effect of changing Z_p from 0 to 1. Cases II, V, VII, IX, and X show that as the anion recedes, the energies of all π orbitals fall. It is clear that the removal of the counter negative charge stabilizes the π system, whereas approach of

the negative charge destabilizes the π system.

As has been observed in the comparison of other calculated properties, the orbital energies calculated for case II agree with those calculated for case I, and those calculated for case X agree with those for case XI. The energies of orbitals ψ_2 , ψ_3 , ψ_4 , and ψ_5 appear to form a set, and these energies appear to decrease uniformly as Z_p is increased. The apparent uniformity can be understood when the behavior of orbital geometry is recalled from the last section. It will be remembered that the geometry of ψ_3 goes to that of ψ_2 and the geometry of ψ_2 goes to that of ψ_1 . In general, with a few notable exceptions, ψ_n goes to ψ_{n-1} . Thus in the conversion from an even to an odd system, each orbital loses one node, and the loss of this node decreases the antibonding character by some standard amount of energy. For the buried π molecular orbitals, the changes in geometry could be expected to stabilize the system by this standard amount.

Analysis of the first MO and the first antibonding MO presents additional considerations. The first MO is also stabilized by loss of a node when the system is converted from even to odd, but additional stability is imparted as the first MO is converted into an atomic orbital. Thus it is set apart from the others with respect to stability. The change in energy that results in the conversion of antibonding II, ψ_7 to nonbonding X, ψ_7 is of additional interest. The first antibonding orbital in II, ψ_7 has six nodes giving rise to six loci of antibonding within the MO. However, in the nonbonding MO of X, ψ_7 , the wave function passes through the center of every even atom (non-starred), and thus the antibonding character is removed or greatly diminished. It is observed that ψ_1 in changing from a molecular to atomic orbital and ψ_7 in changing from an antibonding to nonbonding orbital obtain approximately the same degree of stabilization, i.e., about 2.1 eV.

Figure 3 shows that as the counter negative charge approaches the cation, all of the bonding orbitals are displaced toward higher energy. Thus with respect to the π system, the ground state is destabilized as the counter negative charge approaches. However, it will also be noticed that the energy of the lowest unoccupied orbital, ψ_7 , is displaced toward higher energy more rapidly than the bonding orbitals. This results in the energy of the first excited state being elevated more rapidly than the ground state. Thus the excitation energy will increase as the counter negative charge approaches the cation. With respect to excitation energy, the final picture emerges that the counter negative charge controls the energy of ψ_7 as the charge manipulates this orbital between nonbonding and antibonding as the system passes between odd and even giving rise to large changes in the excitation energy.

Change in Electron Density with Charge. Table III displays the electron density for all 12 atoms in the π system for dodecahexaene (I) and undecapentaenylic cation (XI) plus cases II to X in which the positive charge density on the nitrogen atom is increased. It is clear that cases I and II are similar and cases X and XI are similar. In cases I and II all of the atoms have approximately the same electron density; in cases X and XI the electron density on even atoms tends to remain at unity while it drops on the odd numbered atoms. Once again this is a property of an odd π system, and by observing the change in electron density in going from II to X the conversion from even to odd can readily be followed. The electron density on atom 12 (nitrogen) deserves closer inspection. When Z_p is 0.25, 0.50, 0.75, and 1.00 the electron density is 0.348, 0.662, 0.819, and 0.918, respectively. Thus the calculated electron density on nitrogen is greater than the assigned electron occupancy or the value of the coulomb integral. Thus the nitrogen has a net negative charge in all cases except in the resulting odd cation.

The calculated π -resonance energy shows a linear relationship with Z_p . Values of resonance energy go from 306.51

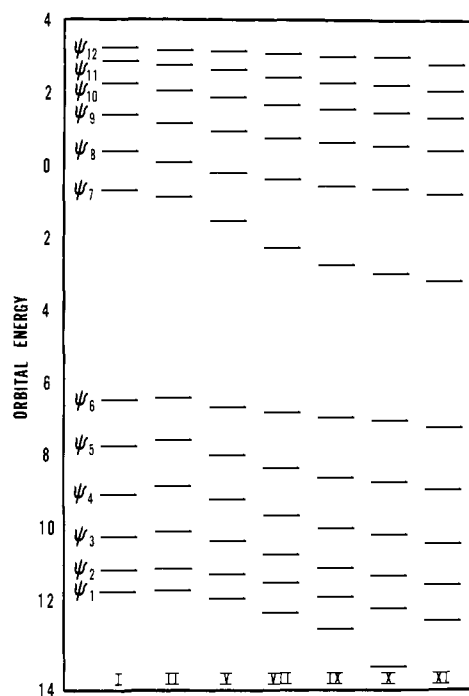


Figure 3. Energies of MO's are plotted for dodecahexaene I, the undecapentaenylic cation XI, and the protonated Schiff base when $Z_p = 0, 0.25, 0.50, 0.75,$ and 1.0 (cases II, V, VII, IX, and X). ψ_1 receives considerable stabilization energy as it is changed from an MO to an atomic orbital. ψ_7 receives an equally large stabilization energy when it is changed from an antibonding MO to a nonbonding MO. The conversion of ψ_7 is responsible for the large decrease in ΔE as Z_p increases.

eV at $Z_p = 0$ to 318.16 at $Z_p = 1$ and linear regression gives a line with a coefficient of determination of 0.985.

Discussion

It has been shown that as Z_p (the fraction of positive charge used in π electron polarization) goes from a value of 0 to +1, a number of molecular parameters undergo a change consistent with conversion of the π system from even to odd. (1) Thus 12 molecular orbitals go to 11 molecular orbitals and one atomic orbital; (2) formal double-single bond alternation decreases, especially toward the center of the newly developed odd system; (3) the evenly distributed electron density of the even system gives way to the kind of alternation of electron density found in odd systems; (4) the lowest unoccupied molecular orbital of the even π system which is an antibonding molecular orbital is converted into a nonbonding molecular orbital; (5) the carbon-nitrogen bond in the even system, which is double, is converted into a single bond thus acting to remove nitrogen from conjugation with the 11 carbon atoms; and finally (6) the π resonance energy is increased in going from even to odd. Thus when the system is converted from even to odd, a number of molecular parameters change, and consequently, the physical and chemical properties based on these parameters also show a change.

The physical property associated with vision that has received virtually all of the attention is the excitation energy. In these studies a relationship has been established between ΔE and Z_p , i.e., $\Delta E \propto (1 - Z_p)^2$ or $\Delta E \propto Z_p^2$. This relationship was given by eq 5 and was predicted previously.⁸ It is particularly interesting that the relationship holds in the face of certain experimental results presented herein. In the original derivation, as a consequence of results from MO calculations, the electrostatic perturbation was applied only to the ground state. The calculations contained herein show that the energy of the lowest unoccupied orbital falls rapidly so that upon increase of Z_p , the excited state is stabilized at a more rapid rate

than the ground state. Consequently the electrostatic perturbation should be applied to both states in a derivation.

The excited state energy can be written:

$$E_x = E_x^\circ - \frac{Z_{ix}Z_a e^2}{\epsilon d} \quad (6)$$

where Z_{ix} is the excited state positive charge engaged in ion bond formation. In the same manner the ground state energy can be written:

$$E_g = E_g^\circ - \frac{Z_{ig}Z_a e^2}{\epsilon d} \quad (7)$$

but $Z_{ig} = d_{og}/d$ and $Z_{ix} = d_{ox}/d$, where d_{og} and d_{ox} are proportionality constants for ground and excited states, respectively. If these values are substituted into (6) and (7) and if (7) is subtracted from (6), we obtain:

$$\Delta E = \Delta E^\circ - \frac{d_{ox}Z_a e^2}{\epsilon d^2} + \frac{d_{og}Z_a e^2}{\epsilon d^2} \quad (8)$$

$$\Delta E = \Delta E^\circ - \frac{Z_a e^2}{\epsilon d^2} (d_{ox} - d_{og}) \quad (9)$$

$Z_a = -1$ and $d_{ox} - d_{og} = \Delta d_o$

$$\Delta E = \Delta E^\circ + \frac{e^2 \Delta d_o}{\epsilon} \left(\frac{1}{d^2} \right) \quad (10)$$

Equation 10 indicates that a plot of ΔE vs. $1/d^2$ should give ΔE° as the intercept, and this value is known to be 2.107 eV or 588.5 nm by an alternate experiment.⁷ Since eq 1 and 10 are identical except for the terms in the slope, the relationship established in eq 5:

$$\Delta E = (\Delta E_{SB} - \Delta E^\circ) Z_i^2 + \Delta E^\circ \quad (5)$$

still holds and with $\Delta E_{SB} = 3.415$ nm and $\Delta E^\circ = 2.107$, eq 5 becomes

$$\Delta E = 1.308 Z_i^2 + 2.107$$

Thus the electrostatic model successfully predicts the outcome of the MO calculations with respect to excitation energy. It is possible to evaluate the parameters d_{og} , d_{ox} , and Δd_o with the experimental evidence we have collected, but this will not be attempted in this already lengthy article.

It has been shown that Z_p controls molecular parameters which in turn control observable chemical and physical properties, and one of these physical properties is excitation energy. At the same time, this all important parameter is determined by Z_i , $Z_p = 1 - Z_i$. Z_i itself is a complicated function and is dependent upon Z_a , d , and ϵ . In other words, the ΔE for any given system is not just a simple function of the exact distance between the centers of positive and negative charge density. Certainly the medium effect or the environmental effect must be taken into consideration. The dielectric and the microscopic reactions of the anion with its environment are of the utmost

importance in λ_{max} considerations, and of course the effect of environment also influences the λ_{max} of the retinylic cation. More detailed consideration of the environmental effect will be postponed until the appropriate experimental results are presented. However, the importance of environment will be recalled in the following example.

NRBAH⁺ salts when dissolved separately in methanol and ethanol exhibit no anion effect, yet these salts absorb at 442 and 447 nm, respectively. The same salts when dissolved in CCl₄ and C₆H₆ exhibit an anion effect, and additionally the chloride salt absorbs at 442 and 437 nm, respectively. One first might be led to conclude that the same mechanism operates in both cases and that the λ_{max} is controlled by the anion. In the case of CCl₄ and C₆H₆ this conclusion is probably correct since the anion would be expected to interact with the cation as an ion pair. The salts are just barely able to stay in solution at about 10⁻⁵ M. On the other hand these solubility circumstances do not prevail when methanol and ethanol are solvents. The salts are freely soluble in large amounts, and first principles suggest they are highly ionized. This would be particularly true in concentrations on 10⁻⁵ M. If the cation's λ_{max} is not controlled by the anion, it must be controlled by solvent-cation interaction. Thus the electron rich centers of oxygen interact with the positive charge on nitrogen by a dipole ion mechanism. The solvent molecules exert the same quantitative influence as a formally charged chloride ion. This is a dramatic example of the solvent environment effect.

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