It would be interesting to vary the structure of the connecting chain and to study its effect on the stability of the triple ion. For example, incorporating oxygen atoms in the chain (*e.g.*, a $(CH_2CH_2O)_n$ linkage) may lead to rather stable intramolecular cyclized triple ions.

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On the Spectral Characteristics of the Odd-Polyenyl Carbonium Ions[1]

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Abstract: Due to the possibility that an odd-polyenyl carbonium ion might play an important role as the wavelength regulator in the chemistry of visual pigments, the spectral behavior of these cations has been investigated with the combined effects of the Pariser–Parr–Pople method and the ω technique. Such a study has enabled us to derive what may be the most appropriate picture of charge distribution in these ions. Particular emphasis has been laid on the undecapentaenylic cation, which is the key cation in the visual pigment rhodopsin.

Among the various mechanisms[2–5] that have been proposed to explain the unique spectral behavior of the visual pigment molecules, the one involving the role of carbonium ions was first postulated by one of us[6a] (P. E. B.) and with modification has been substantiated since then by means of both the experimental as well as theoretical evidence.[7–10] As a result, the emerging molecular model responsible for much of the observed phenomena encompasses the following features. (1) When a π-molecular system with an even number of orbitals, such as a linear polyene, is transformed into one with an odd number of orbitals, corresponding either to its radical, cation, or anion for instance, the optical spectrum is greatly displaced toward longer wavelengths (bathochromic shift). This fact has been associated with the property of visual pigment molecules in which similar large bathochromic shifts are observed when the chromophore molecule (retinal, a polyene aldehyde with λ_{max} 381 nm) is complexed *via* an azomethine type linkage to the visual protein opsin (λ_{max} ranging up to 575 nm). Although in a manner similar to its simple polyene Schiff base counterpart, the chromophore, while still remaining complexed with the opsin, is not a pure carbonium ion. In polyenes such a transformation can be brought about through protonation. (2) The formation of a pure carbonium ion is prevented in the case of Schiff bases because of the proximity of the counteranion which localizes considerable positive charge on the nitrogen atom and thus enables only the leftover fractional charge to delocalize itself over the π structure. By regulating the strengths of the anionic or other electron-rich groups, the charge on the nitrogen and hence that on the chromophore can be controlled indirectly. (3) Whereas the way in which the protein controls the charge on the nitrogen can only be postulated, it must be admitted that this behavior of *N*-substituted charged polyenes differs considerably from that of pure carbonium ions. In the latter, once it is formed, the positive charge is uniformly distributed over the entire ion. Experimental evidence suggests[6b] that carbonium ions have little or no additional polarizability. It is true that the extent by which the N^+ of the Schiff base is in conjugation with the π system is not known. Therefore, it is important to study the two limiting cases in which the nitrogen is completely attached to the π system (*i.e.*, the even orbital heteroatomic polyene) and when it is not (corresponding carbocation—an odd orbital system). These studies can then shed some light on the charge distribution patterns when N^+ is only partially connected to the π system.

It is in connection with this anomaly of charge distribution in carbonium ions that an interesting problem is created and indeed an essential step for understanding the properties of visual pigments. For, once the charge distribution in carbonium ions is known, an exact charge distribution can be derived for the visual chromophore from knowledge of the fractional charge on nitrogen that is available for polarization in the polyene.

Method of Calculation. The success of Pariser–Parr–Pople[11] (the P^3 method) in interpreting the electronic

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spectra of various spectra of various conjugated compounds can hardly be exaggerated. Pople and Brickstock[12] and Pople and Lonquet–Higgins[13] proposed a similar method that can be applied to the unsaturated hydrocarbon radicals and their ions both in their ground and excited states. These methods have been mainly applied to the aromatic and other cyclic cations. Far less is known about the properties of polyenylic cations. This was mainly due to lack of the experimental evidence, since such carbonium ions, with the exception of allyl and pentadienylic cations, were not prepared, and hence their spectra were not known until recently.[7,14] The system of ions for which the spectral data are available has the general formula $C(Me)_2CH(C^+HCH)_nC(Me)_2$; $n = 0–5, 9$. Structures of these ions have been corroborated through known methods of synthesis and the use of nmr and uv spectroscopy. An empirical relation between the observed λ_{max} and the number of double bonds, n', in any of the resonance structures of the cation has been given in the following form[15]

$$\lambda_{max} = 250 + 75n' \qquad (1)$$

The program written to compute the theoretical quantities is based on the approximations of the P[3] method, which mixes all the singly excited configurations to improve the excited states, whereas the ground state essentially remains the same (Brillouin's theorem). The Hückel matrix, the core matrix, the coordinates, and the electron repulsion integrals as calculated by the Mataga–Nishimoto formula[16] are fed to the computer as the input data. The calculations were done on the Sigma Seven of the Xerox Division and on the IBM 360/50 computers.

Theory

On the basis of the resonance theory and the simple HMO, one would expect the excessive positive charge in the cation to be equally distributed only on the starred atoms, whereas there should be no charge on the unstarred ones. This is not in agreement with the results of the SCF method. In fact, Goodman and Hoyland[17] used reminimized orbitals in their SCF calculations, and their results show that the distribution of the excess positive charge is not only nonuniform but that the unstarred atoms show a tendency to acquire excess negative charges. Such a distribution does not conform with the known chemical facts. Such a behavior has also been reported by Mackor, *et al.*,[18,19] who compared their theoretically calculated charge distributions with the charge distributions empirically calculated from the chemical shifts in nmr spectra from eq 2 in

$$\Delta\sigma = a\Delta q \qquad (2)$$

which $\Delta\sigma$ is the change of shielding of hydrogens in these ions, Δq is the excess electron density at that carbon atom, and "a" is proportionality constant, $\simeq 11$ ppm per unit charge. Their results indicate greater delocalization of the positive charge over the entire conjugated structure and not just at the starred atoms. Sorensen[14] used a similar relationship to study the charge distribution, *viz.*

$$\Delta\tau_H = K\Delta\rho \qquad (3)$$

where $\Delta\tau_H$ is the difference between the chemical shift of the protons in the ions and related neutral species and $\Delta\rho = \Delta q$ from the earlier expression. The results obtained by the two methods differ considerably. Sorensen's results are qualitatively comparable to those predicted by HMO except at the end atoms where smaller positive charges appear as a result of the hyperconjugative effects of the terminal methyl groups. Due to such a lack of correlation, we decided to consider various possibilities of parametrization that might lead us to a correct picture of the charge distribution in these ions. The first notion that suggests itself is that in the case of the ions it is not proper to give the Coulomb integrals of all the carbon atoms a common value. One way to adjust the Coulomb integrals is to use Pople's method to determine the corresponding matrix element, F_{ii}, of the Fock matrix as

$$F_{ii} = W_c + (1/2)\gamma_{ii}q_i + \sum_{j\neq i} (q_j - 1)\gamma_{ij} \qquad (4)$$

wherein γ_{ii} and γ_{ij} are one- and two-center electron repulsion integrals, q is electron density, and W_c the valence state ionization potential. Calculating these terms for all carbon atoms of the π system should improve the picture. An easier approach, however, is to use the ω technique[20] which although comparable to the above method differs in the selection of atomic electronegativities relative to one another in the atoms of the cation. The Coulomb integral, α, which stands for the measure of electronegativity of an atom, should be more negative for the relatively more electronegative atom. In the ω technique, this depends upon the amount of positive charge present on that atom. Thus, in case of allyl cation, *e.g.*, the terminal atoms should be more electronegative in the cation than in the neutral radical. This is given by

$$\alpha_i = \alpha_0 + (1 - q_i)\omega\beta_0;$$
$$\text{in allyl cation } |\alpha_1| = |\alpha_3| > |\alpha_2|;\ \omega = 1.4 \qquad (5)$$

In the SCF approach, F_{ii} (see eq 4) stands for the measure of electronegativity of atom i; and in the allylic cation, as shown by Dewar,[21] the results are: $|\alpha_2| > |\alpha_1| = |\alpha_3|$. This is exactly opposite to what the ω technique predicts. It should be remembered that the SCF approach includes electron repulsions and thus results obtained by using this method serve as data from an advance method for comparison. The ω technique compares only vaguely with the SCF approach[22] when all the repulsion integrals, γ_{ij}'s, are neglected except where $i = j$, and this is not apt to happen considering the magnitudes of these terms.

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While the success of the ω technique in calculating, with relative ease, ionization potentials, dipole moments, and energy levels of hydrocarbons, cations, and their heteroatomic derivatives cannot be overlooked, and also since the fact that the SCF approach often leads to excess electron densities and in some cases even to partial negative charges on some unstarred atoms due to their exaggerated high relative electronegativities, it would seem logical to combine the effects of both methods. This can be done simply by taking the electron densities from a pure SCF (P^3) calculation of an ion computed without altering the Coulomb integrals and then substituting them into eq 5 to calculate a new value for each α. Then the SCF calculations are done with these α's to give the final results. These changes can be brought about either by changing the corresponding Hückel matrix elements or by changing Coulomb integrals of the core matrix. We shall call this the modified ω technique (P^3 type).

Protonation of the Schiff base certainly should change effective core charges of the heteroatomic polyene because a $-^{+}NR_3$ is considered as purely inductive. We are, however, considering one of the two limiting cases where the N^+ has gone completely out of conjugation by extracting a pair of π electrons from the π system and thus transforming itself into a neutral configuration, NR_3, and the π system into corresponding carbocation. The inductive effect due to protonation has, therefore, not been taken into consideration.

Results and Discussion

Table I gives the electron densities and the transition energy, ΔE, for the first π,π^* transition as calculated by HMO, ω technique, SCF, and modified ω technique for the allyl cation.

Table I. Comparison between the Results of Various Methods for the Allylic Cation, $\underset{1}{CH_2}\cdots\cdots\underset{2}{\overset{+}{CH}}\cdots\cdots\underset{3}{CH_2}$

	Methods used			
	HMO	ω technique[a]	SCF	Modified ω technique
Electron densities at atom no.				
1	0.500	0.621	0.512	0.584
2	1.000	0.757	0.976	0.832
Energy of transition, ΔE,[b] eV	2.9840	2.1459	4.5592	4.3958

[a] Values after first iteration. [b] Experimental ΔE[14] = 4.06 eV.

Table II gives similar results for the undecapentaenylic cation which has eleven π orbitals and ten π electrons. The results appearing in Tables I and II have been reproduced for various methods mentioned therein by using an identical value for the resonance integral, $\beta = -2.402$ eV [N. L. Allinger, *et al.*, *J. Amer. Chem. Soc.*, **85**, 1171 (1963)]. This was necessary for effective comparison and for establishing validity as well as superiority of the modified ω technique using a standard value. However, for achieving better agreement between experimental and calculated transition energies, we decided to use $\beta = -2.0$ eV. Results appearing in Tables III–VI are the results that we have obtained for various systems using this value of β. Results in Tables II and V cannot be compared, because they have been calculated with different values of β. The data in Tables I and II show how the use of modified ω technique, which is a combination of the ω technique and the SCF approach, enables one to obtain results that are intermediate of the two obtained separately from individual methods. The combined approximation, therefore, serves to modulate the emphasis of choice of electronegativities contradictory to one another and thus presents a more realistic charge distribution which is qualitatively better than that from either ω technique or SCF approach. To see if it can also give quantitatively better results, it would be necessary to compare our results with some experimentally derived values. Table III shows such a comparison for the 2,3-di-*cis*-pentadienylic cation with the charge distribution pattern calculated by using nmr spectra.[18] The agreement is close to the experimentally derived charge distribution and thus seems satisfactory to establish the validity of the modified ω technique. Further, this is the only method among those mentioned in Table III which shows the trend that the positive charge on the starred atoms increases toward the center of the ion.

Table II. Comparison between the Results of Various Methods for the Undecapentaenylic Cation

	Methods used			
	HMO	ω technique[a]	SCF	Modified ω technique
Electron densities at atom no.				
1	0.833	0.951	0.903	0.922
2	1.000	0.904	0.974	0.943
3	0.833	0.916	0.822	0.875
4	1.000	0.884	1.001	0.932
5	0.833	0.905	0.794	0.864
6	1.000	0.879	1.010	0.928
Energy of transition, ΔE,[b] eV	1.2422	0.9935	2.3438	2.1998

[a] Values after first iteration. [b] Experimental ΔE[14] = 1.98 eV.

Table III. Comparison of the Electronic Distributions as Obtained Using the Modified ω Technique and Other Methods with Experimentally Computed Values for the 2,3-Di-*cis*-pentaenylic Cation

	Methods used				
Electron densities at atom no.	HMO	SCF	SCF[a] with doubly excited C.I.	Modified ω technique	Exptl[a] from nmr spectra
1	0.667	0.620	0.64	0.785	0.780
2	1.000	0.960	1.00	0.868	0.840
3	0.667	0.670	0.72	0.694	0.750

[a] Reference 18.

To achieve good agreement in calculated values of transition energies for the whole series of the odd-polyenyl cations, we adjusted the value of β to -2.0 eV, which gave λ_{max} of 625 nm for the undecapentaenylic cation. This value was then held constant for other cations in the series, *viz.*, the allyl, pentadienyl, heptatrienyl, through the β-carotene cation. The agreement between the calculated and the experimental ΔE corresponding to the λ_{max} is given in Table IV.

Table IV. Comparison between the Calculated Lowest Energy Transition and the Experimental Values[a] for the Odd-Polyenyl Cations $C(CH_3)_2CH(C^+HCH)_nC(CH_3)_2$

n	ΔE_{calcd}	$\Delta E_{\text{obsd}}{}^c$
0	4.683	4.060
1	3.471	3.130
2	2.753	2.620
3	2.301	2.260
4	1.980	1.980
5	1.735	1.766
6	1.543	
7	1.387	
8	1.261	
9	1.154	1.194[b]

[a] All values in eV. [b] N. Baumgartner, Ph.D. Thesis, submitted to the University of Wyoming. [c] Reference 14.

It is at once realized that the agreement gets poorer as one goes toward cations with shorter lengths of conjugation; however, considering the fact that only the π electrons are explicitly considered and that inclusion of configuration interaction arising only from mixing of singly excited configurations does not sufficiently improve the wave functions and energy levels of the excited states of these short cations, the results seem satisfactory. The data in Table IV also enable us to predict the $\lambda_{\max}$ for cations with 15, 17, and 19 π orbitals.

Table V shows the charge distribution pattern for the undecapentaenylic cation with $\beta = -2.0$ eV. This is the cation of interest in vision chemistry.

Table V. Comparison of the π Densities as Calculated by the Modified ω Technique and FEMO with the Values Calculated from the Nmr for the Undecapentaenylic Cation

	Methods used		
Atom position	FEMO[b]	Modified ω technique	Empirical[c]
1	0.972	0.925	0.886[a]
2	0.927	0.944	0.963
3	0.846	0.869	0.886
4	0.914	0.938	0.963
5	0.836	0.854	0.886
6	0.949	0.935	0.963

[a] Assuming each of the terminal methyl groups has a positive charge 0.033 on it. [b] D. Oseen, R. B. Flewwelling, and W. G. Laidlow, *J. Amer. Chem. Soc.*, **90**, 4209 (1968). [c] Reference 14.

As remarked earlier, the experimentally derived data in Table V do not compare with either of the calculated, because it resembles the Hückel results. This could be due to lack of complete correlation which can affect the results of this method and thus show deviations in electron density pattern. The difference between our result and that derived from the FEMO is that our result shows increase in the positive charge on both the starred and the unstarred atoms toward the center of the ion, whereas the FEMO, along with other approximations, show increase for the starred and decrease on the unstarred atoms. Also the results of FEMO indicate that the first and ultimate atoms in the π systems have less positive charge than the second and penultimate atoms. This is clearly against current chemical knowledge. Such a behavior can be explained only on the basis of the incorrect estimation of the electronegativities of atoms relative to one another. We observed a similar trend in other schemes of parametrization not mentioned in the present paper. In fact we tried many different approaches such as placing charges nonuniformly, varying bond lengths, and finding other means of evaluating the electronegativities of the atoms; but the results given by the modified ω technique proved to be the best among these. While it is hard to say that this is the best approach there is, it certainly can be said that the real test would be when the modified ω technique can be successfully applied to study the carbonium ions in the visual pigment model which is presently under consideration.

Finally, Table VI shows the bond orders for the ground state of the undecapentaenylic cation calculated with the modified ω technique and that from the HMO. These data show considerable bond alternations resembling more like that of the polyenes. This suggests that there is significant bond alternation in these ions.

Table VI. Comparison between the Bond Orders Calculated from the HMO and from the Modified ω Technique for the Undecapentaenylic Cation

	Methods used	
Bonding atoms	HMO	Modified ω technique
1–2	0.834	0.879
2–3	0.760	0.452
3–4	0.696	0.740
4–5	0.596	0.561
4–5	0.644	0.650

Conclusions

It has been shown that by simple combination of the two methods, *viz.*, the SCF approach and the ω technique, it is possible to obtain results that are better than those individually, because of the inherent limitations of each of these two methods. The effect of combination is compared with other conventional methods and the results are seen to be superior. The knowledge of exact mode of charge distribution in the polyenyl carbonium ions seems to be clear, and this should be helpful in studying the spectroscopic properties of various visual pigments.

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