The spectra of carbonium ions, cyanine dyes, and protonated Schiff base polyenes

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(Received 27 February 1980; accepted 24 June 1980)

The origin of the strong bathochromic shift of the visual pigment supposedly lies in the carbonium ion character of the protonated Schiff base retinal. Following this conjecture, we have carried out a comparative study of the spectra of the carbonium ions, cyanine dyes, and protonated Schiff base polyenes. In our calculation, we have employed PPP (for the carbonium ions) and CNDO/S parametrized Hamiltonians. For a correct description of the electronic excitations in these linear π-systems, we have included all single, double, and in some cases also all triple and quadruple excited configurations in the CI expansion. Our study revealed a close resemblance of the spectral behavior of these three compounds. In particular, we found that higher excitations, accounting for the effect of electron correlation, induce a strong red shift of the main ($S_1 \leftarrow S_0$) absorption band. This behavior is due to the mainly covalent character of the S_1 state which is poorly described by single excited configurations. As in the polyenes, there exists also a weakly absorbing state of double excited character which in contrast to the polyene case lies above the allowed state.

I. INTRODUCTION

An explanation of the bathochromic shift of the visual pigments is regarded as most important for an understanding of the photochemistry of vision. The visual protein, rhodopsin, contains the polyene 11-*cis* retinal, covalently bound to a lysine group as a Schiff base, generally assumed to be protonated.[1] The various rhodopsins occurring in nature have absorption maxima ranging from 430 nm for the worker bee,[2] 500 nm for the human rod pigment,[3] to 610 nm for the red absorbing pigment of a butterfly.[4] These values are to be compared with the 380 nm absorption of unprotonated retinal Schiff bases in solution,[5] i.e., the red shift of the visual chromophore can reach a maximum value of 230 nm.

Red shifts of this magnitude have in fact been observed for polyene systems. The polyene $(CH_3)_2CCH(CHCH)_4CHC(CH_3)_2$, which has 12 conjugated carbon atoms and is isoelectronic to retinal absorbs at 376 nm.[6] The related carbonium ion $[(CH_3)_2CCH(CHCH)_4C(CH_3)_2]^+$ which has only 11 conjugated carbon atoms with 10 π electrons absorbs at 626 nm, i.e., 250 nm to the red of the 12 carbon polyene.[6] This observation suggests that the protonated Schiff base of retinal in rhodopsin may assume some character of a carbonium ion as indicated in Fig. 1. The structure of the protonated Schiff base in Fig. 1 is also similar to that of the cyanine dye $(CH_3)_2CCH(CHCH)_4N(CH_3)_2$ which, in fact, absorbs maximally at 626 nm.[7] It is apparent that an understanding of the red shift of retinal would require (1) an investigation of the spectra of carbonium ions and cyanine dyes, and (2) an answer to the question as to the extent to which the protonated Schiff base of retinal is related to these compounds. In this paper we will address both problems.

Prompted by the observations of low-lying forbidden states in polyenes [summarized in Ref. 8(c)], recent theoretical investigations have demonstrated the general existence of some low-energy excited states of covalent character in conjugated molecules.[8] A prequisite for a complete account of optical transitions in π systems was found to be the inclusion of at least single as well as double excitations in a CI expansion. We have, for this reason, also employed extended CI expansions for carbonium ions and cyanine dyes as well as protonated Schiff bases of polyenes, in one case including all single, double, triple, and quadruple excited configurations. We found that in these compounds *all* excitations are, to a great extent, of *covalent* character. To account for this character, at least double excitations must be included in a CI treatment. In fact, a CI expansion restricted to single excitations describes only part of the red shift between a polyene and its shorter carbonium ion relative.

A much debated problem connected with odd-numbered

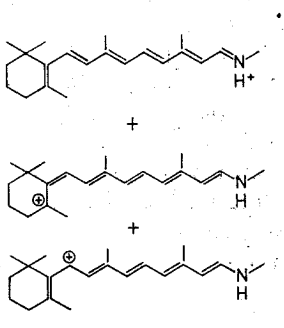

FIG. 1. Contribution of carbonium ion character to the protonated Schiff base of polyenes.

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 0021-9606/80/203927-09$01.00

polyenes regards the question of whether bond alternation exists in the ground state of these compounds. This question, however, can be readily answered by an evaluation of the respective bond orders. Accordingly, we present the bond orders for a series of odd-numbered polyenes. These allow us to determine geometries for the compounds of interest which are used in the ensuing calculations.

For calculations of the electronic excitations of π systems as large as in retinal, one has to rely on semiempirical methods. In general, the PPP Hamiltonian has been found sufficient for the description of polyenes.[8] This Hamiltonian can be extended to carbonium ions without further assumptions regarding the semiempirical matrix elements. However, this does not apply to the cyanine dyes and protonated Schiff bases. For an unbiased parameterization and to account for a possible effect of $\sigma-\pi$ mixing, we have instead applied the CNDO/S method to these compounds. Thus, we report below the results of PPP–SCF–CI calculations on polyenes and carbonium ions (for a comparison of the behavior of these two molecules) and CNDO/S–CI calculations on carbonium ions (to compare with the PPP results), cyanine dyes, and protonated Schiff base polyenes.

Section II of this paper contains a methodological description of our calculations. In Sec. III we consider the problem of ground state bond orders of odd π-orbital systems. In Sec. IV we present the PPP–SCF–CI results on polyenes and carbonium ions and discuss in some detail the electron correlation effects in the latter. In Sec. V we report the CNDO/S–CI results on carbonium ions and cyanine dyes and demonstrate the close relationship between these compounds and protonated Schiff base polyenes. In Sec. VI we provide a short summary.

II. THEORY

A. PPP-SCF-CI calculations

The PPP Hamiltonian has been employed in the representation

$$H=\sum_{n<m}R_{nm}+\sum_{m,\sigma}\left(-I-\sum_{n\neq m}R_{nm}\right)c^{+}_{m\sigma}c_{m\sigma}+\sum_{\substack{n,m,\sigma\\ n\neq m}}t_{nm}c^{+}_{n\sigma}c_{m\sigma}+\frac{1}{2}\sum_{\substack{n,m\\ \sigma,\sigma'}}R_{nm}c^{+}_{n\sigma}c_{n\sigma}c^{+}_{m\sigma'}c_{m\sigma'}\,, \quad (1)$$

where the first term describes the nuclear repulsion, the second term the attraction between electrons and nuclei, the third term the Hückel-type electron delocalization, and the last term the electron repulsion [the sum excluding all terms $(n,\sigma)=(m,\sigma')$]. $c^{+}_{m\sigma}(c_{m\sigma})$ are Fermion creation(annihilation) operators which position the π electrons in an orthonormal set of atomic orbitals. R_{nm} are the effective Coulomb repulsion integrals between orbitals at atom n and m approximated by the formula (Ohno approximation)[9]

$$R_{nm}=14.397\ \text{eV}(1.67+r^{2}_{nm})^{-1/2}\,, \quad (2)$$

where r_{nm} is the corresponding atomic distance in Å. I stands for the effective ionization potential of a π electron at a carbon site chosen to be 11.16 eV and t_{nm} represents the resonance integrals between centers n and m,

$$t_{nm}=-2.6\ \text{eV}+3.21(r_{nm}-1.397)\ \text{eV} \quad \text{for neighboring } (n,m)$$
$$=0 \quad \text{otherwise}. \quad (3)$$

The bond distances r were evaluated in a self-consistent way from the SCF bond orders p by means of[10]

$$r=1.512-0.174p\,. \quad (4)$$

Standard bond angles (120°) were assumed.

For our CI calculations including all single up to all quadruple excited configurations from the SCF ground state, we have employed a new, very efficient algorithm for the evaluation of the Hamiltonian matrix elements.[11]

B. CNDO/S-CI calculations

The CNDO/S method was used employing the Ohno formula (2) for the electron repulsion integrals. The CI calculations including single excitations (S-CI) involved both σ- and π electrons; however, the CI expansion was truncated to a dimension 50. The CI calculations including single as well as double excitations (D-CI) involved solely the π electrons and reached the dimension 703 for the largest molecules discussed. For computational convenience the methyl-substituted polyenes, to which experimental data refer, were replaced in the calculations by the unsubstituted polyenes. The omission of the methyls was also dictated by the intrinsic inadequacy of the CNDO method to correctly handle their inductive effect.[12] The extent to which this affects spectral transitions is discussed below.

For the input geometry, we assumed standard bond angles. For the carbonium ions the Dewar relation (4) between bond length and bond orders was assumed in a *self-consistent* way. For the cyanine dyes, the C–C bond lengths were assumed to be 1.4 Å, the C–N bond lengths 1.3 Å.

III. BOND ORDERS IN ODD-NUMBERED POLYENES

The bond orders in polyenes can be estimated by means of the simple Hückel model, i.e., neglecting any electron repulsion. One can derive the expressions for the bond order $P_{i\,i-1}$ (N is the number of conjugated atoms, $i=2,3,\ldots,N$).

$$P_{i\,i-1}=\left[\frac{1}{N+1}\right]\left\{\frac{1}{\sin[\pi/2(N+1)]}+\frac{(-1)^{i}}{\sin[(2i-1)\pi/2(N+1)]}\right\} \quad n \text{ even}$$
$$=\left[\frac{1}{N+1}\right]\left\{\cot\left[\frac{\pi}{2(N+1)}\right]+(-1)^{i}\cot\left[\frac{(2i-1)\pi}{2(N+1)}\right]\right\} \quad n \text{ odd}\,. \quad (5)$$

This expression exhibits the existence of bond alternation in both even and odd Hückel polyenes. For example,

TABLE I. Ground state bond orders (CNDO/S).

Bond:	1–2	2–3	3–4	4–5	5–6	
$CH_2(CHCH)_1CH_2$	0.96	0.28				
$[CH_2CH(CHCH)_1CH_2]^+$	0.82	0.54				
$[NH_2CH(CHCH)_1NH_2]^+$	0.65	0.62				
$CH_2(CHCH)_2CH_2$	0.96	0.29	0.92			
$[CH_2CH(CHCH)_2CH_2]^+$	0.87	0.47	0.66			
	(0.85	0.48	0.66			PPP–SCF)
$[NH_2CH(CHCH)_2NH_2]^+$	0.62	0.65	0.61			
$CH_2(CHCH)_3CH_2$	0.96	0.30	0.91	0.31		
	(0.95	0.32	0.89	0.34		PPP–SFC)
$[CH_2CH(CHCH)_3CH_2]^+$	0.89	0.43	0.72	0.58		
$[NH_2CH(CHCH)_3NH_2]^+$	0.59	0.68	0.58	0.64		
$CH_2(CHCH)_4CH_2$	0.95	0.30	0.91	0.31	0.91	
$[CH_2CH(CHCH)_4CH_2]^+$	0.90	0.41	0.76	0.53	0.65	
$[NH_2CH(CHCH)_4NH_2]^+$	0.57	0.70	0.56	0.67	0.61	

for $N=7$, i.e., $[CH_2CH(CHCH)_2CH_2]^+$, and $N=8$, i.e., $CH_2(CHCH)_3CH_2$, one obtains the bond orders 0.82, 0.55, 0.65 and 0.86, 0.50, 0.76, 0.53, respectively. One finds the bond alternation to be somewhat more pronounced for the even polyenes.

Table I presents the SCF ground state bond orders resulting from CNDO/S calculations for even and odd polyene systems, as well as the PPP–SCF bond orders for $[CH_2CH(CHCH)_2CH_2]^+$ and $CH_2(CHCH)_3CH_2$. For the latter two compounds one observes close agreement between the CNDO/S and PPP bond orders which both predict bond alternation to be more accentuated than in the Hückel description. Consulting Tables V and VI one finds, however, that ground state electron correlation effects slightly weaken the SCF bond alternation.

Table I demonstrates that bond alternation is greatly attenuated in the cyanine dyes. The origin of this behavior lies in the surplus π-electron charge $q>0.6$ carried by the terminal nitrogens ($P_{NN}=1+q$). This imposes an upper bound to the bond orders P_{NC}. This bound follows from the property of the density matrix

$$\sum_j P_{ij}^2 = 2P_{ii} \tag{6}$$

or

$$\sum_{j\neq i} P_{ij}^2 = 2P_{ii} - P_{ii}^2 = 1 - q_i^2 , \tag{7}$$

i.e., $P_{NC}<0.80$. Hence, the terminal bond in cyanine dyes has to be rather weak, and in contrast to carbonium ions where bond order alternation originates in the terminal bond, bond alternation is greatly attenuated.

Table II shows that protonated Schiff base polyenes exhibit a bond order pattern containing features of both even polyenes and cyanine dyes. Near the terminal carbon bond alternation is as strong as in polyenes, while near the terminal nitrogen the bond order pattern is reminiscent of that found for the cyanine dyes.

It should be noted that the CNDO/S calculations do not include methyl groups for reasons indicated above. In the cases in which their effect was checked, we found no appreciable change for cyanine dye bond orders. For carbonium ions, in particular for the shorter members, the methyl groups were found to reduce the terminal bond orders. Bond alternation in the carbonium ions $[(CH_3)_2CCHCH(CHCH)_nC(CH_3)_2]^+$ may then actually be more attenuated than suggested by our calculations.

IV. ELECTRON CORRELATION IN THE EXCITED CARBONIUM ION (PPP DESCRIPTION)

For an analysis of the spectra of odd carbonium ions, a comparison with the spectra of the even polyenes, which are understood rather well, seems advisable. For this purpose, we have carried out extended PPP–SFC–CI calculations on the polyenes as well as on the carbonium ions. The results presented in Fig. 2 and Tables III–VII will be discussed in this section.

Figure 2 compares the electronic energy levels of octatetraene and the $[(CH_3)_2CCH(CHCH)_2C(CH_3)_2]^+$ carbonium ion resulting from three different CI expansions: (S) including all single excitations from the SCF ground state, (D) including all single as well as all double excitations, and (Q) including all single, double, triple, and quadruple excitations. The results presented for octatetraene differ from previous descriptions (Ref. 8) in that we have chosen the bond length self-consistently (see Sec. II) in order to be consistent with the carbonium ion calculations for which such choice is a necessity. However, the octatetraene bond orders resulting from such a procedure, indicated in Fig. 2, are actually close to the standard values employed in previous calculations, i.e., 1.35 Å for double bonds and 1.46 Å for single bonds. The effect of higher excitations on the spectrum of octatetraene is typical for polyenes.[8] In going from the S-CI to the D-CI description, the (–) states are lowered with respect to the

TABLE II. Ground state bond orders (CNDO/S).

	bonds										
$CH_2(CHCH)_nNH_2^+$	1–2	2–3	3–4	4–5	5–6	6–7	7–8	8–9	9–10	10–11	11–12
$n=1$	0.88	0.43	0.75								
$n=2$	0.91	0.38	0.78	0.51	0.70						
$n=3$	0.93	0.34	0.84	0.43	0.75	0.53	0.69				
$n=4$	0.94	0.32	0.87	0.38	0.81	0.46	0.73	0.55	0.68		
$n=5$	0.95	0.31	0.87	0.35	0.85	0.40	0.80	0.47	0.73	0.56	0.67

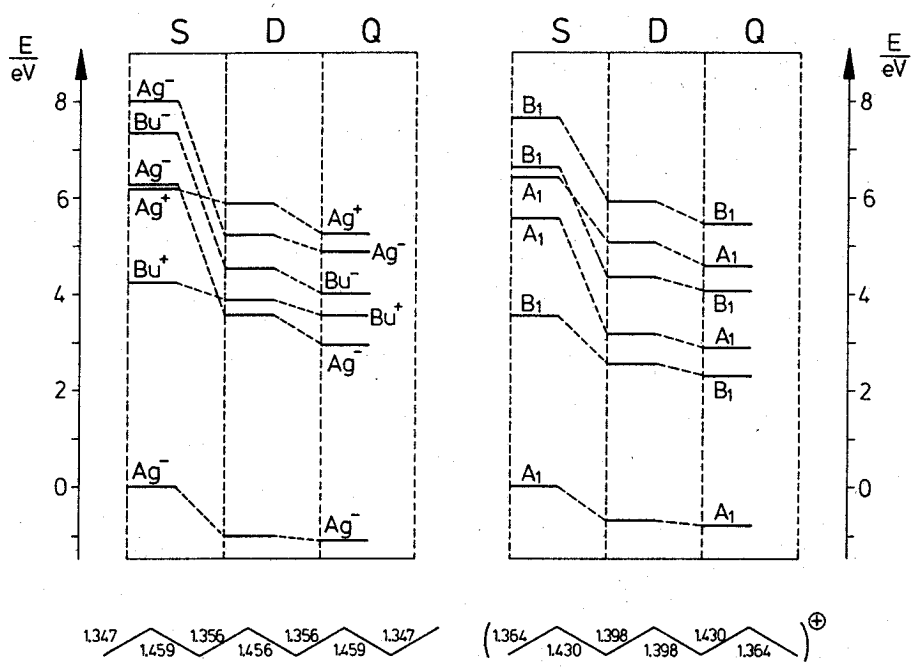

FIG. 2. Energy diagrams for octatetraene and the seven carbon carbonium cation singlet states as described by S-CI, D-CI, and Q-CI calculations with a PPP parameterized Hamiltonian. The bond length values given below the energy diagrams were determined self-consistently for the SCF ground state according to Eq. (4).

(+) states, resulting in a reordering of the spectral transitions. Higher excited configurations (Q-CI) lower all excited states uniformly without generating a spectral reordering. The overall effect of double, triple, and quadruple excited configurations on the first and second excited state is that the optically allowed $1\,^1B_u^+ - 1\,^1A_g^-$ transition is blue shifted by 0.4 eV with respect to the S-CI prediction, and the optically forbidden $2\,^1A_g^- - 1\,^1A_g^-$ transition is red shifted by 2.2 eV. The latter red shift is attributed to the covalent character of the $2\,^1A_g^-$ state, which is poorly described by the S-CI treatment.

In their dependence on the extent of the configuration expansion the CI energy levels of the carbonium ion in Fig. 2 resemble the polyene levels. The inclusion of double excited configurations leads to a reordering of the spectrum, that is, higher excitations give rise to a uniform depression of all energy levels. However, in contrast to the polyene case, these excitations *lower* the $1\,^1B_1 - 1\,^1A_1$ transition by 0.4 eV and, hence, contribute to the red shift of the main absorption band that occurs when octatetraene is transformed to the smaller (seven carbon) carbonium cation. Specifically, the S-CI calculation predicts a red shift by 0.7 eV, the Q-CI calculation a red shift by 1.5 eV, close to the 1.3 eV value reported by Sorenson.[6]

The failure of the S-CI description stems from its poor account of the covalent character of the $1\,^1B_1$ state. In this respect the situation is reminiscent of the S-CI failure to describe properly the $2\,^1A_g$ state in polyenes. However, in contrast to the polyenes, the carbonium ion states are *all*, to a large degree, of covalent character. This argument is illustrated best for the $1\,^1B_1$ state of the three carbon carbonium cation.

Analyzing the wave function of this state as determined by an S-CI and D-CI (i.e., complete CI) treatment we obtain

$$\text{S-CI: } \Delta E(1\,^1B_1 - 1\,^1A_1) = 5.4 \text{ eV},$$
$$\psi(1\,^1B_1) = 0.48(\overset{-}{:}\overset{+}{:}\overset{+}{:} - \overset{+}{:}\overset{+}{:}\overset{-}{:}) + 0.52(.-.\overset{+}{:} - \overset{+}{:}.-.), \quad (8)$$

$$\text{D-CI: } \Delta E(1\,^1B_1 - 1\,^1A_1) = 4.8 \text{ eV},$$
$$\psi(1\,^1B_1) = 0.30(\overset{-}{:}\overset{+}{:}\overset{+}{:} - \overset{+}{:}\overset{+}{:}\overset{-}{:}) + 0.64(.-.\overset{+}{:} - \overset{+}{:}.-.), \quad (9)$$

where $:\!:\!:$ stands for the *ionic* valence bond structure with two electrons on the first carbon, $.-.:$ stands for the *covalent* structure with carbon 1 and 2 occupied such that the electron spins are in an overall singlet state, etc. The result illustrates the increase of the covalent contribution of ψ from 54% to 82% in going from the S-CI to the D-CI description. We should point out that the *definition of ionic character* adopted here refers solely to the occurrence of a *surplus* π-electron charge $-2e$ rather than $-e$ at an atomic site, i.e., $.-.:$ is considered a covalent structure.

In the limit of strong Coulomb repulsion the states $1\,^1A_1$ and $1\,^1B_1$ assume the wave function

$$\psi(1\,^1A_1) - 2^{-1/2}(.-.\overset{+}{:} - \overset{+}{:}-.), \quad (10)$$
$$\psi(1\,^1B_1) - 2^{-1/2}(.-.\overset{+}{:} - \overset{+}{:}.-.). \quad (11)$$

Even in this limit, the transition $1\,^1B_1 - 1\,^1A_1$ between purely covalent states is optically allowed. This is also in contrast to the polyene case where such transitions are optically forbidden. In view of this, it is not surprising that the optically allowed states of the carbonium ions assume rather strong covalent character, this character being underestimated by the S-CI treatment and repaired by the inclusion of higher excitations in the CI expansion.

Figure 2 demonstrates that triple and qudruple excitations lower the excited states relative to the ground state and, thereby, reduce the corresponding excitation

TABLE III. Excitation energies (in eV) for linear polyenes (PPP).[a]

N[b]	S-CI $\Delta E(1\,^1B_u \leftarrow 1\,^1A_g)$	D-CI $\Delta E(2\,^1A_g \leftarrow 1\,^1A_g)$[c]	D-CI $\Delta E(1\,^1B_u \leftarrow 1\,^1A_g)$[c]	obs $\Delta E_{00}(1\,^1B_u \leftarrow 1\,^1A_g)$
6	4.80	4.90	5.18	4.93[d]
8	4.22	4.20	4.50	4.40[e]
		(Q-CI:4.03)	(Q-CI:4.62)	4.08[f]
				3.93[g]
10	3.82	3.75	4.03	3.71[f]
				3.56[g]
12	3.53	3.46	3.67	3.39[f]
				3.30[g]

[a] Results of PPP–SCF–CI calculations as described in the text.
[b] Number of conjugated π orbitals.
[c] Evaluated as $\Delta E(i \leftarrow 1\,^1A_g) = E_D(i) - (5/N)E_D(1\,^1A_g)$ to correct for the effect of higher excitations (see text); $E_D(i)$ stands for the CI energy of state i (relative to the SCF level).
[d] Gas phase spectrum, R. M. Gavin and S. A. Rice, J. Chem. Phys. 60, 3231 (1974).
[e] Gas phase spectrum, R. M. Gavin, Ch. Weisman, J. K. McVey, and S. A. Rice, J. Chem. Phys. 68, 522 (1978).
[f] Unsubstituted polyenes in iso-octane, E. G. F. Sondheimer, D. A. Ben-Efraim, and R. Wolovski, J. Am. Chem. Soc. 83, 1675 (1961).
[g] Methylsubstituted polyene in iso-octane, T. S. Sorensen, J. Am. Chem. Soc. 87, 5075 (1965).

energies. This effect of the higher excitation depends about linearly on the size of the π system.[13] For large systems, the numerical effort for the CI calculations required is prohibitively large and one has to rely on an estimate of this excitation energy reduction. We want to assume that the excitation energy decrement is identical for all transitions $i \leftarrow$ ground and amounts to a certain fraction $-(x/N)$ of the ground state correlation energy as discussed in Ref. 13. x can be estimated by a comparison of the D-CI and Q-CI results in Fig. 2. If one sets $x = 5$, i.e.,

$$\Delta E(i \leftarrow \text{ground}) = E_D(i) - (5/N)E_D(\text{ground}), \qquad (12)$$

one obtains for the seven carbon polyene cation and for octatetraene a satisfactory extrapolation of the D-CI results to the Q-CI results. Since E_D (ground) increases about linearly with the size of small π systems, the energy correction of $-(5/N)\,E_D$ (ground) is nearly independent of N (as required by the results of Ref. 13) and amounts to 0.5 eV for the carbonium ions and 0.6 eV for the polyenes. In Eq. (12) the D-CI energies $E_D(i)$ and E_D(ground) for the excited state i and the ground state, respectively, refer to the *energies with respect to the* SCF *ground state*.

In Tables III and IV we compare excitation energies for the series of linear polyenes and linear carbonium ions as predicted by S-CI and D-CI calculations [in the latter case corrected according to Eq. (12)]. The D-CI results include the lowest B as well as the lowest A excited states. As the latter state is not appropriately described by the S-CI expansion, its S-CI excitation energy has been omitted.

Table III demonstrates that the higher excited π electron configurations induce a blue shift of the $1\,^1B_u - 1\,^1A_g$ optically allowed transition for the series of polyenes hexatriene through dodecahexaene. In addition, the optically forbidden $2\,^1A_g$ state is brought below the $1\,^1B_u$ state. In order to judge the value of our predictions we compare calculated and observed excitation energies for the $1\,^1B_u$ state. Unfortunately, such comparison is handicapped by three difficulties: (1) the calculated spectra refer to vertical transitions in the ground state geometry, i.e., the calculations do not account for an energy lowering of the 0–0 transition (estimated to be less than 0.2 eV) when the mol-

TABLE IV. Excitation energies (in eV) for carbonium ions $(CH_3)_2CCH(CHCH)_nC(CH_3)_2$ (PPP).[a]

$N = 2n+3$[b]	S-CI $\Delta E(1\,^1B \leftarrow 1\,^1A)$	D-CI $\Delta E(1\,^1B_1 \leftarrow 1\,^1A_1)$[c]	D-CI $\Delta E(2\,^1A_1 \leftarrow 1\,^1A_1)$[c]	(f_2/f_1)[d]
5	4.24	3.83	4.53	0.035
7	3.52	3.07	3.70	0.022
		(Q-CI:3.07)	(Q-CI:3.65)	
9	3.03	2.54	3.12	0.015
11	2.67	2.16	2.71	0.012

[a] Results of PPP–SCF–CI calculations as described in the text.
[b] Number of conjugated π orbitals.
[c] Evaluated as in Table III.
[d] Ratio of oscillator strengths $f(2\,^1A_1 \leftarrow 1\,^1A_1)/f(1\,^1B_1 \leftarrow 1\,^1A_1)$ resulting from a D-CI description.

ecule in the $1\,^1B_u$ state is relaxed from the ground state geometry; (2) most absorption data available are for solvated polyenes, the solvent induces a considerable red shift, e.g., up to 0.6 eV for octatetraene; (3) many absorption data also refer to methylated compounds which acquire an additional redshift compared to the parent polyenes. This can be seen in Table III, where it is evident that the gas phase spectra of hexatriene and octatetraene agree rather well with the predicted $1\,^1B_u - 1\,^1A_g$ transition whereas the solvent spectra, in particular those involving methylated compounds, exhibit poor agreement.

Table IV shows that the effect of the higher excited configurations on the spectra of the series of linear carbonium ions is to redshift the main $(1\,^1B_1 - 1\,^1A_1)$ absorption band and to bring the $2\,^1A_1$ state down to a position about 0.6 eV above the $1\,^1B_1$ state. Contrary to the polyene $2\,^1A_g - 1\,^1A_g$ transition the $2\,^1A_1 - 1\,^1A_1$ transition in the carbonium ions is optically allowed. However, the transition carries only a small fraction of the oscillator strength of the main absorption band, this fraction decreasing with increasing π system. Figure 3 compares the excitation energies for the $1\,^1B_1 - 1\,^1A_1$ transition as predicted by our S-CI and D-CI descriptions, and as observed by Sorenson.[6] For the reasons given above, the observations of this author, referring to methylated compounds in solvents, are not directly comparable to calculated energies but are expected to lie at longer wavelengths as is demonstrated in Fig. 3. This diagram shows, however, that the observed chain length dependence of the main absorption band (an increase by about 80 nm for each added pair of carbons) agrees rather well with the D-CI prediction. The S-CI transitions appear, however, at rather short wavelengths and entail only a 55–60 nm increment for each pair of carbons added. As pointed out already, it appears then that higher excited configurations need to be included in a description of the $1\,^1B_1$ state to account for the covalent character and low excitation energy of this state.

Changes in molecular geometry upon electron excitation and the concomitant photochemical activity are dependent upon π-electron bond orders. In Tables V and VI we present ground and excited state bond orders for octatetraene and the seven carbon carbonium cation. For octatetraene the D-CI calculation predicts the $1\,^1B_u - 1\,^1A_g$ transition to weaken the (ground state) double bonds and to strengthen the (ground state) single bonds, both to a considerable extent (cf. Table V). In contrast, the $1\,^1B_1 - 1\,^1A_1$ transition of the carbonium ion largely conserves the (ground state) bond character (cf. Table VI). This conservation of bond character is even more pronounced in the longer carbonium ions. For example, for $N = 11$ one obtains from a D-CI calculation the following consecutive bond orders: $1\,^1A_1$: 0.86, 0.42, 0.73, 0.59, 0.64, 0.64, 0.54, 0.73, 0.24, 0.86; $1\,^1B_1$: 0.82, 0.46, 0.66, 0.53, 0.57, 0.57, 0.53, 0.66, 0.46, 0.82. The difference in the behavior of polyenes and carbonium ions is corroborated by the observation that the width of the main absorption band of the polyenes on an energy scale exceeds the width of the main absorption band of carbonium ions by about a factor 3,[6] an observation which is indicative of a smaller geometry change in the latter case.

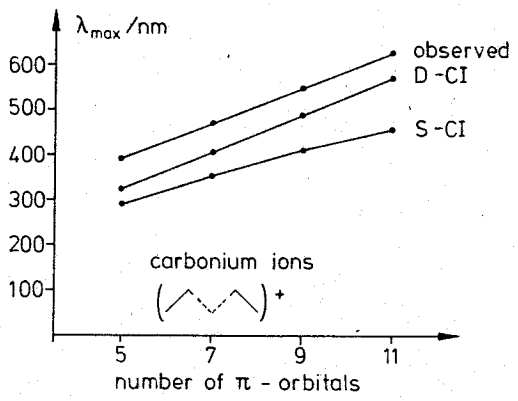

FIG. 3. Comparison of observed and predicted (PPP–SCF–CI) absorption maxima for the series of carbonium ions $[(CH_3)_2CCH(CHCH)_nC(CH_3)_2]^+$ with $2n+3$ π orbitals. The values for λ_{max} are from Ref. 6.

TABLE V. Ground and excited state bond orders of octatetraene (D-CI).[a]

Bond	1–2, 7–8	2–3, 6–7	3–4, 5–6	4–5
Bond order $(1\,^1A_g)$	0.90	0.34	0.84	0.36
Bond order $(2\,^1A_g)$	0.64	0.57	0.41	0.63
Bond order $(1\,^1B_u)$	0.79	0.49	0.58	0.56

[a] Results of a PPP–SCF–CI calculation as described in the text.

The $2\,^1A_g$ and the $2\,^1A_1$ states bring about a change of bond orders which is larger than that of the B states. The change is more pronounced in the polyene where the alteration of bond character as well as the low energy position of the $2\,^1A_g$ state should make this electronic state a favorable starting point for photochemical activity. This statement does not apply to the carbonium ions, unless the $1\,^1B_1$ and $2\,^1A_1$ states cross along a photochemical reaction route (as they do in stilbene, for example).

One should finally note that the carbonium ion π-electron charges are not distributed uniformly in the ground state and that these charges are being redistributed upon electronic excitation. The corresponding π-electron charge densities are presented in Table VII. These charges can mediate strong interactions between excited carbonium ions and their environment. For example, external charges favorable (unfavorable) to

TABLE VI. Ground and excited state bond orders of the carbonium cation with $N = 7$ (D-CI).[a]

Bonds	1–2, 6–7	2–3, 5–6	3–4, 4–5
Bond order $(1\,^1A_1)$	0.82	0.49	0.65
Bond order $(1\,^1B_1)$	0.71	0.49	0.52
Bond order $(2\,^1A_1)$	0.51	0.55	0.53

[a] Results of a PPP–SCF–CI calculation as described in the text.

TABLE VII. π-Electron charge density in ground and excited states of the $N=7$ carbonium ion (D-CI). [a]

State \ C atom	1, 7	2, 6	3, 5	4
$1\,^1A_1$	0.74	1.04	0.71	1.03
$1\,^1B_1$	0.70	0.95	0.89	0.92
$2\,^1A_1$	0.81	0.80	1.01	0.77

[a] Results of a PPP–SCF–CI calculation as described in the text.

the charge redistribution accompanying the $1\,^1B_1 - 1\,^1A_1$ transition should shift the main absorption band to the red (blue), a spectral shift which can be rather strong as judged from the shift for the protonated Schiff base of retinal.

V. ELECTRON CORRELATION IN THE EXCITED CARBONIUM IONS, CYANINE DYES, AND PROTONATED SCHIFF BASE POLYENES (CNDO/S DESCRIPTION)

In order to understand the strong bathochromic shift of retinal in the visual pigments and in bacteriorhodopsin,[14] we have studied the spectral behavior of the cyanine dyes and protonated Schiff base polyenes. To guarantee an unbiased description of the corresponding π systems, which include heteroatoms and a proton charge, we have carried out CNDO/S calculations on these compounds. As above, the CI expansions included all single (S-CI) as well as all single and all double (D-CI) excited π-electron configurations. The effect of electron correlation on the spectra of the cyanine dyes and protonated Schiff base polyenes, as described by double excited configurations, closely parallels the effects on the carbonium ion spectra discussed in the last section. We will therefore give only a brief account of the results obtained and refrain from an analysis of the correlation effects predicted.

For a comparison with the results of the previous section, we present in Table VIII the optical excitation energies of carbonium ions as predicted by CNDO/S S-CI and D-CI calculations. These results are in close agreement with those of Table IV (the PPP excitation energies are consistently lower by about 0.2 eV), supporting our previous conclusions regarding electron correlation effects on the carbonium ion spectrum. For the $N=5$ carbonium ion $[(CH_3)_2CCH(CHCH)_1C(CH_3)_2]^+$ we included also the terminal methyls in our calculation to estimate their effect on the spectral transitions. We determined by a S-CI calculation that the $1\,^1B_1 - 1\,^1A_1$ transition energy is reduced by 0.57 eV with respect to the transition energy of the unmethylated compound; a D-CI calculation predicts a reduction by 0.57 eV. This finding gives a partial explanation for the discrepancy between observed and calculated excitation energies in Fig. 3.

The excitation energies for the cyanine dyes $(CH_3)_2NCH(CHCH)_nN(CH_3)_2$ as predicted by S-CI and D-CI treatments are presented in Table IX. In close analogy to the carbonium ion case, the results show that the inclusion of higher excited configurations in a CI expansion red shifts the $1\,^1B_1 - 1\,^1A_1$ transition relative to that predicted by S-CI. There also exist weakly absorbing $2\,^1A_1$ states of largely double excited character in the cyanine dyes. These states appear about 1 eV above the $1\,^1B_1$ states, i.e., at slightly higher energies than in the carbonium ion spectra. Figure 4 compares the predicted and observed excitation energies for the $1\,^1B_1 - 1\,^1A_1$ transition in the cyanine dyes. The D-CI transitions are found to be close to the observed

TABLE VIII. Excitation energies (in eV) for carbonium ions $[(CH_3)_2CCH(CHCH)_nC(CH_3)_2]^+$ (CNDO/S). [a]

$N=2n+3$ [b]	S-CI $\Delta E(1\,^1B_1 \leftarrow 1\,^1A_1)$	D-CI $\Delta E(1\,^1B_1 \leftarrow 1\,^1A_1)$ [c]	D-CI $\Delta E(2\,^1A_1 \leftarrow 1\,^1A_1)$ [c]
5	4.53	4.13	5.02
7	3.67	3.28	4.06
9	3.16	2.69	3.40
11	2.82	2.27	2.96

[a] Results of CNDO/S–CI calculation as described in the text; the calculation did not account for the terminal methyl groups which were replaced by hydrogens.
[b] Number of conjugated π orbitals.
[c] Evaluated as in Table III.

TABLE IX. Excitation energies (in eV) for the cyanine dyes $(CH_3)_2NCH(CHCH)_nN(CH_3)_2$ (CNDO/S). [a]

$N=2n+3$ [b]	S-CI $\Delta E(1\,^1B_1 \leftarrow 1\,^1A_1)$	D-CI $\Delta E(1\,^1B_1 \leftarrow 1\,^1A_1)$ [c]	D-CI $\Delta E(2\,^1A_1 \leftarrow 1\,^1A_1)$ [c]
5	4.50	4.14	5.40
7	3.65	3.02	4.19
9	3.08	2.39	3.41
11	2.69	1.95	2.88

[a] See Table VIII.
[b] Number of conjugated π orbitals.
[c] Evaluated as in Table III.

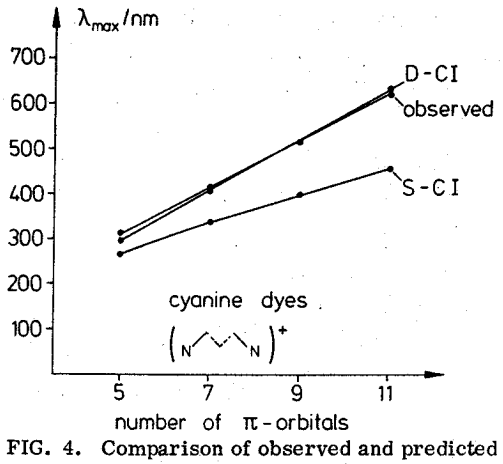

FIG. 4. Comparison of observed and predicted (CNDO/S–CI) absorption maxima for the series of cyanine dyes $(CH_3)_2NCH(CHCH)_nN(CH_3)_2$ with $2n+3$ π orbitals. The values observed for λ_{max} are from Ref. 7.

transitions. This surprisingly good agreement may indicate that the effects of methyl substitution and solvent are rather negligible for these compounds. Our calculations predict, infact, that the spectral shift due to methyl substitution is only about half of the shift predicted for carbonium ions. The D-CI wavelength increment of about 112 nm for each pair of carbon atoms added to the cyanine dye is close to the mean increment of the observed λ_{max} (104 nm), but differs strongly from the S-CI increment found to measure only 62 nm. This discrepancy implies that the S-CI description becomes increasingly inadequate with increasing size of the cyanine π system.

Finally, in Table X we report the S-CI and D-CI optical transitions of the protonated Schiff base polyenes $[CH_2CH(CHCH)_nCHNHCH_3]^+$. The excited states are found to depend critically on the extent of the CI expansion, as was the case for the carbonium ions and the cyanine dyes. Higher excited configurations red shift the main absorption band and bring about a weakly absorbing state at about 1.3 eV above S_1. For $N=12$, the π-electron system corresponds to that of the protonated Schiff base of retinal and its calculated absorption maximum bears directly on the problem of visual pigment spectra. The S-CI excitation energy of 2.96 eV (~420 nm) differs considerably from the D-CI value of 532 nm and the former clearly should not be used as a basis for a discussion of the photophysical properties of visual pigments. A second conclusion evident from Table X is that in protonated Schiff bases, the first excited state is optically allowed, at least for vertical excitations (see also Ref. 15).

TABLE X. Excitation energies (in eV) for protonated Schiff base polyenes $[CH_2CH(CHCH)_nCHNHCH_3]^+$ (CNDO/S). [a]

	S-CI	D-CI	
$N=2n+4$ [b]	$\Delta E(S_1 \leftarrow S_0)$	$\Delta E(S_1 \leftarrow S_0)$ [c]	$\Delta E(S_2 \leftarrow S_0)$ [c]
6	4.24	3.97	5.33
8	3.61	3.18	4.49
10	3.21	2.68	3.96
12	2.96	2.33	3.60

[a] Results of CNDO/S calculations as described in the text; in our calculations the terminal methyl was replaced by a hydrogen.
[b] Number of conjugated π orbitals.
[c] Evaluated as in Table III.

VI. CONCLUSIONS

Our calculations have revealed a great similarity between the spectral behavior of carbonium ions, cyanine dyes, and protonated Schiff base polyenes. We showed that the ground as well as the optically excited state S_1 of these compounds entail mainly covalent character and, therefore, require extended CI expansions for a proper description. This behavior must not be overlooked in future theoretical treatments.

A most noted previous attempt for a consistent description of the spectra of polyenes and cyanine dyes has been given by Kuhn *et al.*[16] These authors obtained by an electron gas model good *agreement with the main absorption band* of these compounds. In our description we aim at a complete account of *all* low-lying excited states. Our finding of a strong lowering of the absorption bands in the cyanine dyes due to the effect of electron correlation as discussed above is in contrast to the finding of Ref. 16 which, in fact, predicts an opposite effect of the electron correlation.

The covalent structures largely characterizing the S_1 state of the red absorbing compounds, e.g., $(\cdot - \cdot\cdot - \cdot\cdot - \cdot \overset{+}{:}) - (\overset{+}{:} \cdot - \cdot\cdot - \cdot\cdot - \cdot \cdot)$ (for an explanation see Sec. IV), may provide an explanation for the photochemical behavior of visual pigments. For example, stabilization of structures appropriate for a bond rotation, i.e., in case of retinal in rhodopsin the structures lacking a covalent singlet link at the 11–12 bond, could provide an efficient route for photoisomerisation. The charge redistribution upon the $S_1 - S_0$ transition opens an avenue for strong spectral shifts through environmental charges.[19]

Still open is the question of how far the ground state of protonated Schiff base polyenes deviates from the normal polyene bond pattern. Resonance Raman spectra reveal that one encounters only relatively small changes of the vibrational frequencies when the main absorption band is red shifted from its polyene position to its carbonium ion position. For example, when the spectrum of retinal is shifted from 380 nm in *trans* retinal to 570 nm in bacteriorhodopsin the C–C stretch frequency changes only from 1580 cm^{-1} (Ref. 17) to 1530 cm^{-1} (Ref. 18). It is not quite clear if the latter frequency can be reconciled with the bond structure indicated by the bond order sequence (for $N=12$) in Table II.

ACKNOWLEDGMENTS

The authors would like to thank P. Tavan for his program to evaluate CI matrices for higher excited configurations. This work has greatly benefitted from a grant by the Kultusministerium des Landes Niedersachsen for a Jerusalem–Göttingen exchange program. The use of the computer facilities of the Gessellschaft für wissenschaftliche Datenverarbeitung is acknowledged. B. H. acknowledges the NSF grant PCM 79-02683.

[1]For a recent review, see B. Honig, Ann. Rev. Phys. Chem. 29, 37 (1978).
[2]H. Autrum and V. von Zwehl, Z. Vergl. Physiol. 48, 357 (1964).
[3]A. König and C. Dieterici, Z. Psychol. Physiol. Sinnesorg. 4, 241 (1893).
[4]G. D. Bernard, Science 203, 1125 (1979).
[5]J. O. Erikson and P. E. Blatz, Vision Res. 8, 1367 (1968).
[6]T. S. Sorenson, J. Am. Chem. Soc. 87, 5075 (1965).
[7]S. Malhotra and M. Whiting, J. Chem. Soc. 1960, 3812.
[8](a) K. Schulten and M. Karplus, Chem. Phys. Lett. 14, 305 (1972); (b) K. Schulten, I. Ohmine, and M. Karplus, J. Chem. Phys. 64, 4422 (1976); (c) P. Tavan and K. Schulten, J. Chem. Phys. 70, 5407 (1979).
[9]K. Ohno, Theor. Chim. Acta 2, 219 (1964).
[10]M. J. S. Dewar and C. de Llano, J. Am. Chem. Soc. 91, 789 (1969).
[11]P. Tavan and K. Schulten, J. Chem. Phys. 72, 3547 (1980).
[12]U. Dinur and B. Honig, J. Am. Chem. Soc. 101, 4453 (1979).
[13]I. Ohmine, M. Karplus, and K. Schulten, J. Chem. Phys. 68, 2298 (1978).
[14]For a possible role of the carbonium ion structure of the protonated Schiff base of retinal in this pigment see, for example, G. Orlandi and K. Schulten, Chem. Phys. Lett. 64, 370 (1979).
[15]R. R. Birge and B. M. Pierce, J. Chem. Phys. 70, 165 (1979).
[16]H. D. Försterling, W. Huber, H. Kuhn, H. H. Martin, A. Schweig, F. F. Seelig, and W. Stratmann, in *Optische Anregung Organischer Systeme* (Verlag Chemie, Weinheim, 1966).
[17]M. E. Heyde, D. Gill, R. G. Kilponen, and L. Rimai, J. Am. Chem. Soc. 93, 6776 (1971).
[18]A. Lewis, J. Spoonhower, R. Bogomolni, R. Lozier, and W. Stoeckenius, Proc. Natl. Acad. Sci. US 71, 4462 (1974).
[19]B. Honig, V. Dinur, K. Nakanishi, V. Balogh-Nair, M. A. Gowinowicz, M. Arnaboldi, and M. Motto, J. Am. Chem. Soc. 101, 7084 (1979).