ON THE NATURE OF EXCITED ELECTRONIC STATES IN CYANINE DYES: IMPLICATIONS FOR VISUAL PIGMENT SPECTRA

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CNDO/S CI calculations are carried out on polyenes and on cyanine dyes. In contrast to polyenes, doubly excited configurations have a strong effect on the first optically allowed excited state in cyanines. Protonated Schiff bases of retinal are closely related to cyanine dyes, with important consequences for models of visual pigment spectra and photochemistry.

1. Introduction

The excited electronic states of linear polyenes have been a subject of interest for many years. They were intensively studied with Hückel and free-electron techniques [1] prior to the development of the PPP theory and have, to some extent, been "rediscovered" due in part to their similarity to retinal, the chromophore of the visual pigments [2]. The earliest theoretical studies provided a satisfactory qualitative description of the spectroscopic properties of linear polyenes (see, e.g., ref. [3]). Polyenilic ions related to cyanine dyes which contain an odd number of atoms have extremely long-wavelength absorption maxima (λ_{max}) which increase linearly with chain length. The series of polyenes with an even number of atoms are considerably blue-shifted relative to cyanine dyes and exhibit an asymptotic curve of λ_{max} versus chain length which levels off near 500 nm.

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In even polyenes, the main absorption band results from a transition to a B_u^+ state and can be successfully described with a semi-empirical π-electron treatment including configuration interaction among singly excited configurations (see, e.g., ref. [4]). However, the inclusion of doubly excited configurations (D CI) is required for a proper description of the manifold of "covalent" states such as the $^1A_g^-$ state which lies close to the main absorption band [5–7]. In contrast to the even polyenes there have been no D CI calculations carried out on odd polyenes such as cyanine dyes. S CI calculations can be parameterized to yield excellent agreement with the experimental λ_{max}— chain length curve, but only when an unusually small resonance integral is used [8]. Thus, it is difficult to obtain a quantitative description of the spectroscopic properties of both odd and even polyenes with a single set of semi-empirical parameters.

Uncertainties as to the proper method of carrying out calculations on polyenes have led to serious difficulties in the interpretation of visual pigment spectra. The chromophore of the visual pigments is the

protonated Schiff base of 11-cis retinal which absorbs in solution at about 450 nm. Protonated Schiff bases of retinal contain an even number of atoms but are nevertheless highly delocalized systems. As such they bear a resemblance tc both even and odd polyenes and it is not clear, a priori, which set of parameters should be used to describe their spectroscopic properties. Calculations using parameters fit from cyanine dyes yield values of λ_{max} in the vicinity of 600 nm [8]. The experimental value of 450 nm is viewed as resulting from a large blue-shift due to a counter-ion or solvent dipoles [8,9]. Calculations [10,11] using a standard set of parameters appropriate to even polyenes yield values of λ_{max} near 450 nm and have not in general accounted for possible effects induced by a counter-ion. Since visual pigments absorb between 430 and 610 nm the uncertainties in the calculations cover the entire range of visual pigment spectra. This introduces obvious complications in any attempt to construct models of chromophore—protein interactions that are based on semi-empirical calculations of electronic spectra.

Our major concern in this paper will be to explain the excited state properties of cyanine dyes. In particular, we will discuss the causes of the failure of standard semi-empirical methods to provide an adequate description of the spectroscopic transition energy in these molecules. To this end we report calculations, using the CNDO/S [12] method, on polyenes, cyanine dyes and the potonated Schiff base of retinal. Our results demonstrate that electronic correlation has very different spectroscopic consequences in polyenes and cyanine dyes. Moreover, protonated Schiff bases of retinal are found to be closely related to cyanine dyes suggesting that semi-empirical methods cannot be applied in their standard form to the study of visual pigment spectra.

2. Method of calculation

The CNDO/S method [12] was employed in this work since the cyanine dyes are ionic molecules and as a result have polarized σ charge distributions. This and the participation of heteroatoms in the π-electron system would have required an ad hoc parameterization had a π-electron method been used. The S CI calculations included the 50 lowest energy configura-

tions and involved both σ and π orbitals (although $\sigma-\pi^*$ excitations made only negligible contributions to the main absorption band). Since all calculations were carried out on planar systems doubly excited configurations in the CI expansion were restricted to include only π orbitals. The CI matrix reached a dimension of 703 for the largest molecules that were treated. The Ohno formula was used to approximate the two-center repulsion integrals as is required when D CI calculations are carried out [6]. Methyl groups were not included and were replaced by hydrogens in the calculations. Single bond lengths of 1.46 Å and double bond lengths of 1.35 Å were assumed for the polyenes. For the cyanines all C—C bonds were set at 1.4 Å and the C—N bonds at 1.3 Å. Standard bond angles of 120° were assumed throughout.

3. Polyenes

The electronic spectra of polyenes have been studied in detail in recent years and it has been found that correlation effects play an important role in determining transition energies [5–7]. It is useful, in order to facilitate comparison to cyanines, to review a number of the conclusions of previous work [5–7] in terms of the CNDO/S results reported in table 1. It is evident that the contribution to the correlation energy from doubly excited configurations is different for the various electronic states. The first excited $^1A_g^-$ state is reduced in energy (relative to the uncorrelated ground state) by approximately 2 eV while the strongly allowed B_u^+ state is stabilized by only 0–0.4 eV, the value increasing with increasing chain length. The result is to place the optically forbidden A_g^- state below the optically allowed B_u^+. The effect of doubly excited configurations on the ground state is also greater than on the B_u^+ state. For example, S CI calculations on octatetraene yield a transition energy of 4.29 eV, close to the experimental value. The inclusion of doubly excited configurations lowers the B_u^+ state by 0.31 eV but lowers the ground state by 1 eV; the net result is a transition energy of 4.99 eV which is clearly two high. In contrast, D CI calculations on butadiene including ground-state stabilization yield a closer fit to the experimental transition energy than do the S CI calculations.

The difference between butadiene and octatetraene

Table 1
Excitation energies [a] (in eV) for polyenes [$CH_2=CH-(CH=CH)_n-CH=CH_2$]

n	Ground state D CI [b]	$^1A_g^-$		$^1B_u^+$		Exp. [c]
		S CI	D CI	S CI	D CI	
0	−0.52	6.81	5.11	5.48	5.48	5.92 [d]
1	−0.77	6.34	4.26	4.75	4.56	4.62 [e]
2	−1.00	5.85	3.73	4.29	3.98	4.08 [e]
3	−1.14	5.46	3.44	3.97	3.59	3.71 [c]
4	−1.46	5.08	3.22	3.75	3.31	3.39 [e]

[a] Taken relative to the uncorrelated ground state (for an explanation see refs. [6,7,21]).
[b] Change in ground-state energy induced by D CI.   [c] All results refer to the $0 \rightarrow 0$ line.   [d] Ref. [18].   [e] Ref. [19].

results from the increasing importance (and number) of triply and higher excited configurations as the size of the molecule increases. Triply excited configurations while contributing to the B_u^+ state have little effect on the ground state since at the Hartree—Fock level all matrix elements between triply excited configurations and the ground state are zero. The actual value of the contribution from higher configurations to the correlation energy of the B_u^+ state can only be determined from extensive and time consuming calculations on the longer polyenes. However, the relatively good agreement between the excitation energy obtained from S CI calculations and from D CI calculations (when the uncorrelated ground-state energy is used) suggests that the unaccounted for correlation energy of the B_u^+ state is comparable in magnitude to the correlation energy of the ground state [6,7]. This conclusion is reinforced by the fact that S CI and D CI calculations succeed quite well in reproducing the experimental relationship between absorption maxima and polyene chain length (table 1).

4. Cyanine dyes

As is evident from table 2, the situation is considerably different than that for even polyenes. In cyanines doubly excited configurations lower the strongly allowed B_2 state much more than they do the ground state. As a result S CI calculations considerably overestimate the transition energy. On the other hand, D CI calculations of the transition energy relative to the SCF ground state yield wavelengths significantly lower than the experimental values, particularly for the longer chained molecules.

One is left then with the problem of developing a semi-empirical scheme that will yield reasonable agreement with experiment for cyanine dyes. An S CI parameterization has in fact been developed for this purpose [8] but, as might be expected, it yields less satisfactory results for the series of even polyenes. Clearly, a semi-empirical scheme appropriate to different classes of molecules must be sought. This will require that the dependence of correlation energy on

Table 2
Excitation energies (in eV) for cyanines [a] [$N(CH_3)_2\overset{..}{=}CH\overset{..}{=}(CH\overset{..}{=}CH)_n\overset{..}{=}N(CH_3)_2$]$^+$

n	Ground state D CI	$^1A_1$		$^1B_2$		Exp. [b]
		S CI	D CI	S CI	D CI	
0	−0.19	9.06	8.25	6.06	5.91	5.53
1	−0.37	6.22	5.03	4.50	3.77	3.96
2	−0.45	5.57	3.87	3.65	2.70	2.98
3	−0.66	5.10	3.04	3.08	2.03	2.39
4	−0.89	4.64	2.48	2.69	1.55	1.98

[a] See footnotes to table 1.   [b] Ref. [20].

chain length be explicitly taken into account. It is interesting in this regard that for the shorter molecules in both the polyenes and cyanines, the D CI result with respect to the *correlated* ground state, yields excellent agreement with experiment (6.0 eV for butadiene and 4.14 eV for the first cyanine in the series). This is the case since for these molecules, doubly excited configurations span most of configuration space while higher excitations have relatively small effects. By studying the effects of higher configurations on the longer chained molecules, it may be possible to arrive at an empirical relationship which accounts for correlation effects in both odd and even polyenes. This will be attempted in a subsequent publication.

The large correlation energy of the $^1B_2$ state in cyanines has an important effect on state ordering. As can be seen from table 2, the optically allowed $^1B_2$ state is predicted to be the first excited state. This may account for the short radiative lifetimes of cyanines [13] which obey the Strickler–Berg relationship. The much longer radiative lifetimes of the even polyenes [14,15] has been attributed to the location of the $^1A_g^-$ state below the $^1B_u^+$ [5–7].

5. Discussion

As mentioned in section 1, in order to construct models for the absorption maxima of visual pigments it is important to determine a reliable theoretical estimate for the excitation energy of the protonated Schiff base of retinal. To this end, we have carried out S CI and D CI calculations of a series of protonated Schiff bases as shown in table 3. We find, in agreement with π-electron studies already reported [16], that the lowest singlet which is responsible for the main absorption band is strongly affected by electronic correlation introduced by doubly excited configurations. The lowering of this state by ≈ 1 eV is comparable to the magnitude of the effect seen in cyanine dyes. It appears then that as for cyanines, S CI calculations which use a standard parameterization scheme [10,11] should not be used as a basis for discussing the protonated Schiff base of retinal. It is possible to use an S CI parameterization scheme appropriate to cyanines [8], or to estimate transition energies from more extensive configuration interaction.

We can obtain an estimate of the excitation energy in the protonated Schiff base of retinal by assuming that the error in the D CI calculations is comparable in magnitude to the discrepancy (0.43 eV) between the theoretical and experimental value for the cyanine with twelve π electrons. Adding this value to the D CI transition energy of 1.82 eV we obtain 2.25 eV (550 nm), in good agreement with the value of 2.05 eV (≈ 600 nm) obtained from S CI calculations which were appropriately parameterized [8]. Since methyl groups were neglected in the D CI calculations, the S CI result of 600 nm seems quite reasonable.

As was discussed above, the fact that the value of λ_{max} for protonated retinal Schiff bases in solution is blue-shifted relative to this theoretical estimate is due to the presence of a counter-ion or solvent dipoles in the vicinity of the protonated nitrogen [8,9]. Since a

Table 3
Excitation energies (in eV) for protonated Schiff bases [a) $[CH_2=CH-(CH=CH)_n-CH=NH_2]$

n	Ground state D CI	$^1A'$		$^1A''$		Exp. [b)
		S CI	D CI	S CI	D CI	
0	−0.32	7.22	6.29	5.26	4.67	4.57
1	−0.50	6.24	4.83	4.24	3.47	3.83
2	−0.71	5.61	3.98	3.61	2.68	3.15
3	−0.93	5.11	3.44	3.21	2.16	2.90
4	−1.14	4.69	3.08	2.96	1.82	2.80

a) See footnotes to table 1. These ions belong to the C_s point group. The state $^1A'$ corresponds to the $^1A_g^-$ state in polyenes and the $^1A_1$ state in cyanines while $^1A''$ corresponds to $^1B_u^+$ in polyenes and $^1B_2$ in cyanines.
b) Ref. [17].

counter-ion is almost certainly present in visual pigments as well, their absorption maxima which range from 430–610 nm, must be due to additional chromophore protein interactions which induce red-shifts relative to the λ_{max} of protonated Schiff bases in solution [8]. Studies with artificial retinals have recently located electrostatic interactions localized near the 11–12 double bond of the chromophore that shift λ_{max} of the protonated Schiff base of retinal to 500 nm in bovine rhodopsin [17].

Acknowledgement

References

[1] H. Kuhn, J. Chem. Phys. 17 (1949) 1198.

[2] B. Honig, Ann. Rev. Phys. Chem. 29 (1978) 31.

[3] H. Suzuki, Electronic absorption spectra and geometry of organic molecules (Academic Press, New York, 1967).

[4] B. Honig, U. Dinur, R.R. Birge and T.G. Ebrey, J. Am. Chem. Soc. (1980), to be published.

[5] K. Schulten and M. Karplus, Chem. Phys. Letters 14 (1972) 305.

[6] K. Schulten, I. Ohmine and M. Karplus, J. Chem. Phys. 64 (1976) 4422;
I. Ohmine, M. Karplus and K. Schulten, J. Chem. Phys. 68 (1978) 2298.

[7] P. Tavan and K. Schulten, J. Chem. Phys. 70 (1979) 6699.

[8] B. Honig, A. Greenberg, U. Dinur and T.G. Ebrey, Biochemistry 15 (1976) 4593.

[9] P. Blatz and J. Mohler, Biochemistry 14 (1975) 2304.

[10] M. Muthukamar and L.J. Weimann, Chem. Phys. Letters 53 (1978) 436.

[11] S. Favrot, J.M. Leclercq, R. Roberge, C. Sandorfy and D. Vocelle, Chem. Phys. Letters 53 (1978) 433.

[12] J. Del Bene and H.H. Jaffé, J. Chem. Phys. 48 (1968) 1507.

[13] N.C.L. Roth and A.C. Craig, J. Phys. Chem. 78 (1974) 1154;
C.J. Trodwell and C.M. Keary, Chem. Phys. 42 (1979) 307.

[14] B.S. Hudson and B.E. Kohler, Chem. Phys. Letters 14 (1972) 299.

[15] J.R. Andrews and B.S. Hudson, Chem. Phys. Letters 57 (1978) 600.

[16] R.R. Birge and B.M. Pierce, J. Chem. Phys. 70 (1979) 165.

[17] B. Honig, U. Dinur, K. Nakanishi, V. Balogh-Nair, M.A. Gawinowicz, M. Arnaboldi and M. Motto, J. Am. Chem. Soc. 101 (1979) 7084.

[18] R. McDiarmid, Chem. Phys. Letters 34 (1975) 130.

[19] E.G.F. Sondheimer, D.A. Ben-Efraim and R. Wolovsky, J. Am. Chem. Soc. 83 (1961) 1675.

[20] S. Malhotra and M. Whiting, J. Chem. Soc. (1960) 3812.

[21] P. Tavan and K. Schulten, Chem. Phys. Letters 56 (1978) 200.