SCF MO Calculations of Polyene Spectra*

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A computationally simple "variable β" procedure within the Pariser-Parr-Pople formalism has been applied with success to the calculation of aromatic hydrocarbon spectra [1]. The method has now been extended to encompass linear polyenes and α, ω-diphenylpolyenes. In the variable β approach the precise molecular geometry need not be specified and it is not necessary to assume bond alternation. Bond lengths were all set at 1.40 Å and bond angles at 120°. The core resonance integrals, $\beta = A_1 p + A_0$, were adjusted at each iteration but the two-center repulsion integrals, $\gamma_{pq} = 14.394/(1.294 + r_{pq})$ eV were kept fixed. $A_1 = -0.51$ eV is appropriate for all C–C bonds [1] and a good fit for the trans-butadiene spectrum is obtained with $A_0 = -2.10$ eV. Since this latter quantity is close to the value used for benzene, it was employed for all bonds in the polyenes and diphenylpolyenes.

Platt has classified the polyene transitions by means of configuration interaction treatment [2]. The transitions to ^1B, ^1D, and ^1F (Platt's $^1D_2$) are allowed. Labeling the occupied orbitals 1, 2, 3 ... (in order of decreasing energy) and the vacant orbitals 1', 2', 3' ... (in order of increasing energy), $^1B \leftarrow {}^1A$ is essentially $1 \rightarrow 1'$, but $1 \rightarrow 2'$ and $2 \rightarrow 1'$, degenerate in the zeroth order, are mixed by configuration interaction to form the ^1C and ^1L_c states. Transitions to both of these states are forbidden in the all-trans isomers, but $^1C \leftarrow {}^1A$ becomes allowed when the center of symmetry is destroyed (cis band) If the SCF MO method with extensive configuration interaction is to be useful for routine computations, the results cannot be greatly dependent on the amount of configuration interaction. To obtain the higher transition energies it is useful to include the nine configurations arising from the set 3, 2, 1 $\rightarrow$ 1', 2', 3'. For convenience in machine calculations additional configurations were included. This only results in an increase in the number of low-lying states of ^1L character, to which transitions are forbidden in all configurations, but the energies and intensities of the allowed transitions are essentially unaltered.

The linear polyene results are compared with experiment in Tab. 1. This comparison is complicated by solvent effects [3], but the results are comparable to those obtained by assuming bond alternation [3, 4]. The oscillator strengths calculated by a "molecules in molecules" method [3] were smaller than those observed, but in the present work the calculated f nos. exceed experiment, a result

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generally obtained in LCAO MO calculations. The bond orders agree closely with those obtained by ADAMS and MILLER [4], and the expected bond alternation is obtained.

In one respect the results are poor. The calculated $^3B \leftarrow {}^1A$ transition energies are much too small, ranging from 1.43 to 0.98 eV as the carbon chain varies from C_4 to C_{22}. This overestimation of singlet-triplet splitting in polyenes has been previously noted [4, 5].

Table 1. *Transition Energies* (eV) *of* H–(CH = CH)$_n$–H *(All-trans Configurations)*

$^1A \rightarrow$	^1B				^1C[b]			^1D		^1F	^1E[b]
n	calc	exp[a]		(c)	calc	exp[a]		calc	exp[a]	calc	calc
		(a)	(b)			(a)	(c)		(c)		
3	4.599	4.62	4.52	4.22	6.767			8.232		8.696	9.415
4	3.928	4.07	4.00	3.76	5.886	5.84	5.46	7.266		7.562	8.127
5	3.481	3.71	3.74	3.38	5.220	5.27	4.88	6.498		6.789	7.482
6	3.163	3.41		3.19	4.724			5.901		6.178	6.863
7	2.924	3.18		2.99	4.337			5.431		5.698	6.339
8	2.742	3.02	2.95		4.028			5.050		5.350	5.907
9	2.599		2.81	2.63	3.771		3.78	4.735	4.8	5.071	5.544
10	2.485	2.77	2.61	2.59	3.558		3.76	4.469	4.6	4.844	5.242
11	2.393			2.57	3.391		3.43	4.242	4.4	4.657	4.980
12	2.319			2.46	3.213		3.26	4.045	4.3	4.502	4.742

[a] (a) H–(CH = CH)$_n$–H in hydrocarbon solvents.
  (b) CH$_3$–(CH = CH)$_n$–CH$_3$ in hydrocarbon solvents.
  (c) Carotenoids in hydrocarbon or alcohol solvents [Ref. 3].

[b] Forbidden in all-*trans* configurations, calculated values for all mono-*cis* isomers are within 0.2 eV of these quantities.

Table 2. *Transition Energies* (eV) *of* φ-(CH CH)$_n$-φ

$^1A \rightarrow$	^1B		^1C		^1D	
n	calc	exp[a]	calc	exp	calc	exp
1	4.103	4.20			5.872	5.39
2	3.633	3.58	5.221	5.17(?)	5.647	5.37
3	3.318	3.36	4.790	4.69	5.547	5.19
4	3.063	3.14	4.412	4.43	5.465	5.39
5	2.871	2.92	4.113		5.139	
6	2.719	2.79	3.835		4.823	

[a] ZECHMEISTER, L.: *Cis-Trans* Isomeric Carotenoids, Vitamins A and Arylpolyenes, New York: Academic Press 1962, and MACCOLL, A.: Quart. Rev. 1, 16 (1947).

The diphenylpolyene results (Tab. 2) are in good agreement with experiment. The bond orders in the phenyl groups are not far from $^2/_3$ and are independent of chain length while the chain bonds alternate strongly and approach the polyene limiting values. The $^1B \leftarrow {}^1A$ transitions are nearly pure $1 \rightarrow 1'$ and these orbitals are delocalized over the entire π-framework.

Although the computed transition energies for the mono-*cis* and di-*cis* isomers differ little (less than 0.2 eV) from the all-*trans* energies, the change in electron

repulsion with greater "coiling" cannot be ignored. An intermediate obtained in the photochemical conversion of stilbene to phenanthrene has been identified, on mechanistic grounds, as a dihydrophenanthrene [6]. This material exhibits an absorption maximum at 447 mμ
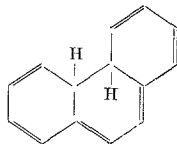
and the calculated $\lambda_{max} = 440$ mμ. This example illustrates the applicabil ityof the SCF MO method to molecules in which the geometries are quite varied, and validates the use of the same variable β formalism for both ring and chain hydrocarbons.

References

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