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VARIABLE-BETA HÜCKEL STUDIES OF THE LINEAR POLYENES

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Abstract—The "variable beta" modification of the Hückel technique is applied to the series of linear polyenes, and the results are shown to be in accord with those of more elaborate approaches. Correlations regarding interatomic distances, spectral properties, ionization potentials and delocalization energies are presented. Incidentally, it is found that, contrary to current statements, the Hückel method does not predict a rapid equalization of bond lengths in long chain polyenes.

INTRODUCTION AND METHOD

THE theoretical work[1-3] devoted to the linear polyenes P_n,* has been concerned with possible changes in interatomic distances caused by lengthening of the chain, and particularly with the question whether the alternation, known in butadiene,[4] persists in longer polyene chains, converging eventually at "single bond" and "double bond" values, or whether the initial differences level out, giving ultimately uniform bond lengths. The first of these possibilities seems now well established:[3] measured ΔE_1 values (for P_4–P_{16} and P_{20}) tend towards a finite limit, which, by FE[5] and LCAO[6] methods, is only possible if the bonds alternate; secondly, both the simple[3] and SCF[7] LCAO methods indicate that the configuration with all bonds equal is, at $n \rightarrow \infty$, the less stable of the two.

In most calculations (see Ref 8), bond alternation had to be explicitly introduced *a priori*, in order to account for the observed properties. If indeed, the characteristic properties of the polyenes are based upon the connectivity of these molecules, then Hückel-type techniques suffice to describe the main phenomena.

The general solution of the Hückel secular matrix has been interpreted[9] as indicating that the bond lengths in the polyenes tend to equality; yet, calculations which we have carried out up to P_{52} do not show such an equalization. It is known[3,6] that bond alternation can be allowed for in the Hückel theory by assigning, *at the beginning*, different resonance integrals to "double" (C_1—C_2, C_3—C_4, etc.) and "single" (C_2—C_3, C_4—C_5, etc.) bonds; however, this procedure begs the question and also assumes the equivalence of all "single", as well as all "double" bonds. The "variable-beta" technique[10] should then constitute a way to meet the difficulty within the realm of Hückel-type methods, as in this technique all resonance integrals are first assumed to be equal, then systematically modified, by successive iterations, dependent upon the calculated bond orders. Thus, the computed properties are determined solely by the ordering of linkages within the molecule ("connectivity").

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* We denote a linear polyene by P_n, so that P_4 is butadiene, P_6-hexatriene, etc. Chain carbon atoms are designated C_1, C_2 . . . , the first singlet–singlet transition-ΔE_1, higher transitions-ΔE_2, ΔE_3.

We have therefore carried out "variable-beta" calculations for the linear polyenes, up to P_{42}, iterations being based upon the relation[10]

$$\beta_{rs} = \beta^0 \exp(0{\cdot}55\, p_{rs} - 0{\cdot}3666)$$

where β_{rs} is the resonance integral at iteration N, p_{rs}—the bond order at iteration (N-1). Upon convergence (tolerance 10^{-4}), bond lengths r_{rs} were obtained either from a relation based upon the interatomic distances in butadiene[4]

$$r_{rs}(\text{Å}) = 1{\cdot}536 - 0{\cdot}204\, p_{rs} \tag{1}$$

or from the standard expression

$$r_{rs}(\text{Å}) = 1{\cdot}524 - 0{\cdot}194\, p_{rs} \tag{2}$$

For the calculation of the spectral properties, it was desirable to introduce neighbouring-atom overlap S. Wheland's technique[11] is permissible if one (a) admits[2] the $\beta(S)$ proportionality, so that $S = S^\circ$ for $\beta = \beta^\circ$ and $S = kS^\circ$ for $\beta = k\beta^\circ$, and (b) considers all iterations, but the last, as a systematic search for realistic β-values, the last one being an ordinary Hückel computation. Choosing now the *convenient* value $S^\circ = 0{\cdot}25$, and denoting orbital coefficients by m (e.g. $\varepsilon = \alpha + m\beta$ for a bonding orbital), one gets

$$\Delta E_1(\gamma) = \frac{32m}{16\text{-m}^2} \tag{3}$$

in view of the pairing property. For small m-values, $\Delta E_1(\gamma) \rightarrow \Delta E_1(\beta)$, and the two energetic indices behave in the same manner.

RESULTS

Hückel bond orders. Hückel bond orders for P_4 (butadiene) are $p_{12} = 0{\cdot}894$ and $p_{23} = 0{\cdot}447$; those for P_{52} and P_{40} are given in columns A and B of Table 1. Alternation persists even for P_{52}, and is especially marked at the ends of the chain. The differences of the data for P_{52} and P_{40} are very small, so that P_{52} appears still far from being an "infinite" polyene, and it cannot be said[12] that the method predicts a *rapid* equalization of bond lengths. The ends of the chain are more stable to lengthening than the inner linkages; stated otherwise, the lengthening of a polyene chain from P_n to P_{n+2} should be considered as the insertion of a vinyl grouping *inside* the P_n chain, *not* as an addition at its end.

"*Beta*" *bond orders.* As already stated, the present approach does not contain any *a priori* assumption as to the regularity governing the nature of the polyene bonds. The computed bond orders (e.g. for P_{40}, Table 1, col. C) indicate indeed that the linkages fall alternately into the double bond ($0{\cdot}92 > p > 0{\cdot}78$) and single bond ($0{\cdot}39 < p < 0{\cdot}48$) domains, and that bonds of either category show a remarkable constancy of length: 1·35–1·38 Å and 1·46–1·44 Å, respectively (by Eq. 1). The method agrees thus with the results of much more elaborate approaches, confirming the distinction between bond types and the absence of equalization in mid-chain.

The orders of the four terminal bonds converge at P_{24} to their final values, corresponding to $r_{12} = 1{\cdot}349$, $r_{23} = 1{\cdot}457$, $r_{34} = 1{\cdot}365$, $r_{45} = 1{\cdot}447$ Å by Eq. (1), or $r_{12} = 1{\cdot}346$, $r_{23} = 1{\cdot}449$, $r_{34} = 1{\cdot}362$, $r_{45} = 1{\cdot}440$ Å, by Eq. (2). These values compare favourably with the SCF values[7] of 1·364 and 1·463, and with the SPO results[13] of

TABLE 1

Bond	A $P_{52}(H)$	B $P_{40}(H)$	C $P_{40}(B)$	D $P_{30}(B)$
1–2	0·849	0·849	0·919	0·919
2–3	0·509	0·509	0·386	0·386
3–4	0·728	0·729	0·838	0·838
4–5	0·565	0·565	0·435	0·435
5–6	0·696	0·696	0·813	0·813
6–7	0·586	0·586	0·454	0·454
7–8	0·681	0·682	0·801	0·801
8–9	0·598	0·596	0·464	0·464
9–10	0·672	0·673	0·795	0·795
10–11	0·604	0·603	0·469	0·469
11–12	0·667	0·668	0·791	0·792
12–13	0·609	0·607	0·472	0·471
13–14	0·663	0·665	0·789	0·790
14–15	0·612	0·610	0·474	0·473
15–16	0·660	0·663	0·787	0·789
16–17	0·614	0·611	0·476	
17–18	0·659	0·662	0·786	
18–19	0·616	0·612	0·476	
19–20	0·657	0·661	0·786	
20–21	0·617	0·612	0·476	
21–22	0·656			
22–23	0·617			
23–24	0·656			
24–25	0·618			
25–26	0·656			
26–27	0·618			

1·347 and 1·463. Bonds further to the interior do not seem to converge up to P_{40}, but the increments with the lengthening of the chain are very small, as can be concluded from the comparison of bond orders in P_{40} (Table 1, col. C) and P_{30} (Table 1, col. D). At high n-values, the order of the middle bond is about 0·476 (r = 1·44 Å, by Eq. 1) for $n = 4q$, or 0·787 (r = 1·38 Å) for $n = 4q + 2$. It should be stated that the orders of "double" middle bonds ($n = 4q + 2$) diminish with the lengthening of the chain, in line with the statement[14] that *trans–cis* isomerization is easier for long than for short polyenes.

Longest-wave absorption band. It is known[1,2] for P_4–P_{16}, P_{20} and similar molecules, that the longest-wave absorption of the linear polyenes undergoes a bathochromic shift with lengthening chain, the increment per C_2-unit gradually diminishing. Calculations based on the general Hückel solution, with two beta values, corroborate this tendency[1] and an appropriate calibration (β_s/β_d = 0·72, β_s = −4·0 eV) yields 553 mμ as the limit wavelength. The longest chain studied experimentally is P_{20}, absorbing at 447 mμ;[15] thus, P_{20} is still far from the limit.

Our $\Delta E_1(\gamma)$ values are reported in Table 2; no convergence is observed, but the increments are small for the longer members of the series. In Fig. 1, calculated $\Delta E_1(\gamma)$ values are plotted against the experimental transition energies; these are

TABLE 2

n	$\Delta E_1(\gamma)$	D
4	1·708	0·236
6	1·296	0·247
8	1·063	0·254
10	0·913	0·257
12	0·809	0·260
14	0·732	0·261
16	0·673	0·262
18	0·628	0·263
20	0·590	0·264
22	0·560	0·264
24	0·531	0·264
26	0·511	0·265
28	0·493	0·265
30	0·476	0·265
32	0·462	0·265
34	0·450	0·265
36	—	—
38	0·433	0·266
40	0·424	0·266
42	0·417	0·266

taken from the literature[2] and may not refer all to the same vibronic sub-level. The data are fitted by the straight line

$$\Delta E(\mathrm{eV}) = 1{\cdot}240 + 2{\cdot}637\ \Delta E_1(\gamma) \tag{4}$$

so that the non-convergence of $\Delta E_1(\gamma)$ does not handicap calculations, at least up to P_{20}, and the theoretical values behave exactly as the experimental ones.

Other electronic transitions. Use of our simple method (see[16]) for the calculation of ΔE_2 and ΔE_3[14, 17] leads, for P_{20}, to the following values: $\varphi_{10} \rightarrow \varphi_{11}$, 0·5905γ

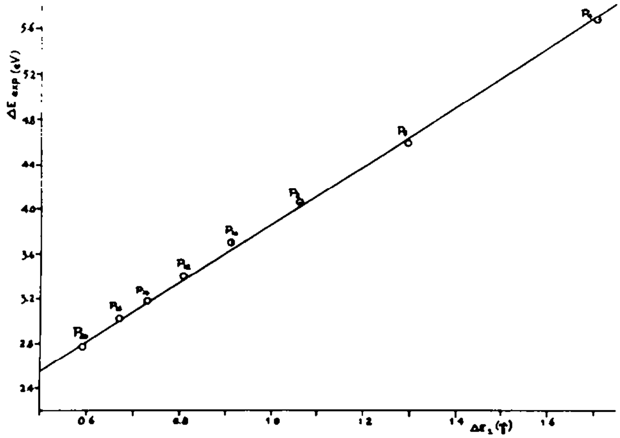

FIG. 1

(2·795 eV by Eq. 4), φ_{10}—φ_{12}, 0·8866γ* (3·576), φ_{10}—φ_{13}, 1·2514γ (4·539), φ_9—φ_{11}, 0·7861γ* (3·312), φ_9—φ_{12}, 1·0822γ (4·093), φ_9—φ_{13}, 1·4471γ* (5·056) (asterisked transitions are forbidden in *all-trans* structures). The calculated bands, $\Delta E_1 = 2{\cdot}8$, $\Delta E_2 = 3{\cdot}3$–$3{\cdot}6^*$ and $\Delta E_3 = 4{\cdot}1$–$4{\cdot}5$ eV, compare favourably with the SCF values:[17] $\Delta E_1 = 2{\cdot}62$, $\Delta E_2 = 3{\cdot}63$ and $\Delta E_3 = 3{\cdot}93$ eV.

One may equally examine Dale's empirical correlation,[14] according to which the band ΔE_s of P_n should approximate ΔE_1 of P(n/s). The values for P_{20}, $\Delta E_2 = 3{\cdot}65$ eV (i.e. ΔE_1 of P_{10}) and $\Delta E_3 = 4{\cdot}50$ (ΔE_1 for hypothetical P(20/3), obtained from a curve based on Table 2), corroborate the relation; however, they do not imply that transitions starting at the next to HOMO should be forbidden, as has been suggested.[14]

Ionization potentials. Ionization potentials correspond, at least approximately, to the energy of the highest occupied molecular orbital[18] and should therefore correlate with its coefficient.[3] As experimental data for the longer polyenes are lacking, we confined ourselves to comparing our values with those obtained by a SCF method.[17] Indeed, plotting the two series of values against each other, we obtained a perfectly straight line, so that also in this respect the "variable-beta" method is equivalent to more advanced approaches. It may be mentioned that the agreement between the SCF results and those obtained from the recently proposed relation[19]

$$\text{I.P. (eV)} = 6{\cdot}924 + 2{\cdot}11\, m_{\text{HOMO}} + \frac{2{\cdot}954}{n}$$

was less good.

Delocalization energy. The delocalization energy index[3] augments regularly with the dimension of the secular matrix and is not of immediate use in a series of closely related structures.[20] We prefer to examine the delocalization energy *per atom*, defined for P_n as

$$D = \frac{n}{2}\Big(\sum_{\substack{i\\ \text{occ}}} m_i - 1\Big)$$

Our D-values, given in Table 2, show but a slight dependence on the length of the chain, being almost constant for the longer polyenes. This is, of course, another manifestation of the bond alternation phenomenon.

CONCLUSION

The main point that emerges from the discussion is that one can employ the "naive" one-electron Hamiltonian for the study of linear polyenes, even without imposing bond alternation from the start. The "variable-beta" technique provides indices which correlate well with results of SCF calculations, showing thus that the main features of these molecules can be elucidated on the sole basis of their connectivity.

REFERENCES

[1] J. N. Murrell, *The Theory of the Electronic Spectra of Organic Molecules.* Methuen, London and New York (1963).

[2] H. Suzuki, *Electronic Absorption Spectra and Geometry of Organic Molecules.* Academic Press, New York and London (1967).

[3] L. Salem, *The Molecular Orbital Theory of Conjugated Systems.* Benjamin, New York and Amsterdam (1966).

[4] W. Haugen and M. Traettenberg, *Selected Topics in Structure Chemistry* Edited by P. Anderson, O. Bastiansen and S. Furberg. Universitetsforlaget, Oslo (1967).

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

[6] M. J. S. Dewar, *J. Chem. Soc.* 3544 (1952).

[7] J. Ooshika, *J. Phys. Soc. Japan* **12**, 1238, 1248 (1957).

[8] J. M. André and G. Leroy, *Theoret. Chim. Acta* (Berl.) **9**, 123 (1967).

[9] J. E. Lennard-Jones, *Proc. Roy. Soc.* **A158**, 280 (1937).

[10] G. V. Boyd and N. Singer, *Tetrahedron* **22**, 3383 (1966).

[11] G. W. Wheland, *J. Am. Chem. Soc.* **63**, 2025 (1941).

[12] H. Labhart, *J. Chem. Phys.* **27**, 957 (1957).

[13] M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.* **87**, 692 (1965).

[14] J. Dale, *Acta Chem. Scand.* **8**, 1235 (1954).

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

[16] J. R. Platt, *J. Chem. Phys.* **18**, 1168 (1950).

[17] O. W. Adams and R. L. Miller, *J. Am. Chem. Soc.* **88**, 404 (1966).

[18] R. S. Mulliken, *Phys. Rev.* **74**, 736 (1948).

[19] K. Vasudevan and W. G. Laidlaw, *Tetrahedron* **25**, 591 (1969).

[20] R. Zahradník, J. Michl and J. Pancíř, *Ibid.* **22**, 1355 (1966).