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A Reevaluation of Side Chain Oscillator Effects in the Polyene Superconductor Model

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SUMMARY

The values calculated for the side chain oscillator interaction energy for the polyene superconductor model have been revised. The use of parallel and perpendicular transitions gives a value for the naphthalene oscillator of 2.1 eV, well within the postulated range for a possibly operable effective interaction.

The macromolecular superconductor concept proposed by Little [1] has been considered from a variety of theoretical points of view. Most of the objections [2-10] which have been suggested seem to be answerable [1, 11] in an acceptable manner. Thus, it does not seem to be essential to require one-dimensionality [4], and the unscreened model [6] gives interaction differentials much too high (above the ionization potential). Also, the thermodynamics of the situation are difficult, if not impossible, to evaluate if the transition occurs at high temperatures. The basic concept, that of electron-electron interaction, appears to present a theoretically valid alternative to the phonon-electron model for the BCS theory of metallic superconductivity.

The original structural proposal [1] for a macromolecular superconductor was that of a polyene spine with doubly alternating, non-cross-conjugated, cyanine side chain substituents. This structure, as does also that with the conjugated aldimine side chain proposed by Salem [7], poses rather difficult problems for the polymer chemist. It is the purpose of this report to consider the characteristics of some alternative macromolecular structures which are more closely related to currently realizable experimental capabilities of polymer science than this cyanine-polyene model. Such structures can be polymers derived from phenylacetylene, diphenylacetylene, and diphenyldiacetylene. Each of these presents a variety of structural and chemical possibilities and limitations which need to be considered.

At present, we wish to present the results of a reconsideration of the values of the effective interaction energy:

$$V_{eff} = V_c(Q) - 2 \sum_n V_n(Q)^2 / W_n \tag{1}$$

when the cyanine side chain oscillator of the Little model is replaced by benzene, naphthalene, or azulene groups for which the necessary data are available for the calculations and which can conceivably be used in standard stereoregular polymerization techniques.

The effective interaction energy, V_{eff}, to be considered is the sum of two terms: the coulombic repulsion, $V_c(Q)$, and the attractive energy assigned to the side chain substituent—the second term of Eq. (1). With the value of Q equal to zero, Little obtains 1.5 eV for $V_c(0)$ based on a screened interaction. The screened interaction seems appropriate for the reasons he has noted; i.e., the unscreened values give unrealistic values in excess of ionization potentials.

The calculation of the side chain attractive interaction involves W_n, the energy of transition of the substituent from the ground state to the nth excited state, and $V_n(Q)$, the matrix element for the attraction between the side chain substituent and the four carbons of the unit cell. Little calculates $V_n(Q)$ by the valence bond method considering the difference between the square of the wave functions of the two resonating forms of the substituent. The calculations are involved, the VB approximation is crude, and for substituents of present interest, the wave functions are not known. Paulus [6] avoided some of these difficulties by calculating $V_n(Q)$ directly from electronic spectral data. This method is simpler and possibly closer to experimental reality, but it is also approximate at best. The approximations result from the necessity of considering the polyene electron as a point charge and assuming the transition dipole to lie at the center of the substituent. We shall proceed with the calculations using the Paulus simplification even though the result may very well only approximate the real value.

To determine $V_n(Q)$ using the Paulus method, the following relation must be evaluated:

$$2\sqrt{N}V_n(Q) = G_{n,1} + 2\sum_{\mu>1} G_{n,\mu} \cos [(\mu - 1)Qa] \quad (2)$$

In this relation, a is the carbon-carbon bond length and N is the number of carbon atoms in the unit cell. The term cos $[(\mu - 1)Qa]$ becomes 1 when, for reasons given by Little, Q is set equal to zero. The value of $G_{n,\mu}$, the interaction between the field of a polyene electron and the transition dipole it induces in the substituent, is determined as:

$$G_{n,\mu} = (e^2/r_\nu^2)\mu_n \cos \theta_{\mu} \quad (3)$$

in which e is the charge on the electron (4.8×10^{10} esu); r is the distance from the dipole to the carbon atoms and is taken by Little as $r_1 = 1.5$, $r_2 = 2.5$, $r_3 = 3$, $r_4 = 4.5$Å for his four-carbon unit cell; cos θ_μ is the cosine of the angle formed by the direction of the dipole and the line binding the dipole to the given carbon atom; and μ_n is the dipole of the transition:

$$\mu_n = (3\hbar^2 f_n 2_m W_n)^{05} \quad (4)$$

in which f is the oscillator strength of the transition $\hbar = 6.6 \times 10^{-28}$ erg-sec/6.28; m is the mass of the electron, 9×10^{-28} g; and W_n is the energy of transition from spectral data (about 38,000 cm^{-1} for benzene derivatives [12], or 76×10^{-13} erg).

In the calculation for benzene, the oscillator strength (f_n) values given by Sklar [12] were used. These values are comparable to that given by Ihaya [13] for toluene but different from that given by Sponer and Love [14]. The V_{eff} calculation is based on Paulus' matrix element, which is double that of Little and must be divided by 4. The value of V_{eff} for benzene as a side chain oscillator, summed over three transitions, is thus

$$V_{eff} = 1.5 - 0.93 = +0.57 \text{ eV}$$

For naphthalene the calculation of the net interaction gives

$$V_{eff} = 1.5 - 3.6 = -2.1 \text{ eV}$$

provided that both parallel and perpendicular transitions are included in the calculation of the oscillator strength. Paulus [6] does not include the perpendicular transitions and obtains a different value: 16.5 eV unscreened; -0.04 eV screened. A similar calculation for azulene gives

$$V_{eff} = 1.5 - 3.5 = -2.0 \text{ eV}$$

It is postulated by Little [1] that the net interactions should be attractive (negative) and in the 1.5 eV range. The values for the naphthalene (-2.1) and azulene (-2.0) as we have calculated them are thus within the postulated range for superconductance.

We now turn our attention to another aspect of the problem presented by the polymer chemistry of the situation. The four-carbon unit cell devised by Little is structurally a head-to-head, tail-to-tail polyene derivable from phenylacetylene. Although this configuration is not that expected of poly(phenylacetylene), it may be presumed that even if it were to become available, the properties of the polymer would not meet the interaction requirements specified by Little. The polymeric structure derivable from diphenylacetylene, perhaps in a helical form, is of possible interest as an alternative structure of a not unrelated type. We have, therefore, calculated the matrix elements and net interaction for the unit characteristic of this structure; e.g, —CPh = CPh—. The coulombic interaction is presumably twice that for Little's four-carbon unit:

$$V_c(Q) = 6/2 = 3 \text{ eV}$$

The attractive matrix element, calculated using the oscillator strength values given above, is evaluated in the same way. The effective interaction for the diphenylacetylene-derived unit is thus

$$V_{eff} = 3 - 0.64 = +2.36 \text{ eV}$$

a value not operable within the scope of Little's assumptions. Similar calculations for the naphthyl analog give

$$V_{eff} = 3 - 2.75 = +0.252 \text{ eV}$$

a value low enough to be of interest.

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