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Vibronic polymers: A novel chemical species

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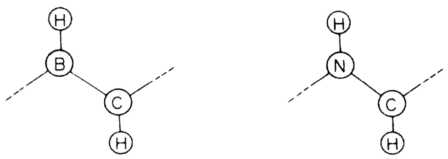
Unusual chemical bonding patterns should appear in polyboracetylene and polyazacetylene as a consequence of strong vibronic instabilities.

Extensive investigations of electrically conducting polymers have been undertaken[1] primarily because of their great technological promise, but some fundamental problems have emerged also. Symmetry breaking and strong coupling both appear in *trans*-polyacetylene (PA); generalizing, Krumhansl predicted[2] the existence of "many new chemical states of matter, with various kinds of conformational symmetry coupled strongly to extended modification in the electronic configuration." However, chemical bonds in PA look rather ordinary,[3] and a better example is needed to make this point clear.

Another major challenge is to synthesize an intrinsically conducting polymer. In a recent Rapid Communication[4] two new candidates were proposed: polyboracetylene (PBA) [Fig. 1(a)] and polyazacetylene (PAzA) [Fig. 1(b)].

In this Rapid Communication, I argue that neither PBA nor PAzA will be metallic, that both of them will be distorted, and that their equilibrium configurations will be rather unusual from the chemist's point of view. Thus these polymers could properly represent the predicted novel "chemical states" of matter.

In more detail, Tanaka *et al.*[4] performed a series of self-consistent-field tight-binding band-structure computations on single stereoregular chains of PBA and PAzA. They allowed the lengths of C—B bonds in PBA to alternate, and studied the dependence of total adiabatic energy on the amplitude of distortion from the equidistant configuration. They found the energy minimum to occur exactly at zero distortion. Analogous computations on PAzA gave the same result. They concluded that in PBA and PAzA there will be no bond alternation and therefore no band gaps between the respective valence and conduction bands, and therefore both polymers will show metallic conductivity without any doping. This result they found to be "rather surprising." Indeed, it opposes a widespread belief that the Peierls theorem ensures that every metallic polymer is unstable. However, in his well-known treatise[5] Peierls considered a monoatomic periodic model chain, i.e., a *simple* polymer, while most actual polymers, including PBA and PAzA, are *complex*—their translation repeat units contain several or many atoms. For a complex polymer with many intracell degrees of freedom it is less easy to guess the proper distortions. In fact, wrong choices have been made so frequently in recent literature that the issue deserves some clarification.



(a) (b)

FIG. 1. (a) Polyboracetylene. (b) Polyazacetylene.

The crucial question here is whether a given distortion $\mathbf{Q}_i$ is linearly forbidden or allowed, i.e., whether the matrix element $A_i = \langle e|\mathbf{Q}_i \cdot (\partial V/\partial \mathbf{Q}_i)_0|e'\rangle$ vanishes by symmetry or not. (Here $|e\rangle$ and $|e'\rangle$ denote the degenerate eigenstates at the Fermi level E_F, and V is the effective one-electron potential.) Namely, if the chain distorts along $\mathbf{Q}_i$ and the distortion amplitude is not too large, the first-order energy corrections—which are proportional to $|A_i|$—are the dominant ones. Experimentally observed[1] distortions of vibronic origin are rather small indeed, 0.01–0.1 Å.

The traditional method[6] of determining the linearly allowed distortions is to decompose the symmetrized Kronecker square $[D_e^2]$ of the irreducible representation D_e of the symmetry group—here, the line group of the polymer under study—according to which the eigenstates $|e\rangle$ and $|e'\rangle$ are transformed into its irreducible constituents, which then identify the allowed modes. An easier and physically more transparent alternative[7] is to utilize the conservation laws for the corresponding quantum numbers —quasimomentum k, quasiangular momentum m, and the parities with respect to reflections in the vertical xz plane and the horizontal xy plane. [These reflections are denoted by σ_v and σ_h, respectively. States which are even (odd) with respect to σ_v are labeled by A (B); the σ_h parity is indicated by + (−).] The latter method is applied below to PA, PBA, and PAzA.

In these polymers the essential physics is conveyed by π electrons of the C, B, and N atoms. With this in mind, I will consider the model polymer shown in Fig. 2(a). Each atom contributes one π orbital, and two π electron bands are formed in either case. For the monatomic chain [i.e., if

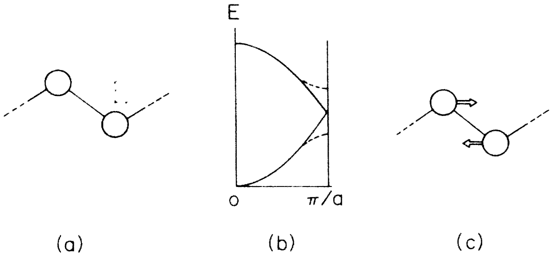


FIG. 2. (a) Model chain investigated in the text. (b) Band shapes of the monatomic polymer (solid lines) and of the diatomic polymer (dashed lines). (c) "Dimerization" of the chain.

the two atoms in Fig. 2(a) are identical], these two bands cross at the Brillouin-zone (BZ) edge—i.e., at $k=\pi/a$, where a is the translation period—to form a "semiloop" shape; see Fig. 2(b). This is required[7] by the $L2_1/mcm$ symmetry of the chain. The band structure of "nondimerized" or "regular" PA indeed consists of such semiloops. In PBA and PAzA the backbone atoms are not identical and the symmetry is reduced to $L1/mm$. The band crossing is avoided, and a gap opens at the BZ edge; see Fig. 2(b).

In PBA there is one π electron per unit cell, which makes the lower band of Fig. 2(b) half filled, i.e., $k_F = \pm\pi/2a$. In PA there are two π electrons per unit cell, the lower band is completely full, the upper one is empty, and $k_F=\pi/a$. In PAzA, there are three π electrons, the upper band is one-half full, and $k_F = \pm\pi/2a$ again. Regular PA is unstable against bond-length alternation [Fig. 2(c)] because of the degeneracy at E_F. In regular PBA and PAzA there are also two degenerate eigenstates, $|e\rangle = |\pi/2\ B\rangle$ and $|e'\rangle = |-\pi/2\ B\rangle$, at E_F. To scatter an electron from $|e\rangle$ to $|e'\rangle$ or vice versa, a phonon must be even with respect to σ_v (which eliminates all out-of-plane distortions), since both states are odd; also, it must have quasimomentum $q=2k_F=\pi/a$. The parity with respect to σ_h is not restricted, since $|e\rangle$ and $|e'\rangle$ are not eigenstates of σ_h. More formally, $D_e = (\pi/2\ B)+(-\pi/2\ B)$ and

$$[D_e^2] \sim (\pi A+)+(\pi A-)+(0A+) \ . \tag{1}$$

Now, the "dimerization" distortion [Fig. 2(c)] which was investigated in Ref. 4, belongs to $(0A-)$; the quasimomentum is not conserved, and this mode is *not* linearly vibronically allowed (LVA). Indeed, any LVA distortion must be of wavelength $\lambda = 2\pi/q = 2a$, so that the translation period is doubled.

The LVA modes of the monatomic model, for the case when the lower (or the upper) electron band is one-half filled, are represented in Fig. 3. As required by the $L2_1/mcm$ line group symmetry, the phonon branches also stick in pairs at the BZ edge: The $\mathbf{Q}_1$ mode is degenerate with $\mathbf{Q}_2$, and $\mathbf{Q}_3$ with $\mathbf{Q}_4$. For the diatomic chain, atomic displacements are renormalized by the respective atomic masses; the four LVA modes still resemble those of Fig. 3, but the degeneracies are lifted.

If we now take into account the hydrogen atoms, each of which can move out of phase or in phase with the backbone atom it is bound to, there are eight LVA modes in PBA, as well as in PAzA.

Each LVA mode $\mathbf{Q}_i$ opens a gap $E_g(Q_i)$ at E_F. If the distortion amplitude is small, $E_g(Q_i)$ is proportional to Q_i. The total adiabatic energy of the polymer is of the form

$$E_{\text{tot}}(\mathbf{Q}) = E_{\text{tot}}(0) + \sum_i \lambda_i Q_i^2 \ln|Q_i| + \sum_i \mu_i Q_i^2 + \cdots \ , \tag{2}$$

where $\mathbf{Q} = \sum Q_i \mathbf{q}_i$ and $\mathbf{q}_i = \mathbf{Q}_i/Q_i$. The constant λ_i is proportional to $|B_i|^2$, where $B_i = \langle e|\mathbf{q}_i\cdot(\partial V/\partial \mathbf{Q}_i)_0|e'\rangle$. The constants μ_i include the elastic response due to the σ electrons. Vibronically inactive phonons are omitted. There is a logarithmic instability along every $\mathbf{Q}$. The constants λ_i and μ_i determine the dominant mode(s). Comparing the force constants, one can exclude the two C—H bond stretching modes, as they appear at much higher frequencies (~ 3000 cm^{-1}) than the remaining six LVA modes (1000–1500 cm^{-1}). The vibronic matrix elements A_i are estimated by Tanaka *et al.*[4] to be "small or virtually zero," because "the dimerized unit cell CHNHCHNH or CHBH CHBH should involve at least three different kinds of C—N (or C—B) bond lengths which is rather unusual from the ordinary chemical point of view."

To assess that estimate, let me calculate explicitly one of these matrix elements—say A_1, which corresponds to the distortion $\mathbf{Q}_1$ shown in Fig. 3—for the monatomic polymer. First I calculate, analytically, the tight-binding π-electron band structure for the polymer distorted along $\mathbf{Q}_1$. Let the upper two atoms be displaced by $+z$ and $-z$, respectively, and let t_0, t_+, and t_- denote the transfer integrals which correspond to the regular, the contracted, and the extended bonds. The distortion opens a gap $E_g = \sqrt{2}|t_+ - t_-|$ at E_F. To the first order, $t_\pm = t_0 \pm Tz$. On the other hand, first-order degenerate perturbation theory gives $E_g = 2|A_1|$. Since A_1 is proportional to z, let $|A_1| = C_1 z$. Thus one obtains $C_1 = \sqrt{2}T$. This result remains valid also for the diatomic polymer. The value of T in PBA will not differ much from its value in PAzA or in PA. Estimating that $\alpha_1 = T/2 = 4.1$ eV/Å, Su, Schrieffer, and Heeger[8] obtained the bond-length difference $\Delta R = R(\text{C—C}) - R(\text{C=C}) = 0.14$ Å and the gap $E_g = 1.40$ eV in PA.[9] This is a rather strong instability; the theoretical transition temperature would be well above the actual polymer dissociation temperature. Other estimates for α_1 are even higher.[10] Finally, one should take into consideration the on-site electron-phonon coupling, since the mode considered induces substantial variations of local charge density at lower row atoms (see the $\mathbf{Q}_1$ mode in Fig. 3); this further increases C_1, roughly by a factor of 2.[11]

Hence the value of C_1 is rather large, of the order of 15–20 eV/Å. The same is true for C_2, C_3, and C_4. The strength of vibronic coupling in PBA and in PAzA is comparable to that in PA. The same is true for the elastic response. One can only conclude that vibronic instabilities should be rather strong in PBA and PAzA, too. Both chains must distort spontaneously. The variation of the backbone bond lengths should be substantial, say $\Delta R > 0.05$ Å.

Such strong instabilities will not be suppressed by interchain interaction, disorder, or impurities. Electron-electron correlations are not decisively important either; the relevant electron bands are rather broad, about 8 eV in PAzA and over 11 eV in PBA according to Ref. 4.

Hence neither PBA nor PAzA are genuine counterexamples[12] to the "Peierls theorem." Indeed, for every metallic polymer there exists an LVA mode $\mathbf{Q}$ which opens a gap $E_g \propto Q$, for small Q, at E_F.[13]

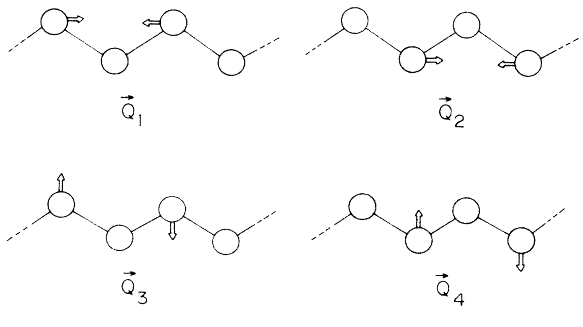


FIG. 3. Vibronically active distortions of the polymer, for $k_F = \pm\pi/2a$.

On the other hand, PBA and PAzA should show unusual chemical bonding patterns. To predict their ground-state configurations precisely, further careful geometry-optimization studies are needed, and they are being undertaken now. But in any case the stabilizing distortion will be a linear combination of the six LVA modes described above, and the predicted structures of PBA and PAzA will be found rather strange by many organic chemists. Take $\mathbf{Q}_1$ as an example—it creates an oscillation (between 3 and 5) of the valence of successive B (or N) atoms. (It does not create three different backbone bonds though, contrary to what is stated in Ref. 4.) Surprisingly or not, polymers with strong vibronic instabilities constitute a new class of physical systems, in which a variety of vibronic effects, static and dynamic, should be expected.[14]

Finally, PA is until now the only polymer known to have degenerate ground states, capable of supporting solitons. Both PBA and PAzA should also have degenerate ground states, and solitons should play a role in electrical transport processes, photoconductivity, etc., in these materials, too. The difference is that in PA solitons arise from the screw-axis symmetry breaking, while in PBA and PAzA only the translational symmetry is broken.

In conclusion, I have shown that vibronic coupling and instabilities in PBA and PAzA should be rather strong. Both polymers should distort considerably into configurations with unusual sequences of chemical bonds. Hence synthesis and characterization of PBA and PAzA (or some other[15] vibronic polymers that can be proposed along the guidelines given here) would be of great interest.

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[*] On leave from the Institute of Physics, Belgrade, Yugoslavia.

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[15] Some of these (e.g., polyacenacene) look perfectly normal chemically—until the actual vibronic distortion is identified.