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Comparative theoretical study of the doping of conjugated polymers: Polarons in polyacetylene and polyparaphenylene

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Defect-state calculations on all-*trans* polyacetylene and polyparaphenylene have been performed in the framework of the adiabatic Hückel Hamiltonian with σ-bond compressibility. In polyacetylene, the study of the energetics of the separation of the radical (neutral defect) —ion (charged defect) pair induced upon doping indicates that the two defects tend to remain in close proximity, resulting in the formation of a polaron. The binding energy of the polaron is estimated to be about 0.05 eV with this model. Absorption spectra at low doping levels are shown to be compatible with polaron formation, thus demonstrating the nonuniqueness of the previously proposed soliton model in explaining these absorption data. At higher doping levels, interaction between polarons leads to the formation of charged solitons carrying no spin. In polyparaphenylene, defects are always correlated in pairs due to the absence of a degenerate ground state. At low doping, polarons with a binding energy estimated at 0.03 eV are formed on ionization of polyparaphenylene. The related deformation of the lattice is relatively soft, in agreement with crystallographic data on biphenyl anions, and extends over about five rings. Increasing the doping level leads to the formation of bipolarons (doubly charged defects) that require a stronger deformation of the lattice and carry no spin. The possibility of a conduction mechanism in polyparaphenylene involving motion of bipolarons is consistent with magnetic data indicative of very low Pauli susceptibility in the metallic regime of SbF_5-doped polyparaphenylene.

I. INTRODUCTION

In recent years, a number of conjugated organic polymers have been discovered that can be made electrically conductive through doping with either strong electron acceptors or donors. Polymers with doped derivatives which have been reported to have conductivities larger than 1 S/cm include polyacetylene,[1] polyparaphenylene,[2] polypyrrole,[3] and various polyphenylene chalcogenides.[4,5] Interest, both academic and industrial, has further increased by demonstration of rechargeable batteries based on doped polyacetylene[6] and polyparaphenylene.[7]

It should be stressed that doped organic polymers, although displaying phenomena in many ways similar to conventional semiconductors, are, in fact, very different from the usual doped inorganic semiconductors.[8,9] These polymers possess highly anisotropic interactions which result in low dimensionality of electronic motion and can lead to collective instabilities typical of quasi-one-dimensional materials, such as Peierls instabilities. In addition, because these are organic compounds, we can anticipate that electronic excitations or charge-transfer processes will markedly affect the atomic geometry, just as in typical organic molecules; therefore, rigid-band models will be incorrect. Finally, the polycrystalline or amorphous character of the present polymers provokes a substantial disorder, which increases further during the doping process. As a result, localized states can play a major role. Note that disorder provides a barrier for determining accurately critical aspects of the structures and properties of conducting polymers. Thus most of the theoretical work on doped organic polymers has been highly idealized and constructed in the framework of crude methods, such as Hückel-type models.

Polyacetylene has been the most studied compound, both experimentally and theoretically. A reason for this is that the degenerate ground state that exists in all-*trans* polyacetylene suggests the presence of topological kinks or so-called soliton defects.[10–14] On the basis of the soliton model, many unusual properties have been predicted for all-*trans* polyacetylene, including a conductivity mechanism involving charged solitons that carry no spin.[12,15] However, other polymers, such as polyparaphenylene, do not possess degenerate ground states and are not expected to accommodate solitons; *nevertheless, doped polyparaphenylene displays transport properties which are very similar to doped polyacetylene.*[2]

In this paper we have studied, within a single theoretical framework, all-*trans* polyacetylene, a system where soliton excitations could appear, and polyparaphenylene, which has no degenerate ground state, in order to make a detailed comparison of the changes in electronic and geometric structures that appear upon doping in both systems. The theoretical model we have used is based on the approaches of Pople and Walmsley[10] and of Su, Schrieffer, and Heeger.[12]

Section II is devoted to polyacetylene (PA). We detail the model and apply it to the study of the energetics of separation of pairs of defects induced upon doping. We compute the interactions between pairs of defects and the band-structure evolution for a lattice of polarons and a lattice of charged solitons. Experimental data for optical absorption of radical anions in finite-chain polyenes are discussed.

In Sec. III, we treat polyparaphenylene (PPP). After pointing out the difference in connectivity between PPP and PA, we describe the energetics of separation of defects and optimization of the bond lengths around the defects. Finally, we emphasize some unusual characteristics of doped PPP.

It must be borne in mind that the models we use are based on a simple one-electron theory and neglect correlation effects which can be important. Interchain interactions and explicit presence of the dopant ions are also neglected. Results should therefore be viewed qualitatively with emphasis on trends and internally consistent comparisons.

II. DEFECT STATES IN POLYACETYLENE

In the framework of one-electron models, all-*trans* PA is Peierls distorted in its ground state, single and double carbon–carbon bonds alternating along the chain. As a result, two energetically equivalent resonance forms (hereafter referred to as phase *A* and phase *B*) can be derived and lead to a double-well potential energy curve, as illustrated in Fig. 1. The potential energy (E) can be expressed as a function of the degree of bond-length alternation (Δr):

$$E = a(\Delta r)^4 - b(\Delta r)^2 + c, \quad a,b > 0 . \tag{1}$$

The experimental estimate of Δr is 0.10 ± 0.03 Å,[16] while *ab initio* double-zeta geometry optimization due to Karpfen and Petkov[17] gives $\Delta r = 0.100$ Å with $r_{C=C} = 1.346$ Å and $r_{C-C} = 1.446$ Å. The Peierls distortion opens up a gap at the Fermi level; the optical absorption spectrum of all-*trans* PA shows an edge at 1.4 eV and peaks at about 1.8 eV.[18]

It has been recognized by Su, Schrieffer, and Heeger[12] (SSH) that because the ground state of the dimerized all-*trans* PA chain is twofold degenerate, solitons[19] can be expected, satisfying a wave equation akin to the ϕ^4 field-theory equation.[20] This can be inferred from relation (1). Solitons are excitations of a system leading from one minimum of the potential to another minimum of same energy. In all-*trans* PA, they correspond to topological kinks that extend over several bonds and gradually lead from a phase-*A* chain segment to a phase-*B* chain segment. Displacement from equilibrium of the atomic positions within the soliton have been usually simulated by a hyperbolic tangent function which is solution of the ϕ^4 field-theory equation.

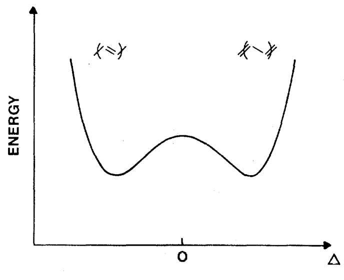


FIG. 1. Sketch of potential energy curve for *trans* polyacetylene showing two energetically equivalent structures.

Note that solitons in PA have peculiar charge-spin relations, since a neutral soliton corresponds to a radical and has spin-$\frac{1}{2}$, while charged solitons carry no spin.[12]

All-*trans* PA appears then unique in having two potential energy minima of the same energy, an indispensable requirement for soliton formation. *Cis* polyacetylene does not possess this characteristic, the *cis*-transoid backbone being slightly more stable than the *trans*-cisoid backbone as suggested by various experiments[21] and by *ab initio* calculations.[22,23]

Study of the energetics of formation of a soliton is usually performed in the context of Hückel theory with σ-bond compressibility. This is true for the SSH adiabatic Hamiltonian as well as for bond-order—bond-length relationships of the Coulson type.[24] In a bond-order—bond-length relationship, which we will use in this paper, the β resonance integral values are expressed as

$$\beta(r)=A\exp(-r/B)\ , \tag{2a}$$

where r is the bond length. The energy of the σ framework is

$$f(r)=C\beta(r)(r-r_0+B)\ , \tag{2b}$$

where A, B, and C are parameters to be optimized, and r_0 usually corresponds to the length of a "pure sp^2-sp^2 single bond" (around 1.50 Å) (Ref. 24) but can also be optimized. We have optimized the parameters in order to reproduce a band gap of 1.4 eV, a total bandwidth of 10 eV and a bond-length alternation of 0.14 Å ($r_{\text{C}-\text{C}}=1.47$ Å; $r_{\text{C}=\text{C}}=1.33$ Å), as in the SSH work.[12] We obtain $A=34.56$ eV, $B=0.531$ Å, and $C=6.78$ Å^{-1}.

With these parameters, we first compute the energy of creation of an isolated soliton defect and compare with previous calculations. We then address the question of the response of the electronic and geometric structure of the chain to the dopant-induced charge-transfer process. For the numerical calculations throughout this paper, we consider mainly the acceptor doping process. However, the discussion and results apply equally well to donor doping. Calculations on polyacetylene are performed on cyclic polyene molecules containing at least 110 carbon atoms—more than enough for the results to be directly compared to the infinite-chain case.

A. Isolated soliton defect

Resonance integral $\beta(r)$ values around the defect are expressed as

$$\beta_{n,n+1}(r)=\beta\Bigg\{1.4+\Bigg[(-1)^n\frac{\Delta r}{2}\times\Bigg[\tanh\frac{n}{l}+\tanh\frac{n+1}{l}\Bigg]\Bigg]\Bigg]\Bigg\}\ , \tag{3}$$

where Δr ($=0.14$ Å) denotes the degree of bond-length alternation far away from the defect, n indicates the site location from the defect, and l is a modulation factor to be optimized and roughly corresponding to the halfwidth of the defect. (We do not use a cutoff procedure such as that used by SSH.[12]) The energy of creation of a soliton excitation is lowest, 0.45 eV, for $l=7$, in excellent agreement with the SSH results. The presence of the soliton introduces a localized electronic state at midgap, i.e., 0.7 eV above the valence-band edge. As a result, the energy of creation of the soliton does not depend on whether the soliton is neutral (state singly occupied), negatively charged (state doubly occupied), or positively charged (state empty). Localization of the electronic state is confirmed by the fact that the total probability density of the radical or charge associated with the soliton is 0.855 over the 15 sites around the defect.

Note that the energy to create a positive isolated soliton defect is 0.25 eV smaller than the 0.7-eV energy required by a vertical ionization process.[12] We also note that ESR experiments on undoped *trans*-PA indicate the presence of about 1 radical (neutral soliton) per 3000 carbon atoms,[25] a ratio much larger than what could be expected on the basis of simple thermodynamics. This implies, as does the fact that this spin concentration shows little temperature dependence, that neutral solitons in undoped *trans*-PA are mainly extrinsic defects created during *cis-trans* isomerization (and trapped with respect to recombination between crosslinks).

B. Interacting defects

We now consider the way the chain can accommodate extra charges created by charge-transfer processes toward acceptor dopants. It is important to recognize that the transfer of an electron from the valence band during the doping creates a polaron, or radical cation on the chain, i.e., a pair of defects and not an isolated defect. (At very low doping levels of course, transfer can also take place from the extrinsic neutral-soliton states, thereby leading to charged solitons on the chain.) It is then relevant to study the energetics of separation of that pair of defects, that can be considered as a soliton-antisoliton pair.

In the region between the two defects, the β values are computed as a function of the product of hyperbolic tangent functions, in the spirit of what has been worked out by Takayama *et al.*[14] as follows:

$$\beta_{n,n+1}(r)=\beta\left[1.4+(-1)^n\frac{\Delta r}{2}\left[\tanh\frac{n}{l}+\tanh\frac{n+1}{l}\right]\left[\tanh\frac{k-n}{1}+\tanh\frac{k-n-1}{l}\right]\right], \tag{4}$$

where k is the number of sites (odd) separating the two defects. Outside that region, $\beta(r)$ values are computed as in relation (3). We have, in addition, made calculations using a difference of tanh functions as is used in Ref. 26 instead of a product as in (4), and find little difference between these and the results using (4).

For the sake of completeness, we have treated the separation of two neutral defects, two positive defects, and a neutral and a positive defect. In every calculation, the value of l has been optimized. Results are presented in Fig. 2. When the two defects are widely separated, we naturally retain the isolated defect results, i.e., the energy of creation of the pair of defects is $2\times(0.45\text{ eV})=0.9$ eV and $l\sim7$.

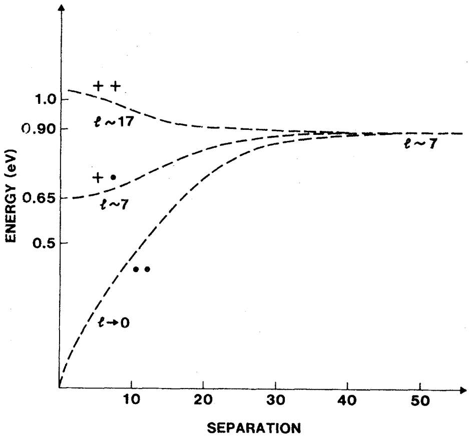


FIG. 2. Energetics of separation of two defects on polyacetylene chain with "··" indicating two radicals (neutral solitons), "+ +" indicating two cations (charged solitons) and "+·" indicating a radical cation (or polaron for small separations). The quantity l defines the extent of the chain deformation due to the defect. The units for the abscissa and l are number of carbon atoms.

1. Separation of two neutral defects

Two neutral defects formed by the breaking of a double bond tend not to separate but to recombine, leaving no deformation ($l\to0$) on the chain.

2. Separation of two positive defects

Two identically charged defects repel each other and lead to two isolated charged solitons. When the two defects are close to each other, the deformation they provoke is strong, extending over 35 bonds ($l\sim17$). When they are widely separated, the corresponding energy is 0.5 eV lower than two vertical ionization processes. Note that Coulomb repulsion is not included in these calculations.

3. Separation of a radical cation (polaron)

We find that the energy is smallest, 0.65 eV, when the two defects are in close proximity, corresponding to the formation of a polaron. Our result that the radical and the ion (i.e., charged and neutral solitons) are attractive is consistent with the trends predicted by Lin-Liu and Maki in the continuum limit for large defect-pair separations.[27] With respect to a vertical ionization process, at 0.7 eV, the polaron binding energy (related to the deformation of the lattice around it) is 0.05 eV. The optimal l value is again about 7, i.e., the deformation is relatively soft, extending over 15 sites for two nearest-neighbor defects. The charge that the polaron carries is also very localized, the 15 sites bearing $0.757e$. The optimal l value (~7) remains the same independent of separation.

It is interesting to note that all these results are fully consistent with the results obtained independently by Bishop *et al.* from a relativistic field-theory approach.[26]

The presence of a polaron introduces two defect levels in the gap, symmetrically placed 0.4 eV above and below the Fermi level rather than both at the Fermi level as for noninteracting defects. This number is in agreement with the purely electronic relaxation energy on electron injection calculated by Su and Schrieffer.[12] For acceptor doping the bonding state is singly occupied and the antibonding state empty. In Fig. 3, we present the difference in band picture going from two isolated defects to two interacting defects. Our results indicate that at low doping levels, the extra charges on the chain form polarons and not charged solitons (except for charge-transfer processes from the few extrinsic neutral soliton defects).

4. *Interactions between polarons*

We now address the question of the interaction between two polarons to understand the evolution when the doping level increases. To study this interaction, we have considered two polarons and located the charged defects at fixed positions, to correspond to the pinning of the plus charges at the positions of the negatively charged dopants. The neutral defects are gradually pulled away from the charged defects, approach each other, and finally recombine leaving two charged solitons (Fig. 4).

For two polarons widely separated [$E \sim 2\times(0.65 \text{ eV}) = 1.3$ eV], that process leads first to the formation of four isolated defects [$E \sim 4\times(0.45 \text{ eV}) = 1.8$ eV], before eventually the recombination of the two radicals leaves only two charged solitons [$E \sim 2\times(0.45 \text{ eV}) = 0.9$ eV]. Thus there is a barrier to recombination as indicated in Fig. 4. At 2.0% (homogeneous) doping level (charges about 50 sites apart), the barrier is still of the order 0.1 eV. The barrier disappears at around 3% doping level (charges about 35 sites apart) and, at 4% doping level, neutral defects readily recombine leading to a lattice of charged solitons.

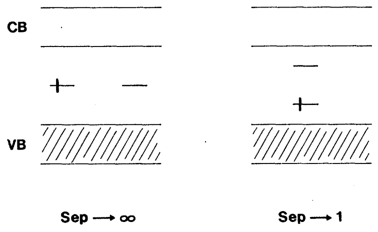


FIG. 3. Interaction of charged and neutral soliton in polyacetylene. States appear at midgap for infinite separation but interact and split as indicated when the separation approaches one bond (polaron formation).

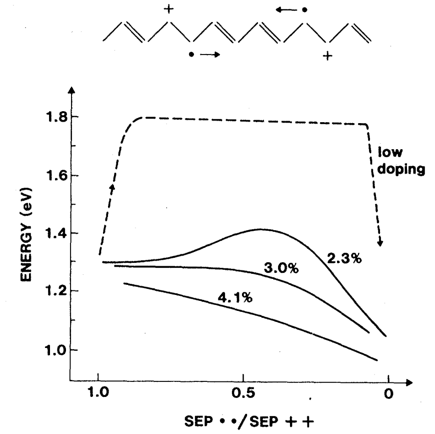


FIG. 4. Interaction between two radical cations (or polarons) in polyacetylene. The horizontal axis is the ratio of the radical separations to the charge separations so that the right extreme of the figure represents the formation of two charged solitions from two polarons. Doping levels as mole per cent are indicated.

Let us consider the evolution of the band structure during the doping process. At low doping levels, we form bonding and antibonding *polaron* states 0.3 eV above the valence band and 0.3 eV below the conduction band. As doping increases, two processes take place: The polaron states form a band [see Fig. 5(a)] and some polarons close to one another will form charged solitons. If the latter process is neglected, the bonding polaron band would merge with the valence band at ~5% doping (and the antibonding polaron band will merge with the conduction band at ~5%). At ~10% doping the gap would disappear. However, the formation of charged solitons intervenes and we shift gradually from a polaron lattice [Fig. 5(a)] to a charged-soliton lattice [Fig. 5(b)]. Note that polarons and charged solitons should coexist until a doping level of 3−4%. The charged soliton states at midgap form a band that may be responsible for the conduction mechanism *without spin* occurring just above the semiconductor-metal (SM) transition (which occurs experimentally at ~1% doping[15]). In our model, the soliton band merges with the valence band at ~10% doping so that carriers with spin can contribute to the conductivity. This is in agreement with the delayed appearance of signifi-

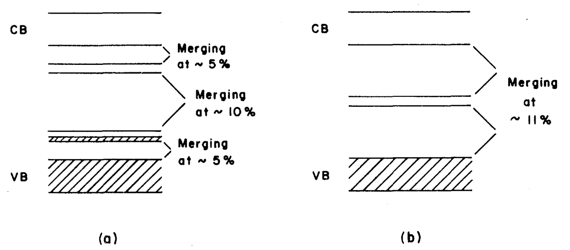


FIG. 5. Band-structure scheme at intermediate doping for a lattice of polarons (a) and a lattice of charged solitons (b). At higher doping levels, bands in the gap broaden and this leads in our model for case (a) to the merging of the bonding (antibonding) band with the valence (conduction) band at ~5% doping level while the bonding and antibonding bands merge at ~10% doping. For case (b), the soliton band merges with the valence and conduction bands at ~11% doping, in agreement with Mele and Rice calculations (Ref. 44). Following these authors, inclusion of interchain coupling could reduce the doping level where merging occurs to below 5% where it is observed experimentally.

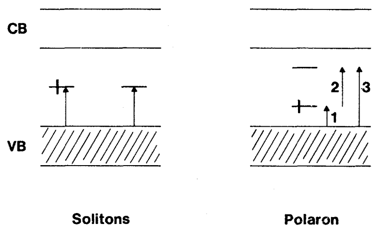


FIG. 6. Schematic representation of doping-induced optical transition in polyacetylene for solitons and polarons.

cant Pauli susceptibility above the SM transition. At very high doping levels, our *ab initio* Hartree-Fock calculations on Li-doped polyacetylene[28] show that bond-length alternation is completely depressed, solitons are no longer present, and conductivity is due to the closure of the Peierls gap.[28,29]

The midgap absorption which appears at about 0.7 eV when polyacetylene is doped[30,31] has been taken as evidence for the generation of solitons on doping. Since our model shows that the formation of polarons is energetically favored over solitons at low doping levels, the question arises as to whether or not polarons are responsible for, or contribute to, the observed midgap absorption. A polaron in polyacetylene introduces three new transitions as depicted in Fig. 6. Table I gives our calculated energies for these transitions (normalized by the energy gap) for radical-ion separations of 1, 3, 5, and 7 bonds. Note that the average absorption energy expected with the polaron model is also about midgap.

We now consider charged-defect absorption observed in model compounds for polyacetylene. We choose the diphenylpolyenes (DPP), $C_6H_5(HC{=}CH)_nC_6H_5$, since there are rather extensive data[32] available for these molecules and their ions with $n=1-6$. Because we are interested in the extrapolation of oligomer data to the polymer, we must appropriately "correct" the DPP data to take into account the fact that the phenyl groups (C_6H_5) effectively extend the conjugation length beyond the polyene sequence. We accomplish this correction by defining an effective conjugation length, $n_{\text{eff}}=n+\nu$, such that the absorption energy of DPP with n double bonds is equal to that of a polyene with $n+\nu$ double bonds.[33] The absorption energies are plotted versus $1/n_{\text{eff}}$, which according to theory and experiment should yield a roughly linear relationship.[34] Results are shown in Fig. 7. We find $\nu=2.7$; in other words, stilbene ($n=1$) absorbs at about the same energy as octatetrene ($n+\nu\approx 4$). The extrapolation to $n_{\text{eff}}=\infty$ yields $E_g=1.8$ eV, in good agreement with experiment.[30]

We also show in Fig. 7 the transition energies for radical anions as obtained by Hoijtink and van der Meij.[32] The data are roughly linear with $1/n_{\text{eff}}$ and extrapolate to 0.5, 0.8, and 1.0 eV. These data, after normalizing by the 1.8-eV band gap, are compared to theory in Table I. These radical anions correspond to negatively charged polarons, i.e., to donor

TABLE I. Energies (E_d), defect level position (ϵ_d), and transition energies for charged defects in polyacetylene. The transition energies (E_1, E_2, and E_3) are normalized by the band-gap energy for comparison to experiment.

Separation	E_d (eV)	ϵ_d (eV)	E_1	E_2	E_3
1	0.652	±0.434	0.20	0.62	0.81
3	0.656	±0.395	0.23	0.56	0.79
5	0.667	±0.357	0.25	0.50	0.75
7	0.680	±0.318	0.28	0.45	0.73
Experiment	· · ·	· · ·	0.30	0.44	0.55

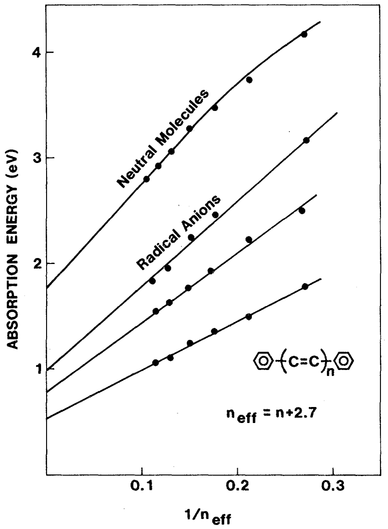


FIG. 7. Optical absorption energy vs the reciprocal of the "effective" number of double bonds for diphenyl polyenes (neutral molecules and radical anions). The solid line through the neutral molecule data represents data for polyenes (with extrapolation) taken from the literature (Ref. 33).

doping of polyacetylene for which a broad (~1-eV wide) transition centered at about 0.7 eV has been observed.[31] Thus the extrapolated radical anion adsorption data are completely consistent with the experimental observations for donor-doped polyacetylene. We may conclude that polaron absorption offers a satisfactory explanation for the midgap absorption in doped polyacetylene and that the soliton explanation is nonunique.

III. DEFECT STATES IN POLYPARAPHENYLENE

Polyparaphenylene consists of benzene rings linked in the para position. Crystallographic data on oligomers[35] indicate that carbon—carbon bond lengths within the rings are about 1.40 Å, and those between the rings are about 1.50 Å. In the solid state, two successive benzene rings are tilted with respect to each other by about 23°. This torsion angle constitutes a compromise between the effect of conjugation and crystal-packing energy, which favor a planar structure, and the steric repulsion between orthohydrogen atoms, which favors a nonplanar structure. The band gap in PPP is about[2] 3.5 eV or about twice that of PA. A resonance form can be derived for PPP that corresponds to a quinoid structure; however, contrary to all-*trans* PA, the benzenoid and quinoid forms are not energetically equivalent, the quinoid structure being substantially higher in energy (Fig. 8).

When we discuss defects in PPP, it is important to recognize that connectivity in PPP makes it very different from *trans*- and *cis*-PA, even at the lowest-order level (Hückel theory). This is demonstrated when we address the possibility of any midgap ($\epsilon=0$) state in PPP, by considering the defect displayed in Fig. 9. As detailed in the Appendix, we find that for physical values of the resonance integrals, a midgap $\epsilon=0$ state as in *trans*- or *cis*-PA, is not possible in PPP. A very important result is that in PPP defects will always be strongly interacting and correlated in pairs; thus a soliton-antisoliton pair will be confined. Also contributing to this confinement is (also true by analogy in *cis*-PA and polydiacetylene) that the more two defects separate, the more rings with quinoid structure of higher energy appear between the two defects. Thus there will be a compromise between the strength and the extension of the relaxation of the lattice due to the presence of defects.

Calculations on PPP are performed on 21 ring chains (126 carbon atoms) in the framework of Hückel theory using a bond-order—bond-length relationship of the Coulson type. Parameters A, B, and C from relations (2) are optimized in order to reproduce in the absence of any defect: (i) the experimental geometry of the benzenoid structure, (ii) the band gap of 3.5 eV, and (iii) the bandwidth of the highest occupied π orbital of the order of 3.2 eV.[9,36] Note that this procedure parallels that used for polyacetylene though the parameters need not be the same. Under these conditions, parameters A, B, and C are, respectively, 46.0 eV, 0.531 Å, and 4.30 Å^{-1}. With this choice of parameters, the total energy difference per ring between the benzenoid structure and a "pure" quinoid structure, where $r_{C=C}=1.38$ Å and $r_{C-C}=1.45$ Å, is 7.2 kcal/mol (0.31 eV), in good agreement with the extended-

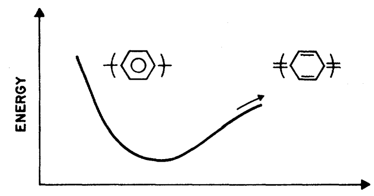


FIG. 8. Sketch of potential energy curve for polyparaphenylene showing energetically inequivalent structures.

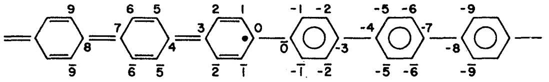
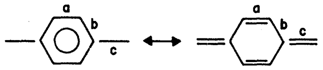


FIG. 9. Sketch of the defect considered when searching for a localized midgap state in polyparaphenylene.

Hückel-theory estimate of Whangbo *et al.*[37]

The model we have chosen to deal with pairs of defects derives directly from what we used for polyacetylene and is consistent with crystallographic data on biphenyl and biphenyl anions.[38] These data indicate that the changes in the geometry in forming the (−1) biphenyl anion are in the direction provided by an increased admixture of the quinoidal resonance form:



The bonds parallel to the chain direction (bonds *a* and *c*) shorten and bonds inclined to that direction elongate. While bonds *a* and *b* are nearly equal in the neutral species ($a=b\cong 1.40$ Å), these bonds differ by about 0.05 Å in the anion ($a\cong 1.38$ Å and $b\cong 1.43$ Å). Bonds *b* and *c*, which in the neutral species differ by about the same amount (0.10 Å) as do adjacent bonds in polyacetylene, become nearly equal in the anion ($c\sim 1.44$ Å).

In our model, we consider that the deformation toward the quinoid structure is maximum in the middle of the defect pair and gradually decreases toward the edge of the defect to lead back to the benzenoid structure (Fig. 10). Such a behavior can be simulated by a product of hyperbolic tangent functions, as in the case of interacting solitons in *trans*-PA. The resonance integral values for the three types of bonds within the defect are expressed as

$$\beta^a_{n,n+1}(r)=\beta\left[1.40-\alpha\left[\tanh\frac{n}{l}\tanh\frac{4N-n}{l}\right]\right], \tag{5a}$$

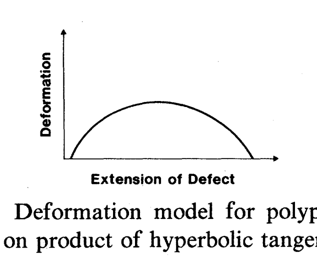


FIG. 10. Deformation model for polyparaphenylene chain based on product of hyperbolic tangent functions.

$$\beta^b_{n,n+1}(\sigma)=\beta\left[1.40+\alpha\left[\tanh\frac{n}{l}\tanh\frac{4N-n}{l}\right]\right], \tag{5b}$$

$$\beta^c_{n,n+1}(r)=\beta\left[1.50-2\alpha\left[\tanh\frac{n}{l}\tanh\frac{4N-n}{l}\right]\right]. \tag{5c}$$

In these expressions, N indicates the number of rings over which the defect extends, n is the site location from one end of the defect ($4N-n$ is then the separation from the other end), l modulates the amplitude of the deformation (note that the larger the value of l, the smaller the deformation), and α denotes the maximum bond-length difference with respect to the original bond lengths. In agreement with the crystallographic data on biphenyl anions,[38] bond *c* is allowed to vary twice as much as bonds *a* and *b*. Optimization of the value of α has led to the choice $\alpha=0.05$ Å. The optimization of the energy for a pair of defects depends on two factors: the number of rings N over which the defect extends and the value of l.

Results for the same three different pairs of defects as studied in PA are presented in Fig. 11 and discussed below.

A. Two neutral defects

In this case, the minimum of energy is obtained for values of l tending to infinity, i.e., there is no deformation left on the chain, the two radicals recombine.

B. Radical cation (polaron)

For a charged defect interacting with a neutral defect, a polaron is formed whose binding energy is of the order of 0.03 eV (to be compared with 0.05 eV in the case of *trans*-PA). The extension of the defect is over about five rings. The deformation of the lattice associated with the polaron is relatively soft ($l=13$ for $N=5$); in the middle of the defect where deformation is largest, the bonds within the ring change by some 0.025 Å, between the rings by 0.05 Å. These changes are fully consistent with the ones observed in the biphenyl anions.[38]

It should be stressed that the relative flatness of the energy curves in Fig. 11 comes from the fact that for each value of N, the l value adjusts in such

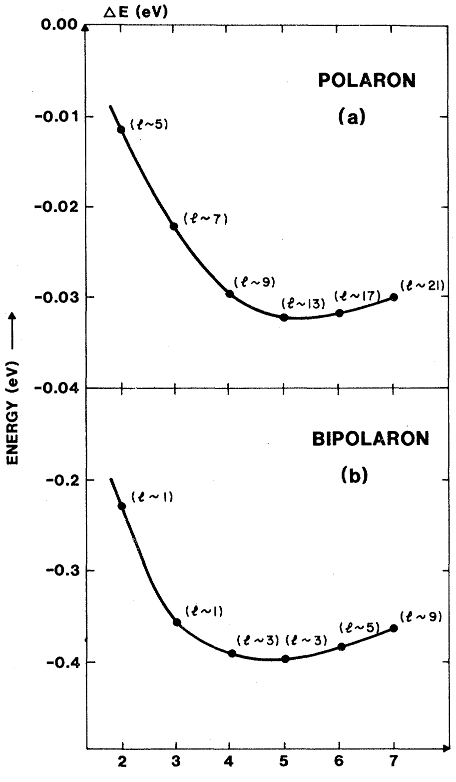


FIG. 11. Energy gain with respect to vertical ionization processes obtained in polyparaphenylene through the formation of a polaron for a singly charged defect (a) and of a bipolaron for a doubly charged defect (b), as a function of the extension of the defect, in number of rings N. For each N value, the optimal l value is shown in parentheses.

a way that the maximal deformation in the middle of the defect is always of the same order. If, for a given N value, the maximal deformation is varied around its optimal value, the energy rises more sharply.

The presence of the polaron introduces two states, bonding and antibonding, in the gap. The bonding state, half-occupied for a radical cation, is 0.2 eV above the top of the valence band. The charge is localized; its probability density over the five rings of the defect is 0.791.

C. Two positively charged defects

Contrary to what happens in *trans*-PA where the two charged defects separate, we observe in PPP the formation of a bipolaron (or correlated charged-soliton—charged-antisoliton pair), Fig. 12. The extension of the bipolaron is of the same order ($N=5$) as that of the polaron, but the deformation is much stronger, about twice as large as for the polaron. The gain in total energy with respect to two vertical ionizations is of the order of 0.4 eV, to be compared with 0.5 eV in the case of two charged solitons in *trans*-PA.

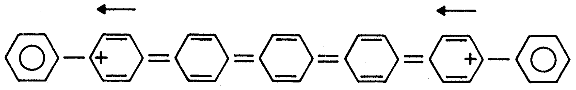


FIG. 12. Bipolaron on polyparaphenylene chain.

Considering explicitly neither Coulomb repulsion nor screening due to the counter ions, the formation of a bipolaron is much preferred over the formation of two polarons (the 0.4-eV energy gain of a bipolaron with respect to two vertical ionizations is to be compared with 2×0.03 eV for two polarons). This can be understood by the fact that the stronger deformation that exists in the bipolaron case pushes up the bonding state in the gap 0.56 eV above the valence band, thereby making the ionization process easier. The charges of the bipolaron are also very localized, being located at 90.6% within the five rings.

Note that as in the case of charged solitons in *trans*-PA, the bipolaron carries no spin and the bonding state it induces in the gap is empty. As the doping level increases, interactions between bipolarons could broaden the bipolaron states in the gap and lead to the formation of a band. Conductivity could arise from the motion of bipolarons carrying no spin. This picture is consistent with recent magnetic data,[39] which indicates a very low Pauli susceptibility in the metallic regime of SbF_5-doped PPP.

The fascinating possibility of formation of bipolarons in doped PPP, whose interest is further increased by the work on bipolaronic superconductivity,[40] calls for more attention to be given to the study of the electronic properties of PPP upon doping. Unfortunately, detailed experimental analyses have so far been hindered by the inhomogeneous character of the doping process in PPP and the impossibility to have precise control of the doping levels. Note that in *cis*-PA, where the same kind of behavior as in PPP could be expected, isomerization takes place upon doping, leading to the *trans* form.

IV. CONCLUSIONS

By model calculations on the defect states induced upon doping in all-*trans* polyacetylene and polyparaphenylene, we have given a picture of the evolution of the electronic properties of both systems upon doping and have shown that, despite the presence in all-*trans* PA of a degenerate ground state which is absent in PPP, PA and PPP are much more similar than generally thought. At low doping levels, polaron formation is expected for both PA and PPP with similar polaron binding energies and defect extensions. At higher doping levels, polarons interact to produce uncorrelated charged solitons in PA and bipolarons or correlated charged-soliton–charged-antisoliton pairs in PPP. As neither charged solitons nor bipolarons carry spin, this is consistent with the absence of significant Pauli susceptibility observed in both systems at doping levels just above the transition to high conductivities (or "semiconductor-to-metal" transition).

We have demonstrated that the response of the atomic geometry to electron excitation processes, i.e., the electron-phonon coupling that we and others have previously emphasized,[8–12,28] plays a fundamental role in the conductivity mechanism of doped organic polymers. This is valid even in the case of the macroscopic SM transition suggested to be due to the percolation threshold of metallic grains.[41]

Finally, we believe more attention should be given to PPP and analogous systems in order to verify the presence of bipolarons and of a conduction mechanism based on them. This is especially significant since it has been recently pointed out that bipolarons, formed by strong electron-phonon interaction can be considered as localized spatially nonoverlapping Cooper pairs and can have, under certain conditions, superconducting properties.[40]

Our results[42] on polyacetylene are in excellent agreement with the field-theoretic results of Bishop and co-workers.[26] Our results on polyparaphenylene, which have not been treated by a continuum field-theoretic model, show that, even in the case of nondegenerate ground states, results qualitatively similar to degenerate-ground-state systems can be obtained when polaron and bipolaron states are considered.

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APPENDIX

We are searching for the condition of appearance of a localized midgap $\epsilon=0$ state in PPP, in the framework of a Hückel Hamiltonian. We consider the defect displayed in Fig. 9 with resonance integral β_1 corresponding to a "long" bond, β_2 to a "short" bond, and β to a "benzene" bond. To the left of the defect, we obtain the following set of equations:

$$\begin{aligned}
EC_0&=C_1\beta_1+C_{\bar{1}}\beta_1+C_{\bar{0}}\beta_1\ ,\\
EC_1&=C_2\beta_2+C_0\beta_1\ ,\\
EC_{\bar{1}}&=C_{\bar{2}}\beta_2+C_0\beta_1\ ,\\
EC_2&=C_1\beta_2+C_3\beta_1\ ,\\
EC_{\bar{2}}&=C_{\bar{1}}\beta_2+C_3\beta_1\\
EC_3&=C_2\beta_1+C_{\bar{2}}\beta_1+C_4\beta_2\ .
\end{aligned}\tag{A1}$$

Imposing $\epsilon=0$ results for a nontrivial solution in all coefficients on odd numbered sites being zero, we get the following relations:

$$\begin{aligned}
C_2&=C_{\bar{2}}=-\beta_1C_0/\beta_2\ ,\\
C_4&=-2\beta_1C_2/\beta_2=2\beta_1^2C_0/\beta_2^2\ ,\\
C_6&=-2\beta_1^3C_0/\beta_2^3\ ,\\
C_8&=4\beta_1^4C_0/\beta_2^4,\\
&\vdots
\end{aligned}$$

or (A2)

$$\begin{aligned}
C_{4n}&=(2\beta_1^2/\beta_2^2)^nC_0\ ,\\
C_{4n+2}&=-2^n(\beta_1/\beta_2)^{2n+1}C_0\ .
\end{aligned}$$

In order to have a localized state, we need

$$2\beta_1^2/\beta_2^2<1 \quad \text{or } \sqrt{2}\beta_1<\beta_2\ .$$

With the short bond taken as 1.35 Å, this implies in our parametrization the long bond should be larger than 1.53 Å (i.e., a C–C bond as in alkanes) or, in Coulson-Golobiewski parametrization,[43] larger than 1.48 Å. This means a very strong quinoid structure of high energy.

Furthermore, it is relevant to consider that the short bonds between the rings are actually longer than the short bonds within the rings. With the introduction for the former of a resonance integral $\beta_3 < \beta_2$, the condition for a localized state becomes

$$\sqrt{2}\beta_1 < \sqrt{\beta_2\beta_3} \ ,$$

thus rendering the condition even more difficult to fulfill.

To the right of the defect, the same process leads to the relations

$$C_{-1} = C_{-\bar{1}} = -\beta_1 C_0/\beta \ ,$$

$$C_{-3} = \beta_1 C_0/\beta \ ,$$

$$C_{-5} = -\beta_1^2 C_0/2\beta^2 \ ,$$

$$C_{-7} = \beta_1^2 C_0/2\beta^2 \ ,$$

$$C_{-9} = -\beta_1^3 C_0/4\beta^3 ,$$

$$\vdots$$

or

$$C_{-(4n+1)} = -\frac{1}{2^n}(\beta_1/\beta)^{n+1} C_0 \ .$$

This constitutes an exponential decrease of the coefficients to the right of the defect.

From the search for a localized state in PPP, we conclude that the $\epsilon = 0$ state does not occur for physical values of the parameters. It only appears if the rings to the left of the defect in Fig. 9 are extremely quinoid, a situation which is energetically highly unfavorable.

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[1] H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, J. Chem. Soc. Chem. Commun. 1977, 578.

[2] L. W. Schacklette, R. R. Chance, D. M. Ivory, G. G. Miller, and R. H. Baughman, Synth. Met. 1, 307 (1979).

[3] K. K. Kanazawa, A. F. Diaz, R. H. Geiss, W. D. Gill, J. F. Kwak, J. A. Logan, J. F. Rabolt, and G. B. Street, J. Chem. Soc. Chem. Commun. 1979, 854.

[4] J. F. Rabolt, T. C. Clarke, K. K. Kanazawa, J. R. Reynolds, and G. B. Street, J. Chem. Soc. Chem. Commun. 1980, 347.

[5] R. R. Chance, L. W. Shacklette, G. G. Miller, D. M. Ivory, J. M. Sowa, R. L. Elsenbaumer, and R. H. Baughman, J. Chem. Soc. Chem. Commun. 1980, 348; L. W. Shacklette, R. L. Elsenbaumer, R. R. Chance, H. Eckhardt, J. E. Frommer, and R. H. Baughman, J. Chem. Phys. 75, 1919 (1981).

[6] D. McInnes, M. A. Druy, P. J. Nigrey, D. P. Nairns, A. G. MacDiarmid, and A. J. Heeger, J. Chem. Soc. Chem. Commun. 1981, 317.

[7] L. W. Shacklette, R. L. Elsenbaumer, J. M. Sowa, R. R. Chance, D. Ivory, G. Miller, and R. H. Baughman, J. Chem. Soc. Chem. Commun. 1982, 361.

[8] C. B. Duke, in *Extended Linear Chain Compounds,* edited by J. S. Miller (Plenum, New York, 1981).

[9] J. L. Brédas, R. R. Chance, R. H. Baughman, and R. Silbey, Int. J. Quantum Chem. S15, 231 (1981).

[10] J. A. Pople and S. H. Walmsley, Mol. Phys. 5, 15 (1962).

[11] M. J. Rice, Phys. Lett. 71A, 152 (1979); M. J. Rice and J. Timonen, *ibid.* 73A, 368 (1979).

[12] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. 42, 1698 (1979); Phys. Rev. B 22, 2209 (1980); W. P. Su and J. R. Schrieffer, Proc. Natl. Acad. Sci. U.S.A. 77, 5626 (1980).

[13] S. A. Brazovskii, Zh. Eksp. Teor. Fiz. 78, 677 (1980). [Sov. Phys.—JETP 51, 342 (1980)].

[14] H. Takayama, Y. R. Lin-Liu, and K. Maki, Phys. Rev. B 21, 2388 (1980).

[15] S. Ikehata, J. Kaufer, T. Woerner, A. Pron, M. A. Druy, A. Sivak, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. Lett. 45, 1123 (1980).

[16] C. R. Fincher, C. E. Chen, A. J. Heeger, A. G. MacDiarmid, and J. B. Hastings, Phys. Rev. Lett. 48, 100 (1982).

[17] A. Karpfen and J. Petkov, Theor. Chim. Acta 53, 65 (1979).

[18] C. R. Fincher, D. L. Peebles, A. J. Heeger, M. A. Druy, Y. Matsumura, A. G. MacDiarmid, H. Shirakawa, and S. Ikeda, Solid State Commun. 27, 489 (1978).

[19] *Solitons in Condensed Matter Physics,* edited by A. R. Bishop and T. Schneider (Springer, Berlin, 1978).

[20] J. A. Krumhansl and J. R. Schrieffer, Phys. Rev. B 11, 3535 (1976).

[21] T. Ito, H. Shirakawa, and S. Ikeda, J. Polym. Sci. Polym. Chem. Ed. 13, 1943 (1975).

[22] A. Karpfen and R. Holler, Solid State Commun. 37, 179 (1981).

[23] J. L. Brédas, J. M. Andre, and J. Delhalle, J. Mol. Struct. 87, 237 (1982).

[24] C. A. Coulson, Proc. R. Soc. London Ser. A 207, 91 (1951); L. Salem, *The Molecular Orbital Theory of Conjugated Systems* (Benjamin, New York, 1966), Chap. 3.

[25] I. B. Goldberg, H. R. Crowe, P. R. Newman, A. J. Heegar, and A. G. MacDiarmid, J. Chem. Phys. 70, 1132 (1979).

[26] A. R. Bishop, D. K. Campbell, and K. Fesser, Mol. Cryst. Liq. Cryst. 77, 253 (1981); D. K. Campbell and A. R. Bishop, Nucl. Phys. B 200, 297 (1982).

[27] Y. R. Lin-Liu and K. Maki, Phys. Rev. B 22, 5754 (1980).

[28] J. L. Brédas, R. R. Chance, and R. Silbey, J. Phys. Chem. 85, 756 (1981).

[29] J. J. Ritsko, Phys. Rev. Lett. 46, 849 (1981).

[30] C. R. Fincher, Jr., M. Ozaki, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. B 19, 4140 (1979); N.

Suzuki, M. Ozaki, S. Etemad, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. Lett. 45, 1209 (1980).

[31] T.-C. Chung, A. Feldblum, A. J. Heeger, and A. G. MacDiarmid, J. Chem. Phys. 74, 5504 (1981).

[32] G. J. Hoijtink and P. H. van der Meij, Phys. Chem. Neue Folge 20, 1 (1959).

[33] R. H. Baughman and R. R. Chance, J. Polym. Sci. Polym. Phys. Ed. 14, 2037 (1976), and references therein.

[34] See, for example, D. Yarkony and R. Silbey, Chem. Phys. 20, 183 (1977).

[35] Y. Delugeard, J. Desuche, and J. L. Baudour, Acta Crystallogr. Sect. B 32, 702 (1976),

[36] J. L. Brédas, R. R. Chance, R. H. Baughman, and R. Silbey, J. Chem. Phys. 76, 3673 (1982).

[37] M. H. Whangbo, R. Hoffmann, and R. B. Woodward, Proc. R. Soc. London Ser. A 366, 23 (1979).

[38] J. H. Noordik, J. Schreurs, R. O. Gould, J. J. Mooij, and J. H. Noordik, Pure Appl. Chem. 51, 73 (1979), and references therein.

[39] M. Peo, S. Roth, K. Dransfeld, B. Tieke, H. Gross, A. Grupp, and H. Sixl, Solid State Commun. 35, 119 (1980).

[40] A. Alexandrov and J. Ranninger, Phys. Rev. B 24, 1164 (1981).

[41] Y. Tomkiewicz, T. D. Schultz, H. B. Brom, T. C. Clarke, and G. B. Street, Phys. Rev. Lett. 43, 1532 (1979); Y. Tomkiewicz, T. D. Schultz, H. B. Brom, A. R. Taranko, T. C. Clarke, and G. B. Street, Phys. Rev. B 24, 4348 (1981).

[42] J. L. Brédas, R. R. Chance, and R. Silbey, Mol. Cryst. Liq. Cryst. 77, 319 (1981).

[43] C. A. Coulson and A. Golobiewski, Proc. Phys. Soc. London 78, 1310 (1969).

[44] E. J. Mele and M. J. Rice, Phys. Rev. B 23, 5397 (1981).