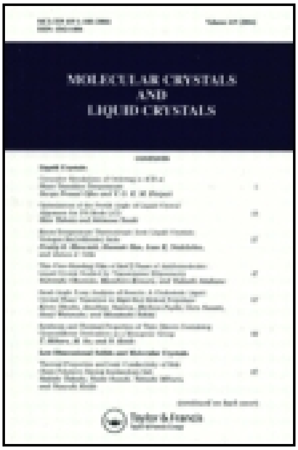

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BIPOLARONS IN DOPED CONJUGATED POLYMERS: A CRITICAL COMPARISON BETWEEN THEORETICAL RESULTS AND EXPERIMENTAL DATA

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Abstract Adopting a language common to both physicists and chemists, we discuss the origin of formation of radical-ions (polarons) and diions (bipolarons) upon doping of conjugated polymers with a nondegenerate ground state. We present a review of some of the calculations we have devoted to the influence of doping on the geometric and electronic properties of the polymer chains. We critically compare the theoretical results with experimental data, such as the evolution of the optical and magnetic properties upon doping. The bipolaron model is shown to provide a coherent and unified picture of the properties of doped conducting polymers.

We point out the relationship between bandgap and bondlength alternation in polymers based on aromatic rings. We demonstrate it is very different from that found in polyacetylene-like compounds and comment on the possibility of obtaining small bandgap conjugated polymers.

I. INTRODUCTION

Until recently, trans-polyacetylene (PA) has been the focus of most work in the conducting polymer area. This was mainly because trans-PA is unique in possessing a degenerate ground state (i.e., two geometric structures corresponding exactly to the same total energy) and can therefore support topological soliton excitations. Increasing interest is, however, currently devoted to other polymers which represent the vast class of compounds having a unique ground-state geometry. Among these systems, polypyrrole (PPy), polythiophene (PT), polyparaphenylene (PPP), and derivatives appear especially interesting. This paper is aimed at: (i) providing a detailed understanding of the bipolaron model that has been proposed a few years ago for doped conjugated polymers with a nondegenerate ground state;[1-3] and (ii) demonstrating that the bipolaron model leads to a coherent and unified picture for the electronic and transport properties of all doped conjugated polymers.

In section II, we discuss in very simple terms the origin of formation of localized charged defects such as polarons and bipolarons (respectively, radical-ions and diions associated with a local geometry relaxation). We also point out the factors that usually cause a bipolaron to be energetically more favorable than two polarons. Section III is devoted to a critical comparison of the theoretical results we have obtained for polymers with a nondegenerate ground state with experimental data which have been recently collected. In section IV, we examine the evolution of the bandgap in polymers based on aromatic rings, as a function of increasing quinoid character.

II. ORIGIN OF THE FORMATION OF POLARONS AND BIPOLARONS UPON DOPING OF CONJUGATED POLYMERS

When conjugated polymers are doped, it is well established that charge transfer takes place between the polymer chains and the dopants. As a result, the chains become ionized. In organic *molecules*, it is known that the equilibrium geometry in the ionized state is usually different from that in the ground state. For instance, the molecule of biphenyl has a benzenoid-like geometry in the ground state but becomes quinoid-like in the ionized state. The energies involved in the ionization process of a molecule are schematically depicted in Figure 1. A vertical, Franck-Condon-like ionization process costs an energy E_0. If a geometry relaxation occurs in the ionized state, an energy E_3 is gained back. Conceptually, going from the ground state to the relaxed ionized state can also be thought of in the following way. We first distort the geometry of the molecule *in the ground state* in such a way that the molecule adopts its optimal geometry of the ionized state. This costs an elastic (distortion) energy E_1 and provokes an upward shift $\Delta\epsilon$ of the HOMO one-electron energy level and a downward shift of the LUMO. Then we proceed to the ionization which now requires an energy E_2.

From Figure 1, we can observe that it is energetically favorable to have a geometry relaxation in the ionized state when the quantity E_0-E_2 (= $\Delta\epsilon$) is larger than E_1; or, in other words, when the gain in ionization energy upon distortion is larger than the elastic energy required to make the distortion.

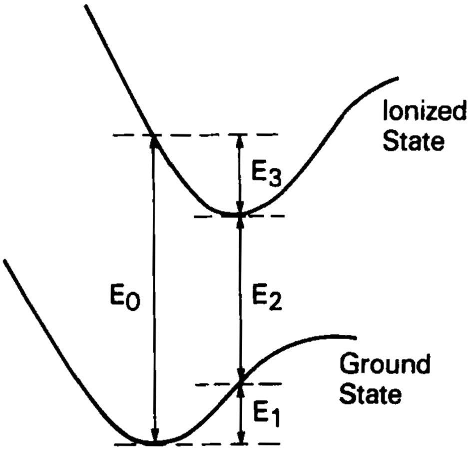

FIGURE 1 Illustration of the energies involved in an ionization process.

In *polymer chains*, a vertical ionization process results in creating a hole (putting an electron) on top of the valence band, VB (in the bottom of the conduction band, CB). In this case, three remarks can be made: (i) the charge is completely delocalized over the whole chain; (ii) no lattice distortion (geometry relaxation) takes place; and (iii) there is appearance of a metallic character.

However, it can be energetically favorable to localize the charge that appears on the chain and to have, around the charge, a local distortion of the lattice. This process provokes the appearance of *localized* electronic states in the gap due to a local upward shift $\Delta\varepsilon$ (downward shift) of the HOMO (LUMO) level. Considering *the removal of an electron from the chain, we gain an energy $\Delta\varepsilon$ in ionization* energy. If $\Delta\varepsilon$ is larger than E_1, the energy required to distort the lattice locally around the charge, this charge localization process is favorable and we obtain the formation of a polaron. The polaron is nothing but a radical-ion (spin 1/2) associated with a lattice distortion and localized electronic states in the gap.

The quantity $\Delta\varepsilon - E_1$ ($= E_3$) corresponds to the polaron binding energy. Calculations have shown that the polaron binding energy is of the order of 0.05 eV in trans-PA,[1,3] 0.03 eV in PPP,[1] and 0.12 eV in PPy.[4] It must be emphasized that in the case of polaron formation, the VB remains full and the CB remains empty; there is no appearance of metallic character (see Figure 2).

The next step is to investigate whether, when two charges are present on a polymer chain, it is more favorable to have the charges separated (i.e. two polarons) or coupled to form a bipolaron. A bipolaron is defined as a pair of like charges (diion) associated with a strong local lattice distortion. (The bipolaron can be thought of as analogous to the Cooper pair in the BCS theory of superconductivity, which consists of two electrons coupled through a lattice vibration, a phonon).

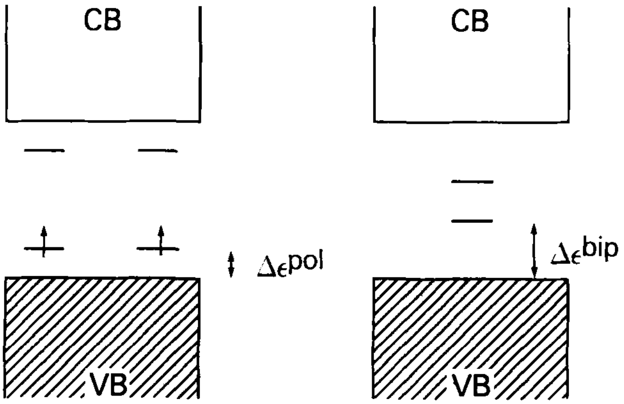

FIGURE 2 Typical electronic structure for a positively charged polymer chain having two polarons (left) and one bipolaron (right).

The electronic structure corresponding to the presence of two polarons and one bipolaron is depicted in Figure 2. The lattice relaxation around two charges is stronger than around only one charge; as a result, E_1^{bip} is larger than E_1^{pol} and the electronic states appearing in the gap for a bipolaron are further away from the band edges than for a polaron.

If we compare the creation energy of a bipolaron relative to that of two polarons, our calculations[1,3,4] for PA, PPP, and PPy indicate that the elastic energy E_1 to form one bipolaron is roughly equal to that to form two polarons. On the other hand, *the gain in ionization energy is much more important in the bipolaron case* ($2 \times \Delta\varepsilon^{bip}$) than for two polarons ($2 \times \Delta\varepsilon^{pol}$). This is the reason why one bipolaron is thermodynamically more stable than two polarons despite the Coulomb repulsion between two similar charges (which is however also largely screened by the presence of dopants with opposite charges). The bipolaron binding energy is larger than that of two polarons by about 0.45 eV in PPy[4] and 0.34 eV in PPP.[1]

Note that because trans-PA has a degenerate ground state, two charges on a trans-PA chain can separate to lower the electrostatic repulsion and form two isolated charged solitons[5,6] rather than a bipolaron. Two charged solitons are favored by 0.40 eV with respect to two polarons.[1,2] In this context, trans-PA can be considered not as the prototype of conducting polymers but rather as a special case.

In case of p-(n-)type doping, the bipolaron levels in the gap are empty (fully occupied), see Figure 2. The bipolarons are thus spinless. The presence of bipolarons on polymer chains result in the possibility of two optical transitions below the gap: for p-type doping, from the VB to the lower bipolaron level and from the VB to the upper bipolaron level. The oscillator strength for the lowest energy optical bipolaron transition has been calculated to be much larger than for the highest energy one.[7] When polarons are present, a third absorption is possible below the gap, corresponding to an optical transition between the two polaron levels.

III. BIPOLARONS IN CONJUGATED POLYMERS WITH A NONDEGENERATE GROUND STATE

Systems such as polypyrrole, polythiophene, or polyparaphenylene possess a nondegenerate ground state; this means their ground state corresponds to only one geometric structure, which is aromatic-like. A quinoid-like resonance structure can be envisioned but is higher in energy. *Ab initio* calculations show that the quinoid structure has a lower ionization potential and a higher electron affinity than the aromatic structure. This explains why on doping the chain geometry relaxes locally around the charges towards the quinoid structure. We have performed a theoretical investigation of the evolution of the PPy band structure as a function of doping level, using methods ranging from highly sophisticated *ab initio* techniques[8] to simple Hückel theory with σ compressibility.[4] Since our aim in this paper is to emphasize the qualitative features, we will mainly discuss the Hückel results[4] (that have however been confirmed and extended by the more elaborate calculations[8]).

The Hückel parameters for the PPy calculations have been optimized on the *neutral* PPy chain in order to reproduce the bandgap (3.2 eV),[9] the bandwidth of the highest occupied π band (3.8 eV)[10] and the *ab initio* optimized geometry.[8]

When we take an electron out of the chain, we obtain the formation of a polaron whose associated geometry relaxation extends over about 4 pyrrole rings. The lower (upper) polaron level coming into the gap is 0.49 eV (0.53 eV) away from the VB (CB) edge. The polaron binding energy is 0.12 eV; this constitutes the difference between the 0.49 eV gain in ionization energy and the 0.37 eV $\pi + \sigma$ energy needed to form the geometry changes.

When a second electron is taken out of the chain, the energetically favorable defect is a bipolaron which also extends over 4 rings. The geometry relaxation is stronger than in the polaron case so that the empty bipolaron electronic levels in the gap are ~0.75 eV away from the band edges. The bipolaron binding energy is 0.69 eV meaning that a bipolaron is favored over two polarons by 0.45 (0.69 - 2 x 0.12) eV. This is supported by ESR measurements on oxygen-doped PPy[11]: (i) at low doping, the ESR signal grows, in accord with the fact that polarons with spin 1/2 are formed; (ii) at intermediate doping, the ESR signal saturates and then decreases, consistent with polarons recombining to form spinless bipolarons; (iii) at high doping, no ESR signal is observed although the system is highly conducting, indicating that the charge carriers in that regime are spinless.

We have also performed a band structure calculation for the 33%-doping level usually achieved in the as-grown PPy films. We then have one 4-ring wide bipolaron per six rings. The corresponding band structure is displayed in Figure 3. Two ~0.4 eV wide bipolaron bands are present in the gap. This is in agreement with the fact that spinless bipolarons could become mobile upon application of an electric field and be the spinless charge carriers suggested by the absence of any ESR signal in the highly conducting regime of the as-grown films. Note that the bandgap has widened from 3.2 ev in the neutral state to 3.6 eV in the 33%-doped state. This is due to the fact that the bipolaron states coming in the gap are taken from the VB and CB edges.

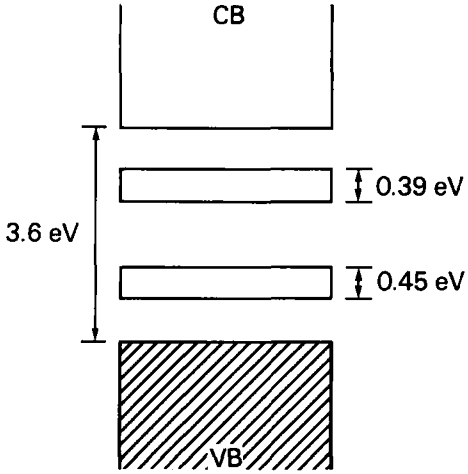

FIGURE 3 Band structure of a 33%-doped polypyrrole chain (after Reference 4).

The whole band structure evolution reproduces very well the evolution upon doping of the optical spectra in ClO_4-doped PPy[4,11] (see Fig.1 in Reference 4) : (i) at low doping, three absorptions are present below the gap at 0.7, 1.4, and 2.1 eV, indicating, as discussed before, the presence of polarons; (ii) at intermediate doping, the 1.4 eV absorption disappears. It also disappears at low doping if one observes its evolution as a function of time;[12] very importantly, in this latter experiment, it has been pointed out that spins are present only as long as the 1.4 eV peak does exist.[12] This is strong experimental evidence that polarons recombine into spinless bipolarons; (iii) at very high doping, two wide optical absorptions peaking at 1.0 and 2.7 eV are present below the gap, in agreement with the existence of two empty bipolaron bands. The bandgap transition has shifted to the blue to 3.6 eV, in excellent agreement with the calculated value.

The bipolaron model for PPy is thus consistent with: (i) the evolution upon doping of the ESR data;[11] (ii) the evolution upon doping[4] or as a function of time[12] of the optical data; (iii) EELS data[13] indicating that the optical transitions in the gap are due to transitions to ~0.5 eV wide electronic bands.

If the bipolaron model is valid for PPy, it should also work for other compounds with a nondegenerate ground state. Recently, measurements of the optical spectra as a function of doping level have been reported for PβDMP,[14] PT,[15,16] and PPP.[17] All these data are consistent with the formation of bipolarons upon doping and in excellent agreement with band structure calculations based on the bipolaron model.[1,8]

IV. RELATIONSHIP BETWEEN BANDGAP AND BONDLENGTH ALTERNATION IN CONJUGATED POLYMERS

The calculations reported in this section have been performed using the Valence Effective Hamiltonian (VEH) technique.[18] We have considered neutral PT, PPy, and PPP chains and varied their geometry from aromatic-like to quinoid-like.

In polyacetylene systems, it is well known within the one-electron model that the smaller the degree of bondlength alternation Δr (i.e. the difference between the length of the long C-C bond and that of the short C-C bond), the smaller the bandgap. The bandgap is expected to vanish if all C-C bondlengths along the chains are equal.

There is a tendency to consider that the same is true for other polymers such as PT, PPy, or PPP, for which one can draw a cis-PA-like path along the chains. Our VEH calculations actually demonstate that the bandgap value *decreases linearly* not as a function of reduced bondlength alternation but *as a function of increasing quinoid character* of the geometry. This is illustrated for PT in Figure 4. The bandgap in PT for the aromatic ground state geometry (Δr = 0.13 Å) is 2.2 eV; it decreases to ~0.15 eV for a strongly quinoid geometry (Δr = -0.07 Å). The bandgap value for the situation where all the C-C bondlengths are equal ($\Delta r \simeq 0$) is of the order of 0.7 eV. Note however that the bandgap does never completely vanish. This is due to the respective symmetries of the highest occupied and lowest unoccupied bands, which prevent them from crossing.[19]

As a result, derivatives where substituents force some quinoid character of the backbone in the ground state will have a smaller bandgap than the parent polymer. This is e.g. the case for polyisothianaphthene, whose bandgap is reported as small as ~1.0 eV [20], i.e. half the polythiophene bandgap.

V. CONCLUSIONS

In summary, we have shown in this paper that: (i) the bipolaron concept in doped conjugated polymers can be very simply understood and is supported by growing experimental evidence indicating that bipolarons play a major role in the electronic and transport properties of conducting polymers; (ii) the bandgap value in systems with an aromatic ground- state geometry decreases as a function of increasing quinoid character.

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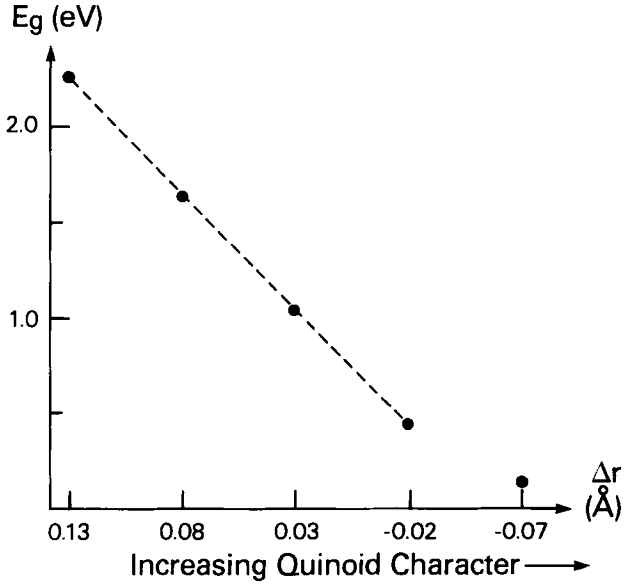

FIGURE 4 Evolution of the bandgap as a function of increasing quinoid character in polythiophene. Abcissa refers to the degree of bondlength alternation between the C-C bonds.

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