Nonlinear Excitations in Pernigraniline, the Oxidized Form of Polyaniline

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The electronic structure of fully oxidized polyaniline, pernigraniline, is investigated in the framework of the Su-Schrieffer-Heeger Hamiltonian, making use of an original renormalization technique. Among the family of polyanilines, pernigraniline is the only form to possess a degenerate ground state. It is shown to accommodate elementary excitations of soliton and polaron types having remarkable properties, in some instances markedly different from those predicted for the so-called *AB* polymer. Nonlinear optical properties of the material are expected to be important.

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Polyanilines have attracted a great deal of attention in the past few years as a new class of organic conducting materials.[1-7] These are polymers of general composition

$$\{(-C_6H_4-NH-C_6H_4-NH)_{1-y}-(-C_6H_4-N{=}C_6H_4{=}N-)_y\}_x .$$

The different polyaniline structures are accessed when one allows for the variation of the relative imine concentration (y), a parameter that also controls the occupied fraction of the valence π band. An important feature of polyanilines is that they are formed by chemically different connecting units: nitrogen atoms (which can be in either amine or imine oxidation state) and carbon rings (which can assume both benzenoid and quinoidlike geometries). This fact has proven to have important implications for the transport properties of polyemeraldine base,[4] the half-oxidized state of polyaniline ($y=0.5$) and its most highly conducting form upon doping.

Theoretical works have been carried out to investigate the electronic structure of the simplest heteroatomic chain, the so-called *AB* polymer. Based on the continuum version of the Su-Schrieffer-Heeger (SSH) Hamiltonian, the properties of the degenerate diatomic chain and its soliton excitations,[8] the polaron solution,[9] the optical absorption spectrum,[10] and the nondegenerate case[11] have been reported. In these models, the physics of the diatomic chain is dominated by two parameters, the electron-phonon coupling (or the dimerization gap) and the difference in site energy between the two units (plus the extrinsic gap for the nondegenerate case[11]). Soliton excitations having fractional charges are predicted for the degenerate *AB* chain[8] and, within a certain range of parameter values, also for the nondegenerate chain.[11] Systems such as polymethineimine, $(-CH{=}N-)_x$,[12] are prototypical of *AB* polymers but unfortunately to date have not been obtained in a well-defined form.

Therefore, in this Letter, we focus on the electronic structure of the fully oxidized polyaniline, polypernigraniline ($y=1$), which has just been synthesized in a pure form.[13] Polypernigraniline, PPN, is the only polyaniline to possess a doubly degenerate ground state. It is thus of high current interest to investigate the way the PPN electronic properties and nonlinear excitations are affected by the difference in electronegativity of the chain units. We find that upon addition or removal of a single electron, polarons are the most stable excitations. Two polarons are, however, unstable towards the formation of a pair of solitons with fractional charges. The intragap optical absorptions arising from these excitations are presented. Implications of the soliton characteristics on the nonlinear optical properties are important.

Ground-state properties and the energetics of defect formation are investigated on the basis of an SSH-type Hamiltonian. The first-neighbor hoppings, $\beta(R)$, and the elastic energy associated to the bonds, $f(R)$, are obtained by the use of bond-order–bond-length relationships of Coulson type.[14] They are written as

$$\beta(R) = -A\exp(-R/B) ,$$

$$f(R) = C\beta(R)(R-R_0+B) .$$

In the above expressions, R is the bond length, A, B, and C are adjustable parameters, and R_0 can be interpreted as the standard single-bond length between sp^2 atoms but can also be optimized. The Green's-function technique is employed to solve the electronic part of the Hamiltonian. This formalism, combined with the use of transfer functions and original renormalization procedures,[15] is very convenient to treat one-dimensional problems in the first-neighbor approximation. Its major advantage is to allow for analytical calculations of the electronic properties, even when localized defects are considered.

A representative set of parameters for PPN was optimized in order to reproduce the valence-effective-Hamiltonian (VEH) band structure[5,16] and the ground-state geometry (for which N−C bonds are 1.30 and 1.41 Å long, benzenoid rings have six equal bonds of 1.407 Å, and quinoidlike rings have four single bonds of 1.46 Å and two double bonds of 1.36 Å[5,7]). Site energies are

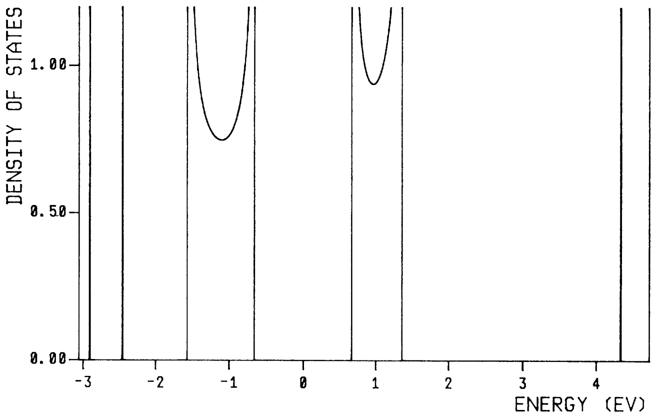

FIG. 1. Polypernigraniline π density of states (arbitrary units). The Fermi level has been shifted to the zero of energies.

fixed in relation to the carbons not connected to nitrogens and are optimized to be -5.5 eV for nitrogens and 1.0 eV for carbons in the para position. Within this choice of parameters, the valence band (VB) and the conduction band (CB) globally extend over 2.9 eV and are separated by a gap of 1.4 eV. The VB originates mostly in the aromatic rings while the major contribution for the CB comes from the N=quinoid=N fragment. These bands are slightly asymmetric with respect to the Fermi level, as can be seen from the density of states displayed in Fig. 1. Note that the Fermi level has been set at the zero of energies. Also shown are the neighboring π bands. We note that the VB and CB appear quite isolated from the rest of the π system. Those neighboring π bands come from molecular levels entirely localized within the rings and are nondispersive. The resulting charge distribution leads to a net charge of $-0.535|e|$ on nitrogens, $+0.948|e|$ on quinoid rings, and $+0.121|e|$ on aromatic rings. These values are in agreement with the fact that phenyl rings tend to adopt a more quinoid structure when they are charged.[17] It is thus a natural consequence of the system geometry that the excess negative charge located on nitrogens mainly come from the quinoid rings.

We searched for an "undimerized" structure and found it to be such that N—C bonds are uniform and 1.355 Å long while the rings adopt a slightly quinoid geometry (four bonds of 1.432 Å and two of 1.390 Å). The ground-state geometry is stabilized by 0.12 eV per two N-ring units relative to the undimerized case. It is notable that, contrary to the behavior of an idealized *AB* chain,[8] the undistorted phase is in the present case obtained to be metallic, a result of the flexibility in the phenyl ring structures.

An infinite PPN chain is calculated to support two kinds of soliton distortions. In both cases, the center of the distortion corresponds to a nitrogen atom. The solitons have the following characteristics: (i) The type-1 soliton has rings around the defect center which possess an aromatic geometry; it introduces a localized state 0.11 eV below the Fermi level. The corresponding wave function is symmetric, having a maximum at the central nitrogen; this state is formed by 74% of a state coming from the VB and 26% of a state from the CB. (ii) In the type-2 soliton, the rings around the defect center have a quinoid structure. The associated electronic localized level appears 0.06 eV above the Fermi level, with an antisymmetric wave function that has a node at the central nitrogen; it has contributions from the VB and CB that exactly compensate those of the type-1 soliton. The optimized soliton geometries are shown in Figs. 2(a) and 2(b). We note that both defects are rather localized, being mainly confined within four rings.

The existence of two types of solitons has an important consequence: The most stable configuration for a

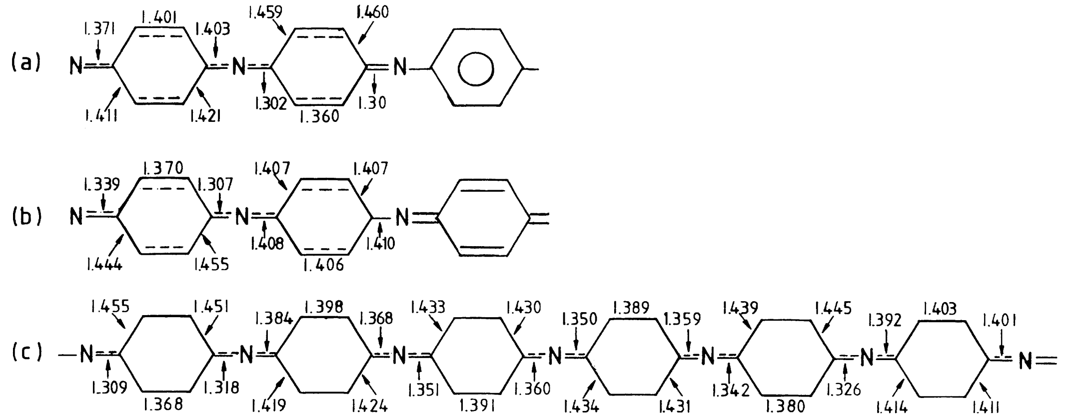

FIG. 2. Defect optimized geometries in polypernigraniline: (a) type-1 soliton and (b) type-2 soliton (the nitrogen to the left corresponds to the soliton center), and (c) polaron structure.

TABLE I. Charge distribution associated with the perfectly dimerized polymer, a pair of neutral, infinitely separated solitons, and positive polaron and negative polaron. N_i and R_i represent, respectively, the ith nitrogen and the ith ring in the chain. In all cases the atom N_0 is placed at the defect center. Charges are given in units of $|e|$.

Perfect polymer			N atoms		Quinoid rings		Aromatic rings		
			−0.535		+0.948		+0.121		
Soliton	N_0	R_1	N_1	R_2	N_2	R_3	N_3	R_4	
Type 1	−0.701	+0.065	−0.527	+0.836	−0.554	+0.105	−0.534	+0.939	
Type 2	−0.510	+1.010	−0.489	+0.250	−0.533	+0.969	−0.529	+0.133	
Polaron	N_{-2}	R_{-2}	N_{-1}	R_{-1}	N_0	R_1	N_1	R_2	N_2
Positive	−0.524	+0.497	−0.515	+0.708	−0.513	+0.666	−0.517	+0.847	−0.516
Negative	−0.532	+0.218	−0.602	+0.395	−0.570	+0.361	−0.539	+0.578	−0.586

soliton-antisoliton pair corresponds to the type-1 soliton level being doubly occupied and the type-2 soliton level left empty, with a total creation energy of 0.64 eV. This results in a net charge of $-0.52|e|$ around the type-1 defect and an opposite charge around the type-2 soliton.[18] The most stable configuration is thus nonmagnetic, contrary to the situation in, e.g., *trans*-polyacetylene. The excitation of a magnetic pair (corresponding to the case where two well separated solitons are each occupied with a single electron) increases the above creation energy by 0.17 eV, i.e., the energy separation between the two localized levels. Table I gives the charge distribution around the solitons in the case of the most stable nonmagnetic pair. The excess negative charge around the type-1 soliton mainly goes to the central nitrogen and to the second rings from the center, while the excess positive charge around the other soliton concentrates on the central rings; i.e., the rings having a quinoid geometry.

Solitons carrying fractional charges have also been predicted for the diatomic chain.[8] However, if *AB* solitons were to possess the same fractional charges as those found here, application of the *AB* polymer model would result in the nonexistence of polarons. Quite the contrary, we predict that the most stable excitation upon addition (or removal) of an electron to PPN is a polaron. The optimized geometry of a polaron is shown in Fig. 2(c). The polarons are remarkably stable, possessing binding energies of 0.14 eV (positive polaron) and 0.21 eV (negative polaron), to be compared to about 0.05 eV in the case of *trans*-polyacetylene. We remark that, due to symmetry constraints, the polaron has a nitrogen at the center instead of a bond, as has been usually found in other systems.[6,19] Two localized levels split from the VB and CB, at 0.38 eV below and 0.30 eV above the Fermi level. The polaron wave functions do not show any symmetry, due to the fact that they combine type-1 and type-2 soliton wave functions which are very dissimilar. Both positive and negative polarons have the usual charge and spin assignments. In Table I, we present the polaron charge distributions. For the positive polaron, the extra charge tends to localize on the rings (nitrogen atoms are hardly affected with respect to the neutral polymer case). On the other hand, the extra charge in the negative polaron goes partly to the nitrogens.

Bipolarons are not found in PPN. A pair of polarons is actually unstable with respect to the formation of a

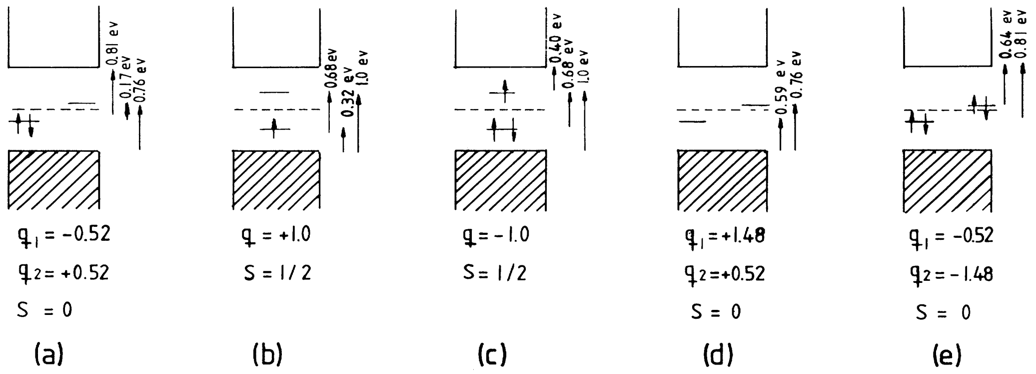

FIG. 3. Charge and spin assignments and intragap optical absorption energies from polypernigraniline excitations: (a) neutral (nonmagnetic) soliton pair; (b) positive polaron; (c) negative polaron; (d) negatively charged soliton pair; and (e) positively charged soliton pair. q_1 and q_2 refer to type-1 and type-2 soliton charges, respectively. Charges are given in units of $|e|$.

pair of charged solitons (by 0.37 eV in the positive case and 0.28 eV in the negative case). Type-1 and type-2 soliton charges are, respectively, $+1.48|e|$ and $+0.52\times|e|$ in the positive case and $-0.52|e|$ and $-1.48\times|e|$ in the negative case.

Figure 3 summarizes the electronic structure of the excitations discussed above. Also shown are the intragap optical absorptions arising from these excitations, which should provide a reference framework for the ir-visible-uv measurements to come on PPN.

Our results demonstrate that PPN, i.e., the polyaniline form possessing a degenerate ground state, presents very special electronic properties, which should lead to interesting experimental developments. This is especially significant since PPN is now becoming available in a pure form. In the neutral state, PPN can develop nonlinear soliton excitations with fractional charge. This appears to be a general property of a degenerate ground-state heteroatomic chain. We note, however, that in the doped state the stability region of a polaron excitation is here markedly different from that derived from the simple *AB* polymer model. Finally, we stress that, very importantly, the nonlinear optical properties of PPN should prove most interesting. It has been indeed shown that high hyperpolarizability values are related to efficient mechanisms for charge separation.[20] In PPN, the (actual or virtual) photogeneration of soliton pairs with fractional charges intrinsically provides for such a mechanism.

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[1] A. G. MacDiarmid, J. C. Chiang, W. S. Huang, B. D. Humphrey, and N. L. D. Somarisi, Mol. Cryst. Liq. Cryst. **125**, 309 (1985).

[2] A. G. MacDiarmid, J. C. Chiang, A. F. Richter, and A. J. Epstein, Synth. Met. **18**, 285 (1987).

[3] J. M. Ginder, A. F. Richter, A. G. MacDiarmid, and A. J. Epstein, Solid State Commun. **63**, 97 (1987).

[4] H.-Y. Choi and E. J. Mele, Phys. Rev. Lett. **59**, 2188 (1987).

[5] D. S. Boudreaux, R. R. Chance, J. F. Wolf, L. W. Shacklette, J. L. Brédas, B. Thémans, J. M. André, and R. Silbey, J. Chem. Phys. **85**, 4584 (1986).

[6] S. Stafström, J. L. Brédas, A. J. Epstein, H. S. Woo, D. B. Tanner, W. S. Huang, and A. G. MacDiarmid, Phys. Rev. Lett. **59**, 1464 (1987).

[7] L. W. Shacklette, J. F. Wolf, S. Gould, and R. H. Baughman, J. Chem. Phys. **88**, 3955 (1988).

[8] M. J. Rice and E. J. Mele, Phys. Rev. Lett. **49**, 1455 (1982).

[9] D. K. Campbell, Phys. Rev. Lett. **50**, 865 (1983).

[10] J. C. Hicks and V. R. Lin-Liu, Phys. Rev. B **29**, 5641 (1984); T. Martin and D. K. Campbell, Phys. Rev. B **35**, 7732 (1987).

[11] A. Saxena and J. D. Gunton, Phys. Rev. B **38**, 8459 (1988).

[12] D. Wohrle, Adv. Polym. Sci. **10**, 35 (1972).

[13] A. G. MacDiarmid (private communication).

[14] L. Salem, *The Molecular Orbital Theory of Conjugated Systems* (Benjamin, New York, 1966), p. 134.

[15] M. C. dos Santos, C. P. de Melo, and H. S. Brandi, Solid State Commun. **52**, 99 (1984); Int. J. Quantum Chem. **30**, 109 (1986); A. L. S. da Rosa and C. P. de Melo, Phys. Rev. B **38**, 5430 (1988).

[16] M. C. dos Santos and J. L. Brédas, Synth. Met. **29**, E321 (1989).

[17] J. L. Brédas and G. B. Street, Acc. Chem. Res. **18**, 309 (1985).

[18] Note that the presence of a type-1 defect in the chain locally takes up 0.74 state per spin from the valence band; for a doubly occupied type-1 level, the total charge around that defect is calculated to be -2 (charge in the defect level) plus 2×0.74 (hole left in the valence band), thus leading to the charge $-0.52|e|$.

[19] J. L. Brédas, R. R. Chance, and R. Silbey, Phys. Rev. B **26**, 5643 (1982); J. L. Brédas, D. S. Boudreaux, R. R. Chance, and R. Silbey, Phys. Rev. B **31**, 652 (1985); D. Bertho and C. Jouanin, Phys. Rev. B **35**, 626 (1987).

[20] A. I. Garito, J. R. Heflin, K. Y. Wong, and O. Zamani-Khamiri, in *Nonlinear Optical Properties of Polymers,* edited by A. J. Heeger, J. Orenstein, and D. R. Ulrich, MRS Symposium Proceedings No. 109 (Materials Research Society, Pittsburgh, 1988), p. 91; M. Sinclair, D. Moses, K. Akagi, and A. J. Heeger, *ibid*., p. 205.