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Protonation process of pernigraniline: A theoretical investigation

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The fully oxidized form of polyaniline, pernigraniline, is studied in the framework of a Su-Schrieffer-Heeger-like Hamiltonian. The protonation process of a long oligomer is investigated. Protonation is modeled by a change in site energies around the protonated site. The results of the calculations indicate that a phase separation occurs between protonated and nonprotonated regions. Inside a protonated region, a charge-density wave (CDW) develops which tends to keep the same periodicity as that of the original CDW of the unperturbed system. As a result, protonation is preferentially produced on every other nitrogen. The present findings are compared to those obtained previously in the case of emeraldine.

The interest in pernigraniline, the fully oxidized form of polyaniline, originates in the fact that this compound has recently been synthesized in a pure form[1] and that fascinating electronic properties have been predicted for this system. Indeed, it has for instance theoretically been shown to possess elementary excitations (solitons) presenting fractional charges[2,3] as a result of the difference in electronegativity between carbon rings and nitrogens.

Recent experimental investigations on the properties of protonated emeraldine, the half-oxidized form of polyaniline, indicate that the proton doping does not occur uniformly.[4-8] At high protonation level, the polymer electrical conductivity has increased by several orders of magnitude up to about 10-50 S/cm;[9] however, properties typical of the metallic state start appearing even in the early stages of protonation.[5] A mechanism, in which protonated phases (the so-called metallic islands) and nonprotonated phases segregate, has been proposed to explain the evolution of the properties of emeraldine to the metallic state as a function of protonation.[6]

Emeraldine corresponds to the most conducting form of polyaniline upon proton doping. The unprotonated form, emeraldine base, is composed of reduced units [$-$NH$-$$B$$-NH-$$B$$-$] and oxidized units [$-N=$$Q$$=N-$$B$$-$], where B and Q denote benzene rings in the aromatic and quinoid geometries, respectively, which are connected to nitrogens in the paraposition. Ideally, the reduced and oxidized units alternate regularly along the chains. Protonation takes place at the imine nitrogens (in the oxidized units) and transforms these imines into positively charged (ionized) amines (NH^+). It is important to stress that the total number of electrons on the chains does *not* change upon protonation. Choi and Mele[10] have carried out calculations at the tight-binding level for emeraldine base, in which only nitrogen sites are taken into account. They have shown that segregation into protonated and nonprotonated phases is expected, due to the heteroatomic nature of this material.

In the case of pernigraniline, only imine nitrogens are present (all units are of the oxidized type defined above). Since pernigraniline has now become available in a pure form and in the light of the interesting emeraldine behavior, it is worth investigating the properties of pernigraniline upon protonation.

We have performed electronic structure calculations based on a Su-Schrieffer-Heeger-like Hamiltonian. It is reasonable to consider that nitrogens in either amine and imine states of oxidation, carbons connected to nitrogens, and carbons not connected to nitrogens all have different site energies. Values for these parameters are optimized in such a way that the tight-binding π-band structures of pernigraniline and leucoemeraldine (the fully reduced form of polyaniline, in which all units are of the reduced type) fit at best those calculated in the framework of valence-effective Hamiltonian theory.[11] In addition, the electron-phonon couplings are adjusted to reproduce suitable ground-state geometries.[12] In order to simplify the parametrization, we have chosen the same electron-phonon couplings for both pernigraniline and leucoemeraldine.

The resulting densities of states, obtained by a Green's-function technique and an exact renormalization procedure,[2,13] are shown in Fig. 1. The site energy values that allow us to match at best the relative positions of the Fermi energies, the band gaps, as well as the widths of the bands closest to the Fermi energy are given in Fig. 2. The effect of protonation of an imine nitrogen is simulated by a change in the site energies of the protonated nitrogen and the nearest-neighbor carbons. We note that, even though neutral and ionized amines should correspond to different species, we are not able to distinguish them at this level of theory. This approximation, however, is not to alter in any significant way the main results of our work.

The protonation process has been carried out on a long pernigraniline oligomer including up to 30 nitrogens and 30 carbon rings. The protonation of a first nitrogen is calculated to increase the π energy by 0.82 eV. Note, however, that in terms of total energy, the stabilization of the nitrogen lone pair due to the N$-$H bond formation should compensate the increase in π energy, but is not taken into account in our study. Geometry modifications induced by protonation are found to be restricted to the bonds surrounding the protonated site. These NH$-$C bonds

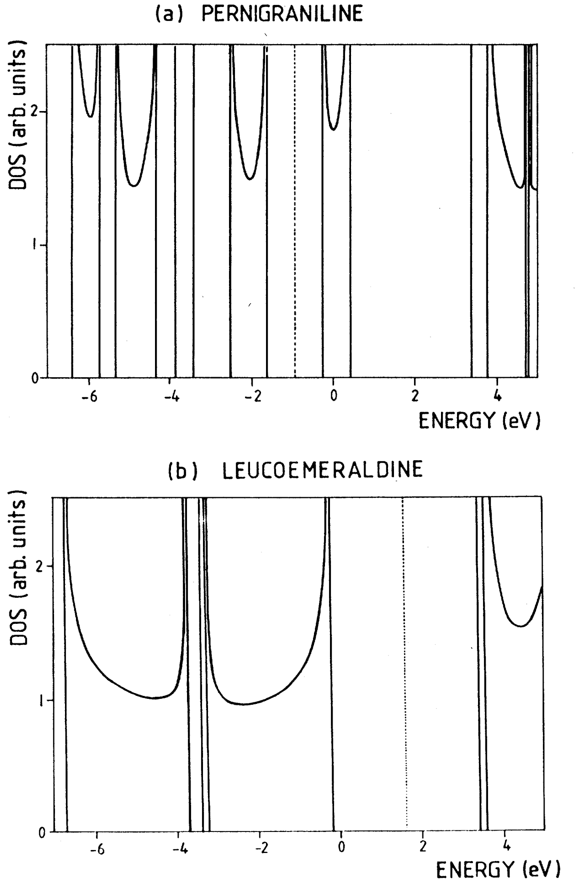

FIG. 1. Densities of electronic states (arbitrary units) vs energy (eV) obtained from Green's-function calculations: (a) pernigraniline and (b) leucoemeraldine. Dotted lines indicate the position of the Fermi energies.

shorten with respect to their original values (1.28 Å vs 1.30 Å for the original double bond and 1.39 Å vs 1.41 Å for the single bond). This result is an indication that we have overestimated the electron-phonon coupling of the NH—C bonds, since more elaborate quantum chemical geometry optimizations have indicated an elongation of the original N=C double bond upon protonation.[14] The elastic properties of polyaniline chains are thus modified by protonation. Local changes of the elastic properties do not alter the trends in the present theory since the perturbations on the electronic spectrum are mainly concerned with the diagonal disorder in the Hamiltonian (which is the way the proton doping has been simulated).

The ground-state charge-density wave (CDW) of pernigraniline is locally affected by protonation. The main modification consists in a charge transfer of $-0.18|e|$ ($|e|$ is the magnitude of the electron charge) from the protonated site towards the neighboring quinoid ring. The present model is of course exclusively concerned with π-density rearrangements; the sigma charge redistribution which is expected as a consequence of N—H bond formation upon protonation has not been explicitly treated.

Several protonation-induced localized electronic states appear in the density-of-states spectrum: One of these states resides inside the central gap of pernigraniline, just above (≤ 0.01 eV) the top of the valence band. We have also calculated the effect of protonating one site and adding one electron at the same time. A polaron distortion is then created in the chain to accommodate the excess electron. However, there occurs an interaction of the polaron states with the protonation-induced localized state in the gap which increases the polaron binding energy (0.24 eV with respect to 0.21 eV in the absence of any proton[3]). Thus, we find that protonated sites act as trapping centers to the polaron motion, even though it can be activated by thermal effects.

We now turn to a discussion of the energy required to protonate a second site as a function of the distance to the first protonated site. The results are presented in Fig. 3. Similar evolutions are found for successive protonations. The most important result is that a clear preference is obtained for *protonation to occur on every other site.* This behavior determines a well-defined pattern of protonated and nonprotonated nitrogens and leads to phase separation, as illustrated in Fig. 4.

The origin of this effect can be simply rationalized by taking account of the charge distribution. Each protonation takes some negative charge from a nitrogen to

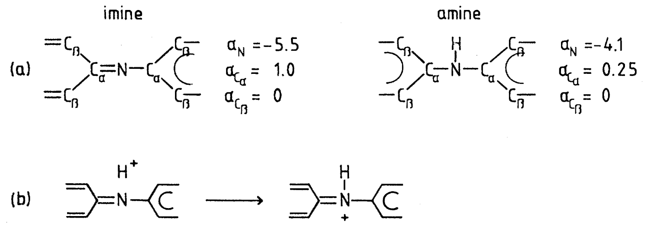

FIG. 2. (a) Sketch of the basic units of pernigraniline (imine) and leucoemeraldine (amine), and their optimized site energies (in eV). (b) Illustration of the protonation reaction transforming the imine nitrogen into a positively charged amine.

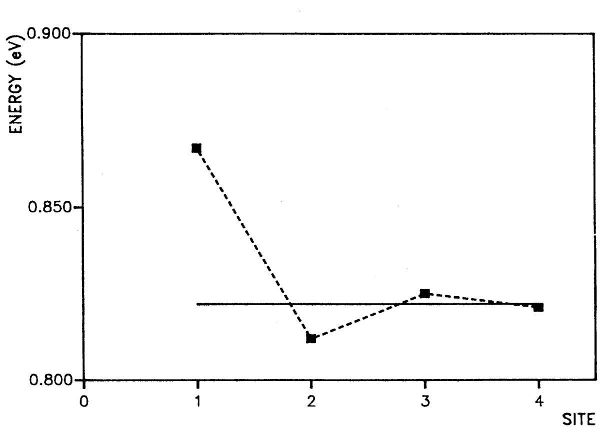

FIG. 3. Energy associated to the second protonation when site 0 is protonated, as a function of the distance between the protonated sites. The solid line represents the energy of the first protonation.

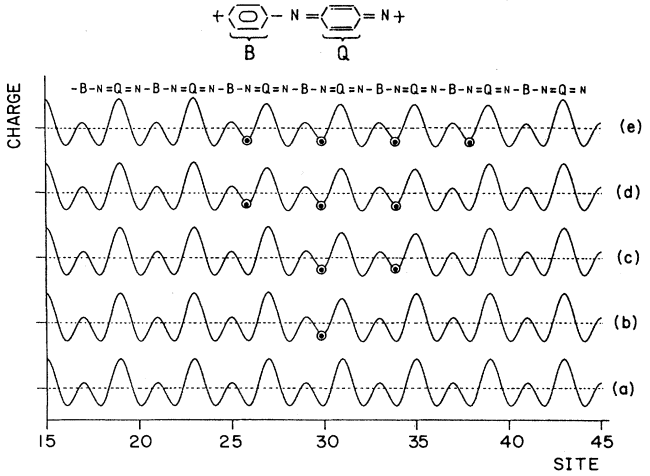

FIG. 4. Evolution of the charge-density-wave pattern upon protonation: (a) ground-state CDW, and (b) first, (c) second, (d) third, and (e) fourth protonations. In these figures, the dashed lines represent the zero of charge and amplitudes vary from $-0.54|e|$ to $0.95|e|$. The circles on the curves indicate the positions of the protonated sites.

transfer it to the neighboring quinoid ring. This affects the original charge distribution, presented in Fig. 4(a), even though *the total number of π electrons remains the same.* As the period of the CDW is determined by the band filling, the new CDW which develops on the chain due to protonation tends to keep the same period as that of the original (unprotonated chain) CDW, since *the band filling has not changed* (see Fig. 4).

The present result is therefore consistent with that theoretically predicted by Choi and Mele[10] for emeraldine base. These authors have suggested that, upon protonation, there should first appear a phase of the kind $[\mathrm{NH}-B-\mathrm{NH}-B-\mathrm{NH}^{+}=Q=\mathrm{N}-B-]_x$, which corresponds to a CDW periodicity of order 4, as determined by the $\frac{3}{4}$ band filling of emeraldine base. This intermediate step of proton doping should be completed before total protonation can be achieved, at least at low temperature. As in our calculation, see Fig. 3, differences in protonation energies of distinct sites are found by Choi and Mele[10] to be of the order of, or slightly larger than, the thermal energy at room temperature.

Very recently, protonation doping experiments have been carried out on pernigraniline. The experimental data suggest that protonation actually leads to some degree of crosslinking between pernigraniline chains.[1] For such a crosslinking to be achieved, however, it is necessary that protonation does not start to occur on adjacent nitrogens. This behavior is thus consistent with our theoretical result.

At this stage, it is interesting to draw a comparison between the protonation doping (acid-base chemistry) and the more conventional charge transfer doping (redox chemistry) of conducting polymers. The latter chemical process *changes the band filling without altering the chemical composition of the polymer chains.* The excess charge therefore introduces discommensurations along the chains. *Proton doping,* on the other hand, changes the chain properties in a different fashion: *it does modify the polymer chemical composition* (since, for instance, in the case of polyanniline, imine nitrogens are modified to form ionized amines) *while the band filling is kept constant.* Hence, charge rearrangements which occur as a consequence of protonation are constrained to conserve the periodicity of the underlying CDW due to the conservation of number of electrons in the process. Phase separation between protonated and nonprotonated regions can thus arise from this feature, even though it could be affected by temperature.

The appearance of metallic properties in protonated polyanilines is also influenced by the heteroatomic nature of these polymers. The semiconducting gap in these materials has two main contributions, one arising from the Peierls instability of one-dimensional systems and the other coming from the CDW amplitude (which is not present in most of the charge transfer doped conducting polymers). The existence of electronic states around the Fermi energy upon protonation is thus expected to correspond to a mechanism which differs from that proposed for redox doping.[15] A full account of the interplay between the protonation-induced electronic states and the states related to elementary excitations (solitons, polarons) will be presented elsewhere.

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