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Role of ring torsion angle in polyaniline: Electronic structure and defect states

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The role of phenyl-ring torsion angle in determining the nature of the ground and charged-defect states of polyaniline is explored. The coupling of the transfer integral between nitrogen atom and phenyl-ring constituents of the polyaniline chain to the dihedral angle of the rings competes with the substantial steric repulsion between adjacent rings in determining the conformation of these systems. The ring conformation of the leucoemeraldine-base (LB) form of polyaniline is described by a novel ring-torsion-angle order parameter. The anharmonicity of the interring steric potential leads to a temperature-dependent mean order parameter, and thus to the prediction of thermochromic effects consistent with experiment. Furthermore, changes in optical spectra accompanying derivatization of the rings can be understood by the response of the substituted polymer to modifications of the steric potential. The existence of two degenerate ring-torsion-angle phases in LB implies that both polaronic and solitonic ring-angle-alternation defect states may be relevant in describing the charged states in polyaniline. As these defects involve substantial changes in ring torsion angle, they are expected to possess large kinetic mass, in agreement with photoinduced absorption experiments on polyaniline. The anticipated Peierls ground state of the oxidized pernigraniline-base form of polyaniline can be regarded in part as a ring-torsion-angle dimerized state; consequently, the charge states of this material are also expected to be massive defects in the ring-rotational order. The importance of ring rotations in other ring-containing electronic polymers, such as poly(paraphenylene sulfide), is discussed.

I. INTRODUCTION

Polyaniline has been recognized recently as an interesting and unusual member of the class of π-conjugated conducting polymers. Unlike many other members of this class—polyacetylene, polydiacetylene, and polythiophene—whose electronic properties are well understood solely by considering their conjugated carbon backbones,[1] a nitrogen heteroatom is incorporated between phenyl (C_6H_4) rings in the polyaniline backbone. The chemical flexibility provided by the nitrogen heteroatom allows access to several insulating ground states that are distinguished by their oxidation level:[2] reduced leucoemeraldine base (LB), partially oxidized emeraldine base (EB), and fully oxidized pernigraniline base (PNB), Fig. 1.

An initial focus of polyaniline studies was the relatively stable emeraldine oxidation state; it was found that EB [Fig. 1(b)] could be doped to the emeraldine salt (ES) form by treatment with protonic acids such as HCl, increasing the room-temperature conductivity 11 orders of magnitude to $\sim 10\ (\Omega\,\mathrm{cm})^{-1}$,[3] and inducing the appearance of a metallic-like Pauli paramagnetic susceptibility.[4] Based on audio-[5] and microwave-[6] frequency conductivity and dielectric-constant studies, together with magnetic experiments,[4] it was proposed that charge hopping among fixed polaron and bipolaron sites was the primary charge-transport mechanism in the lightly protonated EB system; at high doping (protonation) levels the polarons are arrayed to form a polaron lattice[4] with metal-like transport within the partially filled polaron energy band.[7] *In situ* electron-paramagnetic-resonance experiments demonstrated that polarons are also produced by the electrochemical oxidation of LB toward ES.[8] Theoretical studies of the polaron lattice[9] indicated that the severe asymmetry of the valence and conduction bands in polyaniline leads to only one broad defect band within the energy gap, in contrast to the symmetric pair of defect bands expected[1] for polarons or bipolarons in charge-conjugation-symmetric systems.

Photoinduced optical studies of LB and EB have given insight into the charged defects formed upon the insertion of electrons and holes into the polymer backbone.[10–17] For EB, similar photoinduced features are observed whether pumping into the 3.8-eV π-π^* band-gap absorption or the 2.0-eV absorption ascribed to interring charge transfer associated with excitations from benzenoid to quinoid moieties.[10,14] Bleachings of these existing transitions are observed upon photoexcitation of EB; photoinduced-absorption (PA) peaks are found at 0.9, 1.4, and 3.0 eV. While the 0.9-eV peak is relatively short lived, the 1.4-eV absorption and a light-induced electron spin-resonance signal[16,17] indicative of polarons are found to be long lived, a substantial population existing for many hours after excitation at liquid-nitrogen temperature. The relative weakness of the associated photoinduced infrared-active vibrations (IRAV), contrasting substantially with the intense photoinduced IRAV due to solitons in polyacetylene[18] and polarons or bipolarons in

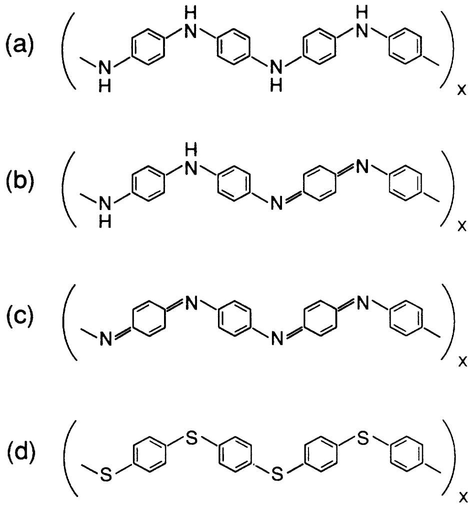

FIG. 1. Chemical structures of the (a) leucoemeraldine-base (LB), (b) emeraldine-base (EB), and (c) pernigraniline-base (PNB) forms of polyaniline; (d) poly(paraphenylene sulfide) (PPS).

polythiophene,[19] implies that the photoinduced excitations in polyaniline are quite massive: application of the amplitude-mode theory to the measured PA of EB yielded an estimate of the effective mass of ~60 electron masses.[13] The existence of this unusually large mass and long-time-scale dynamics led to suggestions that these effects might be due to the ring degrees of freedom in the polyaniline chain.[10,11,13–15]

The Su-Schrieffer-Heeger (SSH) Hamiltonian[20] and its variants have been widely used to study the electronic structure of the carbon-backbone polymers, successfully describing the ground state of such systems in terms of a Peierls distortion augmented by an extrinsic contribution to the ground-state energy gap, i.e., one-electron effects, in the case of the nondegenerate–ground-state polymers like polythiophene.[1] Initially applied to carbon p_z-electron systems, this approach was extended to alternating heteroatomic chains, the so-called "*A-B*" polymers.[21] Since the electron-lattice interaction was based on coupling to longitudinal modes of the polymer chain, the charge-storing states were found to be defects—solitons, polarons, and bipolarons—in the ground-state pattern of bond alternation.[22] Later studies emphasized the important roles of Coulomb interaction[23] and interchain coupling.[24]

Despite the success of the SSH model in understanding the electronic structure of the carbon backbone polymers, it has proved necessary to go beyond its simple electron-phonon coupling in order to study the role of conformational changes on ground-state properties. For example, the thermally induced and solvent-induced changes in the optical spectra observed in the polydiacetylenes,[25] polysilanes,[26] and substituted polythiophenes[27] have been explained[28,29] by induced rotations of the π-conjugated molecular units out of the energetically favored planar conformation, reducing the interunit transfer integral and thus increasing the π-π^* band gap.

Several theoretical studies have shown that ring-rotational conformation is important in determining the ground-state electronic structure and geometry of PNB and other forms of polyaniline.[30–33] In addition, an excited-state ring rotation was invoked to explain the interring charge-transfer exciton energy in EB.[34–37] Despite the experimental evidence for long-lived, massive charged defects in polyaniline, as well as the demonstration of the importance of ring flipping as a relaxation mechanism,[38] the role of ring conformational changes in the self-trapping of charged defect states has received little attention.[39,40] The substantial electron-lattice coupling originating from phenyl-ring rotations, together with the severe charge-conjugation asymmetry[41] of the valence and conduction bands of the LB, EB, and ES forms of polyaniline, suggests that the geometry, electronic structure, and dynamics of the defect states in polyaniline are quite different than those of the carbon-backbone conjugated polymers.

In this paper, the role of ring torsion angle in determining the electronic and structural properties of the reduced LB and oxidized PNB forms of polyaniline is investigated. In order to emphasize the importance of the ring-rotational degrees of freedom, we make use of a simple model that highlights the role of ring torsion angle. Though the filled-band LB system exhibits no tendency toward Peierls dimerization, LB nonetheless possesses two degenerate ground states corresponding to two different phases of ring-angle rotation. An order parameter is developed to represent the spatial variation of ring-angular order. The magnitude of the order parameter in the ground state depends strongly on the steric repulsion between atoms of neighboring rings. Consequences of the angular dependence of the steric potential energy include the increase in average ring torsion angle upon increasing temperature or upon derivatization, both leading to observable changes in the electronic structure. Defect states in LB—polarons and solitons—are associated with localized changes of the ground-state ring-torsion-angle order parameter, i.e., ring rotations toward planar conformations for polarons[39] and a reversal of the sign of the ring-torsion-angle order parameter for solitons. Due in part to the relatively large moment of inertia of the rings, the kinetic mass of these polarons is very large, ~50–100 electron masses, at least one order of magnitude greater than typical defect masses in systems with bond-length distortions only; ring-torsion-angle soliton masses are even larger. The relevance of these massive ring-rotational defects to recent experiments on polyaniline and other ring-containing polymers such as poly(paraphenylene oxide) (PPO) and poly(paraphenylene sulfide) (PPS) [Fig. 1(d)] is explored.

Consequences of the ring-rotational degrees of freedom for the oxidized PNB form of polyaniline are also investigated. PNB, a half-filled-band system, is anticipated to undergo dimerization to a semiconducting Peierls ground state.[42] A dimensionless electron-ring-angle coupling constant is derived[43] in order to compare the importance of ring-rotational and bond-length changes in affecting the electronic structure. At least a portion of the Peierls gap likely originates from ring-angle dimerization;[44] consequently, the polaronic and solitonic species important to charge storage likely possess a ring-rotational component, thus exhibiting a larger effective mass than the usual bond-alternation defects.

Section II presents the model used to explore the general implications of ring torsion angle and the interring steric potential for polyaniline. In Sec. III, the effects of the ring-torsion-angle degrees of freedom on the electronic structure and defect states—polarons, bipolarons, and solitons—are outlined. The consequences of these additional degrees of freedom are summarized in Sec. IV, together with a generalization to other polymer systems.

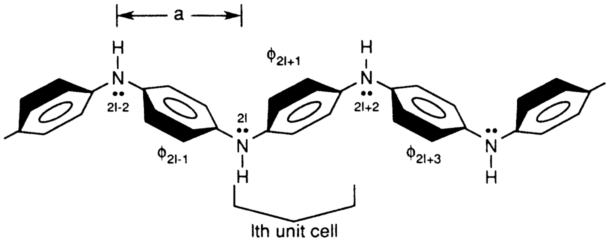

FIG. 2. Sketch of lth LB unit cell and its neighbors; the cell contains the $2l$th nitrogen atom and benzene ring at angle ϕ_{2l+1} with respect to the C—N—C plane.

II. THE MODEL

A. Electronic Hamiltonian

We explore the role of the ring-torsion-angular degrees of freedom using for the system Hamiltonian a sum of electronic and steric contributions: $\mathcal{H}=\mathcal{H}_{\mathrm{el}}+V_{\mathrm{steric}}$, where electron-lattice coupling, electron-electron interactions, etc., are incorporated into $\mathcal{H}_{\mathrm{el}}$ and V_{steric} includes only steric interactions between neighboring phenyl rings. The model is developed initially for the reduced form of polyaniline, LB, Fig. 1(a). Ignoring the zig-zag structure of the polymer chain, the repeat unit of the polymer is a single ring-NH unit of length $a \simeq 4.9$ Å, a being the projection of the N-N distance along the chain axis. Each nitrogen atom is assumed to possess two electrons in a p_z orbital perpendicular to the C—N—C plane, while each C_6H_4 ring contributes six p_z electrons. Figure 2 shows the polymer backbone structure and site labeling; the unit cell is numbered by l, while the nitrogen and phenyl subunits are numbered consecutively. The $(2l+1)$th phenyl ring is twisted at a dihedral torsion angle ϕ_{2l+1} out of the plane of the nitrogen atoms. The treatment of the A-B polymer[21] is generalized to include six molecular orbitals at the "B" site, i.e., the molecular orbitals of an unperturbed benzene ring; the nitrogen p_z is thus at the "A" site. For simplicity, and in order not to obscure the essential physical concepts involved, a tight-binding approximation is utilized to describe the electronic Hamiltonian. Using a one-dimensional linear combination of molecular orbitals approach,[45] the electronic part of the Hamiltonian can be written as

$$\mathcal{H}_{\mathrm{el}}=\sum_{l,s}\alpha_{\mathrm{N}}a^{\dagger}_{2l,s}a_{2l,s}+\sum_{l,s}\sum_{j}\varepsilon_j b^{j\dagger}_{2l+1,s}b^{j}_{2l+1,s}$$
$$-\sum_{l,s}\sum_{j}[t^{j}_{2l,2l+1}(a^{\dagger}_{2l,s}b^{j}_{2l+1,s}+b^{j\dagger}_{2l+1,s}a_{2l,s})+t^{j}_{2l+1,2l+2}(b^{j\dagger}_{2l+1,s}a_{2l+2,s}+a^{\dagger}_{2l+2,s}b^{j}_{2l+1,s})] \ . \tag{1}$$

The operator $a^{\dagger}_{2l,s}$ ($a_{2l,s}$) creates (destroys) an electron of spin s on the nitrogen atom in the lth unit cell, with site energy α_{N}, and $b^{j\dagger}_{2l+1,s}$ ($b^{j}_{2l+1,s}$) creates (destroys) an electron of spin s in the jth molecular orbital of the lth benzene ring, with site energy ε_j. We make two reasonable assumptions[46] about the transfer integral $t^{j}_{2l,2l+1}$ between the $2l$th nitrogen p_z and the jth molecular orbital of the $(2l+1)$th benzene ring: first, that it is proportional to the cosine of the angle between the nitrogen and ring p_z-electron lobes, i.e., $\cos\phi_{2l+1}$; and second, that it is proportional to the coefficient of the jth molecular orbital at the *para*-carbon atom neighboring the nitrogen (including first-near-neighbor hopping only). We define $t^{j}_{2l,2l+1}\equiv t^{j}_{+}\cos\phi_{2l+1}$ and $t^{j}_{2l+1,2l+2}\equiv t^{j}_{-}\cos\phi_{2l+1}$; $t^{j}_{+}=\pm t^{j}_{-}$, the plus (minus) sign being appropriate to those benzene molecular orbitals that are even (odd) under interchange of the para carbon atoms. In order to focus on the novel effects of ring rotation, the more usual electron-phonon coupling via bond-length modulation is not explicitly included.

In order to minimize the steric repulsion between adjacent phenyl rings, the LB ring-torsion angles ϕ_{2m+1} alternate in sign, as is reported in crystallographic studies of the analogous polymers PPO (Ref. 47) and PPS (Ref. 48) and in the emeraldine forms of polyaniline.[49] Therefore, an order parameter ψ_{2m+1} is defined such that $\phi_{2m+1}=(-1)^m\psi_{2m+1}$. Since no tendency towards Peierls dimerization exists in the filled-band LB system, the ground state consists of ring angles which are all of equal magnitude ψ_0 and alternating in sign, so that there exist two degenerate ground states, $\psi_{2m+1}\equiv+\psi_0$ and $\psi_{2m+1}\equiv-\psi_0$, as shown schematically in Fig. 3. The existence of degenerate A $(+\psi_0)$ and B $(-\psi_0)$ structural phases suggests that topological defects—ring-rotational polarons and solitons—are important excited states in LB.

The electronic Hamiltonian is transformed to a momentum representation using the Bloch operators

$$a_k=\frac{1}{\sqrt{N}}\sum_{l}e^{-ikla}a_{2l,s}, \qquad b^{j}_{k}=\frac{1}{\sqrt{N}}\sum_{l}e^{-ikla}e^{-ika/2}b^{j}_{2l+1,s} \ . \tag{2}$$

Periodic boundary conditions for a chain of N nitrogen-phenyl repeat units are used, with Brillouin-zone boundaries at $\pm\pi/a$. $\mathcal{H}_{\text{el}}$ becomes

$$\mathcal{H}_{\text{el}}=\sum_{k,s}\alpha_{\text{N}}a^{\dagger}_{k,s}a_{k,s}+\sum_{k,s}\sum_{j}\varepsilon_j b^{j\dagger}_{k,s}b^{j}_{k,s}\sum_{k,s}\sum_{j}\cos\psi[(t^j_{+}+t^j_{-})\cos(ka/2)(a^{\dagger}_{k,s}b^{j}_{k,s}+b^{j\dagger}_{k,s}a_{k,s})$$
$$+i(t^j_{+}-t^j_{-})\sin(ka/2)(a^{\dagger}_{k,s}b^{j}_{k,s}-b^{j\dagger}_{k,s}a_{k,s})]\ . \tag{3}$$

In order to obtain analytic solutions for the energy bands and to avoid obscuring the origin of the electronic phenomena to be discussed, the hopping term of the Hamiltonian is treated within second-order perturbation theory, appropriate for weak coupling between nitrogen and benzene molecular orbitals (MO's). The nitrogen p_z energy-band dispersion is found to be

$$E_{\text{N}}(k)=\alpha_{\text{N}}+\cos^2\psi\sum_{j}\frac{(t^j_{+}+t^j_{-})^2+(t^j_{+}-t^j_{-})^2}{2(\alpha_{\text{N}}-\varepsilon_j)}$$
$$-\cos^2\psi\sum_{j}\frac{(t^j_{+}+t^j_{-})^2-(t^j_{+}-t^j_{-})^2}{2(\alpha_{\text{N}}-\varepsilon_j)}\cos(ka)\ , \tag{4}$$

while the jth benzene molecular-orbital band dispersion is given by

$$E_j(k)=\varepsilon_j+\cos^2\psi\frac{(t^j_{+}+t^j_{-})^2+(t^j_{+}-t^j_{-})^2}{2(\varepsilon_j-\alpha_{\text{N}})}$$
$$+\cos^2\psi\frac{(t^j_{+}+t^j_{-})^2-(t^j_{-}-t^j_{-})^2}{2(\varepsilon_j-\alpha_{\text{N}})}\cos(ka)\ . \tag{5}$$

Both the effective site energy (i.e., the energy of the band center) and the effective transfer integral (i.e., the bandwidth) of each molecular orbital are modulated by the ring angle ψ. Figure 4 is the band structure obtained with $\psi\simeq56°$, $t_{\text{C-C}}=3.5$ eV,[50] $t_{\text{C-N}}=0.8t_{\text{C-C}}$,[46] and $c_{\text{N}}=-2.0$ eV;[51] the energies are measured with respect to the carbon p_z site energy $\alpha_{\text{C}}=-11.4$ eV.[51] The ring angle ψ was chosen to yield a π-π^* band gap (~3.5 eV) and valence-band width (~2.3 eV) in agreement with spectroscopic studies[14,15] and band-structure calculations[31,52,53] on LB; $\psi\simeq56°$ is similar to that found experimentally for PPO (Ref. 47) and PPS.[48]

An effective one-band electronic Hamiltonian describing the valence band and including the resonance-energy increase of the bands derived from the benzene-ring molecular orbitals is inferred from the energy-band dispersions, i.e.,

$$\mathcal{H}_{\text{eff}}=\{\alpha_{\text{N}}+[\alpha_{\text{eff}}-2t_{\text{eff}}\cos(ka)]\cos^2\psi\}$$
$$\times\sum_{k,s}c^{\dagger}_{k,s}c_{k,s}-\sum_{k,s}\alpha_{\text{eff}}\cos^2\psi\ , \tag{6}$$

where

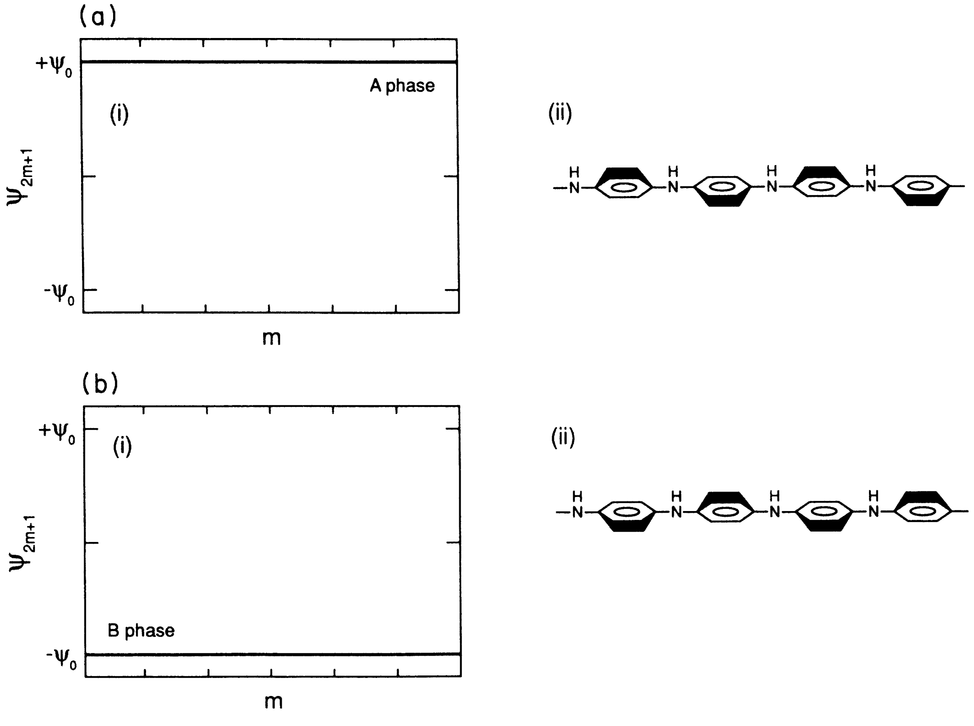

FIG. 3. Spatial variation of (i) the order parameter and (ii) schematic ring torsion angle for the degenerate (a) *A* and (b) *B* phases of LB.

$$\alpha_{\rm eff} \equiv \sum_j \frac{(t^j_+ + t^j_-)^2 + (t^j_+ - t^j_-)^2}{2(\alpha_{\rm N} - \varepsilon_j)} , \tag{7}$$

$$t_{\rm eff} \equiv \sum_j \frac{(t^j_+ + t^j_-)^2 - (t^j_+ - t^j_-)^2}{4(\alpha_{\rm N} - \varepsilon_j)} , \tag{8}$$

and $c^\dagger_{k,s}$ ($c_{k,s}$) is the valence-band creation (annihilation) operator for electrons of wave vector k and spin s. The last term in the effective Hamiltonian accounts for the resonance energy gain of the lower filled energy bands. With the transfer and site energy parameters used to generate Fig. 4, $\alpha_{\rm eff}=2.76$ eV and $t_{\rm eff}=1.81$ eV; the value of $t_{\rm eff}$ is nearly identical to that utilized in an earlier study.[50]

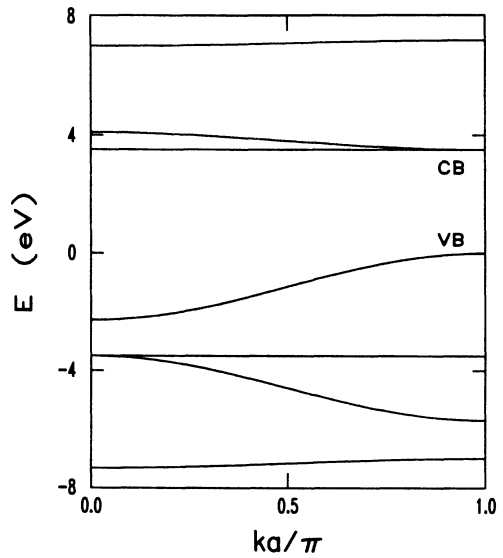

FIG. 4. Calculated band structure for LB; parameters are specified in the text.

In order to facilitate the study of the charged defects arising from the creation of holes in the filled valence band, the Hamiltonian is transformed back to real-space variables and hole creation ($h^\dagger_{2l,s}$) and destruction ($h_{2l,s}$) operators are introduced,

$$\mathcal{H}_{\rm eff} = -\sum_{l,s} \left[\frac{\alpha_{\rm N}}{2} + \frac{\alpha_{\rm eff}}{2} \cos^2\psi_{2l+1} \right] (h^\dagger_{2l,s} h_{2l,s} + h^\dagger_{2l+2,s} h_{2l+2,s}) + t_{\rm eff} \sum_{l,s} \cos^2\psi_{2l+1} (h^\dagger_{2l,s} h_{2l+2,s} + h^\dagger_{2l+2,s} h_{2l,s}) - \varepsilon_{\rm res} \sum_l \cos^2\psi_{2l+1} . \tag{9}$$

Here

$$\varepsilon_{\rm res} \equiv \sum_s \sum_{\substack{\rm unocc \\ j}} \frac{(t^j_+ + t^j_-)^2 + (t^j_+ - t^j_-)^2}{2(\varepsilon_j - \alpha_{\rm N})} \tag{10}$$

is the resonance-energy gain[46] per repeat unit due to conjugation with the backbone nitrogen p_z electrons. With the parameter values used above, $\varepsilon_{\rm res}=3.07$ eV.

B. Lattice potential energy

In polyaniline, the π-electron delocalization energy $\varepsilon_{\rm res}$ that favors phenyl rings in the plane of the nitrogen atoms is countered by a substantial steric repulsion between adjacent rings, forcing them out of the plane. A common treatment of steric effects in molecules is to sum the interaction energies pairwise over atoms from the interacting subunits, e.g., assuming a Lennard-Jones interaction potential between atoms.[54] The study of double-rotor molecules like diphenylsulfide, $(C_6H_5)_2S$, and diphenyl ether, $(C_6H_5)_2O$, has led to the use of a two-dimensional Fourier series to parametrize the dependence of the total molecular energy on ring orientation.[55,56] Since the phenyl rings in polyaniline possess twofold symmetry about the C—N axis, only terms that are even with respect to 180° rotations of either ring contribute; both even and odd terms are included for asymmetric ring-derivatized polyanilines such as polyorthotoluidine (C_6H_4 units replaced by $C_6H_3CH_3$). A useful approximation for the angular variation of the total energy is obtained by retaining several low-order terms of the series expansion,[39]

$$V(\psi_{2l-1}, \psi_{2l+1}) \simeq -\frac{V_{2,0}}{2} (\sin^2\psi_{2l-1} + \sin^2\psi_{2l+1}) + \frac{V_{4,0}}{2} (\sin^4\psi_{2l-1} + \sin^4\psi_{2l+1}) + V_{1,1} (\sin\psi_{2l+1} - \sin\psi_{2l-1})^2 + \text{const} , \tag{11}$$

where $V_{2,0}$, $V_{4,0}$, and $V_{1,1}$ are constants. The $\sin^2\psi$ term includes contributions from steric repulsion as well as from the resonance energy $\varepsilon_{\rm res}$. A variation of the C—N bond length—and thus the bond elastic energy—on the cosine of the ring-torsion angle is anticipated from the rotational dependence of single bond lengths in model molecules such as biphenyl;[46] consequently, the elastic energy of the C—N bonds is implicitly included in $V_{2,0}$. Furthermore, lattice strain involving deviations from equal bond lengths and valence bond angles will contribute to the value of $V_{1,1}$.

Conformational studies of diphenyl ether[56] are particularly germane to this study because C—O and C—N bond lengths are comparable (~1.40 Å), and thus the steric energy of this molecule should be nearly identical to that for the interaction between two adjacent phenyl rings in LB. As anticipated, the total energy is minimized in a skewed conformation,[56] in which adjacent phenyl rings are tilted out of the nitrogen plane by equal

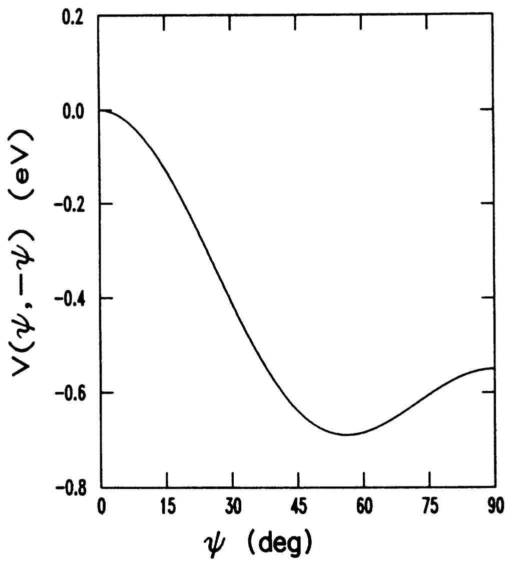

FIG. 5. Approximate total energy per site vs ring torsion angle ψ for LB, with equal-magnitude near-neighbor angles assumed.

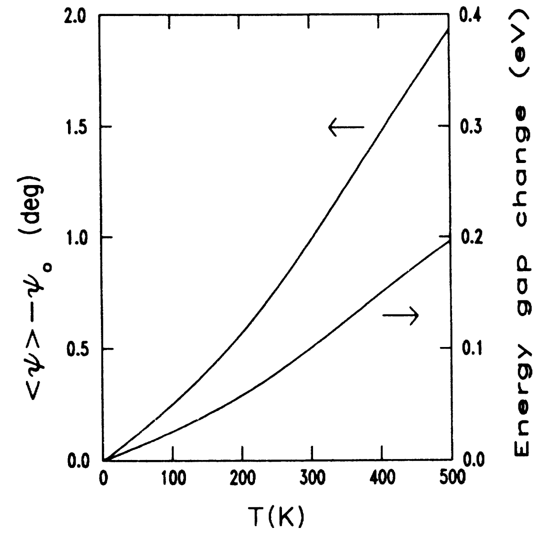

FIG. 6. Calculated variations of the thermal-average ring angle and energy gap with temperature in LB.

but opposite angles. Approximate values of the steric parameters appearing in the total-energy function [Eq. (11)], $V_{2,0} \simeq 1.58$ eV and $V_{4,0} \simeq 1.45$ eV, are chosen to yield the same depth and angular position of the energy minimum obtained from these quantum-chemical calculations on diphenyl ether; $V_{1,1} \sim 0.2$ eV is also estimated from these results. Setting $V_{2,0} \simeq 2.0$ eV yields $\psi_0 \simeq 56°$, producing the 3.5-eV tight-binding band gap expected for LB. The larger value of $V_{2,0}$ in LB than in diphenyl ether is consistent with the decreased resonance energy $\varepsilon_{\mathrm{res}}$ upon replacing the oxygen atom with the less electronegative[51] nitrogen atom. Figure 5 shows the approximate total-energy dependence on ring torsion angle appropriate to LB.

III. IMPLICATIONS OF THE RING-ROTATIONAL DEGREES OF FREEDOM

A. Consequences of the steric potential

Within the adiabatic approximation, the variation of the total energy with torsion angle serves as an effective steric potential energy. Associated with the potential-energy minimum is a Raman-active torsional mode in which adjacent phenyl rings oscillate out of phase; with the moment of inertia $I \simeq 89$ amu Å^2 for phenyl-ring rotations about the C—N axis, the classical frequency of this mode is ~ 90 cm^{-1}. Since it modulates the energy gap, the torsional mode is anticipated to be resonantly enhanced for Raman excitation energies near the band gap.

The angular dependence of the steric potential energy is anharmonic, with larger angles becoming more probable as the temperature is increased. The thermal average of the angular displacement from the zero-temperature equilibrium torsion angle, $\langle \psi \rangle - \psi_0$, is calculated using the Boltzmann distribution function,

$$\langle \psi \rangle - \psi_0 = \frac{\int (\psi - \psi_0) e^{-V(\psi,-\psi)/k_B T} d\psi}{\int e^{-V(\psi,-\psi)/k_B T} d\psi} ; \qquad (12)$$

see Fig. 6. The thermally induced change in energy gap, Fig. 6, is calculated within the tight-binding scheme by neglecting fluctuations in the distribution of ring angles[28] as well as by ignoring the likelihood that the LB chain takes on a coiled conformation as the temperature is increased,[29] i.e., by assuming that all nitrogen atoms remain in a plane; inclusion of these effects would further enhance the calculated temperature dependence of the optical transition energy. The dependence of the valence-band width and band center on ring-torsion angle itself leads to a calculated thermochromic blue shift of the band-gap transition of ~ 0.1 eV from 0 to 300 K. Experiments on EB solutions[57,58] and films[16] reveal an upward shift of the π-π^* band-gap transition of this magnitude, while the 2-eV (benzenoid to quinoid) transition blue shifts to an even greater degree. More detailed studies of EB solutions show that, at room temperature and above, the 2-eV transition shifts linearly with temperature with a temperature coefficient $\sim 7 \times 10^{-4}$ eV/K.[58] This linear shift with temperature is unlike the sharp thermochromic transitions observed in polydiacetylenes[25] and polysilanes,[26] but is in accord with the thermal expansion of the ring-torsion angles resulting from the anharmonic steric potential.

The sensitivity of the electronic structure to ring torsion angle is also manifest in the optical spectra of polyaniline derivatives. Solution and solid-film spectra of polyorthotoluidine reveal increased transition energies as compared with the spectra of the corresponding unsubstituted polymers.[59,60] The enhanced steric repulsion between H and the bulkier CH_3 on adjacent rings increases the average ring-torsion angle, decreasing the valence-band width and thus increasing the π-π^* transition energy.[60,61]

B. Ring-rotational defects

The complete Hamiltonian, combining the electronic, steric, and ring kinetic-energy terms, is

$$\mathcal{H}=\sum_l \tfrac{1}{2}I\left[\frac{\partial\psi_{2l+1}}{\partial t}\right]^2+\sum_l\left[V_{1,1}(\sin\psi_{2l+1}-\sin\psi_{2l-1})^2-V_{2,0}\sin^2\psi_{2l+1}+V_{4,0}\sin^4\psi_{2l+1}\right]$$
$$-\sum_{l,s}\left[\frac{\alpha_{\mathrm{N}}}{2}+\frac{\alpha_{\mathrm{eff}}}{2}\cos^2\psi_{2l+1}\right](h^\dagger_{2l,s}h_{2l,s}+h^\dagger_{2l+2,s}h_{2l+2,s})+t_{\mathrm{eff}}\sum_{l,s}\cos^2\psi_{2l+1}(h^\dagger_{2l,s}h^\dagger_{2l+2,s}h_{2l,s})\ . \tag{13}$$

Minimizing $\mathcal{H}$ with respect to arbitrary ring angle ψ_{2m+1} for stable solutions,

$$\frac{d\mathcal{H}}{d\psi_{2m+1}}=0=2V_{1,1}(\sin\psi_{2m+3}+\sin\psi_{2m-1}-2\sin\psi_{2m+1})-2V_{2,0}\sin\psi_{2m+1}$$
$$+4V_{4,0}\sin^3\psi_{2m+1}+2\sin\psi_{2m+1}\left[\frac{\alpha_{\mathrm{eff}}}{2}(h^\dagger_{2m}h_{2m}+h^\dagger_{2m+2}h_{2m+2})-t_{\mathrm{eff}}(h^\dagger_{2m}h_{2m+2}+h^\dagger_{2m+2}h_{2m})\right]\ . \tag{14}$$

Within the continuum approximation, the stability equation [Eq. (14)] becomes

$$V_{1,1}\frac{d^2\sin\psi_{2m+1}}{dm^2}+2V_{4,0}\sin\psi_{2m+1}(\sin^2\psi_{2m+1}-\sin^2\psi_0)$$
$$=-\sin\psi_{2m+1}\left[\frac{\alpha_{\mathrm{eff}}}{2}(h^\dagger_{2m}h_{2m}+h^\dagger_{2m+2}h_{2m+2})-t_{\mathrm{eff}}(h^\dagger_{2m}h_{2m+2}+h^\dagger_{2m+2}h_{2m})\right]\ , \tag{15}$$

where $\sin^2\psi_0\equiv V_{2,0}/2V_{4,0}$. In the ground state, $\sin\psi_{2m+1}\equiv\pm\sin\psi_0$, as expected.

The expectation value of the Hamiltonian (13) is varied with respect to an adiabatic hole wave function $h^{(0)}_{2m}$; introducing the staggered wave function $h^-_{2m}=(-1)^m h^{(0)}_{2m}$, one obtains

$$(\varepsilon+\alpha_{\mathrm{N}})h^-_{2m}=-\frac{\alpha_{\mathrm{eff}}}{2}(\cos^2\psi_{2m+1}+\cos^2\psi_{2m-1})h^-_{2m}$$
$$-t_{\mathrm{eff}}(\cos^2\psi_{2m-1}h^-_{2m-2}$$
$$+\cos^2\psi_{2m+1}h^-_{2m+2})\ . \tag{16}$$

The stability equation [Eq. (14)] is similar to the field equation of ϕ^4-field theory, since the steric potential [Eq. (11)] possesses an explicitly broken symmetry in the ground state: $\psi_{2l+1}\leftrightarrow-\psi_{2l+1}$. The excitations of certain ϕ^4 models have been shown to be polarons and solitons.[63] In the following subsections, some solutions specific to the present model are discussed.

C. Hole polarons

Iterative solutions of the discrete equation (16) for a hole polaron (P^+) wave function have been found, utilizing the *ansatz* that the polaron ring-angular order parameter varies with position as

$$\sin^2\psi_{2m+1}\equiv\sin^2\psi_0-A\ \mathrm{sech}[(m-m_0)/l]\ , \tag{17}$$

where l and A are dimensionless length and depth parameters, respectively, and m_0 is the site index of the polaron center. Solutions corresponding to a single energy-level split off into the band gap by an energy ε_P from the valence band are found, reminiscent of the Holstein polaron.[64] Figure 7 shows the variation of ring angle and hole charge density with position of the minimum-energy solution for $\varepsilon_P\simeq0.8$ eV, with the defect length $l\simeq1.5$ and depth $A\simeq0.19$. Essentially the same characteristics are found for ring or nitrogen-centered defects. These ring-rotational polarons are predicted to be stable, since the associated increase in steric energy is $\simeq0.2$ eV, yielding a binding energy $\varepsilon_B\simeq0.6$ eV, not accounting for changes in the valence-band density of states induced by the defect. Assuming that the polaron translates without distortion along the chain at a velocity v_{pol}, its effective mass M_{pol} is estimated by equating its translational kinetic energy with the sum of the rotational kinetic energies of the rings associated with the polaron, i.e.,

$$\tfrac{1}{2}M_{\mathrm{pol}}v^2_{\mathrm{pol}}=\tfrac{1}{2}I\sum_m\left[\frac{d}{dt}\psi(m-v_{\mathrm{pol}}t/a)\right]^2\ , \tag{18}$$

where $I\simeq89$ amu Å^2 is again the moment of inertia for phenyl-ring rotations about the *para* axis. The above expression simplifies to

$$M_{\mathrm{pol}}=\frac{I}{a^2}\sum_m\left[\frac{d\psi(m)}{dm}\right]^2\ ; \tag{19}$$

for the defect considered here, $M_{\mathrm{pol}}\sim50m_e$, where m_e is

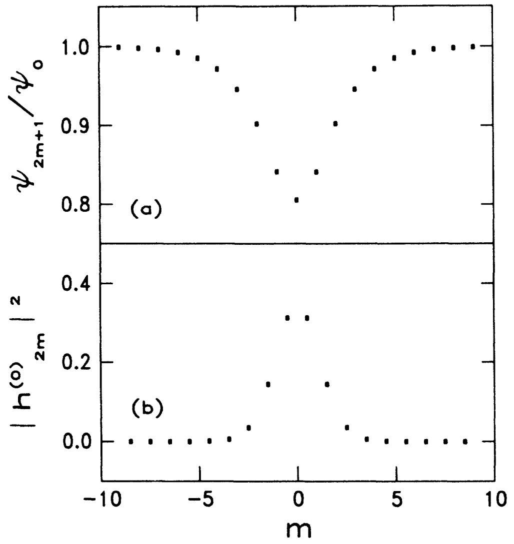

FIG. 7. Spatial variation of the (a) order parameter and (b) hole charge density for a ring-rotational polaron in LB.

a free-electron mass. Removal of a second electron from the polaron yields a spinless bipolaron exhibiting increased ring-torsion-angle distortion—analogous to the increased order-parameter deviation in bond-order bipolarons—and thus possessing an even larger effective mass.

As shown in Fig. 8, *two* in-gap optical transitions, whose energies sum to the gap energy, are associated with the P^+ energy level; by contrast, a polaron induces *three* optical transitions in nearly-charge-conjugation-symmetric systems.[65] Near-steady-state photoinduced-absorption studies on LB,[14] revealing induced absorptions at 0.75 and 2.85 eV upon pumping into the π-π^* band gap, are consistent with this defect-level scheme. Similarly, both photoinduced[66] and doping-induced[67] studies of PPS reveal two optical transitions whose energies sum to ~3.9 eV, the peak of the π-π^* transition, further supporting the role of ring-rotational polarons. The importance of ring-rotation-stabilized radical cation states in triphenylamine[68] and in diphenylsulfide[69] provides an analog of the ring-rotational polarons in model molecular systems.

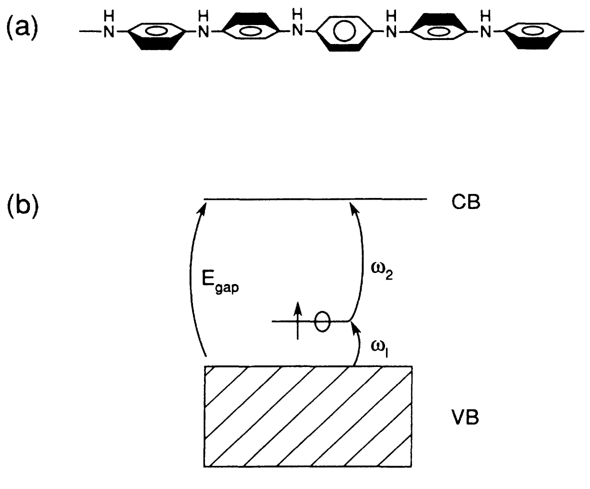

FIG. 8. Schematic (a) structure and (b) energy-level diagram for a ring-rotational hole polaron in LB, showing the *two* associated optical transitions ω_1 and ω_2.

D. Solitons in LB

Another class of excitations supported by the model Hamiltonian are soliton defects in the order parameter, as shown schematically in Fig. 9. An uncharged soliton possesses a hyperbolic-tangent order parameter[70]

$$\sin\psi_{2m+1} = \pm\sin\psi_0 \tanh[(m-m_0)/\xi] \, , \qquad (20)$$

where $\xi^2 = V_{1,1}/V_{2,0}$ is the square of the dimensionless soliton length and m_0 is the site index about which the soliton is centered. Charged solitons in LB are anticipated to induce a single energy-level split off from the valence band into the gap. Unlike the solitons of *trans*-polyacetylene, LB solitons possess conventional spin-charge statistics as a consequence of the unity band filling in this system. The creation energy of both neutral and charged solitons in LB is quite large, since the associated phase reversal of the order parameter requires near-zero ring-torsion angles involving substantial steric energy; consequently, thermal generation is not likely to be an important mechanism of soliton creation in LB. Nevertheless, it is plausible that some solitons are formed during the conversion[2] to LB from the as-prepared oxidized forms of polyaniline.

E. Implications for dynamics

The concept of ring-torsional polarons, which connects the electronic structure of charged defects with the local chain conformation, can reconcile the existence of extremely long-lived, massive polarons inferred from several photoinduced absorption[10–14,16] and photoconductivity[11,15] experiments with NMR studies,[38] demonstrating that large-amplitude ring rotations are thermally activated: polarons are likely trapped by various constrained chain-packing arrangements, their recombination hindered by lack of free volume for ring rotation. Consideration of the ring degrees of freedom in polyaniline thus links the dynamical processes in conducting polymers with those in classical polymers like polycarbonate, in which ring motions are also very important relaxation processes.[71] A distribution of environments in the amorphous regions of the polymer may account for the dispersive decays of photoinduced-absorption features in various forms of polyaniline on picosecond[72] and millisecond[10] time scales, memory phenomena reported for protonation of EB,[49] and the hysteresis observed in electrochemical doping experiments.[73]

F. Electron polarons

A consequence of the severe change-conjugation asymmetry in LB is the difference in the origin of self-trapping for electron (P^-) and hole (P^+) polarons. While ring rotations are effective in splitting off an energy level from the valence band into the gap, binding a P^+, they do not alter the energy of the lowest unoccupied molecular orbital which comprises the conduction-band states and thus cannot provide any binding for electrons. Self-trapping of electrons can occur, however, by a quinoid distortion of both the C—N and ring bond lengths. The resulting polaron is similar in character to the polarons in polyparaphenylene (PPP):[74] one energy level is split off from each of the valence and conduction bands into the energy gap, yielding a nonzero polaron binding energy and three polaron-induced optical transitions. The magnitude of the energy splittings, which are not symmetrical because of charge-conjugation-symmetry breaking, are anticipated to be of the same order as for PPP, i.e., ~0.2 eV.[74] Photoinduced-absorption experiments on polyaniline have not produced evidence for defect transition energies of this magnitude, perhaps reflecting the difficulty of discerning the defect absorption features or the short lifetimes of such defects. Indeed, a short P^- lifetime is inferred from near-steady-state photoinduced-absorption measurements on LB, which suggest[14] that on a millisecond time scale the photoexcited electrons have recombined with holes or are trapped at residual quinoid rings. It is noted that self-trapping of P^+ due to ring rotations may also be enhanced by contributions from ring bond-length changes toward a quinoid geometry.

G. Pernigraniline

The electronic structure of PNB has been characterized in terms of a Peierls ground state that supports soliton and polaron defects.[42] The half-filled π band, estimated to have a full width $W=2.9$ eV, is split by a calculated[42] energy gap $E_g=1.4$ eV caused by an effective bond-length alternation, resulting in the constituent C_6H_4 (phenyl) rings of the polyaniline backbone taking on an alternating quinoid-benzenoid character analogous to the double-bond–single-bond alternation in dimerized *trans*-polyacetylene. The resulting degenerate ground state of PNB was shown[42] to support bond-alternation defects, particularly solitons and polarons, which were anticipated to accommodate doping-induced and photoinduced charge in the polymer.

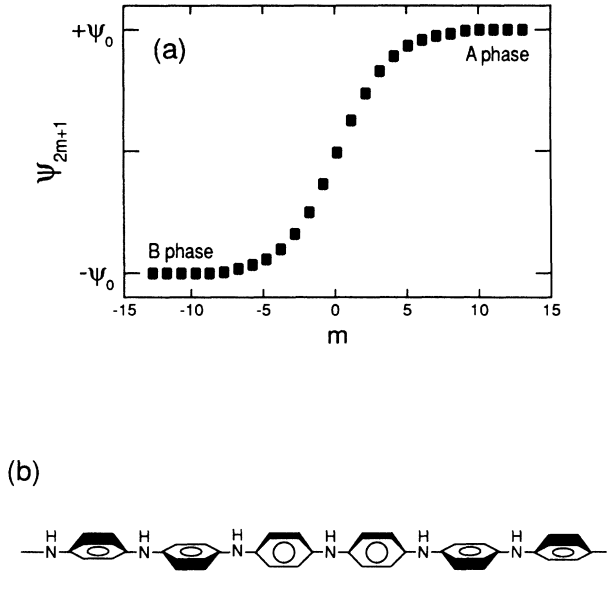

FIG. 9. Spatial variation of the (a) order parameter and (b) schematic ring torsion angle for a soliton in LB.

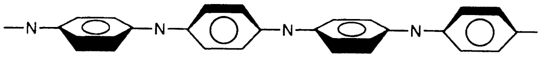

FIG. 10. Schematic dimerization of ring torsion angle in PNB.

An alternate perspective on the ground and defect states in PNB is provided by *ring-rotational* dimerization.[44] Rotation of adjacent rings to different torsion angles ψ_1 and $-\psi_2$, Fig. 10, will cause a dimerization of the effective valence-band transfer integral[75] and thereby induce a nonzero E_g in the otherwise half-filled valence band. In the second-order perturbation-theory limit, for example, these changes in ring angle can be related to the magnitude of the dimerization gap; using the approximate dependence of the steric energy on torsion angle [Eq. (11)], it can be shown that the lattice energy increase is given by

$$E_{\mathrm{latt}}/N \simeq (V_{4,0}+V_{1,1}/\sin^2\psi_0)\cos^4\psi_0(E_g/W)^2 \;, \qquad (21)$$

where ψ_0 is the ring-torsion angle before dimerization. In this limit, the correspondence of the ring-rotational dimerization in PNB with the bond-length dimerization in, e.g., *trans*-polyacetylene, implies that the energy gap is given by

$$\frac{E_g}{W}=\frac{4}{e}\exp\left[-\frac{1}{2\lambda_{\mathrm{tors}}}\right] , \qquad (22)$$

where

$$2\lambda_{\mathrm{tors}} \equiv \frac{4t_{\mathrm{eff}}\tan^2\psi_0}{\pi(V_{2,0}+2V_{1,1})} \qquad (23)$$

is the effective electron-ring-torsion-angle coupling constant. A similar expression is obtained if the coupling constant is defined by linearizing the angular dependence of the transfer integral and steric restoring force about ψ_0.[43] With the constants used previously, and assuming $\psi_0 \sim 30°$ for PNB,[30] $2\lambda_{\mathrm{tors}} \sim 0.4$ is estimated, comparable to the electron-phonon–coupling constants estimated for polyacetylene[18] and polythiophene.[19] We conclude that the electron-ring-torsion-angle coupling in polyaniline is substantial. Though developed for large ring angles, the torsion-angle dependence of $2\lambda_{\mathrm{tors}}$ suggests that the electron-ring-torsion-angle coupling is nearly zero in ring-containing polymers like polythiophene and polypyrrole, for which the rings are nearly planar ($\tan^2\psi_0 \sim 0$).

The energy gap and bandwidth predicted from bond-length dimerization[42] can be reproduced by alternating ring angles of 40° (−40°) and −63° (63°) within the present model; the charge-storing defect states are thus expected to be ring-alternation-defect solitons and polarons possessing large effective masses. The *trans*-$(\mathrm{CH})_x$ bond-alternation soliton mass expressed in SSH (Ref. 20) can be extended to unit cells containing more than one atom, assuming that the soliton length l is the same for all J atoms in the unit cell:

$$M_{\mathrm{sol}} = \frac{4}{3l} \sum_j^J M_j \left[\frac{u_0^{(j)}}{a} \right]^2 , \tag{24}$$

where M_j and $u_0^{(j)}$ are, respectively, the mass and displacement from the undimerized position of the jth atom in the unit cell, and a is the unit cell length. The undimerized and dimerized bond lengths quoted by dos Santos and Brédas for PNB (Ref. 42) yield $u_0^{(j)}$ for the carbon and nitrogen constituents of the chain; the dimerization amplitude for the nitrogen atom is $|u_0^{\mathrm{N}}| \simeq 0.054$ Å, for the *ortho*- and *meta*-carbon atoms $|u_0^{\mathrm{C}}| \simeq 0.032$ Å, and for the *para*-carbon atoms $|u_0^{\mathrm{C}}| \simeq 0$. Taking $l \sim 2$ units [within the continuum limit, $l = W/E_g$ (Ref. 76)], $M_{\mathrm{sol}} \sim 5m_e$ is obtained.

Equating the soliton kinetic energy to the kinetic energies of rotation of the phenyl rings, the effective mass for a ring-rotational soliton can be calculated. Assuming dimerized ring angles $\psi_0 + \delta$ and $-\psi_0 + \delta$, and a hyperbolic-tangent-shaped soliton of length l, the soliton mass is

$$M_{\mathrm{sol}} \simeq \frac{4}{3l} \frac{I}{a^2} (\psi_0^2 + \delta^2) . \tag{25}$$

With the torsion-angle dimerization stated above, $M_{\mathrm{sol}} \sim 10^4 m_e$. As a ring-rotational *polaron* involves no reversal of the order parameter, it is anticipated to possess a smaller effective mass than the soliton, similar in value to that of polarons in LB ($M_{\mathrm{pol}} \gtrsim 50m_e$).

As in *trans*-$(\mathrm{CH})_x$, the smallness of the atomic displacements relative to the unit cell spacing in PNB results in small bond-length soliton masses. By contrast, the ring-rotational soliton mass is determined by the large moment of inertia of the phenyl rings as well as the substantial difference in ring angles in the two phases of ring-angle alternation. The large effective masses expected for ring-angle-alternation defects are consistent with the observation of relatively weak infrared activity induced by photoexcited charged defects in the LB,[14] EB,[13] and PNB (Ref. 77) forms of polyaniline, and in PPS.[66]

The actual Peierls-distorted state is expected to contain both ring- and bond-dimerized components, since the infrared-absorption spectrum of PNB exhibits an intense 1600-cm^{-1} mode that is indicative[11–14] of a quinoid-like distortion of the phenyl-ring bond lengths. However, the ring-torsion-angle dimerization dominates the effective masses of the defect states.

IV. SUMMARY

Significant consequences of the ring-rotational degrees of freedom exist for the electronic structure and defect states of polyaniline and other ring-containing polymers. An order parameter describing the spatial variation of the ring angle was developed. The competition between delocalization energy and steric repulsion between rings in determining the ground-state value of the order parameter was emphasized; the anharmonic nature of the steric interaction is consistent with the thermochromism observed in polyaniline. The charge-carrying hole states in LB are solitonic and polaronic defects in the ring-rotational order parameter; associated with the polarons is a single level in the energy gap responsible for two induced absorptions, consistent with experimental observation. For simplicity, the tight-binding approach was utilized; it possesses limited capability for the accurate prediction of transition energies and equilibrium geometries. Moreover, overlap between the π and σ electrons, which has been suggested[78] to play a role in determining the equilibrium chain conformation of some conjugated polymers, is not treated at the simple Hückel level. Electron-electron interactions, also neglected in the model Hamiltonian, may lead to very different phenomena in LB than in *trans*-$(\mathrm{CH})_x$;[24] for example, that LB possesses an even number of electrons per site suggests that removal of one electron may increase the stabilization of the resulting hole polaron via the reduced on-site Coulomb repulsion.

The disorder expected in real polyaniline samples is likely to have important effects on the tendency toward polaronic self-trapping; furthermore, interchain interactions may affect not only the electronic band structure but also the steric potential experienced by each phenyl ring. Though the consequences of interchain interaction may be represented to first order by a renormalization of the steric parameters utilized in this paper, a complete theoretical treatment entails a complex many-body problem.

The results obtained here were derived within second-order perturbation theory, valid in the limit that the ring-N transfer integrals are small compared to the relevant energy differences between ring and N orbitals. While this approach overestimates the π-electron delocalization energy gain with decreasing ring angle, it is anticipated that the existence and character of the ring-rotational defects introduced here will remain unaltered within more accurate levels of calculation.

The ring-rotational degrees of freedom in the half-filled band PNB system provide an alternative to a bond-dimerized Peierls distortion, i.e., ring-rotational dimerization. Estimates of the electron-ring angle coupling constant suggest that it is comparable to the usual electron-phonon coupling constant in polyacetylene. The charged defect states in PNB are associated with distortions of ring angles and thus are likely to possess a substantial kinetic mass, in contrast to the bond-alternation solitons in *trans*-$(\mathrm{CH})_x$.

The coupling of the electronic state to the chain conformation provides a means to understand the substantial effective masses and lengthy relaxation times inferred for photoexcitations in polyaniline, and connects the dynamics of this conducting polymer with classical polymer systems. These lifetime effects may be important for, e.g., the development of optical information-storage technology based on the polyanilines.[79]

The ring-torsional degrees of freedom are important for PPO and PPS, as they are isostructural and isoelectronic to LB. Their importance has also been recognized in describing thermally induced changes in ground-state properties—thermochromism— in the polydiacetylenes and polythiophenes. It is suggested that ring rotations may prove to be an important component of the excited states of many polymers, particularly in those systems[80] in which steric interactions force deviations from planarity in the ground state.

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