PHYSICAL REVIEW B VOLUME 38, NUMBER 8 15 SEPTEMBER 1988-I

Electronic properties of polyacene

Andrea L. S. da Rosa and Celso P. de Melo
Departamento de Física, Universidade Federal de Pernambuco, 50 739 Recife, Pernambuco, Brazil

(Received 5 October 1987; revised manuscript received 6 May 1988)

We initially use a recently developed method based on the combination of transfer-function technique and renormalization ideas to investigate the electronic structure of polyacene within a first-neighbor tight-binding Hamiltonian. It is found that at this level of approximation the electronic structure of the material closely resembles that of two interacting polyacetylene chains. In particular, it is shown that the wave function associated with a conformational defect in one of the lateral chains of polyacene is identical to that of a similar soliton in polyacetylene. An extended-Hückel-theory crystalline-orbital study of polyacene is then performed to establish the relative stability of its different isomers, and the resulting band structure is used to construct the joint density of states for the valence and conduction bands. The results suggest that the optical properties of polyacene should be remarkably different from those of polyacetylene.

I. INTRODUCTION

Polyacene, $[C_2H_4)_n]$, is a yet to be synthesized polymer consisting of condensed aromatic rings of linearly fused structure (Fig. 1). Chains of low molecular weight ($n \lesssim 6$) can be obtained by thermal or photoinduced polymerization[1] and display dark conductivity of 10^{-15} $\Omega^{-1}\text{cm}^{-1}$. In spite of earlier reports that longer members of this family of polymers could present much higher conductivities,[2] to our knowledge well-characterized samples have not been produced and the mechanical and environmental properties of polyacene are still uncertain.

The electronic structure of infinite polyacene (PANE) has long been the object of theoretical interest; as in the case of polyacetylene (PA), controversy existed whether or not a central gap resulting from bond alternation would occur.[3-8] In their pioneering tight-binding study of the electronic structure of polyacenes, Salem and Longuett-Higgins[2] concluded that the ground-state configuration of the polymer should correspond to a nonalternant structure. Whangbho *et al.*[4] included long-range interactions through an extended-Hückel-theory crystalline-orbital (EHCO) method to compute the band structure of PANE in its different configurations; their result pointed to the alternant *trans* form as the most stable, with a corresponding gap of the order of 0.45 eV. This could be understood as a consequence of the allowed symmetry mixing of occupied and virtual bands[5] as a result of the pattern of alternating single and double bonds between carbon atoms in each lateral chain of the *trans* form. This conclusion has been later confirmed by the complete-neglect-of-differential-overlap crystalline-orbital (CNDO CO) study of Tanaka *et al.*,[6] who have suggested that due to its dopantphilic nature and the presence of a small band gap PANE should be a promising electrically conductive material. In fact, PANE meets simultaneously the four criteria recently enumerated by Bredas[9] for a polymer to present high conductivity at low voltages, since it possesses (i) a high degree of π-electron conjugation, (ii), a very simple structure, (iii) forms a planar system, and (iv) is expected to have a very low ionization-potential value associated with a very large bandwidth.

The high symmetry of PANE's unit cell has led Kivelson and Chapman[10] to consider the possibility that strong electron-phonon interactions could suppress the Peierl's gap present in the alternant isomers of the material. On the other hand, PANE can also be seen as consecutive to PA in the series of polymers terminating with graphite and whose structures "result" from the coupling of an increasing number of parallel polyenic chains:[11] Kertsez and Hoffman[12] have used simple symmetry arguments to predict that the central gap in these systems should scale

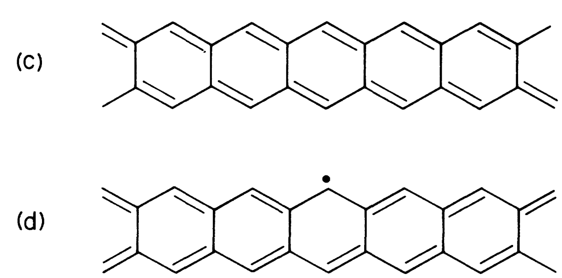

FIG. 1. Possible configurations for polyacene (PANE): (a) nonalternant, (b) alternant *cis*, and (c) alternant *trans;* (d) single-site defect in one of the lateral chains of polyacene.

with the inverse of the number of coupled chains. Although the question of whether or not a novel ground-state configuration could result from vibronic interactions in the infinite polymer is by no means settled,[13] as a first approximation one could expect that the electronic structure of PANE should not depart remarkably from that of PA. Considering the importance that structural defects play in the electronic properties of the latter,[14] it is surprising to notice that not much attention has been given in the literature to the study of the electronic structure of polyacenic chains presenting defects.[15]

In this paper we initially examine the electronic properties of PANE using a recently developed technique for the calculation of the electronic structures of complex polymers.[16–18] It is shown that within a first-neighbor tight-binding approximation PANE can be formally reduced to a one-dimensional chain of two different kinds of "atoms" disposed in an alternate bonding pattern and coupled up to second-neighbor interactions. An exact solution to the electronic structure of this latter problem is then found after the introduction of transfer functions similar to those used previously to describe PA.[19] The treatment is finally extended to examine the modifications introduced in the electronic structure of PANE by the presence of a defect [Fig. 1(d)] resulting from the breaking of the pattern of alternation between single and double bonds in one of the lateral chains. Our results indicate that a damped spin-density wave identical to that of a soliton in PA (Refs. 14 and 20) occurs and that, at least at this level of approximation, for a nonrelaxed (single-site) defect this disturbance in the spin polarization of the system is entirely confined to a single lateral chain. As a consequence, if correlation effects[21,22] are neglected one can expect the transport properties of PANE to be very similar to those of PA.[13]

This should not be the case for the optical properties of these two polymers. As shown by Flytzanis and collaborators,[23,24] below a certain critical temperature T_c a chain-pairing interaction could have drastic effects on the one-and two-photon absorption spectra of polydiacetylene polymer crystals due to the doubling of the unit cell in the direction transverse to the chain. If ever synthesized, PANE would be a physical realization of this system presenting very high T_c. The actual properties of PANE will depend on which of its configurations would come out to be the most stable; in any case, however, its optical properties can be expected to differ substantially from those of PA. In the final part of this paper we use EHCO band-structure results to compare the joint density of states for the valence and conduction bands of this polymer to a similar result for PA. The observed differences stress the importance of further studies in the linear and nonlinear optical properties of PANE.

II. RENORMALIZATION-TECHNIQUE RESULTS

A. Defect-free chain

It has been recently shown that renormalization ideas can be combined to a transfer-function technique to yield a simple yet powerful scheme for the treatment of the electronic structure of one-dimensional polymers.[16–18] The method was originally applied to the so-called "chain-bridged" polyenes. All members of this class of polymers were formally reduced to a polyacetylenic structure and hence, the electronic-structure problem could be solved at once in a generic way. Then, after appropriate substitution of parameters, one was able to get the corresponding density of states for each individual polymer. An important feature of the method is that it also provides an analytical way of calculating the wave functions associated with conformational defects along the polymeric chain. The presence of these kinds of defects (solitons and polarons) seems to play an essential role in the transport properties of conjugated polymers. Here we will apply the technique to investigate the electronic structure of PANE. Since the carbon atoms in PANE cannot be connected through a topological one-dimensional path, this is conceptually a new problem.

We will consider initially the case of regular (i.e., with no conformational defects) PANE chains, as this will allow us to investigate the effect of the different geometric parameters upon the electronic structure of the polymer while introducing the transfer functions to be used later in the soliton calculation. Within a first-neighbor tight-binding approximation, PANE can be thought of as resulting from the lateral interaction between two parallel PA chains. In this model, only the $2p_z$ (perpendicular to the plane of the molecule) orbitals in each carbon atom are considered. Assuming that they form an orthonormal basis, the corresponding Hamiltonian can be written as

$$H=\sum_{i}\varepsilon_i a_i^{\dagger}a_i+\sum_{i,j}(v_{ij}a_i^{\dagger}a_j+\text{c.c.})\ , \tag{1}$$

where the nondiagonal coupling only extends to first neighbors. Then, three hopping parameters, v_1, v_2, and v_3 [Fig. 2(a)], can be defined (the first two are related to

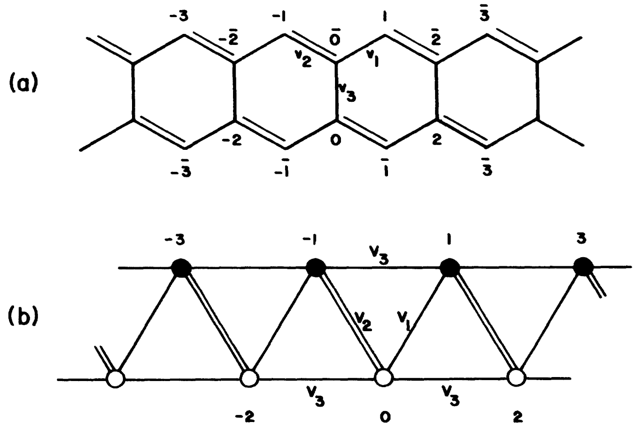

FIG. 2. (a) Off-diagonal coupling terms in regular polyacenic chain. (b) Interactions in renormalized chain; note that longer-range interactions (V_3) are introduced in the process of renormalization.

the degree of bond alternation in each lateral chain, while the latter measures the strength of the coupling between the chains), and by choice of adequate parameters one can describe all configurations of Fig. 1. As is usual in the treatment of homocyclic compounds, the eigenenergies ε_i of all carbon atoms are assumed identical,[25] and for convenience will be here taken equal to zero. In the site representation the Green's operator $\mathbf{G}=(E-\mathbf{H})^{-1}$ will give an infinite set of coupled equations. Adopting the notation introduced in Fig. 2(a), we will have

$$\begin{aligned}
EG_{-\bar{1},0}&=-v_1G_{0,0}-v_2G_{-2,0}\ ,\\
EG_{0,0}&=1-v_1G_{-\bar{1},0}-v_2G_{\bar{1},0}-v_3G_{\bar{0},0}\ ,\\
EG_{\bar{1},0}&=-v_2G_{0,0}-v_1G_{2,0}\ ,\\
EG_{\bar{0},0}&=v_1G_{1,0}-v_2G_{-1,0}-v_2G_{0,0}\ .
\end{aligned}\tag{2}$$

After eliminating references to the sites designated by overbars, we can write for the remaining "renormalized" sites [Fig. 2(b)]

$$\begin{aligned}
&\ldots\ ,\\
&(E-\alpha)G_{0,0}=1+V_1G_{1,0}+V_2G_{-1,0}+V_3(G_{2,0}+G_{-2,0})\ ,\\
&(E-\beta)G_{1,0}=V_1G_{0,0}+V_2G_{2,0}+V_3(G_{3,0}+G_{-1,0})\ ,\\
&\ldots\ ,
\end{aligned}\tag{3}$$

or, for a generic $n>0$ site,

$$\begin{aligned}
(E-\alpha)G_{2n,0}=V_1G_{2n+1,0}+V_2G_{2n-1,0}&\\
+V_3(G_{2n+2,0}+G_{2n-2,0})\ ,&
\end{aligned}\tag{4a}$$

$$\begin{aligned}
(E-\beta)G_{2n+1,0}=V_1G_{2n,0}+V_2G_{2n+2,0}&\\
+V_3(G_{2n+3,0}+G_{2n-1,0})\ ,&
\end{aligned}\tag{4b}$$

where

$$\alpha=\frac{v_1^2+v_2^2+v_3^2}{E}\ ,\tag{5a}$$

$$\beta=\frac{v_1^2+v_2^2}{E}\ ,\tag{5b}$$

$$V_1=\frac{v_1v_3}{E}\ ,\tag{5c}$$

$$V_2=\frac{v_2v_3}{E}\ ,\tag{5d}$$

and

$$V_3=\frac{v_1v_2}{E}\ .\tag{5e}$$

The structure of Eq. (4) above is similar to those corresponding to a topologically one-dimensional chain of alternate species of atoms and bonds within a second-neighbor interaction approximation. An exact solution to this problem can be found in the same way as in the case of a homoatomic chain after introduction of the transfer functions[19]

$$T_1=\frac{G_{2n+1,0}}{G_{2n,0}}\tag{6a}$$

and

$$T_2=\frac{G_{2n,0}}{G_{2n-1,0}}\ ,\quad n=0,1,2,\ldots\tag{6b}$$

with $t=T_1T_2$. Substitution of (6) in (2) allows, after some algebra, to obtain the explicit form of T_1 and T_2 as

$$T_1=\frac{b(1+at)}{\xi_2-y}\tag{7a}$$

and

$$T_2=\frac{b(a+t)}{\xi_1-y}\ ,\tag{7b}$$

where

$$a=\frac{V_2}{V_1}\ ,\tag{8a}$$

$$b=\frac{V_3}{V_1}\ ,\tag{8b}$$

$$\varepsilon=\frac{E}{V_1}\ ,\tag{8c}$$

$$\xi_1=\varepsilon^2-(1+a^2+b^2)\ ,\tag{8d}$$

$$\xi_2=\xi_1+b^2\ ,\tag{8e}$$

$$y=\xi_2\pm b\varepsilon\ ,\tag{8f}$$

and

$$t=\frac{y\pm(y^2-4a^2)^{1/2}}{2a}\ .\tag{8g}$$

As usual, in order to obtain physically meaningful results the signs of y and t are chosen such that the condition $|t|<1$ is satisfied.

Similar expressions can be found for the sites on the negative part of the chain, through the use of the transfer functions

$$F_1=\frac{G_{-2n,0}}{G_{-2n+1,0}}\tag{9a}$$

and

$$F_2=\frac{G_{-2n-1,0}}{G_{-2n,0}}\ ,\quad n=1,2,\ldots\ .\tag{9b}$$

If we proceed as above, we easily obtain

$$F_1=\frac{b(1+at)}{\xi_1-y}\tag{10a}$$

and

$$F_2=\frac{b(t+a)}{\xi_2-y}\ .\tag{10b}$$

Finally, after substitution of expressions (6)–(10) in Eq. (3) we obtain

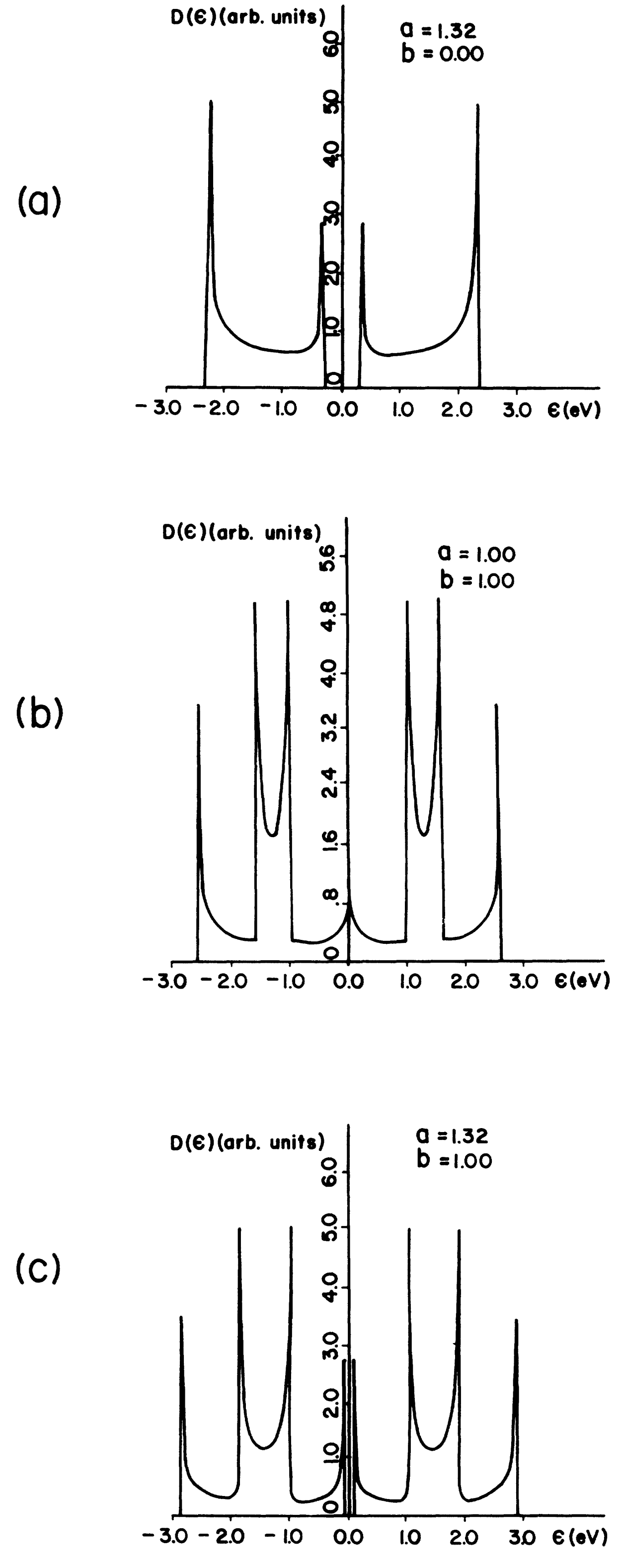

FIG. 3. Local density of states per unit cell (in arbitrary units) for polyacene for different values of parameters a and b. (a) If $b \to 0$, the system resembles two weakly interacting polyacetylene (PA) chains, (b) if no bond alternation in each lateral chain occurs ($a = 1.0$) the central gap vanishes, and (c) the central gap appears for $a \neq 1.0$.

$$G_{0,0} = \frac{\varepsilon}{(\xi_1 - bT_1 - abF_2 - 2bt)} \tag{11a}$$

and

$$G_{1,1} = \frac{\varepsilon}{\xi_2 - bF_1 - abT_2 - 2bt} \ . \tag{11b}$$

The local density of states (LDOS) per unit cell can then be determined as

$$D(\varepsilon) = -(1/\pi)[\mathrm{Im}G_{0,0}(\varepsilon) + \mathrm{Im}G_{1,1}(\varepsilon)] \ . \tag{12}$$

We present the calculated LDOS per unit cell for different values of the parameters a and b in Fig. 3. As is usual for neutral conjugated π-electron systems, the Fermi level is at the middle of the total π bandwidth. In the limit of vanishing coupling between the lateral chains ($b \to 0$) the LDOS reduces to the case of two isolated PA chains of corresponding a, as it should. The parameter b controls the degree of superposition of the two bands inside each set of valence and conduction bands. The degree of alternation in each lateral chain in PANE (measured by a) determines the existence of the central gap between valence and conduction bands. However, the value of this central gap depends simultaneously on the values of a and b.

A caveat should be introduced here in that the crudeness of the adopted first-neighbor model does not allow for any reliable predictions concerning the relative stabilities of the different configurations; this point will be discussed later (Sec. III), when we will present the extended-Hückel-theory (EHT) calculations. For now, we should just call attention to the fact that even for an alternant geometry the gap between the valence and conduction bands of PANE is much smaller than for the corresponding PA polymer of the same degree of bond alternation. As discussed by Kivelson and Chapman,[10] if the ground-state configuration of PANE turns out to be associated to a small band gap, the proximity of the Van Hove singularities at the edges of the valence and conduction bands near the Fermi level could give rise to additional instabilities in the electronic distribution.

B. Soliton wave function

We now turn to the problem of a conformational defect in the polyacenic chain (Fig. 4). After the seminal work of Su, Schrieffer, and Heeger,[14] the study of solitons in condensed matter has experienced explosive growth. In particular, transfer-function techniques have proved to be an important tool for the investigation of the electronic structure associated with single-site[20] and relaxed[26] defects in PA. Here we are interested in the comparison of the qualitative features of polyacenic and polyacetylenic chains: We will consider then the simple case of a nonrelaxed solitonlike defect in one of the lateral chains of PA. For a first-neighbor Hamiltonian, the *cis* and *trans* configurations of PANE are energetically equivalent, and hence the defect represented in Fig. 4(a) connects two isoenergetic chains.

To obtain the change in the electronic structure of the system introduced by the presence of the defect centered at site 1, we adopt the same notation as before and write

$$EG_{1,1}=1-v_1(G_{\bar{2},1}+G_{\bar{0},1})\ , \tag{13}$$

where

$$G_{\bar{2},1}=\frac{-(v_1G_{1,1}+v_2G_{3,1}+v_3G_{2,1})}{E} \tag{14}$$

and

$$G_{\bar{0},1}=\frac{-(v_1G_{1,1}+v_2G_{-1,1}+v_3G_{0,1})}{E}\ . \tag{15}$$

Substitution of (14) and (15) in (13) will give the expression for the diagonal element of the Green's function only in terms of renormalized sites,

$$(E-\alpha_s)G_{1,1}=1+V_1(G_{0,1}+G_{2,1})+V_3(G_{3,1}+G_{-1,1})\ , \tag{16}$$

with

$$\alpha_s=\frac{2v_1^2}{E}\ . \tag{17}$$

It is easy to show that for $i>1$ the periodic structure of the chain is restored and therefore the transfer functions (6) can be introduced. Since the problem now has inversion symmetry with respect to site 1, we obtain directly (in units of v_1)

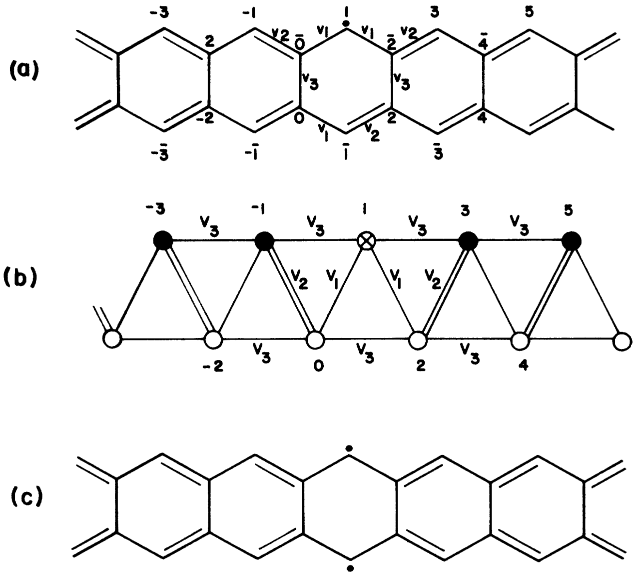

FIG. 4. (a) Coupling parameters for single-site defect in one of the lateral chains of polyacene (PANE), and (b) equivalent renormalized chain. (c) Possible polaron-type defect in polyacene.

$$G_{1,1}=\frac{\varepsilon}{\varepsilon^2-2(1+bT_2+at)}\ ,$$
$$=\frac{-\varepsilon\mp b}{(1-a^2)\pm[\varepsilon^4-2\varepsilon(1+a^2)(\varepsilon\pm b)+b\varepsilon^2(b\pm 2\varepsilon)+(1-a^2)^2]^{1/2}}\ . \tag{18}$$

A similar procedure would give the diagonal elements of the Green's function at any site, and the LDOS associated with any particular cell could be calculated as before. In Figs. 5(a) and 5(b) we present the LDOS for the cell comprising sites 0 and 1 for different values of a and b.

Solitons represent a disruption in the translation symmetry of the polymer, and therefore the corresponding changes in the electronic structure of the system should appear as a localized state. It can be shown[27] that the weight of the localized electronic state of energy ε centered at site i decays along the chain as

$$\frac{\psi_i(\varepsilon)}{\psi_j(\varepsilon)}=\frac{R_{i,i}(\varepsilon)}{R_{j,j}(\varepsilon)}\ , \tag{19}$$

where $R_{j,j}(\varepsilon)$ is the residue of the diagonal Green's-function element at site j. For the solution of physical interest the denominator of (18) vanishes for $\varepsilon\rightarrow 0$, and the corresponding residue at this point can be shown to be

$$R_{1,1}(0)=\lim_{\varepsilon\rightarrow 0}G_{1,1}(\varepsilon)=\frac{a^2-1}{a^2+1}\ . \tag{20}$$

The wave function associated with the defect (a spin-density wave) should have a maximum at site 1. If we take advantage of the symmetry of the problem, the value of the soliton wave function at any site can be shown to be

$$\begin{gathered}\psi_{2n+1}(0)=(T_1T_2)^n\psi_1(0)\ ,\\ \psi_n(0)=a^{-|n-1|/2}\cos[\pi(n-1)/2]\psi_1(0)\ .\end{gathered} \tag{21}$$

An important conclusion can be drawn from the above results: Since the soliton wave function vanishes at all sites pertaining to the lower lateral chain and its weight on the remaining sites does not depend on b, its properties are entirely determined by the characteristics (i.e., bond alternation) of the upper chain. We note that the wave function (21) above exactly satisfies the normalization condition, and therefore it rigorously vanishes at the intermediate sites eliminated in the process of renormalization.

For this single-site defect, the wave function is depicted in Fig. 5(c). Comparison to the soliton wave function in PA (Ref. 20) shows that at this level of approximation the soliton properties in PANE are identical to those of an equivalent defect in a polyacetylenic chain: The latter has been extensively studied in recent years and therefore much of the properties of solitons in polyacenes can be inferred from the comparison between the two systems. As discussed previously, relaxation of the width of the potential barrier between the two alternating patterns should lead to a broadening of the localized state.[26] Also, correlation has been shown to lead to a nonvanishing spin density at all sites;[22] due to the electronic delocalization in the aromatic ring, we expect correlation effects to play in PANE a much more important role in the structure and dynamics of solitons than in PA. Since these effects have not been included here, our model should then be seen as a first approximation to the description of the electronic structure of defects in polyacenes (PANE).

III. EXTENDED-HÜCKEL-THEORY RESULTS

In view of the crucial effects that the suppression of the Peierls distortion in the ground state of PANE could have upon the electronic properties of the polymer, it is pertinent to proceed to a systematic study of the relative stability of its different isomers. As noticed before, the first-neighbor tight-binding model used above does not give realistic values for the electronic and total energies of the system. For example, one has to include at least a second-neighbor interaction in order to distinguish between the *cis* and *trans* configurations of PANE. On the other hand, long-range interactions are naturally includ-

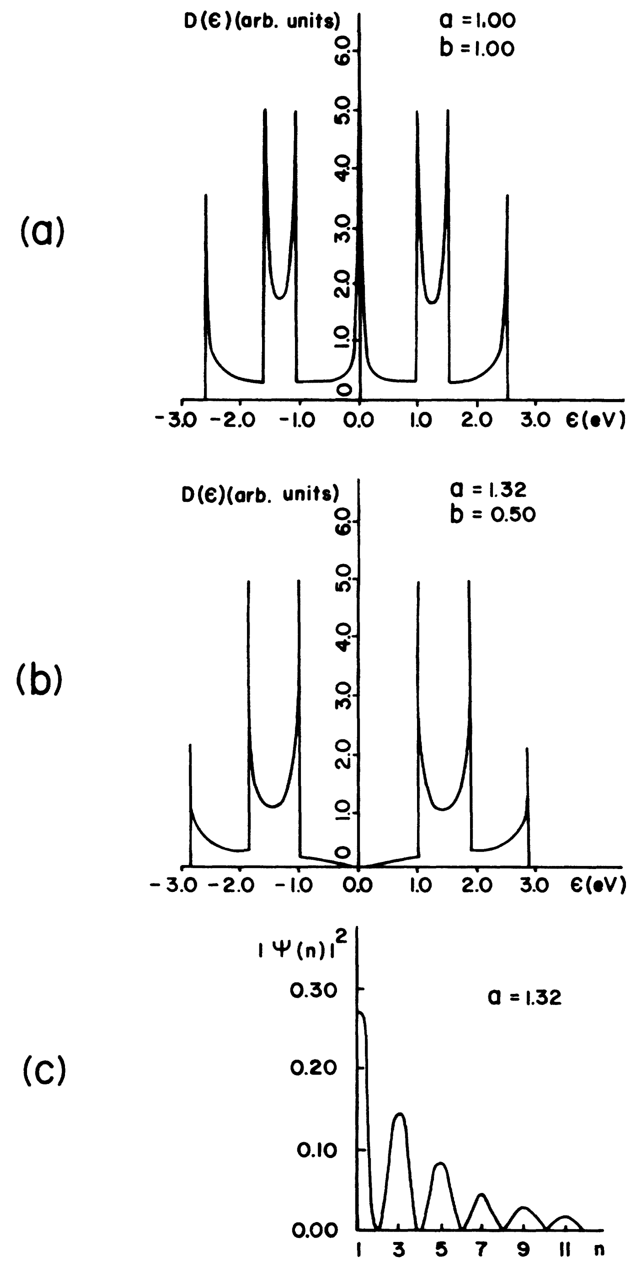

FIG. 5. (a) and (b) Local density of states (in arbitrary units) for a polyacene (PANE) chain presenting a single-site defect. (c) Wave function associated with the localized state.

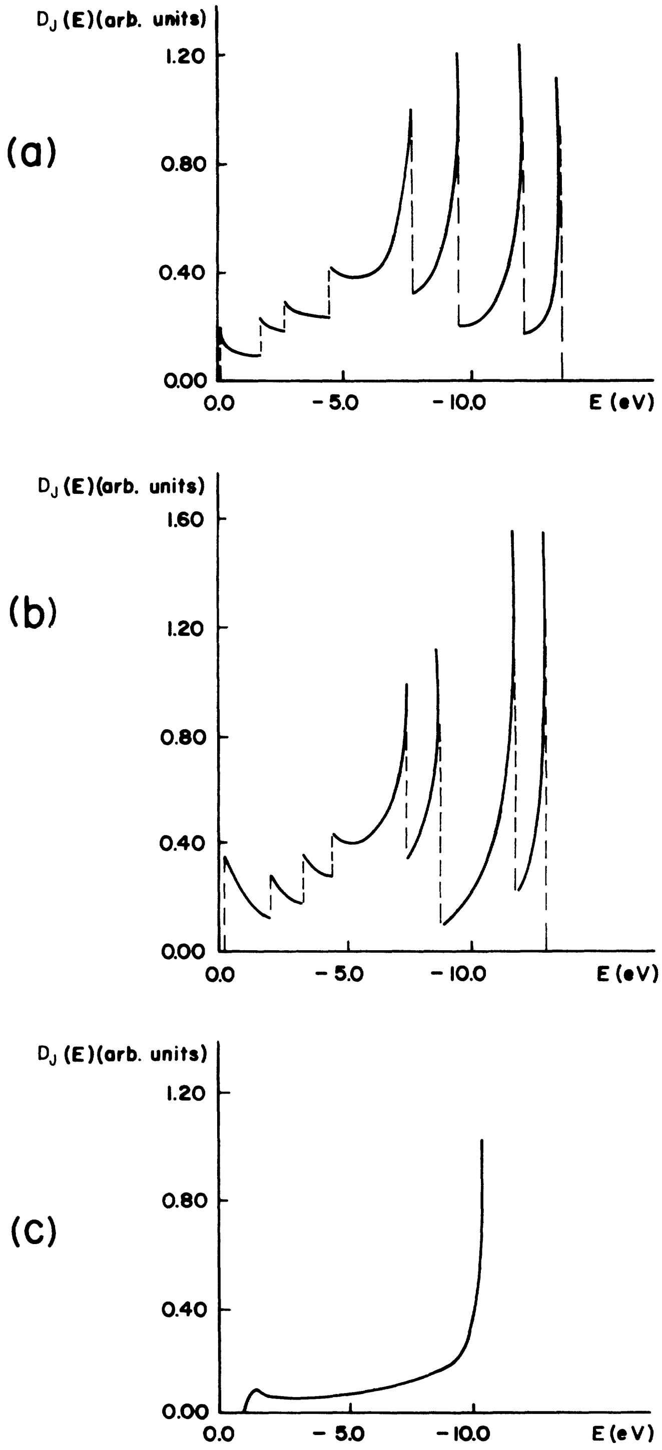

FIG. 6. Joint density of states for (a) *cis*-PANE (b) *trans*-PANE, and (c) *trans*-PA.

ed in the extended-Hückel-theory approximation, which assumes the coupling between different atoms to be proportional to the overlap of their respective atomic wave functions.

We decided then to perform an EHCO investigation of the electronic structure of the PANE isomers. The program utilized[28] uses a standard parametrization with a Slater-type-orbital (STO) minimal basis set. The polymer was assumed to have a planar structure with bond angles of 120°, and the CH bond lengths were taken as 1.08 Å. A homogeneous CC bond length of 1.42 Å was adopted for the regular structure; for the alternant isomers, on the other hand, double and single bonds of lengths equal to 1.35 and 1.45 Å, respectively, were considered along each lateral chain, while the distance between the chains, r_3, was taken as a free parameter. Failure to properly take the lattice sums to convergence can lead to spurious results, as pointed out before;[12] here, these sums were carried out to four neighboring cells, since previous exploration had indicated that beyond this range of interaction results do not suffer appreciable change. For all values of r_3 examined the *trans* isomer was found to be the most stable of the alternant forms. When the distance between lateral chains corresponds to a single bond length ($r_3 = 1.45$ Å), the energy per unit cell of the *trans* configuration is 0.19 eV lower than that of the *cis* isomer. For comparison, the energy per unit cell of the regular structure is 0.22 eV higher than that of the $r_3 = 1.45$ Å *trans* PANE. For this latter geometry a gap of 0.38 eV is predicted between occupied and unoccupied bands. The calculated π-band structure essentially agrees with that of Ref. 4 and will not be reproduced here.

Of increasing interest in recent years is the investigation of the optical properties of conjugated polymers.[29] In particular, due to the high polarizability and anisotropy of their electronic distribution, these systems are expected to present remarkable nonlinear-optical properties. A quantity relevant to the study of the optical-absorption profile is the joint density of states (JDOS) for the valence and conduction bands, as it probes the number of states accessible for electronic transition induced by a photon of energy $\hbar\omega$. The JDOS can be defined as[30]

$$\rho_{vc}(\hbar\omega) = \frac{1}{4\pi^3} \frac{dS}{|\nabla_k(E_c - E_v)|_{E_c - E_v = \hbar\omega}} , \tag{22}$$

where $E_c(k)$ and $E_v(k)$ describe, respectively, the conduction and valence bands of interest, and S is a surface of constant energy in **k** space.

We have used the calculated EHCO band structure to compute the JDOS for the *trans* and *cis* isomers of PANE Results of $r_3 = 1.45$ Å are presented in Fig. 6, where comparison to PA is made. As expected, most of the transitions will take place at the critical points near the band edges where $E_c - E_v$ is stationary and the gradient in the denominator of (23) vanishes. The final absorption profile will depend not only on the JDOS at each k, but also on the corresponding oscillator strengths; however, one can already see from the comparison of the low-energy regions of the curves of Fig. 6 that the optical-absorption properties of PANE should differ substantially from those of PA. This is consistent with the fact that PANE possesses a smaller band gap, larger bandwidth, and a larger number of π bands than the latter system.

IV. CONCLUSION

In this paper we have shown that if long-range interactions are neglected the electronic structure of polyacene can be obtained in a simple and analytical way through the combination of renormalization ideas with the use of adequate transfer functions. It is interesting to note that although the renormalized problem consists of a polymeric chain involving second-neighbor interaction, the electron-hole symmetry (reflected by the symmetric forms of valence and conduction bands) is still present. This is a different result from the previous application of the method where the introduction of long-range interactions disrupted this symmetry,[19] since then the pairing theorem of alternant hydrocarbons could not be applied.[21,22] In our case the symmetry was present in the original polyacene model, but the fact that it is preserved through the final results is an indication that no fictitious effects associated with the intermediary Hamiltonian are introduced in the renormalization process. The problem examined here also shows that the technique can be applied to systems other than the polymers of one-dimensional topological nature treated before.

If only first-neighbor interactions are included, conformational defects as the one introduced in Fig. 4(a) can be considered to be of soliton nature. It is shown that the wave function associated with the localized state is identical to the corresponding defect in polyacetylene. Hence, at this level of approximation the transport properties of the two systems can be expected to be similar. If longer-range interactions are included, the two semi-infinite chains connected by the single-site defective aromatic ring become energetically inequivalent. For this case a defect such as that suggested in Fig. 4(c) would be the simplest form of a mobile kink in PANE. This defect resembles one of the Dewar structures for benzene[25] and would be interesting in itself since it would present a spin-charge relationship characteristic of polarons. However, delocalization effects are expected to be much more important in these aromatic polymers and correlation effects have to be included if more realistic predictions are required.

Finally, an EHCO structure calculation for the different isomers of PANE is performed. It is shown that the *trans* configuration should be the most stable form of the polymer, and the band structure was used to construct the joint density of states for the valence and conduction bands of the polymer. The results suggest that the optical-absorption properties of PANE should be substantially different from those of PA.

It is important in this context to refer to the work of Agrawal *et al.*[24] who, in order to explain the low-temperature optical-absorption profile of polydiacetylene crystals, have considered the pairing of parallel chains of the polymer, forming structures similar to PANE. This doubling of the unit cell below a certain critical temperature T_c would account for the observed doubling of the peaks corresponding to π-electron transitions. In the present case, PA and PANE would be the physical realization of the two different phases of the same polymer, and a similar analysis of the differences in the corresponding spectra could be performed here.

We conclude by noting that although in Ref. 24 it is affirmed that selection rules would operate in different ways for the *cis* and *trans* configurations of the PANE phase (hence leading to substantially different absorption properties for these two forms of the polymer), that analysis was based on a first-neighbor approximation. Since the symmetry restrictions used to rule out certain one- and two-photon transitions at the band edges of the *trans* isomer become invalid once long-range interactions are included in the Hamiltonian,[12] one could expect transitions to occur at all peaks of Fig. 6, with intensity modulated by the respective oscillator strengths. This conclusion reinforces the importance of further investigation of the linear and nonlinear optical properties of polyacenes.

ACKNOWLEDGMENTS

This work was partially supported by the Brazilian agencies Financiadora de Estudos e Projetos (FINEP) and Conselho Nacional de Desenvolvimento Científico e Technológico (CNPq). We acknowledge useful discussions with Dr. F. Moraes and Dr. M. C. dos Santos.

---

[1] H. Meier, *Organic Semiconductors* (Verlag-Chemie, Weinheim, 1974).

[2] A. Rembaum, Encycl. Polymer Sci. Technol. **11**, 318 (1969).

[3] L. Salem and H. C. Longuett-Higgins, Proc. R. Soc. London, Ser. A **255**, 435 (1960).

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

[5] M. R. Boon, Theor. Chim. Acta **23**, 109 (1971).

[6] K. Tanaka, K. Ozheki, S. Naukai, T. Yamabe, and H. Shirakawa, J. Phys. Chem. Solids **44**, 1069 (1983).

[7] B. Pietrass, in *Proceedings of the 13th Annual International Symposium on Electronic Structure of Metals and Alloys, Johnsbach, 1983,* edited by P. Ziesche (Technical University, Dresden, 1983), p. 176.

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

[9] J. L. Brédas, in *Handbook of Conducting Polymers,* edited by T. A. Skotheim (Dekker, New York, 1986), Vol. 2, p. 859.

[10] S. Kivelson and O. L. Chapman, Phys. Rev. B **28**, 7236 (1983).

[11] J. K. Burdett, Prog. Solid State Chem. **15**, 173 (1984).

[12] M. Kertesz and R. Hoffman, Solid State Commun. **47**, 97 (1983).

[13] I. Božović, Phys. Rev. B **32**, 8136 (1985); **33**, 5956 (1986).

[14] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **42**, 1608 (1979); Phys. Rev. B **22**, 2099 (1980); **28**, 1338(E) (1983).

[15] Although the existence of solitons in PANE has been suggested before [see, for example, W. A. Seitz, D. J. Klein, T. G. Schmalz, and M. A. Garcia-Bach, Chem. Phys. Lett. **115**, 139 (1985), and Ref. 13], to our knowledge no calculations have been actually performed.

[16] M. C. dos Santos, C. P. de Melo, and H. S. Brandi, Solid State Commun. **52**, 99 (1984).

[17] M. C. dos Santos, C. P. de Melo, and H. S. Brandi, Int. J. Quantum Chem. **30**, 109 (1986).

[18] A. L. S. da Risa, Master thesis, Universidade Federal de Pernambuco, 1986.

[19] C. P. de Melo, A. A. S. de Gama, and G. Brandi, Theor. Chim. Acta **65**, 91 (1984).

[20] H. S. Brandi and C. P. de Melo, Solid State Commun. **44**, 37 (1982).

[21] For a discussion of the implications of the alternant character of the conjugated system on its electronic properties, see A. J. Heeger and J. R. Schrieffer, Solid State Commun. **43**, 207 (1983).

[22] As discussed in Ref. 21, the pairing theorem also cannot be strictly applied when electron-correlation terms are present. See, for example, M. C. dos Santos and C. P. Melo, Synth. Met. **17**, 23 (1987).

[23] C. Cojan, G. P. Agrawal, and C. Flytzanis, Phys. Rev. B **15**, 909 (1977).

[24] G. P. Agrawal, C. Cojan, and C. Flytzanis, Phys. Rev. Lett. **38**, 711 (1977).

[25] A. Streitweiser, *Molecular Orbital Theory for Organic Chemists* (Wiley, New York, 1961).

[26] C. P. de Melo, A. A. S. da Gama, and H. S. Brandi, Theor. Chim. Acta **63**, 1 (1983).

[27] C. T. Papatriantafillou, Phys. Rev. B **7**, 5386 (1973).

[28] M. C. dos Santos and C. P. de Melo, Solid State Commun. **50**, 389 (1984).

[29] See, for example, *Non-Linear Optical Properties of Organic and Polymeric Materials,* edited by David J. Williams, American Chemical Society Symposium Series No. 233 (ACS, Washington, 1983).

[30] See, for example, F. Wotten, *Optical Properties of Solids* (Academic, New York, 1972).