Solitons and polarons in polyacetylene: Self-consistent-field calculations of the effect of neutral and charged defects on molecular geometry

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Semiempirical self-consistent-field calculations are carried out on various polyenes with emphasis on defect configurations designed to simulate soliton and polaron excitations in polyacetylene. For defect-free polyenes, the calculated bond-length alternation ($\Delta r = 0.106$ Å) is in close agreement with generally accepted values for polyacetylene. Solitons and polarons are simulated on polyene radicals, ions, and radical ions by the introduction of appropriate symmetries and by charging; these are viewed as neutral (radical) and charged (cation and anion) defects in the polyene structure. The equilibrium geometries and charge distributions of varying-length polyenes and defect-containing polyenes are calculated. The extent of disruption of the bond-length alternation pattern of the carbon backbone is predicted to be about half as large as previously thought for neutral defects (solitons) and even smaller for anionic defects. Positively charged solitons are of larger extent. These results are consistent with known conductivity—doping-level relationships. A spatially damped charge-density wave is associated with the charged solitons and a spin-density wave with the neutrals; in both cases the wave extends farther than the lattice kink itself. Polarons and bipolarons, studied as soliton-antisoliton pairs (radical cations and radical anions) on the same model molecule, are also found to exhibit charge-density-wave solutions. The bipolaron is shown to be unstable to the formation of a like-charge soliton-antisoliton pair. Strong interchain coupling is expected as a result of the large dipole moments associated with the unique form of the lattice polarization due to the damped charge-density wave in charged solitons and polarons.

I. INTRODUCTION

Polyacetylene has received a great deal of attention both experimentally and theoretically because it is, at first sight, the simplest of the interesting class of highly conducting, doped organic conductors.[1] Elegant models of conduction mechanisms have been given which account for, among other things, the absence of Pauli susceptibility at the beginning of the high conductivity regime, around 1% doping level; but there is still considerable controversy as to even qualitative aspects of the physical processes operating in such materials. One of the most fascinating suggestions is that conductivity in polyacetylene is controlled by the properties of soliton defects.[2] Since there are two energetically degenerate possibilities for its ground-state bond-alternation pattern $\cdots -C=C-C=C-C=C- \cdots$ and $\cdots =C-C=C-C=C-C= \cdots$, polyacetylene has a structure which supports the soliton, defined as an excitation of the system connecting a section of the polymer chain in one ground state to another section in the other. Topologically, it is clear that the region of polymer in which the soliton de-

fect is localized must contain a radical carbon site (one with only three bonds); therefore a neutral soliton is an open-shell system with spin $\frac{1}{2}$ which, in principle, requires no net work to propogate through the medium.[2] Charged solitons have spin 0. More recently it has been shown[3-7] that a likely possibility is that doping induces polarons (which can be viewed as an interacting charged-soliton—neutral-antisoliton pair) on the polyacetylene backbone; at higher doping levels the polarons interact, their radicals recombine, and the process leads to charged solitons. On more complex organic polymers which become conducting with suitable doping (polyparaphenylene, polypyrole, and various polyphenylene chalcogenides), solitons cannot be created because these polymers lack the degenerate ground state of polyacetylene. They could however, and apparently do, support doubly charged polarons (bipolarons) which have been proposed as the spinless charge carriers in such systems.[3,4,7-10]

The detailed physics of soliton and polaron excitations is complicated by the organic nature of the polymers although recent papers have suggested how their physics could serve to explain various experimental observa-

tions.[11,12] It is typical of organics that excitation or charge transfer causes significant modification to the atomic geometry, and energies associated with the geometric distortions must be included in physical descriptions, i.e., important effects due to electron-phonon coupling are expected. It is the primary purpose of this paper to determine accurately the geometries of the various defects which may be associated with excitation or charge transfer in polyacetylene.

There have been estimates of the geometric distortions but with relatively simple theories of molecular quantum chemistry. Such work has served as an important guide to the construction of theory but focused only on soliton excitations; this paper is the first to seriously address the geometric distortions associated with polarons. Most previous work has been based on a simple adaptation of Hückel theory: The simplest possible Hamiltonian is postulated whose diagonal elements are the π orbital binding energies and whose only nonzero off-diagonal elements are between bonded orbitals. The values of the matrix elements are adjusted to fit known properties of the polymer system. One simple extension is made in the application of such concepts to studies of defects in polyenes. The off-diagonal parameters representing the strength of a bonding interaction are assumed to have an exponential dependence on the length of the bond between atoms; this includes in the simplest way the relationship between bond strength and orbital overlap. The calculation is not carried out self-consistently with respect to the parameters describing the electronic structure other than the bond-length dependence described above. More specifically, the fundamental procedure used in previous work is to diagonalize the modified Hückel Hamiltonian for a series of assumed molecular geometries and to select that geometry which produces the lowest total energy. In this way the electron lattice interaction is simulated and it can be said that such a calculation is self-consistent with respect to the electron-phonon interaction. Since there is no dependence on orbital occupancy in this non-self-consistent scheme and no explicit treatment of electron-electron interactions, it is not possible to distinguish between charged and uncharged defects (except via perturbation theory). There is every reason to expect that oppositely charged defects will undergo different geometric relaxations; e.g., $CH_3^{\cdot}$ and CH_3^+ hybridize as sp^2, while CH_3^- hybridizes as sp^3 (see Ref. 13). It is worth stating clearly also that only the p_z orbitals are explicitly included in the modified Hückel calculations (so that sp^3 hybridization effects cannot be taken into account) and that the effect of σ bonds (crucial to geometry determination) is poorly represented. Finally, note that geometry optimization is limited by the range of atomic configurations considered in the search for the minimum total energy. In practice a specific functional dependence has to be assumed for atom positions (e.g., a tanh function is used for solitons) and the best one can hope for is a local energy minimum on the potential surface described by such an assumption.

Very recently, the Pariser-Parr-Pople (PPP) Hamiltonian has been applied to polyacetylene.[14] In this case the Hückel Hamiltonian is extended to include "on-site" and "off-site" electron-electron repulsion plus nearest-neighbor exchange. Thus it is basically a π electron, approximate self-consistent-field method. Within this approach, it is possible to distinguish between neutral and charged defects but not between positively and negatively charged defects. The results to be presented below agree qualitatively with those from the PPP calculations but extend and quantitatively improve upon them.

In the present work we focus on geometries of solitons and polarons as the fundamental excitations and we apply more sophisticated quantum chemical methods. We report the geometric details of both neutral and charged solitons and find an interesting oscillation of charge on approach to a defect site. This oscillation [damped charge-density wave (CDW)] extends further than the lattice kink itself as does a damped spin-density wave (SDW) associated with the neutral defect. Similar but more complicated effects appear in the structure of polarons. We relate them specifically to the π electron system as it relaxes to screen the defect. A preliminary version of this work has been recently published.[15]

II. METHOD OF CALCULATION

We focus exclusively, in this paper, on all-trans polyacetylene which is modeled by finite polyenes of varying length. Previous work has studied very long[2,16-19] and cyclic polyenes[3] by the theoretical approach originally suggested by Pople and Walmsley[20] and adapted by Su, Schrieffer, and Heeger,[2] basically Hückel theory with σ bond compressibility as described above. The beauty of this approach is that it permits relatively simple computations to be carried out and/or can be cast into the form of well-studied field theories with elegant solutions.[7,18] Though interesting physics can and has been extracted from such work, at certain points the conclusions are based on quantities whose numerical values can be unreliable. (For example, Hückel theory does not predict geometry very well.[21])

In an effort to improve upon this situation, we have carried out calculations using the MNDO scheme of Dewar and Theil.[22] MNDO (modified neglect of differential overlap) is a semiempirical method for finding the self-consistent-field solutions of the Hartree-Fock Hamiltonian (expanded in Slater-type orbitals), i.e., containing a kinetic term, the nuclear attraction term and the nonlocal exchange, and Coulomb repulsion term. All valence σ and π electron interactions are included. The computational feasibility comes from neglecting certain selected sets of multicenter integrals and parametrizing some of the remaining ones. The parameters are chosen to optimize the predictive capabilities of the scheme for molecular geometries and heats of formation; in effect, the parameters build in some allowance for the electron correlation neglected by the Hartree-Fock theory.[23] The method has been tested on a large number of molecules and exhibits particularly notable success for hydrocarbons. While it is an approximate scheme with limitations, it is computationally feasible where *ab initio* methods are not and in many cases the MNDO geometry predictions are closer to

experiment than *ab initio*. As important is the fact that the limitations (and some peculiarities) are known and can be dealt with.

The computations proceed by providing the molecular connectivity and initial estimates for the various bond lengths and angles. In the present case we report results for exactly planar molecules because our more elaborate calculations allowing for nonplanar structures inevitably predicted planarity even for anions. We model nondefective oligomers of polyacetylene by polyene molecules: an even cardinality sequence of C—H units terminated at each end by CH_2. Various length polyenes have been considered in order to assess the range of the effect of the termination units. The soliton defects studied here are topological kinks (domain walls) in the polyene chain caused by a phase shift in the bond alternation pattern. The site of the defect is a carbon atom with equal bonds to each of its neighboring carbons. In the absence of chain end effects such a model is equivalent to a soliton excitation on an infinite chain. The neutral soliton carries spin $\frac{1}{2}$ (the carbon atom at the defect site has one half-filled orbital and is chemically described as a radical) and is expected to require very little energy to move from site to site.[2] To simulate these defects in finite chains we add one C—H unit to a polyene, $\cdots -C=C-C=C-C=C-C=C- \cdots$, to form $\cdots -C=C-C=C-\dot{C}-C=C-C=C- \cdots$ and impose a symmetry by insisting that the length of the two bonds adjacent to the site of the defect be equal. Equivalently a plane of symmetry can be used if the defect is at the middle site of the model molecule and considerable simplifications result in the computation; the point group of such models is C_{2v}. The increase in the number of C—H units is necessary to accomodate the same termination units: $=CH_2$. The geometry is otherwise unconstrained and adjusted to minimize the total energy of the radical. Note that such a defect need not be located at the geometric center of the molecule. The radicals are open-shell systems with only one electron in the highest occupied molecular orbital. We have also done calculations on charged soliton defects (ions) by simply adding or removing one electron from the highest occupied molecular orbital followed by a complete geometric relaxation of the system; in the case of either a cation or an anion all orbitals are doubly occupied resulting in a charged, spin-0 defect which has been invoked to explain various experimental observations.[24] We have also considered the simplest polaron states on polyacetylene. These are simulated by charging the nondefective polyenes and relaxing them to optimum geometry subject to the restriction that inversion symmetry be maintained about a point through the middle of the central bond; the point group symmetry of these models is C_{2h}.

It should be noted that MNDO has been tested less rigorously for radical and ion geometries, the principal reason being the lack of experimental information. We are, however, confident that the application of MNDO to defects in polyacetylene is a substantial improvement over the previous Hückel treatments. Where data has been available, MNDO predictions have been quite good.[22,25] It is found that a restricted Hartree-Fock (RHF) treatment, modified to deal with open shell systems (by placing "$\frac{1}{2}$ electron" of each spin in the open shell to avoid problems associated with the form of the variationally optimized wave function[26]) produces results that are superior to the use of an unrestricted Hartee-Fock (UHF) treatment; the reason for this likely comes from the fact that UHF MNDO, using parameters optimized for an RHF scheme, overestimates electron correlation in conjugated systems because some of the correlation is already included in the parameters.[23,27] The failure of UHF schemes as applied to polyenes is more general; it is widely found that they produce non-bond-alternant ground-state solutions since the largest energy gains using UHF are obtained for the equidistant cases.[28]

III. RESULTS AND DISCUSSION

A. Polyenes

To verify the relationship of the present scheme to previous numerical estimates, we determined the optimum geometry of polyenes containing $2,4,6,\ldots,20$ double bonds; i.e., for the planar molecules: C_4H_6, $C_8H_{10},\ldots,C_{40}H_{82}$. The most significant result is the bond-length alternation pattern: the single bonds are 1.4628 Å while the double bonds are 1.3568 Å (in the middle of the oligomer) for a difference of $\Delta r_\infty = 0.1060$ Å. (In the notation of the Su, Schrieffer, and Heeger[2] paper, $u_0 = 0.0306$ Å; those authors calculated $u_0 = 0.04$ Å.) This compares to an experimental estimate[29] of $u_0 = 0.03$ Å (adjacent-bond-length difference of $\Delta r_\infty = 0.104$ Å) and to double-ζ *ab initio* calculations by Karpfen and Petkov[30] of $\Delta r_\infty = 0.100$ Å (C=C, 1.346 Å; and C—C, 1.446 Å) or in the alternate notation $u_0 = 0.029$ Å. There are additional details from the *ab initio* studies that show the quality of the geometry predictions of the MNDO scheme. The C—C=C bond angle is calculated by Karpfen and Petkov at 125.3° while our result is 124.9°. In addition we find, very interestingly, that the H atoms are inclined towards the single bonds by 4.4°; this parameter has not been optimized in the *ab initio* calculations. Our results are the same for all but the smallest polyene (variations occur within three C atoms of the chain ends). Thus in the 40-carbon-atom chain, there is a quite long section of the finite molecule which has the periodic repeat pattern of polyacetylene.

B. Solitons and radicals

Radicals have been inserted into the geometric center of the polyenes as described in the preceding section. This avoids end effects and makes maximum use of symmetry but we treat noncentered defects shortly. The radicals studied have 8, 10, 14 and 20 double bonds, i.e., from $C_{17}H_{19}$ to $C_{41}H_{83}$; in each case a full geometry optimization has been carried out, including all bonds and angles. We are primarily interested in the changes to the ground-state geometry and in particular the effect of the defect on the pattern of bond-length alternation. Results are displayed in Fig. 1 where we plot the difference in adjacent bond lengths, Δr, versus the position of the carbon
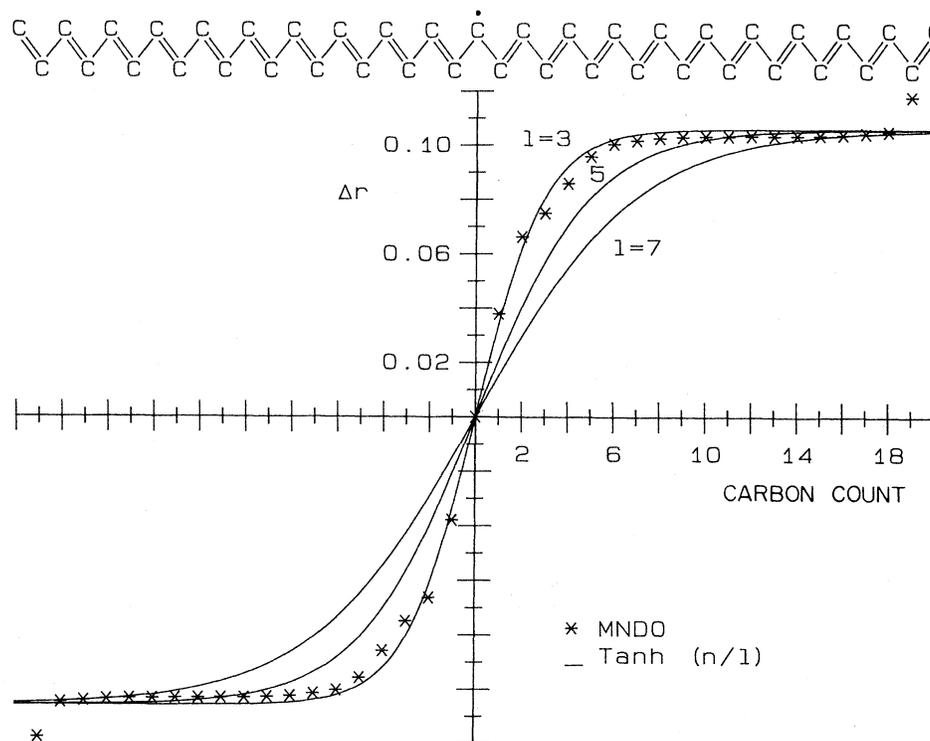
FIG. 1. Bond-length alternation around neutral defect site. The difference in adjacent bond lengths Δr is plotted against carbon site distance from defect. The continuous curves are the form predicted by Su, Schrieffer, and Heeger (Ref. 2) $\Delta r = \Delta r_\infty \tanh(n/l)$; their Hückel results suggested $l=7$ as the minimum energy configuration. The asterisks are based on MNDO calculations described in the present paper.

atom common to the adjacent bond pair; $\Delta r = 0$ implies no bond alternation. The data points shown by asterisks are from the 20 double-bonded radical chain $(C_{41}H_{83})$. The defect is centered at carbon number 21 and lies in the plane of symmetry under C_{2v}. Therefore, atom 21 has $\Delta r = 0$ by definition. Also plotted are three curves given by $\Delta r = \Delta r_\infty \tanh(n/l)$ where n is the number of the carbon atom counted relative to the defect site as zero, l determines the defect extent and $\Delta r_\infty = 0.106$ Å. This hyperbolic tangent function is the model of the bond alternation associated with the geometric distortion due to solitons on an infinite chain as used originally by Su, Schrieffer, and Heeger[2] (SSH); this choice is dictated because it is the solution of the solitary wave equation in ϕ^4 field theory.[7,18] Their work as well as that of others[3,16−19] had suggested a value of $l=7$ for the extent of the defect; i.e., beyond 7 carbon atoms on either side of the defect center, the bond-length pattern had returned to about 70% of the infinite chain value. Our results clearly show a much more localized defect, best characterized by $l=3$ although the shape of the curve imposed in the simpler theory remains a good approximation.

The energy-level spectrum produced by the MNDO self-consistent-field calculation for the minimum energy geometry qualitatively shows the behavior expected, namely a half-filled orbital at mid-gap (the Fermi level).

The bandwidth of the occupied π band is calculated to be 5.3 eV which is quite reasonable with respect to other calculations,[31] but the band gap is far too wide. This problem is well known in Hartree-Fock—based theory and is due to the treatment of an electron in an excited orbital as experiencing the potential due to N other electrons rather than $N-1$. In the rest of this paper we therefore measure the position of levels in the gap relative to the band edges in fractions of the gap energy.

In order to probe the effect of the chain ends more carefully a 17-carbon-atom radical has been studied as the defect is moved from the middle of the chain (at carbon atom 9) successively toward the end (to atoms 7, 5, and 3). The results are depicted in Fig. 2. The effect of the lattice kink on the bond-length pattern is translated without appreciable distortion until very near the chain end. The total energy of the model molecules has also been monitored and is indicated in the figure. The rise is insignificant until the last stage when the defect is only 3 units from the end. Of course, this is consistent with the values $l=3$ assigned to the soliton width. A similar analysis was performed by Su[32] using the SSH Hamiltonian as a basis but with energy increases approximately double those found here. We wish to stress that these data do not provide any information about the energy required to promote a defect centered at one site to the next available site; the only
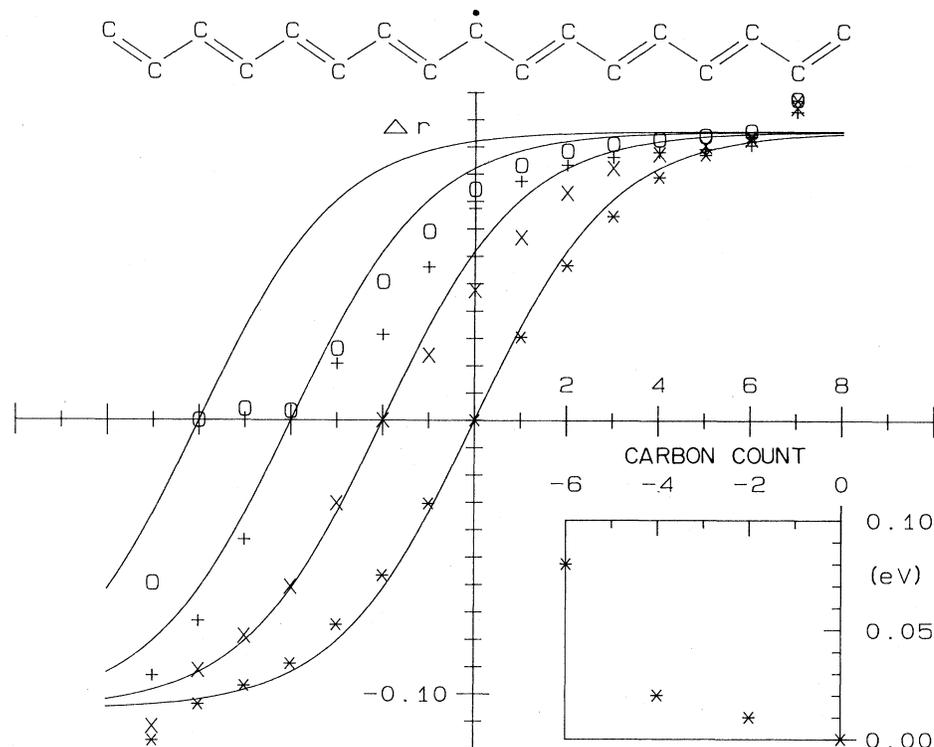
FIG. 2. Effect of defect moving toward the end of a chain is exhibited for a 17-carbon-atom model. The bond-length alternation pattern is shown for the defect located at carbon atoms 9 (*), 7 (×), 5 (+), and 3 (○). The total molecular energy is also shown (inset) as a function of position; no significant change occurs until the defect is within 3 units of the chain end where distortion of the tanh(n/l) shape begins to appear.

available information on this point is the original estimate of Su, Schrieffer, and Heeger[2] of ~0.002 eV.

C. Charged solitons

An intrinsic limitation of the Pople and Walmsley[20] and the Su, Schrieffer, and Heeger[2] approach is that no distinction is possible between neutral and charged isolated defects. This is because the creation of the defect automatically places a half-filled orbital at the Fermi energy. One can think of all π orbitals as being paired into bonding and antibonding levels falling and rising, respectively, into the valence and conduction bands except for that single unpaired orbital at the defect site which remains at its original position since it corresponds to a noninteracting state. Because it is at the Fermi energy, changing the occupancy of this level (charging the defect) requires no energy and hence has no associated geometry change. Our approach improves the picture for charged defects since it is self-consistent. We have studied both cationic and anionic defects in the same way as for neutral defects; an electron is simply added to or deleted from the highest occupied level (the one at the Fermi energy) and the resulting system is subjected to a complete geometry optimization. Figure 3 shows the results for the bond-length alternation pattern for ions of 20 double bond chains. Clearly the positive defect is considerably more diffuse than the

neutral ($l \sim 5$) and the negative more compact ($l < 3$). The curves depart from the simple hyperbolic tangent form by exhibiting a tail at large n which goes like l/n as might be expected for charged species. In order to understand, possibly, the compactness of the negative soliton, we refer to the intuitively appealing picture of solitons given by Rebbi,[33] in which the extent of the defect is determined by a competition between a potential energy and an intrinsic energy. Everything else remaining the same, the negative charge on the anion could cause the intrinsic energy to increase because it tends to provoke sp^3 hybridization and therefore could force the width of the soliton to decrease. Again the energy-level spectrum is too broad but behaves qualitatively in the right way; the mid-gap level moves closer to the valence-band edge for a negative defect (level doubly occupied) and further away for positive (level empty) as expected from our restricted Hartree-Fock treatment. The effect of charging is also consistent with the experimental facts that higher concentrations of donor dopants are required to produce equivalent conductivities in all-trans polyacetylene; if increased conductivity is due to overlaping defects forming a band, then clearly one would require fewer positive than negative defects because of their different spatial extent. We also wish to note that in the π electron models previously applied to this problem the Hamiltonian is charge conjugation symmetric[18]; as a result, for every state below the Fermi level there is
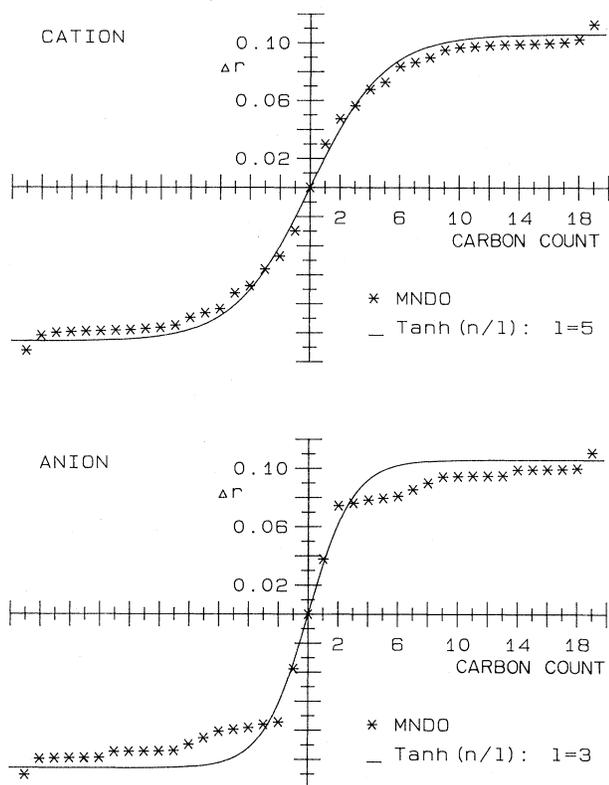
FIG. 3. Bond-length alternation patterns around charged defects: top, for cations and bottom, for anions. The cations are more diffuse than the neutral defects, the anions more compact. The prediction of this effect is beyond the capabilities of earlier calculations.
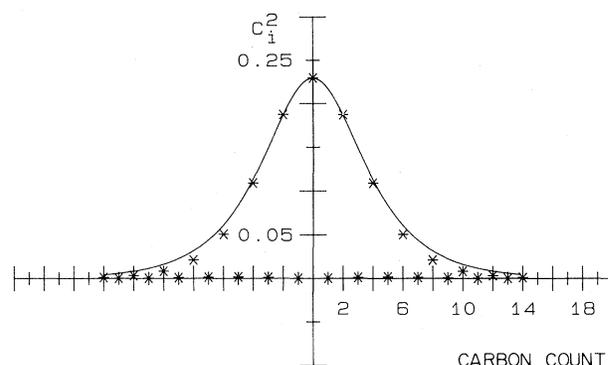

FIG. 4. Spin-density-wave solution of a neutral defect on a 19-carbon-atom model. The square of the coefficients of singly occupied p_z orbitals on the carbons is plotted vs carbon number. Also shown is a line proportional to $\mathrm{sech}^2(n/l)$ with $l=5$; this is the form consistent with the $\tanh(n/l)$ behavior of the bond-length alternation.

another at exactly the same energy above. This forces charged solitons to be identical in such models. The study of oppositely charged states via perturbation theory[34−36] to include electron-electron interactions (breaking the charge conjugation symmetry) conclude that positive and negative solitons are only slightly different as should be expected from a perturbation analysis. There is no such symmetry in all valence electron models and we stress that our conclusions are not the results of perturbation analysis.

Going beyond the distortion of the backbone geometry, we have studied the orbital corresponding to the mid-gap level. The only nonzero components of its eigenvector are carbon p_z coefficients. For the neutral soliton the orbital describes a damped (SDW) as indicated in Fig. 4. All other orbitals are doubly occupied or empty in our RHF treatment and so contribute nothing to the net spin. Here the square of the coefficients of the p_z orbitals is plotted versus the carbon number for a 29-carbon-model molecule. Note that the orbital only has amplitude on every other carbon. This is a reflection of the topological constraint that the soliton with nonzero coefficients on the "top" carbons cannot mix with an antisoliton having nonzero coefficients on the "bottom" carbons. The solid

line in the figure is proportional to $\mathrm{sech}^2(n/l)$ with $l=5$; this functional dependence is consistent with the $\tanh(n/l)$ dependence of the lattice kink but the SDW is more extended than the kink. This is compatible with the results of Fukutome and Sasai,[14] based on the PPP Hamiltonian, which imply a width of $l \sim 6$. Recent ESR results[37] have been interpreted as requiring widths $(2l)$ between 10 and 17 in agreement with our calculations since the ESR experiment specifically probes the SDW rather than the lattice kink. An SDW solution of approximately the same width was obtained by Kivelson and Heim[35] and by Subbaswanny and Grabowski[36] in a perturbation treatment of the SSH Hamiltonian. They find a nonzero component of spin on alternant sites due to the inclusion of an on-site Hubbard term, as one's intuition would suggest. Such results are prohibited by the RHF treatment in the present work; if it were possible to perform properly parametrized UHF calculations we would expect a similar result.

The anionic and cationic defects exhibit a similar and very interesting (CDW) as shown in Fig. 5. Here we have plotted the total excess charge per C—H unit as a function of atomic distance from the site of the defect. Again the CDW is considerably more extended $(l \sim 8)$ than the lattice kink and even more extended than the SDW on the neutral species; also the CDW's for positive and negative defects are of comparable width. Interestingly all of the units on one side of the chain are positive while all units on the other are negative. Chemical intuition suggests that a partial negative charge will be induced on the carbons next to the positively charged carbons due to polarization of the π bonds next to the charged site. However the magnitude of the polarization is surprising. This effect is not to be found in non-self-consistent approaches even qualitatively. The alternation of sign is due to an enhancement of Coulomb repulsion between orbitals on different atoms compared to that between orbitals on the same atom as documented by Dewar.[38] Analysis of the density matrix for the charged defects clearly reveals a

CATION
ΔQ
0.25
* CHARGE/CH UNIT

0.05

2   6   10   14   18
CARBON COUNT

ANION
ΔQ
0.25
* CHARGE/CH UNIT
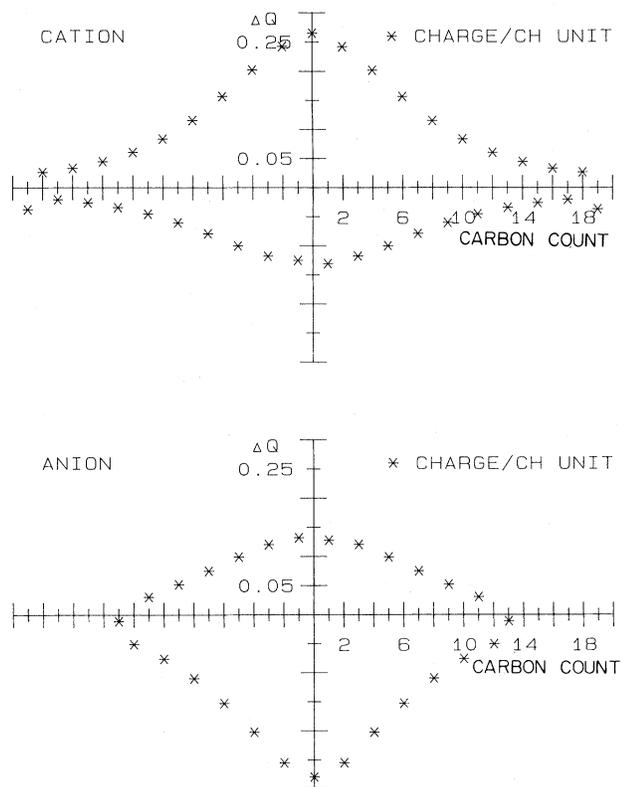
0.05

2   6   10   14   18
CARBON COUNT

FIG. 5. Net charge per C—H unit along the chain as a function of distance from a charged defect. Oscillations are predicted from site to site which are of such a periodicity as to cause a gap in the energy spectrum even if all bonds were of equal length. This effect was not expected on the basis of earlier theories due to their lack of self-consistency.

simple physical picture of the origin of the charge oscillation as a screening response to the charge at the defect site; the alternant π bonds polarize in a direction to form a screening field just as should be expected because they comprise that component of the charge distribution which is least tightly bound and most diffuse. Another way of saying the same thing is to consider populating (or depopulating) the orbital responsible for the SDW state of the neutral defect (cf. Fig. 4); as a result net negative (positive) charge exists on the even-numbered carbon sites; then consider the total electronic system self-consistently adjusting to this change. Excess positive (negative) charge is induced on the odd-numbered carbon sites so that the net electric field of the resulting array of charges on sites $(\pm 1, \pm 2, \pm 3, \dots)$ is in a direction such as to screen the defect at site zero. To see this consider the array as a set of electric dipoles aligned along the C=C bonds; the field of each such dipole has a component in the direction opposite to the field of the defect charge. In other words, if the defect is negative, there is a component of electric field along the molecular axis directed towards the defect site; each induced C=C dipole however has the component of its field along the molecular axis directed away

from the defect. The sum of molecular axis components of dipole fields exactly cancels the molecular axis component of field due to the defect. Perturbation theory has also been applied to the study of charged defects[35,36] obtaining considerably different results because the electrostatic interactions are not treated self-consistently.

There are significant consequences of the existence of CDW solutions. First, the periodicity of the oscillations are such as to make possible an energy gap even on a chain with all bond lengths equal. To estimate the magnitude of this effect we have returned to Hückel theory using parameters known to reproduce the band widths and gap in polyacetylene[3]: β designates resonance integrals proportional to bonding and α designates orbital binding energies. The unequal β's which are normally chosen to reproduce the observed band gap, $2|\beta_1 - \beta_2|$ on an alternant chain, are replaced with their average value (2.5 eV) and the α's are alternated in order to produce a charge oscillation of $0.320e$ to match MNDO predictions. The result is that the charge oscillation alone yields a gap of ~ 0.6 eV; further, we find that even with bond-length alternation (unequal β's) the charge oscillation substantially increases the gap although the two effects are not purely additive. A second point of significance is that the charge oscillation produces a polarization sufficiently large to produce strong interchain coupling. Therefore, a localized defect on one chain could have a profound effect on defect diffusion along neighboring chains.

D. Polarons and bipolarons

Our calculations include results for positive and negative polaron simulations. The model is a polyene radical ion with an imposed inversion symmetry about the central C=C bond, i.e., it has the symmetry of the point group C_{2h}. This model relates to equilibrium interactions of soliton-antisoliton pairs with one of the members charged. Because of the interaction neither soliton has a clearly defined center making it impossible to define an equilibrium separation; in combination, however, they reduce the bond-length alternation, Δr, as shown in Fig. 6. The phase of the bond-length alternation is the same on the left and on the right of the defect but there is a depression in the middle. The negative polaron has a stronger effect on suppressing the bond alternation ($\Delta r_{\text{middle}} = 0.31 \Delta r_{\infty}$) than the positive ($\Delta r_{\text{middle}} = 0.49 \Delta r_{\infty}$). As was the case with solitons the negative polaron is narrower (more localized) than the positive and both defects lead to similar lattice polarizations of approximately the same width extending over ~ 36 C—H units. Also shown in Fig. 6 are fitted curves based on an appropriate extension of the tanh functional form used for isolated solitons. The positive polaron is best fit with $l=9$ while the negative polaron is fit with $l=7$. The value deduced from Hückel theory[3] was $l=7$ and it is interesting to note that MNDO does not always predict smaller values of l than the simpler theory.

Owing to the center-of-inversion symmetry of the polarons, the lattice polarization takes a different form from the soliton case as shown in Fig. 7. The four sites closest to the symmetry point carry charges of the same sign; oscillation of charge sign from site-to-site starts from the
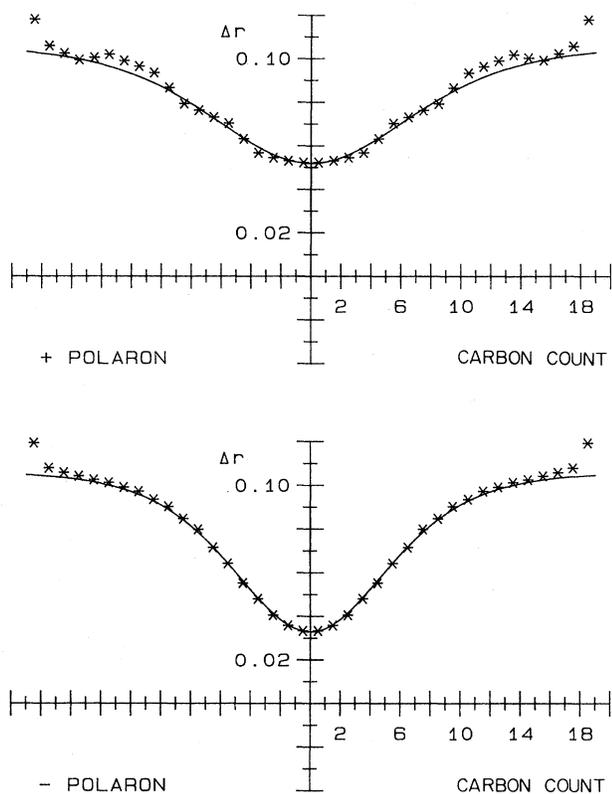
FIG. 6. Bond-length alternation pattern for negative and positive polarons. As for solitons the negative defect is more localized. The smooth curves through the lattice points correspond to the function $\Delta r_\infty [1 - \alpha \, \text{sech}^2(n/l)]$ with $\alpha = 0.51$, $l = 9$ for the positive polaron (radical cation) and $\alpha = 0.69$, $l = 7$ for the negative polaron (radical anion).
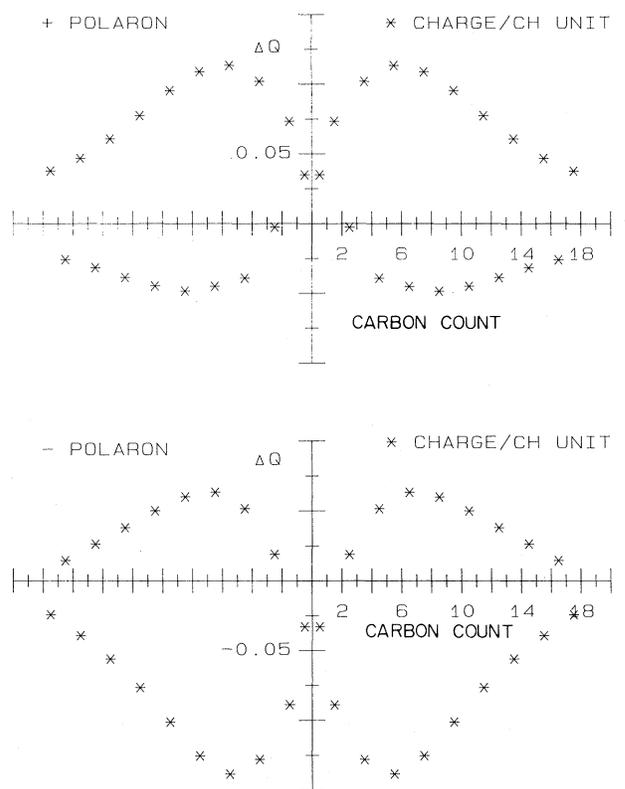

FIG. 7. Lattice polarization (net charge per C—H unit) for positive and negative polarons modeled as radical cations and anions on a model molecule $C_{40}H_{82}$. The extent of the polarization along the molecular axis is approximately the same for both polarons.

third site away from the middle of the defect and, very interestingly, the largest charges ($\Delta Q \sim 0.15e$) are obtained on the sixth and seventh sites away from the middle. Thus strong coupling between polyacetylene chains is also expected in the case of polarons. Both polaron models are open-shell systems which result in a half-filled level in the gap. For radical cations (anions) the level is pulled from the valence- (conduction-) band edge about 20% of the gap energy. If we take the experimental value for the gap (1.4 eV), this would place the polaron level about 0.3 eV from the appropriate band edge which is in fact the same value obtained in earlier calculations.[3]

Motivated by the interest in bipolarons[3] (doubly charged radical ions) for the more complex conducting polymers which cannot support isolated solitons, we went one step further in the calculation described above. Starting from the positive polaron, one more electron was removed from the system and the geometry completely optimized under exactly the same symmetry conditions. The results are shown in Fig. 8. Clearly the bipolaron consists of a soliton-antisoliton pair about 24 carbon atoms apart. The l value for tanh functions fitted through each is 5, exactly the same as for the isolated positive soliton. The lat-

tice polarization for each is also similar to the isolated species. The interpretation of this result is that the two like-charged soliton defects repel each other; in the absence of end effects of the finite model molecule, the bipolaron is unstable to the formation of a separated soliton-antisoliton pair. A corrolary is that MNDO predicts the charged-soliton—neutral-antisoliton pair (polaron) to be bound. In polymers more complex than polyacetylene (those with nondegenerate ground states) the Coulombic repulsion of the pair of charged solitons would be compensated by the increase in energy of the section of molecule between the defects and thus an equilibrium distance would be established characteristic of each polymeric system.

The MNDO method normally produces reliable numbers for total molecular energy[22] or heat of formation; however the introduction of topological kinks causes some problems. The kink forces the formation of a level whose eigenfunction is composed partly of a level pulled from the valence-band edge and partly of a level pulled from the conduction-band edge; as the Hartree-Fock theory has intrinsic difficulties in dealing with conduction-band states (see Introduction) this causes difficulties in obtaining accurate energies for the gap state. In turn the total
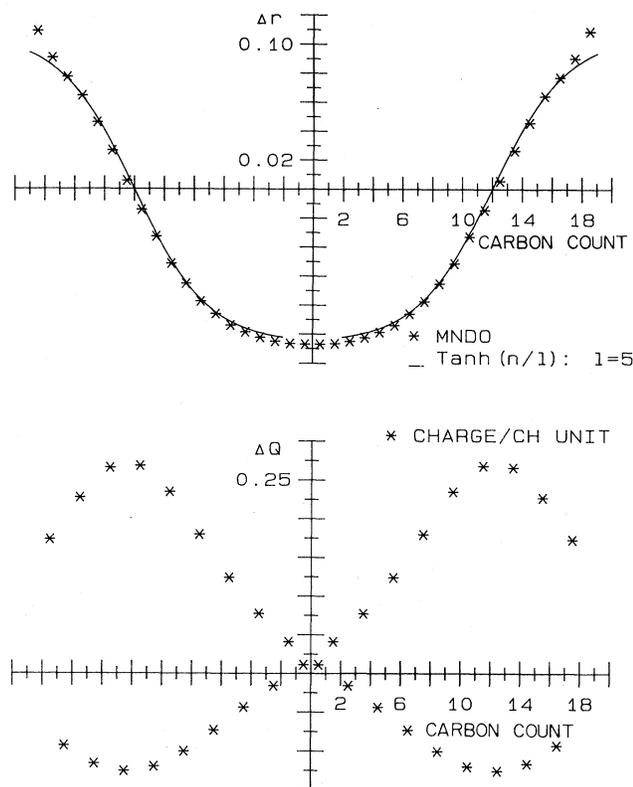
FIG. 8. Bond-length alternation pattern (top) and lattice polarization for a positive bipolaron on a molecular model containing 40 carbon atoms. The polaron is unstable to the formation of a pair of positively charged solitons each of which has the same width (smooth curves drawn have $l=5$) and charge distribution as their isolated counterparts. The calculation for this result is the same as for Figs. 6 and 7 except that one more electron is removed.

molecular energy is a function of, among other things, the orbital energies and one is inevitably left with inaccuracies. It would still be possible to compare energies on a relative basis (as was done in the discussion of moving defects toward the end of the chain) but it is difficult to compare the polyenes to the radicals because the chain termination effects force the two to have different numbers of atoms. We have made some preliminary estimates of the formation energy of the neutral soliton defect by comparing the total energy of the model molecular radical to that of an hypothetical molecule. The hypothetical molecule is constructed so as to have the same number of atoms as the radical but its geometry is constrained so that each bond and angle is given the value from the closed-shell polyene with the same number of double bonds. This is the closest we have come to the "vertical" process which is the inverse of the energy gained by molecular relaxation upon defect formation. Our present estimate for the relaxation is 0.35 eV which is based on

similar calculations on chains with 8, 10, 14 and 20 double bonds. This is 0.10 eV larger than the value predicted by Su, Schrieffer, and Heeger.[2] We have attempted to obtain a more quantitative assessment of excitation energies by creating and separating defect pairs on an extended chain with the inclusion of some configuration interaction to eliminate the errors in the total energy described above; we were unable to find self-consistent solutions to this problem.

IV. SUMMARY

We have reported details of the geometric distortions of polyene chains containing radical or ion sites (solitons) or radical ions (polarons) and have related the data to the physics of polyacetylene chains. For solitons the distortion of the bond-length alternation pattern is more localized than previously thought and, even more importantly, the distortions are different for different charges states, a fact which has not previously been discussed. In the case of the ions we have shown that an oscillation of charge can exist from site to site which may have profound influence on interchain interactions. The calculations on which our conclusions are based are of a semiempirical nature and as a result subject to possible numerical inaccuracy. However, we have taken great pain to determine that none of the effects we describe are due to computational artifacts; this is done by identifying in detail the physical process underlying each of our predictions and its qualitative correctness. Although some modifications to our arguments may be required if dopant atoms are specifically taken into account, they are fully relevant in the case of charge injection processes. Finally, we note that in comparing the results of this or any similar calculation to experiment, one should consider the effect of quantum tunneling between degenerate ground states.[39,40] In general the physics is preserved with a diminution of the expected value of the bond-length alternation.

Note added in proof. Since the completion of the manuscript, we have been able to study the biradical excitations (a pair of neutral well-separated solitons) on a polyene backbone. Comparing the total energies of the biradical to the bond-alternant polyene ground state, we calculate 0.61 eV for the excitation of a single isolated soliton defect. This compares to 0.45 eV deduced by Hückel theory and is sensible for our more compact defect geometries.

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