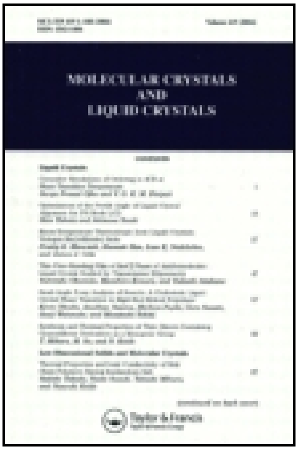

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The Dependence of The Electronic Structure of Polymers on Their Molecular Architecture

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THE DEPENDENCE OF THE ELECTRONIC STRUCTURE OF POLYMERS ON THEIR MOLECULAR ARCHITECTURE

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Abstract A molecular orbital theory of the electronic structure of polymer macromolecules is developed and applied to interpret UV photoemission and absorption spectra of polyacetylene, poly(p-phenylene), and polypyrrole. The degree of localization of injected charges and excitons in these materials is deduced from spectral measurements and the role of localization in achieving "conducting" polymers by doping is indicated.

INTRODUCTION

In this paper we examine the dependence of the electronic structure of certain organic polymers on the molecular architecture of these polymers. The systems which we examine are polymers which can be charge transfer doped, using strong donors or acceptors, to obtain large increases in electrical conductivity. Polymers such as polyacetylene (PA),[1] poly(p-phenylene) (PPP),[2] and polypyrrole[3] exhibit conductivity enhancements of nearly twelve orders of magnitude after doping, thus becoming transformed from insulators into "organic" metals (with conductivities of 1-10^3 S/cm). The technological opportunities offered by the control of the electrical conductivity over such a vast range has not been overlooked.[3-5] In addition, these materials exhibit the added feature of reduced dimensionality which gives rise to an assortment of collective phenomena, not characteristic of traditional semiconductors,[6] which are thought to play an important role in the transport, magnetic and optical properties of the polymers. Low energy electronic excitations of the collective ground state, e.g. solitons,[7] polarons,[8] and bipolarons[8] arise from the interactions between the valence electrons, the dopant molecules and the polymer backbone.

To describe transport in doped "conductive" polymers it is necessary to construct a quantitative model of the electronic structure of the pristine polymers before the addition of the dopant molecules. We present such a model herein, focusing on two issues. First, we examine how the details of the molecular architecture influence the valence electronic structure. Four topics are considered: the degree of conjugation, the length of the polymer chains, the role of heteroatoms, and the effects of linkage groups. Second, we indicate the influence of disorder on the electronic structure of polymers. The polymers of interest are not prepared as single crystals. Consequently, the polymeric conformation will not be regular over macroscopic dimensions even prior to doping. Upon doping, further conformational variations probably occur.[9] In order to investigate the consequences of such variations we present calculations which describe the alterations of electronic structure induced by prescribed changes in macromolecular conformation.

Our work is motivated in part by the importance of the derivation of a set of simple, visualizable "molecular design rules" for the selection of conducting polymeric materials, as emphasized previously.[6,10,11] Because the synthetic chemist has some control over the details of the molecular architecture, it is important to understand how those details might be advantageously employed in the design of conducting polymer/dopant systems. In addition, the interpretation of valence band photoemission and UV absorption spectra of organic systems relies heavily upon accurate theoretical models. We report herein the development of an accurate molecular orbital model, properly extended to deal with "infinite" systems, which is suitable for both new-materials evaluation and the quantitative analysis of spectral data.

THEORETICAL MODEL

The model used in our calculations is a complete neglect of differential overlap (CNDO) self-consistent field method. This model, to which we refer as CNDO/S3, is a spectroscopically parameterized method first introduced by Lipari and Duke[12] for interpreting the ultraviolet photoemission and electromagnetic absorption spectra of small organic molecules. It subsequently has been applied to many other organic molecules,[13] e.g. the polyenes, the polyacenes, the paracyclophanes, TCNQ, the porphins, the phthalocyanines, and most recently to polymer macromolecules.[14-16] Aside from the description of ultraviolet photoemission (UPS) and ultraviolet absorption (UVA) spectra, the model has also been used to determine the electron interactions with the molecular vibrations of benzene[17] and TCNQ,[18] useful for the analysis of line shapes found in gas phase photoemission and for the construction of models of electronic charge transport in the solid state. The parameterization of the model proceeds in two steps: First, one computes a density of valence states (DOVS) for a given set of parameters and compares this with measured gas phase UPS spectra for a group of selected small molecules. Secondly, a limited, configuration interaction (CI) calculation is performed, usually using only the outer valence pi levels, to obtain the lowest energy excitations of the model molecules. These two steps are performed iteratively until a satisfactory fit is obtained for the whole family of small molecules. The resulting parameters are transferred without further modification to other, larger molecules sharing similar bonding configurations. For elements in rows one and two of the periodic table six parameters are described for each atom. The parameters used in this work are listed in Refs. 14-16. A more general tabulation can be found in the Ref. 13. The DOVS are computed by convoluting a given eigenvalue spectrum with a Gaussian of width β to model the inter- and intramolecular relaxational broadening of the one-electron levels[6,11] and the intrinsic resolution of the spectrometer. Typically β is chosen to have a value near 0.7eV for condensed phase spectra and 0.3eV for gas phase spectra. The success of this approach suggests that no theory of the cross-sectional dependence of the individual levels is required for the analysis of ultraviolet (as opposed to X-ray) valence electron photoemission in terms of the calculated DOVS.

A polymer can be viewed as being formed from a linked assembly of individual monomeric molecular units. Consequently, it is important that our theoretical model yield a highly accurate description of the electronic states of these molecular units. The CNDO/S3 model has been tested and "calibrated" for a number of systems, as noted above, and has been shown to yield an accurate analysis of photoemission and optical absorption spectroscopies. Since the phenyl-based aromatic systems studied in this paper exhibit similar

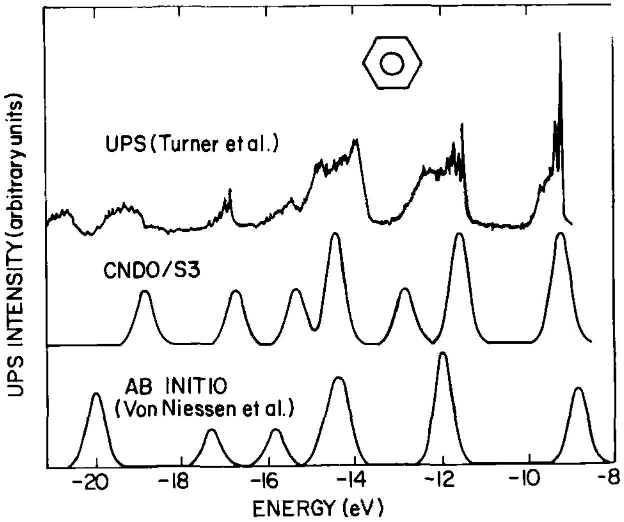

FIGURE 1. *Top panel: UPS gas-phase spectrum of benzene;*[19] Middle panel: DOVS computed using CNDO/S3; Bottom panel: DOVS computed from the results of a renormalized Green function method.[20]

bonding to that found in benzene, we discuss first the analysis of benzene. In Fig. 1 we show a comparison between the gas-phase UPS benzene spectrum of Turner, et al.[19] to the DOVS computed using CNDO/S3. The calculation yields an accurate description of the data in the outer valence region. Also indicated in the figure is a DOVS computed from the eigenvalues obtained by von Niessen, et al.[20] from a highly accurate ab initio renormalized Green function calculation. The occupied level symmetries computed using the CNDO/S3 model, unlike other semi-empirical models,[20] agree completely with those predicted by the ab initio calculation.[16] Finally the CNDO/S3 ultraviolet excitation energies are in good agreement[12,16] with the observed transition energies and are more accurate than those determined using ab initio CI methods.[21]

Similarly, in order to discuss polypyrrole it is necessary to describe the pyrrole monomer. Pyrrole and polypyrrole have been studied recently using CNDO/S3 by Ford, et al.[15] who achieved a theoretical description of the pyrrole molecule comparable in quality to that of benzene. The results reported herein use the parameters obtained from studies of these two molecules.

The transferability of this molecular CNDO/S3 model to the infinite polymer can be examined using the first optical transition of the diphenyl polyenes.[22] These molecules have been characterized spectroscopically and moreover, model the oligomer sequence leading to polyacetylene. In Fig. 2 we show the first optical transition of the diphenyl polyenes as a function of the number of double bonds in the polyene chain linking the phenyl end groups and compare these values to the lowest ultraviolet transition predicted by the CNDO/S3 model. The agreement is excellent over the range of extant data and serves to support the application to large molecular systems of parameters obtained from "small" molecules.

Polymeric macromolecules are too large to treat using a molecular orbital framework even with the simplifying assumptions of CNDO. Consequently, we regard the polymers as infinite chains and in so doing transform the molecular orbital model into a crystal orbital model, one appropriate to the infinite crystal boundary conditions.[23] For CNDO/S3 this has been done by Ford, et al.[14] In their paper the energy levels of the infinite polymer are reported using band diagrams, traditional in solid state physics, where the

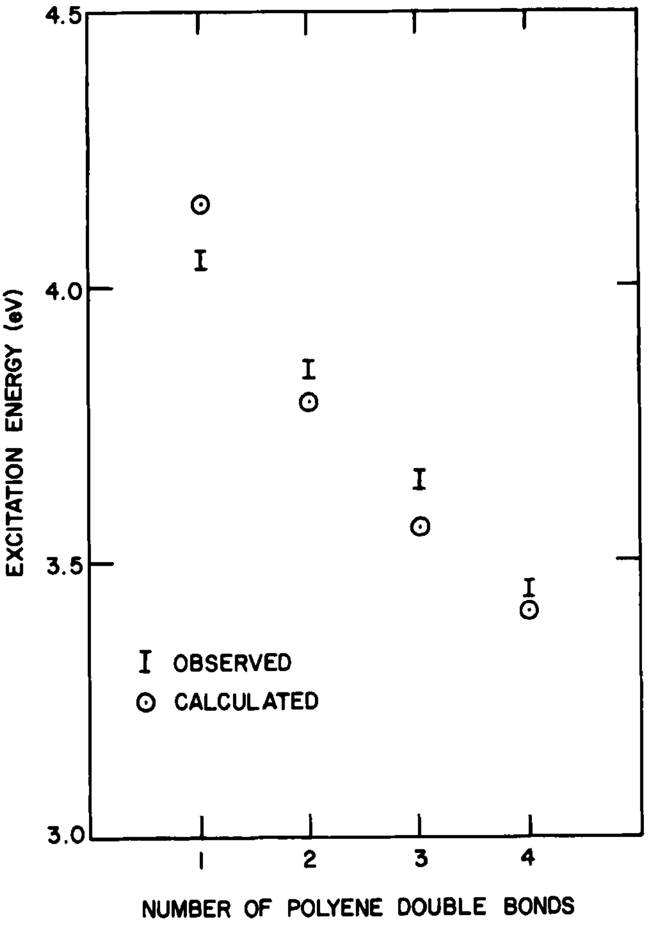

FIGURE 2. Energies of the first allowed optical transitions of the diphenyl polyenes versus of the polyene length compared with the energies predicted by the CNDO/S3 model.[22]

energy of the states, in principle, a continuum of states, are displayed as a function of the quantum index k called the wave number, which describes the translational symmetry of the level. We utilize their analysis herein to describe macromolecules of polyacetylene, poly(p-phenylene), poly(p-phenylene vinylene) and polypyrrole.

SIMPLE CONJUGATION

The effects of increasing chain lengths for conjugated systems are most transparent in polyacetylene and poly(p-phenylene). For such highly conjugated polymers the valence pi electrons can become delocalized because of the larger intermolecular electron overlap integrals.[6] Hence one might expect to analyze the electronic and transport properties of such polymers, using a band model, provided that the reduced dimensionality of macromolecular chain does not change the physics markedly.

The first example we discuss is polyacetylene (PA). The CNDO/S3 crystal orbital band structure[14] is shown in Fig. 3. The pi-bands, indicated by dashed lines, constitute the highest occupied and lowest unoccupied states of the pristine polymer. The overall width of the two bands is approximately ten electron volts. The gap of 4.9eV evident in Fig. 3 is the SCF single particle gap. It cannot be identified as the predicted optical band gap since in the crystal orbital calculation particle-hole correlation has been neglected. Correlation must be included in this model through a CI calculation in order to analyze optical properties. The strong optical absorption band of polyacetylene predicted from an extrapolation of CI calculations for polyene oligomers occurs at 2.0eV in satisfactory corres-

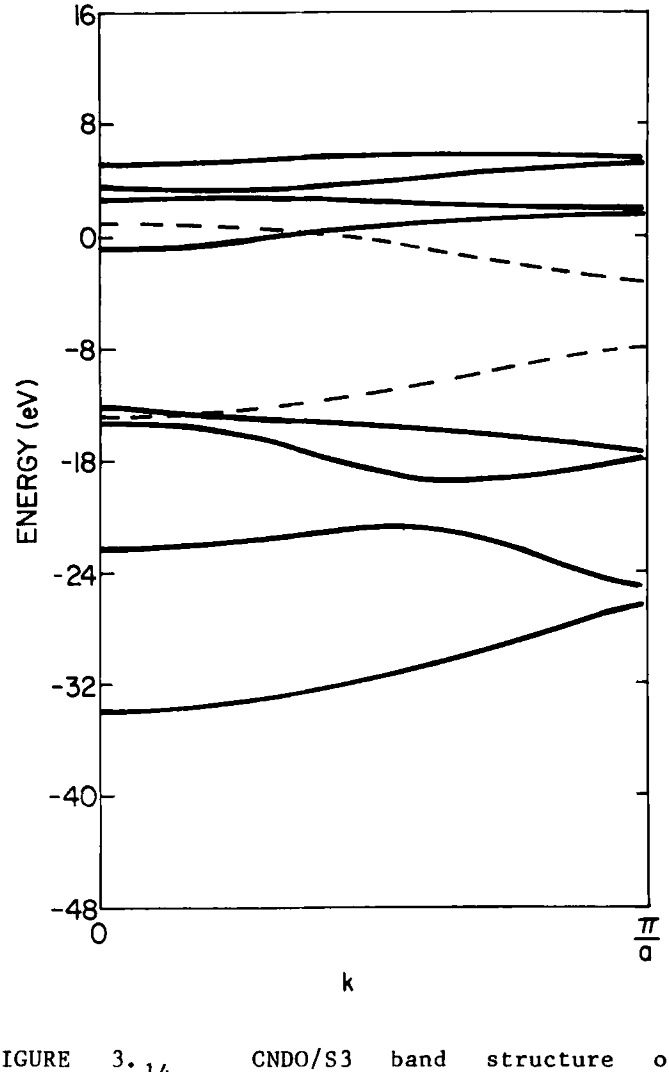

FIGURE 3.[14] CNDO/S3 band structure of trans polyacetylene. The solid curves denote sigma states and the dashed ones represent pi states.

pondence with the measured band gap of 1.5eV.[24] In Fig. 4 we compare the CNDO/S3 DOVS for a sequence of polyene oligomers with the *trans*-polyacetylene UPS spectrum measured by Salaneck et al.[25] The DOVS curves for $C_{12}H_{14}$ and for the infinite macromolecule predict that UPS will not be sensi-

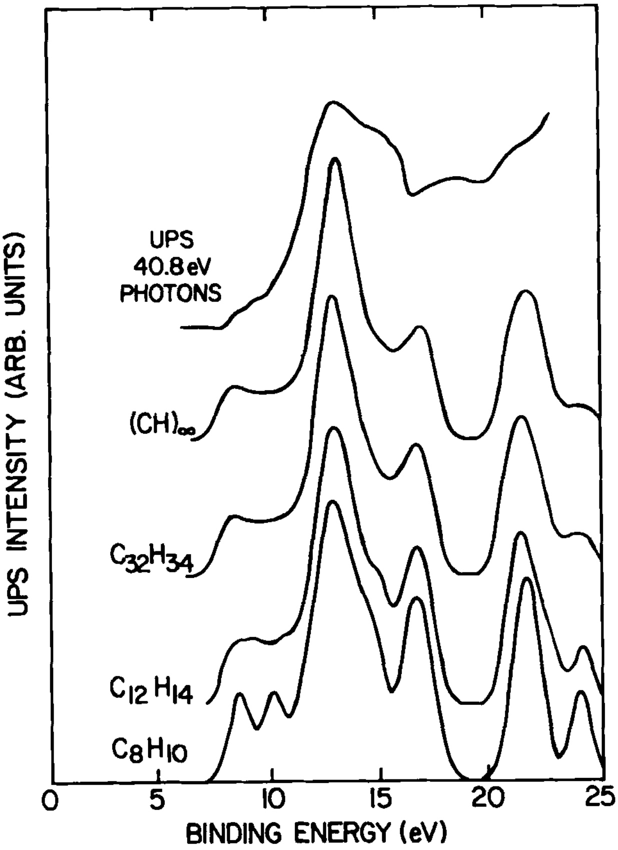

FIGURE 4. DOVS of a polyacetylene oligomer sequence computed using β =0.7eV are contrasted[14] to the UPS condensed phase spectrum of *trans* polyacetylene.

tive to photogenerated radical cation states which extend over more than twelve or so C=C bonds. More importantly it is evident that without modification the infinite-chain does not describe the low binding energy region of the UPS data in which there is no hint of a pronounced shoulder predicted theoretically. Since the pi-electron radical cations are highly extended along the polymer, they are sensitive to topological defects and general disorder, suggesting that the localization of these states near the top of the pi band is responsible for the failure of the infinite-chain DOVS to describe the low-binding-energy radical cations. A quantitative description of the role of disorder in polymeric systems has been given by Duke.[26]

Poly(p-phenylene) (PPP) also is a relatively simple polymer, being constructed of a chain of phenyl rings. It differs from PA in that the conjugated phenyl moieties create both "bonding" and "non-bonding" pi-electron states. The bonding states are comprised of pi states which have considerable overlap between phenyl groups, whereas the non-bonding states have nodes at the phenyl-connecting bond sites. In PPP these two bands of states arise from the degenerate e_{1g} states of benzene.[16] Thus the pi electron system of PPP is fundamentally different from that of PA in that it possesses two pi-electron bands contributing to highest energy valence-electron ionizations. The bonding states, having considerable overlap with each other, form a wide band while the non-bonding states form a narrow, dispersionless band. The band structure of PPP[16] is presented in Fig. 5 from which it is clear that the first 4eV region below the Fermi level is dominated by these two pi electron bands. The width of the bonding band is 5.0eV whereas the

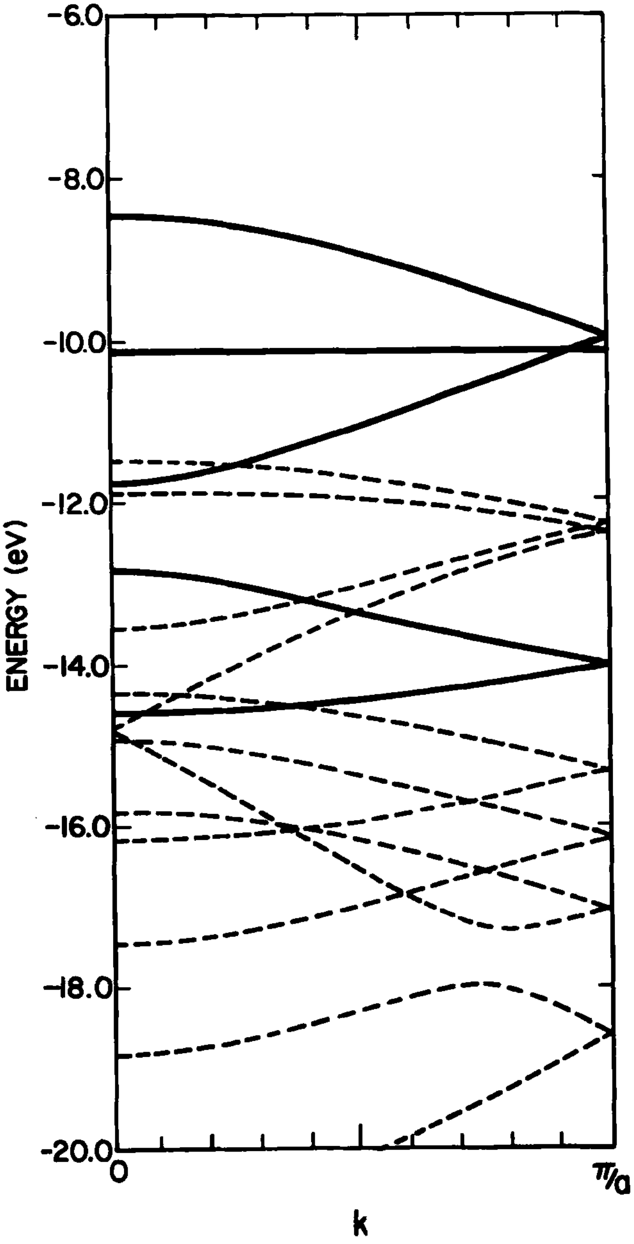

FIGURE 5. CNDO/S3 band structure of poly(p-phenylene)

width of the non-bonding band is only 0.02eV. This band structure is computed using two phenyl groups per unit cell and a planar geometry. The implications for photoemission is evident in the calculated DOVS which is displayed in Ref. 16. The non-bonding pi-band yields a spectrum-dominating peak that dwarfs the small, low-binding-energy shoulder generated by the bonding pi-states. Examining the changes of the DOVS as a function of oligomer length[16] the emergence of the bonding shoulder with increasing chain length is obvious but the position of the non-bonding peak does not change. The net effect in the photoemission is predicted to be a broadening of the low energy peak with increasing chain length. The optical absorption on the other hand will be sensitive to the length of the PPP chains, with the first allowed optical transition decreasing with increasing chain length to a value of about 3.6eV for the infinite polymer from a value of 4.8eV for biphenyl.[16]

EFFECTS OF LINKAGE GROUPS

The choice of group linking successive aromatic moieties along a macromolecular chain has serious consequences for the electronic characteristics of the resultant polymer. If the choice is such that conjugation is retained, delocalized valence states will occur favorably impacting the electrical conductivity of the polymer. Conversely, if the choice is such that conjugation is destroyed, delocalized valence states will not arise. Rather localized molecular-like states will dominate the physical properties. Finally, if the linkage group is a heterogroup or a heteroatom, such as sulfur or oxygen, which introduces a lone-pair or other unique hybridization, conjugation may be disrupted but extended, crystalline states may still arise.[10]

In this section we illustrate the first two alternatives noted above by comparing two similar polymers, poly(p-phenylene vinylene) (PPV) and poly(p-xylylene) (PPX). PPV forms a chain similar to PPP except that the phenyl groups are linked by unsaturated, vinyl groups. The pi-electron system now includes both the pi-electrons of the phenyl ring and those of the vinyl linkage group. The conjugated electron system thus extends between the phenyl moieties with the consequence that two wide bands of states are formed of delocalized bonding pi electron levels whereas in PPP there is only one. In Fig. 6a the CNDO/S3 band diagram of PPV is presented. It reveals the presence of the expected two rather broad bonding pi bands, each having a width of approximately 2.0eV. Unlike these bonding pi states which exhibit pi charge accumulation at the carbon atoms of the linking groups, another set of pi states are formed which have nodes at those atoms. This set of states consists of the non-bonding levels and gives rise to the dispersionless band near-10.2eV in Fig. 6a. The charge densities of these states are essentially identical to those of the analogous states in PPP. Aided by the wide, bonding bands, PPV can be charge-transfer doped and achieves a conductivity of circa 3 S/cm, although lower than the circa 500 S/cm reported for PPP. Comparing PA, PPP, polypyrrole (vide infra) and PPV we observe a systematic correlation between the bonding pi-electron bandwidths predicted using the CNDO/S3 model and the highest currently achieved conductivities showing that as the bandwidth is decreased the conductivity also decreases. (Bredas, et al.[32] have also observed this trend for similar systems using another theoretical model.) Such a trend supports the use of one-electron models to interpret the physics of conducting polymers.

Poly(p-xylylene) (PPX) is similar in chemical structure to PPV but has instead a saturated, ethyl linkage group connecting its phenyl rings. This group does not add electrons to the pi system but instead serves to separate the pi systems on neighboring phenyl rings.[27] Thus the conjugation is broken and no extended pi-electron crystalline states arise. In Fig. 6b we display the CNDO/S3 band structure for PPX. Evidently, two dispersionless bands of states dominate the outer valence energy region. Contrary to the case of PPV where bonding and non-bonding bands of states evolve from the degenerate e_{1g} benzene levels, PPX instead exhibits two non-bonding bands emanating from these levels. Not surprisingly, PPX has not been successfully charge-transfer doped, although it has been made conducting via chemical vapor codeposition procedures.[27] The electrical properties of this polymer resembles those of polystyrene and other insulators where states localized to the aromatic rings dominate the electronic properties.[28] A discussion of the role of molecular chain length on the DOVS of oligomers of p-xylylene has been given by Duke et al.[27]

EFFECTS OF HETEROATOMS

The introduction of atoms other than carbon and hydrogen into the molecular structure can induce important changes in the polymeric electronic properties. As mentioned above, a heteroatom or heterogroup appearing as a linkage group may introduce extended crystalline states in non-planar polymers. Appearing in the aromatic ring, a heteroatom can effect mixing of the bonding and non-bonding bands, i.e.

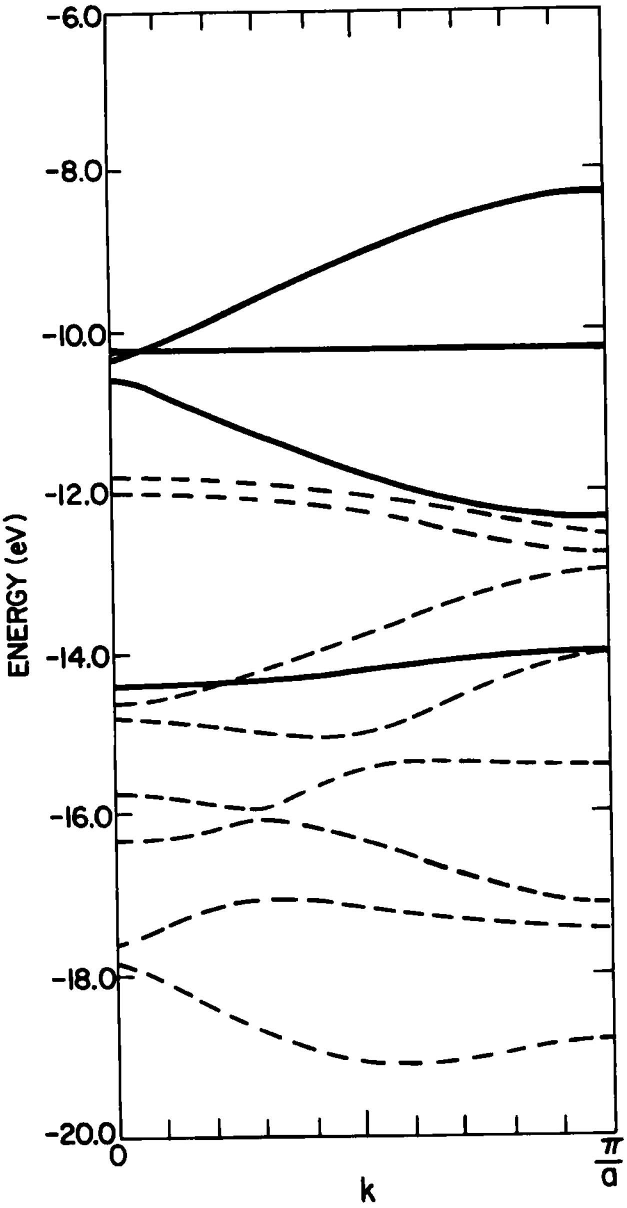

FIGURE 6a. CNDO/S3 band structure of poly(p-phenylene vinylene).

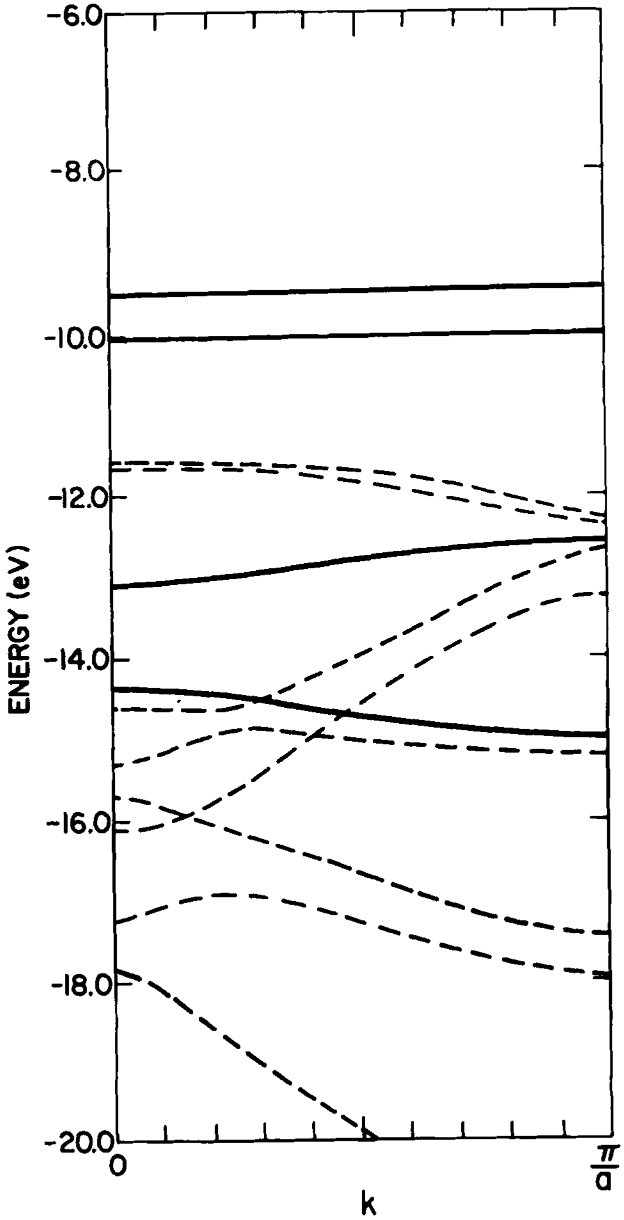

FIGURE 6b. CNDO/S3 band structure of poly(p-xylylene).

cause orbital hybridization of the bonding and non-bonding crystalline states. This hybridization influences the relative energies of the non-bonding band with respect to the bonding bands. Indeed, in an extreme case the hybridization obscures the differences between the two classes of states. The magnitude of the changes incurred depends on the detailed chemistry of the substituent heteroatom.

In this section we analyze the effect of substituting a heteroatom in the aromatic ring, using polypyrrole as a model. The consequences of heteroatom linkages in poly(p-phenylene oxide) and poly (p-phenylene sulfide) have been described elsewhere.[6,11] Polypyrrole and PPP have similar band structures except for changes due to the presence of a nitrogen atom in the aromatic pyrrole rings.[15,16] The crystalline pi-states of polypyrrole[15] consist of a set of bonding orbitals (which exhibit charge densities peaked on the carbon atoms of the pyrrole chain and nodes at the nitrogen atoms) and of a set of non-bonding orbitals (which exhibit charge maxima at the nitrogen atoms and the β carbon atoms but nodes at the connecting, α atoms). The bonding states of polypyrrole are analogous to those of cis-polyacetylene just as in the case of poly(2,5 thienylene).[6] The CNDO/S3 band structure of polypyrrole is presented in Fig. 7, from which it is obvious that the pi-electron system dominates the outer valence energy region. Two effects due to the nitrogen atom are evident: First, the bonding and non-bonding bands have become hybridized in the region of -10.2eV. Secondly, the non-bonding band now appears at a greater binding energy relative to the top of the valence band than was the case for PPP. Consequently, in poly(pyrrole) we expect the DOVS to be dominated by contributions due to the non-bonding states and to exhibit an extended, low-

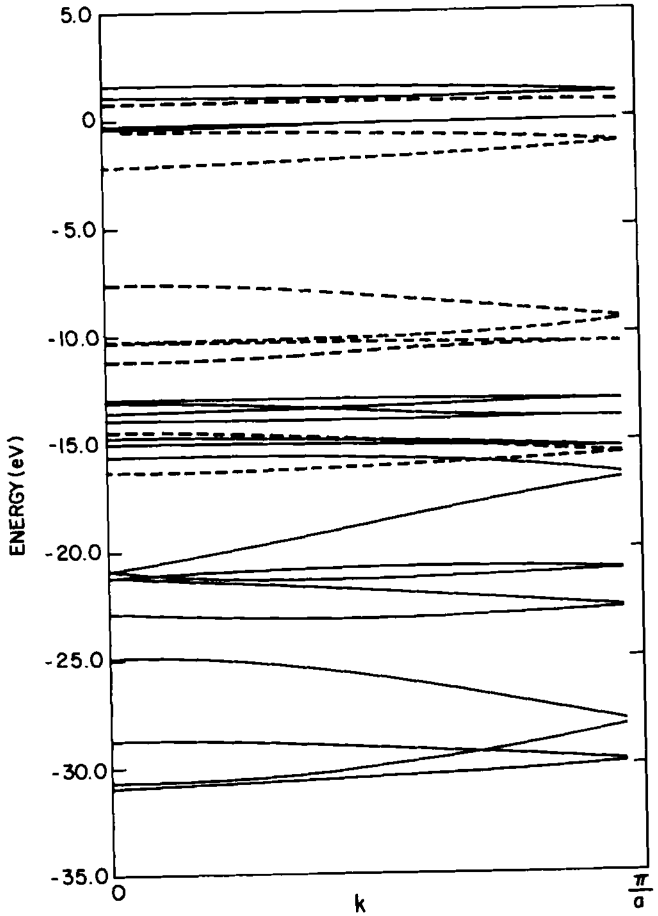

FIGURE 7. CNDO/S3 band structure of polypyrrole.[15]

binding-energy shoulder due to the bonding states. In Fig. 8 we show the development of the DOVS for pyrrole oligomers of increasing length. In going from the monomer to the dimer the main peak in the outer valence region shifts to increased binding energies and a small low-binding-energy shoulder appears. As the polymer is formed the dominant peak due to the non-bonding orbitals appears nearly stationary, shifting

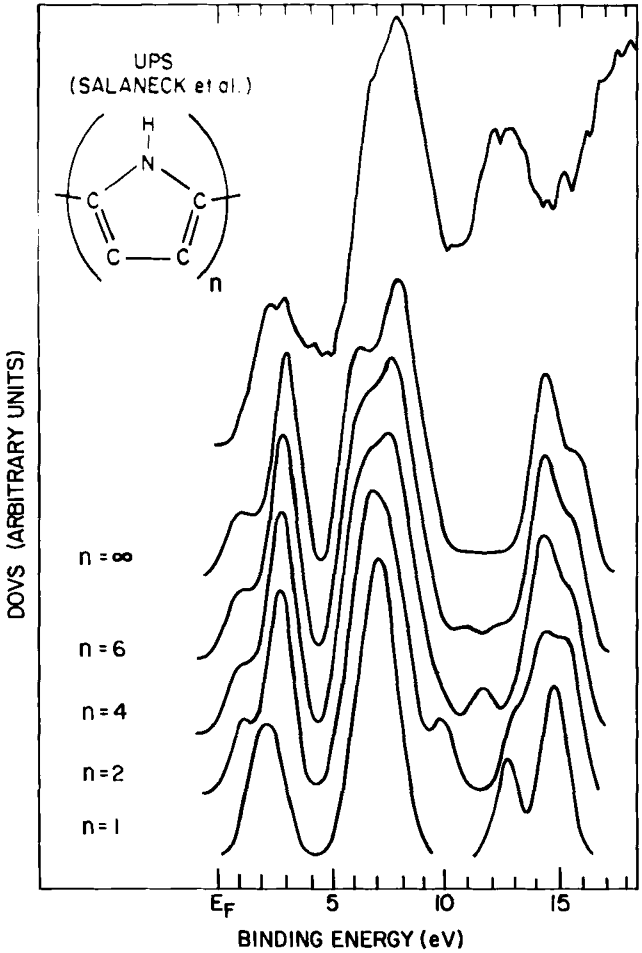

FIGURE 8. The theoretical UPS spectrum of oligomers of pyrrole for chains of n=1,2,4 and 6 pyrrole units and for polypyrrole is contrasted to[15] the observed UPS spectrum of a thin film of the polymer. The DOVS is computed with a β =0.7eV.

approximately 0.5eV to higher binding energies. The shoulder due to the bonding levels develops toward lower binding energies. This comparison allows us to predict a shift and a broadening of the dominant peak of the UPS spectrum, which subsequently has been observed.[16,29] Comparing the theoretical curves to the experimental spectrum given in this figure the absence of the predicted low-binding energy shoulder is apparent, as was the case above for polyacetylene. Disorder and relaxation effects can be invoked to explain this absence for polypyrrole, also.

The position of the non-bonding band is important since it helps to define the maximum Fermi energy for the doped polymer. With increasing acceptor doping the Fermi level will move lower in the bonding pi-band of these polymers, until it enters the region of non-bonding states. Here it will appear to pin due to the high density of states created by the narrow, non-bonding bands. In polypyrrole the bandwidth of the bonding states above the non-bonding region is approximately 2eV and that of the overall pi-electron region is only circa 2.5eV. In PPP on the other bond, the non-bonding band more or less splits the 5.0eV side bonding band in half. Thus the effect of nitrogen in polypyrrole is to increase the width of the bonding band above non-bonding level.

SENSITIVITY TO CONFORMATION

The conducting polymers of interest here are disordered materials, often made as amorphous films. Consequently, the nature of the real physical system must be considered in our model calculations. With the framework of our CNDO/S3 model we now discuss the effect of conformational disorder on the electronic structure of polymers, in particular PPP and polypyrrole. The types of disorder which we have examined consists primarily of changes of the details of the bonding geometry which may arise due to solid state effects.

Considering first PPP we have examined the changes in the electronic structure induced when the individual rings along the chain are twisted back and forth. A twisted conformation rather than a planar one is thought to be the physical one.[30] With twists of 0°, 11°, and 23° neither the pi electron contributions to the DOVS nor the first optical transition changes appreciably. Thus UPS and UVA will not be highly sensitive to the differences between a planar geometry and a twisted one.

We also examined the quinoid form of PPP which is expected to arise in localized regions of the chain when the polymer is doped.[31] The major change induced in the DOVS using this geometry is an extension to lower binding energies of the bonding pi-band shoulder of the non-bonding peak. The insensitivity to this geometrical change of the non-bonding peak itself is easily understood because the non-bonding states are localized, having very little overlap between phenyl moieties. Thus they do not respond to the change in geometry while the bonding states, which have considerable charge overlap between phenyl groups, are quite sensitive to geometric modification. The band gap, which is determined by the position of the bonding (and anti-bonding) levels, is greatly reduced using this geometry. Therefore the UPS response is dominated by contributions from the non-bonding states and is predicted to be insensitive to a quinoid lattice defect, but the optical properties of the polymer is predicted to be significantly effected.

The microscopic structure of polypyrrole is not well characterized. All of the bond lengths are not known, and the average chain length has not been determined. In our calculations we consider the polymer to be a planar, linear chain of pyrrole units having alternating orientation. As in the case of PPP, we studied how the electronic structure of polypyrrole might be effected if the pyrrole units were twisted back and forth. We predict essentially no major modifications to the UPS and UVA spectra compared to the that of the planar polymer.

It is also possible that long chains of polypyrrole could be formed from nearly planar, open rings of pyrrole monomers, roughly analogous to porphin geometries. Our calculations of the UPS and UVA spectra using this configuration indicate that such a defect cannot be differentiated from the ideal, linear conformation. Thus both must be considered when characterizing the polymer using UPS and UVA spectroscopies. The electron excitations of polypyrrole are sensitive to both the chain length of the polymer and the bond length connecting two pyrrole moieties, i.e., $d_{\alpha\alpha}$. In Fig. 9 we show the results of our CI calculations of the first optical transition in polypyrrole as a function of chain length for three choices of $d_{\alpha\alpha}$.[15] The energy of this transition is quite sensitive to the chain length, changing by nearly one electron volt over the range of chain lengths used for each choice of bond length. The physical values of the transition energy are somewhat lower than those calculated.[15] The lowest-energy observed optical transition is near 3.0eV for undoped polypyrrole.[33] From Fig. 9 the sensitivity of the model predictions to these two conformational features is apparent and thereby suggests the predictive potential of the model once one of the two unknown

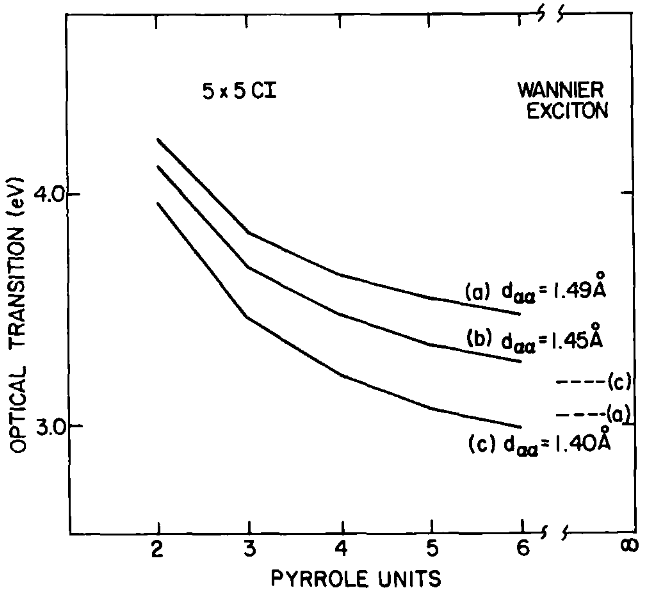

FIGURE 9. Lowest energy dipole allowed optical transition energies of oligomers of pyrrole as a function of the number of pyrrole units in the oligomer. The three curves labeled (a)-(c) correspond to $d_{\alpha\alpha}$ of 1.49, 1.45 and 1.40A, respectively. Also displayed are the predicted Wannier exciton excitation energies obtained using a simplified effective mass theory.

parameters is determined independently.

SYNOPSIS

The extent to which polymers, as well as traditional semiconductors, can be made conducting by doping is determined by the nature of the electronic states found in the material, with extended states leading to wide bandwidths and high conductivities. In polymers extended states result from increased conjugation along the polymeric chain. However, the nature of the conjugation is strongly influenced by the details of the macromolecular architecture, as we have demonstrated in this paper. The length of polymer chain is an important determinant for the electronic structure as demonstrated for polyacetylene and poly(p-phenylene). Using the examples of poly(p-xylylene) and poly(p-phenylene vinylene) we illustrated the importance of the choice of linkage group when constructing the chain. Finally we indicated the important impact of heteroatoms on the electronic structure using the example of polypyrrole. Several types of conformational disorder likely to occur in real systems were also investigated with results reported for poly(p-phenylene) and polypyrrole.

All of our discussions have been based on an accurate theoretical model, CNDO/S3, which is particularly well suited to the analysis of the ultraviolet photoemission and optical absorption spectra. Hence, we are able to make quantitative predictions regarding the results of spectroscopic measurements on real polymers. In some cases, e.g. polypyrrole, unexpected predictions have been verified by subsequent measurements.

The outer valence electronic structure of the polymers considered consists mainly of contributions from pi-electrons which therefore determine most of the transport, optical and magnetic properties of the polymer. Except for PA, these levels can be grouped into two classes: bonding and non-bonding. The non-bonding bands dominate the predicted UPS spectra. The photoelectron spectroscopic importance of the bonding bands is diminished both for this reason and because the extended, bonding states are most sensitive to the presence of disorder. The bonding bands, on the other hand, play a dominant role in the ultraviolet optical properties of the polymer as well as in the transport properties. The CNDO/S3 model does, therefore, provide the basis for quantitative interpretation of the spectroscopic and transport properties of extended linear-chain polymers. Moreover, it also affords valuable insight into the role of molecular architecture in determining the electronic states of the macromolecular chain. It is such insight which permits the suggestion of promising candidates for conducting polymer/dopant systems on the basis of the molecular structure of the polymer, and thereby achieves the technological objectives of this research effort.

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