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A nonempirical effective Hamiltonian technique for polymers: Application to polyacetylene and polydiacetylene

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The recently proposed *ab initio* effective Hamiltonian technique is extended to polymer calculations and applied to various conformations of polyacetylene (all-*trans*, *cis*-*transoid*, and *trans*-*cisoid*) and polydiacetylene (acetylenic and butatrienic backbones). Band structures, density of states (DOS), and XPS theoretical spectra are presented. Comparison of the band structures and DOS with those obtained by *ab initio* SCF (self-consistent-field) Hartree-Fock calculations of double zeta quality is excellent. The XPS theoretical spectrum for all-*trans* polyacetylene is in good agreement with experiment. In polyacetylene, it is found that the π bands are quite similar for all three backbone conformations, though the σ bands differ significantly. For polydiacetylene, low ionization potentials are predicted—a few tenths of an eV larger than polyacetylene for the acetylenic backbone and a few tenths of an eV smaller than polyacetylene for the butatrienic backbone.

I. INTRODUCTION

Conjugated organic polymers have recently been the focus of enormous interest. This interest is mainly due to the discovery that certain of these polymers, when doped with electron donors or acceptors, can increase their conductivity by many orders of magnitude up to near metallic levels. Such systems include doped polyacetylene, $(\text{CH})_x$,¹ poly(*p*-phenylene), $(\text{C}_6\text{H}_4)_x$,² poly(*p*-phenylene sulfide), $(\text{C}_6\text{H}_4\text{S})_x$,^{3,4} and polypyrrole, $(\text{C}_4\text{H}_3\text{N})_x$.⁵

It has been demonstrated that an understanding of the electronic properties of polymeric compounds can be aided by quantum chemical calculations.⁶ However, *ab initio* Hartree-Fock methods, which have proved successful in the determination of the ground state properties of molecules, are already time consuming for middle- and large-sized molecules. As a result, they become almost prohibitively expensive when one wants to apply them to polymers of interest. Cheaper semi-empirical techniques could in principle replace them but suffer from crude approximations and arbitrary simplifications, which sometimes result in difficult interpretative work. This is especially true when one has to discriminate between a possibly interesting chemical effect and an artifact of the method. For instance, extended Huckel calculations yield reasonable band structures of hydrocarbon polymers but usually with too large an overlap between σ and π bands; they

fail when applied to polar systems such as fluoro-polymers.⁷ CNDO-2 methods provide nonmeaningful density of states, even in the reference polyethylene case.⁸ Other parametrizations in the CNDO scheme (CNDO/S3) have given encouraging results for oligomers of polyacetylene,⁹ but have yet to be applied to the polymer. Therefore, it is highly desirable to find a method affording a reasonable compromise between the computationally fast semiempirical schemes and the more reliable *ab initio* techniques.

For that purpose, methods based on the simulated *ab initio* molecular orbitals (SAMO)¹⁰ and on the application of linear combination of localized orbitals (LCLO)¹¹ techniques have been proposed. The principle of these methods is to build the Fock matrix elements of the polymer from transferable *ab initio* data obtained from model molecules. The advantages are the speed and the *ab initio* character of the approach. However, these methods suffer from: (i) a tedious generation of a huge number of matrix elements; (ii) the need of rather large model molecules to get transferable parameters; and (iii) the impossibility of interpreting persistent discrepancies in band shapes and widths.¹²

Recently a new approach has been proposed by Nicolas and Durand (ND).¹³ In contrast to the semi-empirical, SAMO, and LCLO techniques, which each have approximations at the level of matrix elements, ND have suggested the use of approximate one-electron valence effective Hamiltonians (VEH). They developed a methodology to derive such Hamiltonians and applied their technique to various hydrocarbon molecules. They find

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excellent agreement with SCF double zeta *ab initio* results.¹³ The advantages of the model are: (i) it is completely theoretical; (ii) it is nonbasis set dependent; (iii) it gives *ab initio* quality results with negligible computer time, due to the evaluation of only one-electron integrals and the complete avoiding of SCF iterative cycles.

Hence, this method appears very attractive for extension to polymer calculations, as has already been pointed out by André *et al.*¹⁴ They have extended the VEH formalism to polymers and presented preliminary results for polyethylene and polyacetylene. The purpose of this paper is the assessment of the quality of the non-empirical VEH technique as applied to polymer calculations on unsaturated hydrocarbon systems, exemplified by polyacetylene and polydiacetylene.

Section II is devoted to the determination of universal atomic potentials for carbon and hydrogen, as obtained from calculations on model molecules including ethane, butadiene, and acetylene. Universal atomic potentials are intended to be reliable for saturated as well as unsaturated compounds with double and/or triple bonds. In Sec. III, we briefly describe the extension of the VEH method to polymer calculations. In Sec. IV, we apply the technique for polymers to (i) three forms of polyacetylene chains: all-*trans*, *cis-transoid*, and *trans-cisoid* (see Fig. 1); (ii) various backbones of polydiacetylene chains ranging from the so-called acetylenic skeleton to the butatrienic one (Fig. 2). Band structures along with density of states and XPS theoretical spectra are presented and discussed in connection with recently performed SCF *ab initio* calculations of double zeta quality and with experimental data where available. Conclusions are presented in Sec. V.

II. UNIVERSAL ATOMIC POTENTIALS FOR CARBON AND HYDROGEN ATOMS

The complete methodology for obtaining molecular one-electron effective Hamiltonians from first principles has been developed in Ref. 13. The effective Fock Hamiltonian of a molecule is assumed to be the

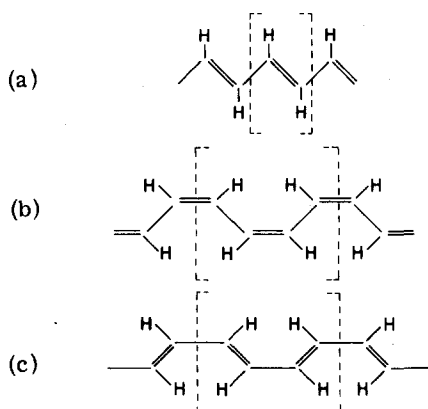


FIG. 1. Structure of polyacetylene: (a) all-*trans*; (b) *cis-transoid*; (c) *trans-cisoid*.

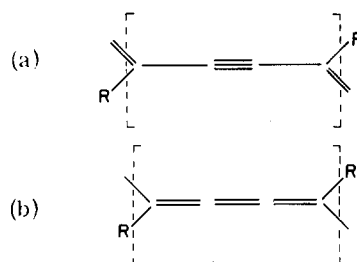


FIG. 2. Structure of polydiacetylene: (a) acetylenic backbone; (b) butatrienic backbone. R is a substituent group which is taken to be H in our computations; experimentally, the R groups for known systems are quite bulky, containing up to 30 atoms, but having a saturated carbon connection with the backbone.

sum of the kinetic energy and of the various atomic potentials in the molecule:

$$F_{\text{eff}} = -\frac{\Delta}{2} + \sum_{\text{A}} V_{\text{A}}, \quad (1)$$

where V_{A} is the effective potential of atom A. For computational reasons, simple nonlocal atomic potentials are chosen of the form:

$$V_{\text{A}} = \sum_l \sum_m \sum_{i,j} C_{ij,lm}^{\text{A}} | \chi_{ilm}^{\text{A}} \rangle \langle \chi_{jlm}^{\text{A}} |. \quad (2)$$

The summations over l and m define the angular dependence of V_{A} . The numerical coefficients $C_{ij,lm}$ are independent of m in the case of spherical symmetry, which we consider throughout this paper. The χ_{ilm} 's are normalized Gaussian functions:

$$\chi_{ilm} = N_i r^l \exp[-\alpha_i r^2] Y_{lm}(\Theta, \varphi). \quad (3)$$

N_i is the normalization factor and $Y_{lm}(\Theta, \varphi)$ indicates the usual spherical harmonics. Only 1s and 2p Gaussian Cartesian functions are used.

The parametrization of universal atomic potentials for carbon and hydrogen has been carried out, according to the techniques described in Ref. 13, on model molecules: ethane, butadiene, and acetylene. In a first step, valence SCF calculations are performed for these three molecules by a theoretical pseudopotential method¹⁵ with first a minimal basis set of Slater orbitals¹⁶ and then a double zeta basis set.¹⁷ For each molecule the Fock operator is:

$$F = \sum_{\nu} \epsilon_{\nu} | \varphi_{\nu} \rangle \langle \varphi_{\nu} |, \quad (4)$$

where the summation is over all occupied levels. F is constructed with the valence orbitals φ_{ν} determined from the minimal basis set, whereas the corresponding energies ϵ_{ν} are those obtained from the double zeta basis set. The choice of the above theoretical Fock operator leads to valence effective Hamiltonians [Eq. (1)] which provide mono-electronic energies of double zeta accuracy when solved within a minimal basis set. Some information is lost for the wave functions but this is of little consequence for e.g., the comparison of calculated one-electron energies with the corresponding data from XPS experiments.

In a second step, parametrization of atomic potentials

TABLE I. Potential parameters of C and H atoms in the hydrocarbon series [Eq. (2)].

Atom	l	m	i	j	α_i	$C_{ij,lm}$
C	0	0	1	1	3.63	-10.075
			2	2	0.33	-1.178
			1	2		2.077
	1	-1, 0, 1	1	1	6.50	-11.468
			2	2	0.52	-0.443
			1	2		-0.185
H	0	0	1	1	5.00	-4.696
			2	2	0.49	-0.500
			1	2		0.646

for the carbon and hydrogen atoms is determined by minimizing the quantity

$$\begin{aligned} & [(F - F_{\text{eff}} | F - F_{\text{eff}})_{\text{ethane}} + (F - F_{\text{eff}} | F - F_{\text{eff}})_{\text{butadiene}} \\ & + (F - F_{\text{eff}} | F - F_{\text{eff}})_{\text{acetylene}}] . \end{aligned} \quad (5)$$

In Eq. (5), $(F - F_{\text{eff}} | F - F_{\text{eff}})$ denotes the scalar product of $F - F_{\text{eff}}$ with itself in the subspace of the occupied valence orbitals.¹³ The linear coefficients $C_{ij,lm}$ of V_A in Eq. (2) are obtained by solving a linear system of equations with the Fourier techniques developed in Ref. 13, whereas the determination of the nonlinear α_i exponents of the Gaussian functions of Eq. (3) requires the direct minimization of the quantity defined by Eq. (5). Parameters of potentials V_C and V_H for carbon and hydrogen atoms are given in Table I. These potentials are universal in the sense that they can be used with a good accuracy in the whole series of the hydrocarbon compounds. It must be stressed again that these potentials do not contain any experimental data and that they have been completely determined from first principles.

Table II compares the VEH and the double zeta SCF orbital energies of the three model molecules. The

agreement is quite good, the standard deviation being on the order of 0.01 a.u. We obtain very similar results for methane, ethylene, propene, and propyne, thus demonstrating the transferability of the effective potentials. The highest occupied levels are especially well reproduced for all the molecules considered. This gives confidence in obtaining, for instance, accurate relative ionization potentials in a series of similar polymers. On the other hand, the lowest valence level is found consistently lower in energy in the VEH technique. In the polymer calculations, this will tend to lower the bottom of the valence band and lead to overestimations of total valence bandwidths.

Note that no information pertaining to the excited states is included in the atomic potentials. This could in principle be done, as has been demonstrated in Ref. 13, but would not be very useful in the framework of the Hartree-Fock Hamiltonian, since Hartree-Fock excited states are known to bear little meaning. As a result, no special attention is to be given to the unoccupied levels. It should be added however that, in propene and butadiene, excited σ^* levels do appear too close to the highest occupied π levels. It is our experience that this fact sometimes leads, in polymer calculations, to the presence of spurious σ^* bands unusually low in energy.

III. EXTENSION OF THE METHOD TO POLYMER CALCULATIONS¹⁴

In the LCAO theory of chain polymers,¹⁸ the crystalline one-electron orbitals $\psi(k)$ are expressed as linear combinations of ω Bloch functions, where k is a point in the first Brillouin zone of the polymer:

$$\psi(k) = \varphi(k) C(k) . \quad (6)$$

The band structure $E(k)$ is obtained as eigenvalues of the set of secular equations:

TABLE II. Comparison of valence molecular energies (a. u.) obtained with VEH and double zeta SCF Hartree-Fock calculations.

Ethane		<i>Trans</i> -butadiene		Acetylene	
Effective Hamiltonian	SCF	Effective Hamiltonian	SCF	Effective Hamiltonian	SCF
$e_g - 0.501$	-0.487	$b_g - 0.322$	-0.318	$\Pi_u - 0.412$	-0.410
$a_{1g} - 0.507$	-0.496	$a_u - 0.437$	-0.445	$\Sigma_g - 0.661$	-0.679
$e_u - 0.620$	-0.601	$a_g - 0.476$	-0.498	$\Sigma_u - 0.758$	-0.762
$a_{2u} - 0.824$	-0.840	$b_u - 0.546^a$	-0.547	$\Sigma_g - 1.056$	-1.041
$a_{1g} - 1.050$	-1.022	$a_g - 0.523^a$	-0.550		
		$b_u - 0.644$	-0.642		
		$a_g - 0.662$	-0.644		
		$b_u - 0.756$	-0.761		
		$a_g - 0.794$	-0.822		
		$b_u - 1.004$	-1.007		
		$a_g - 1.137$	-1.102		
\bar{x}^b	-0.011		+0.003		+0.001
σ_x^c	0.015		0.018		0.012

^aNote incorrect ordering.

^bMean error on the valence molecular orbital energies (a. u.).

^cStandard deviation of the error (a. u.).

$$\mathbf{F}(k) \mathbf{C}(k) = \mathbf{S}(k) \mathbf{C}(k) \mathbf{E}(k) \quad (7)$$

The matrices $\mathbf{F}(k)$ and $\mathbf{S}(k)$ are the Fock and overlap matrices between Bloch functions $\varphi(k)$ constructed from atomic orbitals χ :

$$\begin{aligned} F_{pq}(k) &= \int \varphi_p^*(k) h \varphi_q(k) dv \\ &= \sum_j e^{ikja} F_{pq}^j, \end{aligned} \quad (8)$$

$$\begin{aligned} S_{pq}(k) &= \int \varphi_p^*(k) \varphi_q(k) dv \\ &= \sum_j e^{ikja} S_{pq}^j. \end{aligned} \quad (9)$$

The summation over j extends over all the unit cells; h is a one-electron operator; a indicates the length of the polymer unit cell; F_{pq}^j and S_{pq}^j are matrix elements, respectively, of the one-electron operator and the unity operator, between the atomic orbital χ_p centered in the origin unit cell and the atomic orbital χ_q centered in cell j .

In the effective Hamiltonian model, h is expressed as:

$$h = -\frac{1}{2} \Delta + \sum_g \sum_A V_A^g, \quad (10)$$

where the summation over g and A extend over, respectively, the polymer unit-cells and the atoms present in one cell. Making use of the expression for the atomic potentials (Eq. 2), we have for the matrix elements F_{pq}^j :

$$\begin{aligned} F_{pq}^j &= \langle \chi_p | T | \chi_q^j \rangle \\ &+ \sum_g \sum_A \sum_i \sum_m \sum_{t,u} C_{tu,im}^A \langle \chi_p | \chi_{tim}^{Ag} \rangle \langle \chi_{uim}^{Ag} | \chi_q^j \rangle. \end{aligned} \quad (11)$$

This expression has excellent convergence properties. The kinetic term $\langle \chi_p | T | \chi_q^j \rangle$ decays \sim exponentially with the square of the distance between χ_p and χ_q^j . The summation over g rapidly decreases due to the exponential decrease of the overlappike terms $\langle \chi_p | \chi_{tim}^{Ag} \rangle$ and $\langle \chi_{uim}^{Ag} | \chi_q^j \rangle$. In practice, the summations over j in Eq. (8) and Eq. (9) are performed out to the cell where all Fock matrix elements are smaller than a threshold value, usually set at 10^{-8} a.u. The process leads to properly stabilized Fock matrix elements. Note that the long-range coulombic interactions problem, which exists in *ab initio* calculations,¹⁹ is not present in VEH calculations. The diagonalization procedure [Eq. (7)] is usually performed for 21 equidistant k points in half the first Brillouin zone of the polymer.

IV. APPLICATION TO POLYACETYLENE AND POLYDIACETYLENE

Polyacetylene and polydiacetylene have been chosen for our test calculations. Both systems are currently the focus of great interest. Among doped polymeric systems polyacetylene compounds exhibit the highest conductivities obtained so far ($> 10^3$ S/cm). Polydiacetylenes, substituted with bulky ligands, provide the unique feature of being synthesized as macroscopic

single crystals with low level of defects. Their one dimensional extended π systems lead to very interesting linear and nonlinear optical properties.²⁰

As a result of the interest in these two polymeric systems, numerous *ab initio* calculations have already been performed.²¹⁻²³ Recently, double zeta quality studies have been reported.^{24,25} This allows a close comparison between VEH and double zeta SCF calculations. It should also be pointed out that the combination of single, double, and triple bonds in these systems offer a good framework for testing the universal atomic potentials.

A. Polyacetylene

Polyacetylene can be obtained in two conformations: the *cis* conformation, generally produced through the Ziegler-Natta catalized reaction of acetylene at low temperature (-78°C), and the all-*trans* conformation, usually obtained by thermal annealing of the *cis* compound.²⁶ Two backbones can be envisioned for the *cis* structure: *cis-transoid* and *trans-cisoid* (Fig. 1). Note that the *ab initio* calculations^{27,28} that correctly indicate the larger stability of the all-*trans* form²⁹ predict a very small energy difference between the two *cis* backbones (of the order of a few tenths of kcal/mol—the *cis-transoid* being slightly favored). Other calculations,^{30,31} which fail to reproduce the *trans* form as most stable, are probably less reliable.

1. All-*trans*-polyacetylene

In order to closely compare the VEH calculation with the double zeta calculation of Karpfen and Petkov (KP),²⁴ we used the same geometry as the one they optimized: R_{C-C} : 1.346Å; R_{C-C} : 1.446Å; $\angle C-C-C$: 125.3° . In Fig. 3 we display the VEH band structure of all-*trans*-polyacetylene, as well as the density of states (DOS) computed from the band structure by the method due to Delhalle.³² The comparison with KP double zeta results (Fig. 4 from Ref. 24) is excellent, not only for the band structure but also for the DOS which represents a finer probe of the band shapes (being the inverse of the derivatives of the energy bands with respect to k).

Table III collects the VEH absolute band positions at $k=0$ and $k=\pi/a$ along with the STO-3G (minimal basis set, 4th neighbor interaction) and 8s/4p (double zeta basis set, 2nd neighbor interaction) values from KP.²⁴ When comparing these values, some caution is needed, since the KP 8s/4p calculations contain only 2nd neighbor interactions. KP have observed that, in this non-polar system, the effect of including more neighbors is essentially to induce a rigid upward shift of the absolute positions of the bands. At the STO-3G level, going from 2nd to 4th neighbor interaction, they found this shift to be of the order of 0.02 a.u.²⁴ A similar shift can be expected for the double zeta basis set. It should also be noted that the KP 8s/4p basis set is slightly different from the double zeta basis set we used to parametrize the atomic potentials.

Taking this into account, we can make the following observations from Table III: (i) as could be expected from the trends observed on the model molecules,

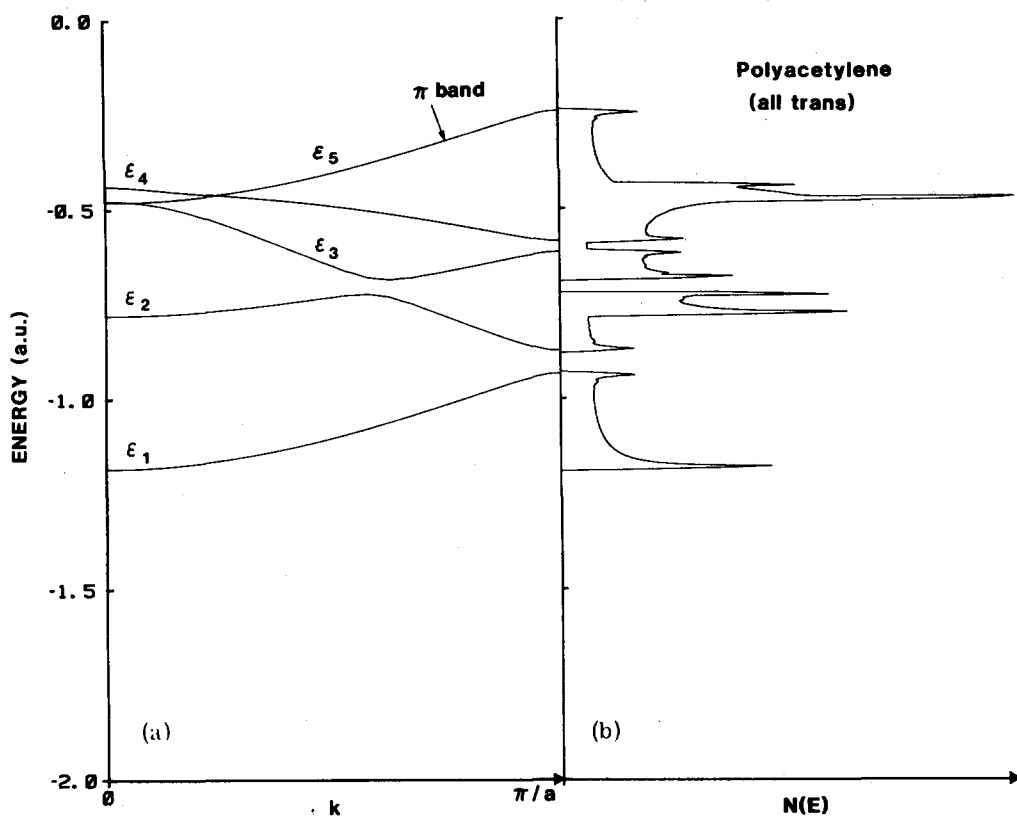


FIG. 3. All-*trans*-polyacetylene: (a) band structure; (b) density of states.

the position of the top of the effective Hamiltonian valence band is in excellent agreement with the SCF double zeta value [-0.243 a. u. with respect to $-0.262 + (\sim 0.02)$ a. u.] while the bottom of the band is too low in energy; (ii) for the inner bands, the agreement in widths is generally better with the SCF STO-3G than the $8s/4p$ values, probably as a consequence of the use of an STO-3G basis set in the VEH calculations; and (iii) the overall agreement is very satisfactory.

The XPS theoretical spectrum of all-*trans*-polyacetylene is displayed in Fig. 4 along with the experimental spectrum.³³ The theoretical spectrum is computed from the DOS following the method due to Delhalle.³⁴ In this method, the DOS curves are corrected for the photoionization cross-section factors according to

Gelius' model,³⁵ and convoluted by a Gaussian function whose half-width is chosen in order to take into account the resolution of the spectrometer. For solid state spectra, the half-width is usually taken as 0.7 eV. This method has given excellent results in previous instances³⁶⁻³⁸ and provides an elegant way of interpreting the experimental XPS data. Agreement of the theoretical spectrum with the rather poorly resolved experimental data³³ is quite good (Fig. 4). (It should be pointed out that a XPS spectrum has already been published on all-*trans*-polyacetylene,³⁹ but is considerably less well resolved than that displayed in Fig. 4.) Experimental peak relative positions and intensities are well reproduced in the theoretical spectrum. The only exception comes from the position of the peak corresponding to the bottom of the valence band. As

TABLE III. Comparison of the absolute band positions at $k=0$ and $k=\pi/a$ for all-*trans*-polyacetylene for calculations based on (a) VEH technique; (b) SCF STO-3G, fourth neighbor interaction²⁴; (c) SCF double zeta $8s/4p$, second neighbor interaction.²⁴ All values in a. u.

Band	VEH			SCF STO-3G			SCF $8s/4p$		
	$k=0$	$k=\pi/a$	Δ^a	$k=0$	$k=\pi/a$	Δ	$k=0$	$k=\pi/a$	Δ
ϵ_1	-1.186	-0.937	0.249	-1.102	-0.918	0.184	-1.194	-1.010	0.184
ϵ_2	-0.781	-0.876	0.095	-0.759	-0.863	0.104	-0.836	-0.962	0.126
ϵ_3	-0.479	-0.616	0.137	-0.497	-0.587	0.090	-0.592	-0.664	0.072
ϵ_4	-0.441	-0.588	0.147	-0.450	-0.577	0.127	-0.542	-0.658	0.116
ϵ_5 (π band)	-0.482	-0.243	0.239	-0.480	-0.195	0.285	-0.554	-0.262	0.292

^a $\Delta = |E_{k=0} - E_{k=\pi/a}|$ does not necessarily correspond to the bandwidth.

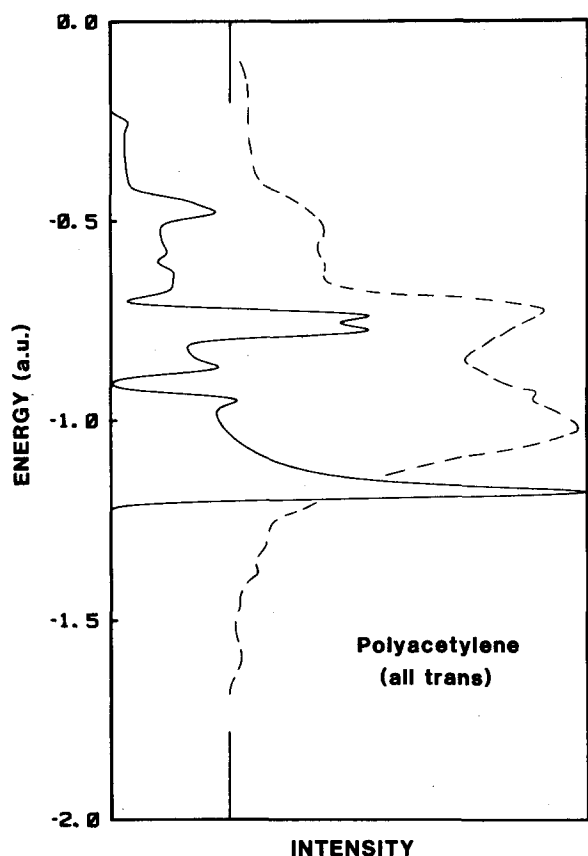


FIG. 4. All-*trans*-polyacetylene: XPS theoretical spectrum (solid line) and XPS experimental data (dashed line).³³ The origins of both spectra have been made coincident and the experimental peak positions have been rescaled (multiplied by a factor of 1.3) in order to obtain a better fit between theory and experiment.

already mentioned, the latter is usually located at too low an energy in an effective Hamiltonian calculation. The experimental peak positions presented in Fig. 4 have been rescaled (multiplied by a factor of 1.3) in order to obtain a better fit between theory and experiment on the energy scale. Note that the cross section of a carbon $2p$ electron is ~ 13 times smaller than for a carbon $2s$ electron.³⁵ As a result, the bottom of the valence band is enhanced and the π bands are almost completely smeared out in the XPS spectrum.

2. *Cis*-polyacetylene

To our knowledge, no *ab initio* quality band structures have yet been published on *cis*-polyacetylene. Our calculations on the *cis*-transoid and *trans*-cisoid backbones have been performed with the same bond lengths used for the all-*trans* conformation. The C-C-C angle has however been chosen 2° larger, in order to be consistent with the *cis*-polyacetylene crystal packing calculations due to Baughman *et al.*⁴⁰ The slight opening of the C-C-C angle is due to steric interactions between neighboring hydrogen atoms. It has been shown^{27, 40} that despite these steric interactions, the backbone of *cis*-polyacetylene remains essentially planar due to the electronic stabilization of the planar conjugated structure.

The band structures and XPS theoretical spectra of *cis*-transoid and *trans*-cisoid polyacetylene are displayed in Figs. 5 and 6. It should be pointed out that a screw axis runs along both *cis* backbones (Fig. 1). This symmetry results in the degeneracy of the bands two by two at the end of the Brillouin zone. Unfolding

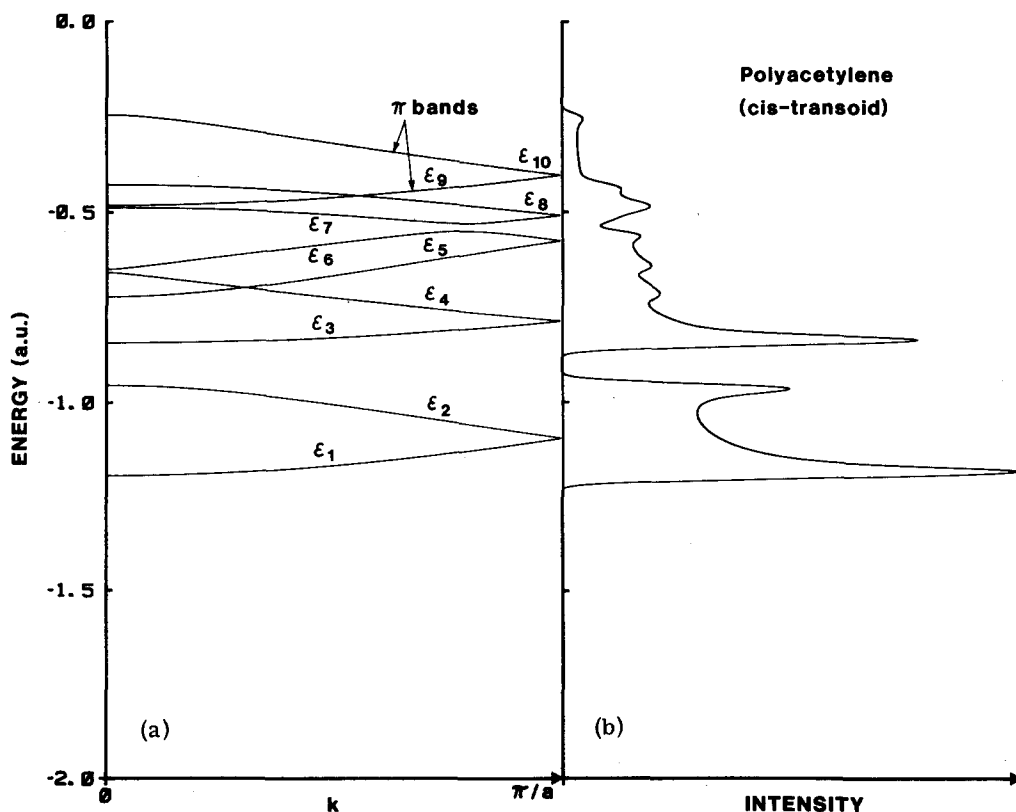


FIG. 5. *Cis*-transoid polyacetylene: (a) band structure; (b) XPS theoretical spectrum.

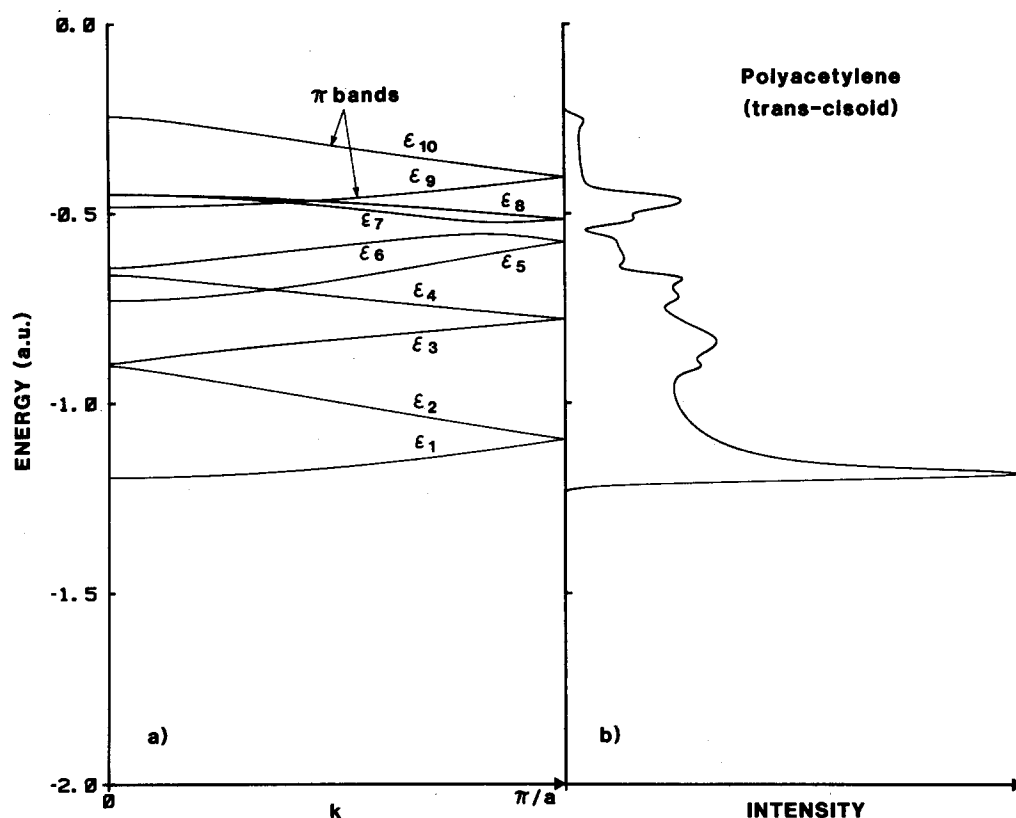


FIG. 6. *Trans*-cisoid polyacetylene: (a) band structure; (b) XPS theoretical spectrum.

these bands leads to a band structure directly comparable with the all-*trans* band structure.

Two major differences are observed between the *cis*-transoid and *trans*-cisoid band structures: (i) the gap, at $k=0$, between bands 2 and 3 is much smaller in *trans*-cisoid (0.006 a.u. vs. 0.108 a.u. in *cis*-transoid); (ii) the separation between bands 7 and 8 is larger in *cis*-transoid, for instance, at $k=0$, 0.061 a.u. vs. 0.001 a.u. Both trends can also be found in the CNDO/2 calculations by Yamabe *et al.*⁴¹ (Note however the incorrect avoided crossing found by these authors between bands 4 and 5 in both structures; this crossing is actually allowed by symmetry.) These two major band structure differences show up markedly in the theoretical XPS spectra and should be experimentally observable. No XPS experimental data have been reported so far for *cis*-polyacetylene.

When comparing all three polyacetylene band structures (Figs. 3, 5, and 6), we are led to a striking observation: in all three structures, the π bands have almost identical shapes, widths and absolute positions, as shown in Table IV. Thus, the conformation appears to have major effects only for the σ electrons. As a result, the ionization potential is about the same for all three conformations. Applying Koopmans' theorem, it amounts to 6.61 eV, 6.69 eV, and 6.58 eV for respectively all-*trans*-, *cis*-transoid, and *trans*-cisoid polyacetylene. This corresponds for all-*trans*-polyacetylene to a value ~ 1.9 eV higher than the experimental value of 4.7 eV as determined by XPS experiments.³⁹ This 1.9 eV difference can be accounted for, at least partly, by relaxation effects but numerous other effects can play a role in addition to the inherent limita-

tion of our theoretical model. It is our experience however that, in other VEH calculations, the subtraction of ~ 1.9 eV to the Koopmans ionization potential value provides good agreement with experimental data. This topic will be covered in a forthcoming publication.⁴²

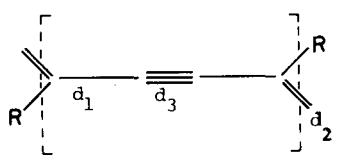
B. Polydiacetylene

The backbones of polydiacetylene chains are generally divided into two groups: acetyleniclike and butatrieniclike (Fig. 2). The actual compounds possess bond lengths intermediate between ideal acetylenic and butatrienic structures.⁴³ A majority of the polydiacetylenes are more acetyleniclike, such as PTS with substituent group $R = \text{CH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3$; a few are butatrieniclike, such as TCDU with $R = (\text{CH}_2)_4\text{OCONHC}_6\text{H}_5$. The bond lengths of PTS and TCDU, two of the most studied diacetylene compounds, are collected in Table V along with the bond lengths recently optimized by Karpfen²⁵ at the SCF *ab initio* double zeta level for pure acetylenic

TABLE IV. π band characteristics in all-*trans*-, *cis*-transoid, and *trans*-cisoid polyacetylene, from effective Hamiltonian calculations. Unit cell is C_2H_2 (for the *cis* conformations, this means unfolding of the two π bands is applied). All values are in a.u.

	Absolute band positions			Bandwidth
	$k=0$	$k=\pi/2a$	$k=\pi/a$	
All- <i>trans</i>	-0.482	-0.405	-0.243	0.239
<i>Cis</i> -transoid	-0.482	-0.404	-0.246	0.236
<i>Trans</i> -cisoid	-0.482	-0.404	-0.242	0.240

TABLE V. Bond lengths, in Å, in some polydiacetylene compounds.



	d_3	d_1	d_2
PDA ^a	1.194	1.425	1.321
PTS ^b	1.21	1.43	1.36
TCDU ^c	1.24	1.38	1.42
PBT ^a	1.248	1.319	1.444

^aResults of a geometry optimization by Karpfen with an SCF *ab initio* 7s/3p method.²⁵

^bX-ray structure from D. Kobelt and E. F. Paulis, *Acta Crystallogr. B*30, 232 (1973).

^cX-ray structure from V. Enkleman and J. B. Lando, *Acta Crystallogr. B*34, 2352 (1978).

(PDA) and butatrienic (PBT) backbones. Karpfen finds the PDA structure more stable than the PBT one by some 12 kcal/mol per C_4H_2 unit. Karpfen's calculations, as well as most other computations on polydiacetylene systems, consider only the case $R=H$. The solid-state synthesis procedure used to prepare single crystal polydiacetylenes has thus far restricted available compounds to those having rather bulky substituent groups, such as PTS and TCDU.

We have performed VEH calculations on all four backbone structures presented in Table V, using the universal atomic potentials for carbon and hydrogen. We will restrict considerations to the $R=H$ case. The larger R groups should provide only a minor perturbation of the results, since they are usually linked to the backbone by saturated groups.

1. PDA and PBT backbones

We first consider the optimized structures from Karpfen so that a direct comparison to his results can be made. The VEH band structures, DOS and XPS theoretical spectra of PDA and PBT are displayed in Figs. 7 and 8. The band structures and DOS are directly comparable with the SCF *ab initio* double zeta (7s/3p basis set) results (Figs. 3 and 4 from Ref. 25). The agreement is as good as in all-*trans*-polyacetylene case. In particular, the two major differences between PDA and PBT according to the 7s/3p band structures are: (i) a larger gap between bands 2 and 3 at $k=0$ in PDA; (ii) a lowering of band 6 with respect to the lower π band when going from PDA to PBT. Both differences are correctly reproduced in the VEH calculations and translated in the DOS and XPS theoretical spectra.

The VEH, SCF *ab initio* STO-3G (3rd neighbor interactions)²⁵ and 7s/3p (1st neighbor interactions)²⁵ absolute band positions are presented in Tables VI and VII respectively for PDA and PBT. Extrapolating to an infinite number of neighbors, Karpfen estimates that the upward shift on the 7s/3p values is of the order of 0.06 a.u. for PDA and 0.03 a.u. for PBT. From the tables we observe: (i) the agreement of the VEH inner

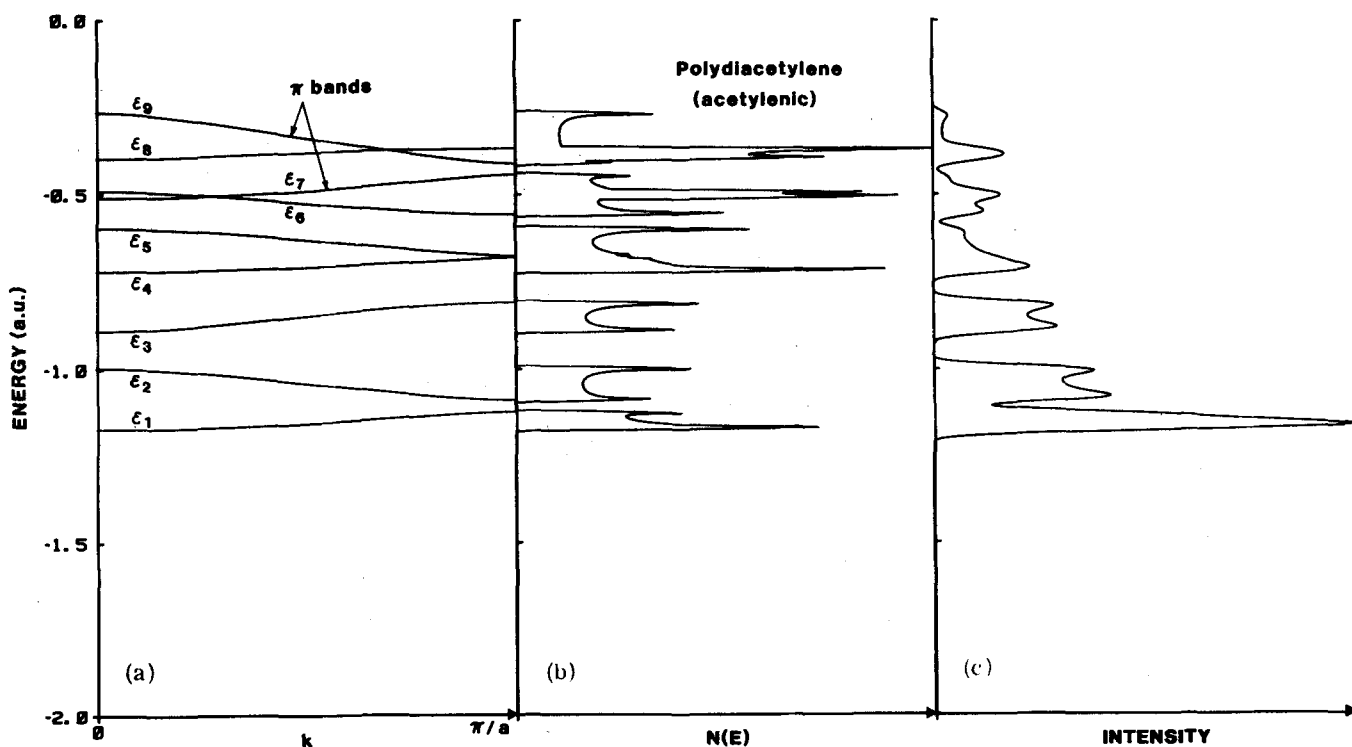


FIG. 7. Polydiacetylene, acetylenic backbone: (a) band structure; (b) density of states; (c) XPS theoretical spectrum.

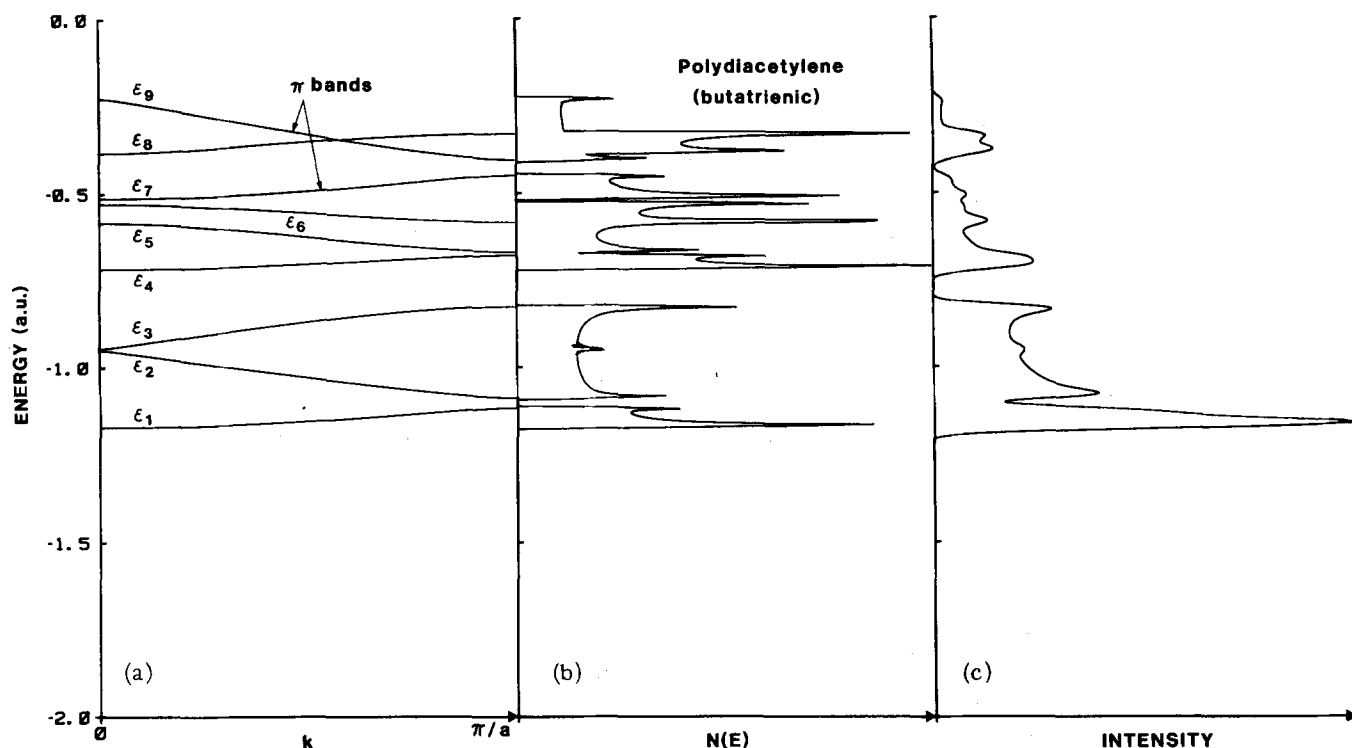


FIG. 8. Polydiacetylene, butatrienic backbone: (a) band structure; (b) density of states; (c) XPS theoretical spectrum.

band positions with the SCF ones is very satisfactory, generally better with the SCF STO-3G positions; (ii) the bottoms of the VEH Hamiltonian valence bands are significantly lower than the STO-3G values but match the $7s/3p$ values when the shift is taken into account; (iii) the top of the VEH valence band is in excellent agreement with the $7s/3p$ value in PBT (-0.227 a.u. vs $-0.260 + \sim 0.03$ a.u.); this is not the case in PDA (-0.266 a.u. vs $-0.358 + \sim 0.06$ a.u.). However, the difference in ionization potentials between PDA and PBT is predicted by the $7s/3p$ calculations to be of the order of 1.9 eV. The VEH calculations predict a difference of 1.05 eV. The latter value seems more

reasonable, for instance when we consider that 1.9 eV represents the difference in ionization potentials between a conjugated system like polyacetylene (4.7 eV)³⁹ and polybenzyl ($C_6H_4-CH_2$)_x (6.6 eV),⁴⁴ a compound where consecutive phenyl groups are perpendicular to each other and separated by a saturated methylene unit.

Application of Koopmans' theorem leads to an ionization potential ~ 0.4 eV lower for PBT and ~ 0.6 eV larger for PDA compared to all-*trans*-polyacetylene. Assuming that a similar reduction of ~ 1.9 eV from the Koopman's theorem values takes place as in polyacetylene, we predict ionization potentials of the order

TABLE VI. VEH, SCF *ab initio* STO-3G (third neighbor interactions)²⁵ and $7s/3p$ (first neighbor interactions)²⁵ band absolute positions for PDA. All values in a. u.

	VEH			STO-3G			$7s/3p$		
	$k=0$	$k=\pi/a$	Bandwidth	$k=0$	$k=\pi/a$	Bandwidth	$k=0$	$k=\pi/a$	Bandwidth
ϵ_1	-1.171	-1.123	0.048	-1.099	-1.071	0.027	-1.245	-1.217	0.027
ϵ_2	-0.997	-1.090	0.093	-0.945	-1.023	0.077	-1.088	-1.165	0.077
ϵ_3	-0.891	-0.810	0.081	-0.864	-0.788	0.076	-1.005	-0.923	0.082
ϵ_4	-0.721	-0.680	0.041	-0.700	-0.657	0.043	-0.819	-0.797	0.022
ϵ_5	-0.597	-0.677	0.080	-0.606	-0.657	0.050	-0.746	-0.789	0.043
ϵ_6	-0.491	-0.558	0.067	-0.519	-0.558	0.038	-0.633	-0.661	0.028
ϵ_7 (π)	-0.510	-0.444	0.066	-0.502	-0.421	0.081	-0.616	-0.549	0.067
ϵ_8	-0.398	-0.369	0.029	-0.382	-0.364	0.018	-0.491	-0.481	0.010
ϵ_9 (π)	-0.266	-0.412	0.146	-0.250	-0.418	0.169	-0.358	-0.532	0.174

TABLE VII. VEH, SCF *ab initio* STO-3G (third neighbor interactions)²⁵ and $7s/3p$ (first neighbor interactions)²⁵ absolute band positions for PBT. All values in a. u.

	VEH			STO-3G			$7s/3p$		
	$k=0$	$k=\pi/a$	Bandwidth	$k=0$	$k=\pi/a$	Bandwidth	$k=0$	$k=\pi/a$	Bandwidth
ϵ_1	-1.172	-1.118	0.054	-1.091	-1.048	0.043	-1.204	-1.163	0.041
ϵ_2	-0.951	-1.089	0.138	-0.914	-1.034	0.120	-1.023	-1.143	0.120
ϵ_3	-0.946	-0.827	0.119	-0.900	-0.793	0.107	-1.015	-0.903	0.112
ϵ_4	-0.717	-0.679	0.038	-0.686	-0.649	0.037	-0.775	-0.759	0.016
ϵ_5	-0.585	-0.670	0.085	-0.585	-0.648	0.063	-0.705	-0.748	0.043
ϵ_6	-0.530	-0.585	0.055	-0.536	-0.567	0.031	-0.617	-0.643	0.027
$\epsilon_7(\pi)$	-0.514	-0.449	0.065	-0.501	-0.425	0.076	-0.584	-0.506	0.078
ϵ_8	-0.383	-0.328	0.055	-0.370	-0.322	0.048	-0.452	-0.417	0.035
$\epsilon_9(\pi)$	-0.227	-0.404	0.177	-0.167	-0.393	0.226	-0.260	-0.490	0.230

of ~ 4.3 eV for PBT and ~ 5.3 eV for PDA.

Following Boudreaux and Chance,⁴⁵ Karpfen has observed that the highest occupied and lowest unoccupied π bands change symmetry when going from PDA to PBT. At $k=0$, the symmetry is Au in PDA and Bg in PBT for the highest occupied π band and *vice versa* for the lowest unoccupied one (see Fig. 5 from Ref. 25). The VEH calculations reproduce exactly the same symmetry inversion.

2. PTS and TCDU backbones

The VEH band structures and theoretical XPS spectra corresponding to the backbones of PTS and TCDU

are displayed in Figs. 9 and 10. Some characteristics pertaining to the highest occupied π band are presented in Table VIII. The values of ionization potentials and π bandwidths make PTS acetyleniclike and TCDU butatrieniclike, in agreement with the respective bond lengths of these compounds. However, the symmetry of TCDU highest occupied π band is the same as PTS and PDA. This suggests that all three systems belong to the same electronic potential curve and that no electronic phase transition has to take place when going from a PTS backbone to a TCDU backbone, in agreement with the predictions of the molecular model calculations due to Boudreaux and Chance.⁴⁵ From an electronic structure point of view, the TCDU backbone can rather

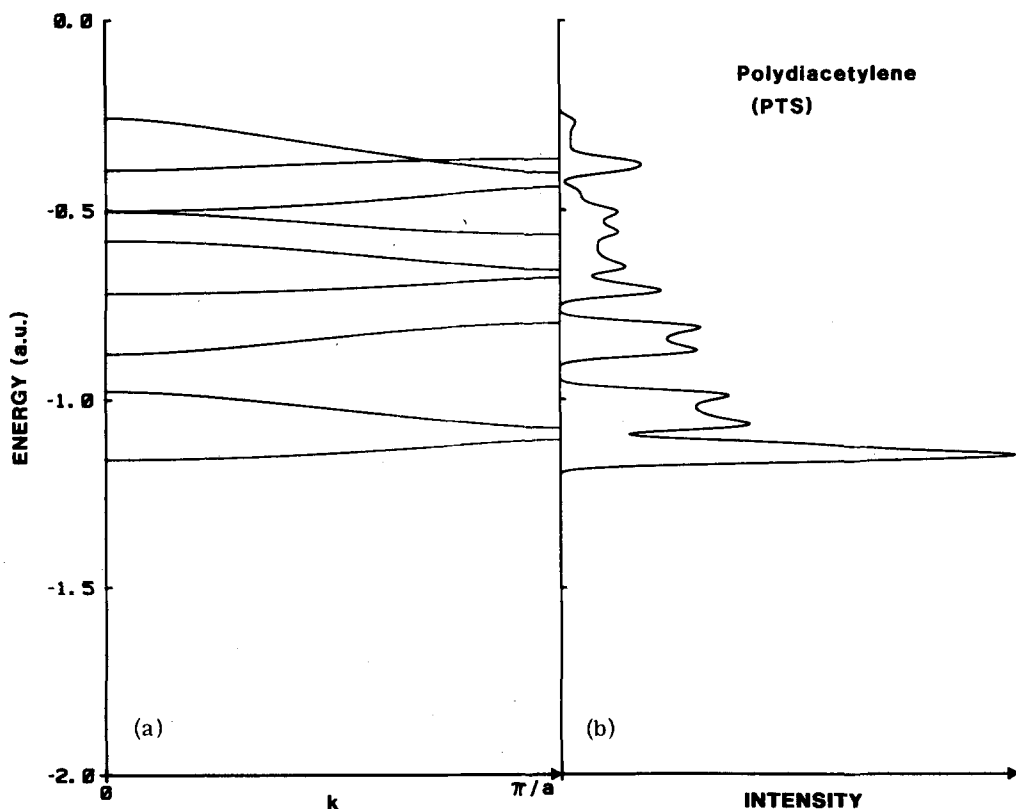


FIG. 9. Polydiacetylene, PTS: (a) band structure; (b) XPS theoretical spectrum.

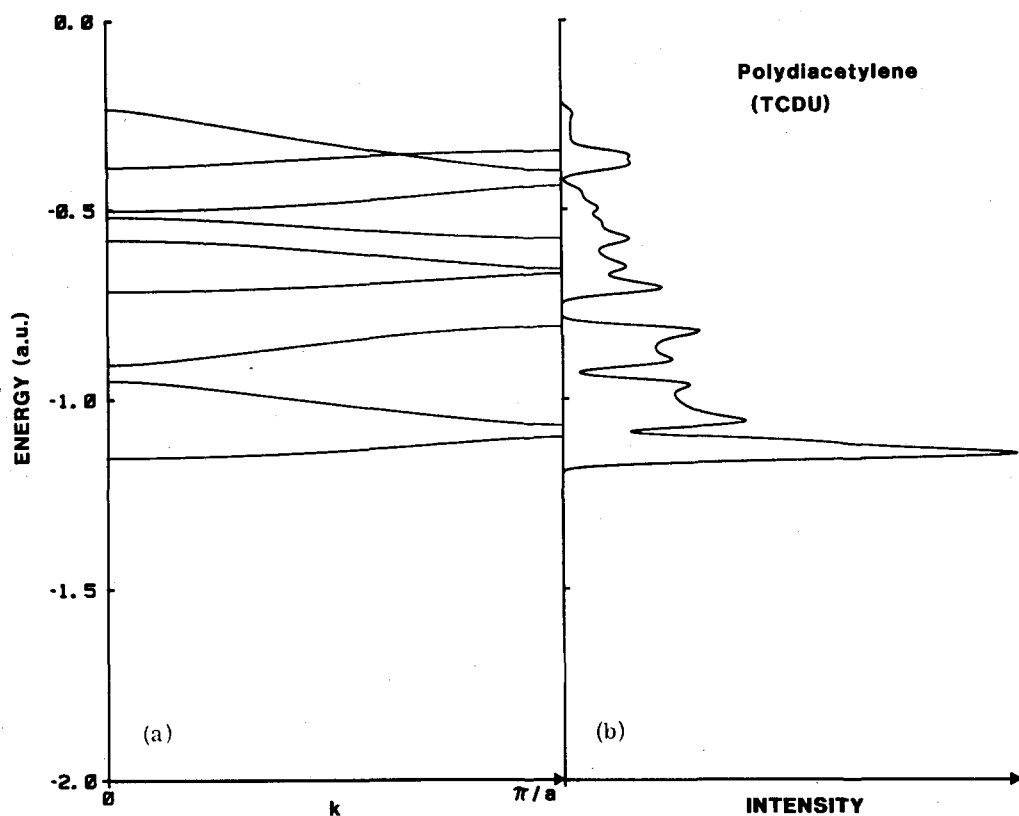


FIG. 10. Polydiacetylene, TCDU: (a) band structure; (b) XPS theoretical spectrum.

be viewed as a strained acetyleniclike backbone, as has been suggested by recent experiments.⁴⁶

XPS spectra of some polydiacetylene compounds have been published.⁴⁷ Unfortunately, no direct comparison with the theoretical spectra is possible because the experimental data are dominated by contributions coming from the bulky side-groups and are not very well resolved.

Applying Koopmans' theorem and again assuming a reduction of ~ 1.9 eV, we predict ionization potentials of 5.1 eV for PTS and 4.4 eV for TCDU. The carrier injection experiments of Spanring⁴⁸ yield 5.4 ± 0.5 eV for PTS while preliminary photoionization experiments on PTS from Arnold⁴⁹ yield ~ 5.2 eV, in excellent agreement with our theoretical results. No measurements for TCDU have been reported.

Thus our theoretical results and available experi-

mental results suggest that polydiacetylenes have ionization potentials which are quite similar to polyacetylene. Therefore, similar behavior with acceptor doping would be expected for the two polymers. This is not the case, however, since no polydiacetylene has, as yet, formed a conducting complex with $\sigma > 10^{-5}$ ohm $^{-1}$ cm $^{-1}$, though numerous materials and a variety of dopants have been tried (including strong electron acceptors).⁵⁰ We suggest that the electronic properties of the backbone cannot be the limiting factor and that the reason for the contrasting results for polyacetylene and polydiacetylene must involve structural and/or chemical interference from the substituent groups.

V. CONCLUSIONS

Valence effective Hamiltonian calculations with universal atomic potentials for carbon and hydrogen have

TABLE VIII. Highest occupied π band characteristics in PDA, PTS, TCDU, and PBT. Values in a. u.

	Absolute band positions		Ionization potential	Bandwidth	Symmetry at $k=0$
	$k=0$	$k=\pi/a$			
PDA	-0.266	-0.412	0.266	0.146	A_u
PTS	-0.258	-0.403	0.258	0.145	A_u
TCDU	-0.233	-0.399	0.233	0.166	A_u
PBT	-0.227	-0.404	0.227	0.177	B_g

been performed on all-*trans*-, *cis*-*transoid*, and *trans*-*cisoid* polyacetylene and various polydiacetylene backbones. The agreement with SCF *ab initio* double zeta quality calculations is excellent. Thus the VEH method offers a simple way to obtain double zeta quality band structures and related ground state properties at very low cost. Typical CPU times on the VAX 11/780 mini-computer are: ~1 min for all-*trans*-polyacetylene and ~4.5 min for polydiacetylene.

The parameterization can easily be extended to other atoms, including heavier elements. The range of applicability of the method will then be much broadened and this will allow quite inexpensive double zeta quality calculations on polymers containing for instance nitrogen, oxygen or sulfur atoms. Furthermore, the method yields a good description of the top of the valence band, and thus provides reliable estimates of relative ionization potentials in a series of similar polymers.

ACKNOWLEDGMENTS

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