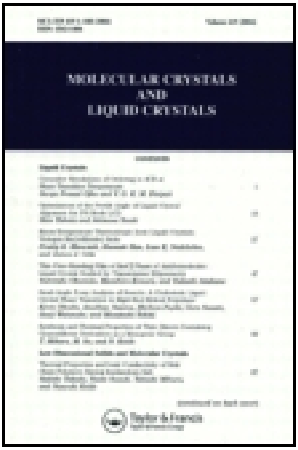

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# Electronic structure of highly conducting polymers

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# ELECTRONIC STRUCTURE OF HIGHLY CONDUCTING POLYMERS

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Results of ab initio SCF LCAO crystal orbital calculations are presented for pure and doped polyacetylenes, polydiacetylene backbones, stacked TCNQ and TTF columns and for linear chains of $(SN)_x$. The structural parameters of five different polyacetylene chains were fully optimized at the Hartree-Fock level and the cis-trans isomerisation energy was calculated by taking into account interchain interactions in the 3D crystal including dispersion. Several one-particle properties are discussed both for symmetry adapted and symmetry breaking solutions (bond- and spin density waves, Peierls distortion) and the effect of electronic correlation on those quantities is demonstrated. The effect of n-type doping with Li and Na was investigated in both cis- and trans polymers. Besides charge transfer the impurity atoms fundamentally change the geometrical structure (transforming the Peierls distorted chains to equidistant ones) and substantially reduce the fundamental gap. Four different polydiacetylene backbones are also compared from the point of view of stability and their one-electron properties are discussed. Finally, the effect of randomly distributed hydrogen impurity in $(SN)_x$ on the electronic structure is investigated with the help of the CPA method.

## INTRODUCTION

We give in this paper a short review of the results of crystal orbital calculations performed recently in our Laboratory for four different classes of polymeric substances: polyacetylenes, polydiacetylenes, stacked infinite columns of TCNQ and TTF, and single chains of $(SN)_x$. Emphasis will be laid on the ab initio nature of the computational schemes applied in these calculations. The starting point in these studies is the computation of reliable wavefunctions within the framework of the one-electron approximation (various Hartree-Fock schemes[1]) from first principles i.e. without introducing any empirical information besides structural data. This fact allows, on the one hand, also the study of chemically unusual situations (like the interaction of impurities with the polymer chains) and provides a reasonable basis to investigate conformational properties, electronic charge distribution, etc. On the other hand, it makes possible a systematic treatment of the electronic correlation effects which have to be taken into account in the calculations of more accurate single particle gaps, optical properties, etc.

## POLYACETYLENES

### Single Chain Structure Optimization

A recent preliminary study of the electronic structure of different polyacetylene (PA) models[2] has shown that several conformers of the cis- and trans modification of this polymer differ from each other only on the milihartree (or kcal/mol) scale. Detailed structural data are not available even for pure (undoped) PA's. Since, on the other hand, the calculated values of nearly all physical properties depend very sensitively on them, it is inevitable to perform as first step a structure optimization within the framework of the given computational scheme. For this prupose we used a minimal (STO-3G) atomic basis set and the restricted Hartree-Fock (HF) method with proper truncation of the infinite lattice sums[2]. Both for the trans- and cis isomers a four-dimensional energy hypersurface has been investigated using as variables the C-C distances $R_1$ and $R_2$, respectively (see Figure 1), the C-C-C angle and the C-H distance[3].

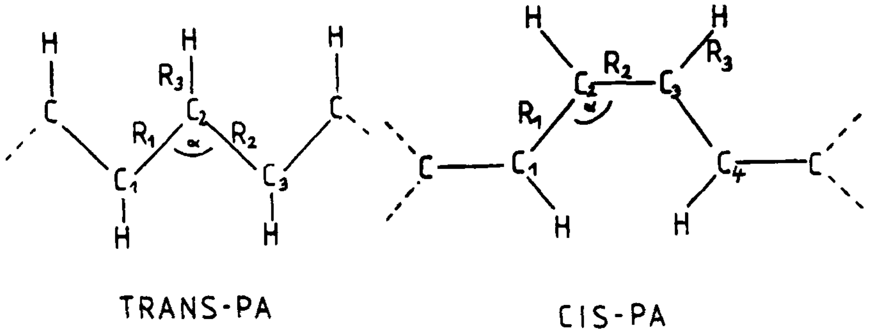

Figure 1: Trans- and cis-polyacetylene single chains showing the structural parameters which have been optimized. The unit cell consists of a $C_2H_2$ group for the trans-chains and of a $C_4H_4$ group for the cis-chains, respectively.

The most important parameters characterizing the five physically interesting local minima are shown in Table 1. Two of them belong to trans-PA, the other three to cis-PA. We found also for these optimized parameters (as in Ref. 2) that the bond alternating structures are energetically more stable for both isomers (the cis-transoid being the stable cis modification). It is interesting, however, that among these five structures the most stable is the trans-alternating one. On the other hand,in our previous study[2] in

Table 1 Optimized Single-Chain Structural Parameters and The Corresponding Total Energy Values Per $C_2H_2$ Units For Five Different Polyacetylene Models[a]

| Polyacetylene chain | $R_1^{opt.}$(Å) | $R_2^{opt.}$(Å) | $\alpha^{opt.}$(degree) | Energy/$C_2H_2$ unit(hartree) |
|---|---|---|---|---|
| equidistant-trans | 1.390 | 1.390 | 125.12 | -75.935765 |
| alternating-trans | 1.325 | 1.481 | 124.10 | -75.947121 |
| equidistant-cis | 1.395 | 1.395 | 126.75 | -75.933784 |
| cis-transoid | 1.479 | 1.333 | 126.31 | -75.944058 |
| trans-cisoid | 1.327 | 1.484 | 124.16 | -75.942055 |

[a] For the meaning of the variables $R_1$, $R_2$ and see Fig. 1.

which 'standard' values for the bond lengths and bond angles were applied, we have found the cis-transoid structure as the most stable one. This experience shows that for accurate conformational predictions careful structure optimization is needed in these systems.

## One-Electron Properties And the Effect of Symmetry Breaking

From the point of view of transport calculations in these polymers the most important electronic indices are the one-particle energies summarized in Table 2. It can be seen that the pure cis- and trans isomers are quite similar in this respect both having broad valence bands of ~7 eV and conduction bands of ~9-10 eV, separated by a too large gap of ~9 eV.

Table 2 Some One-Electron Properties Of Polyacetylene Chains: Ionization Potentials (IP), Electron Affinities (EA) Valence Band Width ($\delta E_V$), Conduction Band Width ($\delta E_C$) And Single-Particle Gap ($\Delta E_{gap}$). All Energy Values Are Given In eV.

| Polyacetylene chain | IP | EA | $\delta E_V$ | $\delta E_C$ | $\Delta E_{gap}$ |
|---|---|---|---|---|---|
| equidistant-trans | 0.399 | -0.399[a] | 25.202[b] | - | 0. |
| alternating-trans | 4.828 | 4.068 | 7.221 | 9.025 | 8.896 |
| equidistant-cis | 2.877 | 1.918 | 8.115 | 11.606 | 4.795 |
| cis-transoid | 4.928 | 3.964 | 7.099 | 9.478 | 8.892 |
| trans-cisoid | 4.923 | 4.056 | 6.616 | 9.385 | 8.979 |

[a] Position of the Fermi level.

[b] Half-filled band.

The use of more extended atomic basis sets reduces its value only by ~1 eV[4]. There are no reliable experimental values for this very important quantity in pure PA, but from the position of the first singlet exciton state in long polyenes (~2.2 eV) we can estimate its value to lie around 3 eV i.e. the remaining error of ~5 eV has to be assigned to the error introduced by a restricted (closed shell) HF calculation in the position of the virtual levels and to correlation effects.

To understand the driving forces of Peierls-type metal-insulator transitions in polymers it is very instructive to study space-symmetry breaking HF solutions. As an example we show in Table 3 the total energies per cell, the single particle gap and the bond orders connecting two neighboring $\pi$-orbitals in trans-PA. In the first two cases the carbon-carbon bond lengths are equal through the whole polymer, while the wave function of the first solution is rigorously symmetry adopted ($P^o_{\pi,\pi} = P^+_{\pi,\pi}$), this requirement is not fulfilled by the second one. The relaxation of the spatial symmetry of the wave function (using still doubly occupied Bloch orbitals) lowers the energy and introduces a gap of ~4.4 eV as compared with the first metallic solution (no gap). The existence of such bond density wave (BDW)-type instabilities[5] seems to be a precursor of the Peierls transition also in other polymers. In fact, we can see from the third line of Table 3 that the reduction of the symmetry in the nuclear framework (bond alternation) further decreases the energy and increases the gap to ~8.9 eV. The symmetry of the wave functions can be reduced also by putting electrons with different spins for different spatial Bloch orbitals (unrestriced-HF scheme[6]). This leads to a spin density wave (SDW)-type solution whose energy lies substantially deeper since this state accounts for a certain

Table 3 Some properties of Symmetry Adapted And Symmetry Breaking HF Solutions In Trans-Polyacetylene: Total Energy Per $C_2H_2$ Units ($E_{tot.}$), Single Particle Gap ($\Delta E_{gap}$), Density Matrix Elements (Bond-Orders) For Two Neighboring $\pi$-Electron Bonds ($P^o_{\pi,\pi}$, $P^+_{\pi,\pi}$).

| symmetry | | | | | |
|---|---|---|---|---|---|
| nuclei | wave function | $E_{tot.}$(hartree) | $\Delta E_{gap}$(eV) | $P^o_{\pi,\pi}$ | $P^+_{\pi,\pi}$ |
| equidistant | symm.adapted | -75.935765 | 0. | 0.474 | 0.474 |
| equidistant | BDW[a] | -75.939089 | 4.444 | 0.644 | 0.290 |
| alternating | symm.adapted | -75.947121 | 8.894 | 0.735 | 0.153 |
| equidistant | SDW[b] | -75.965899 | 13.442 | 0.364[c] | 0.364[c] |

[a] Bond density wave solution calculated with the spin-restricted HF method.

[b] Spin density wave solution calculated with the spin-unrestricted HF method.

[c] Sum of electrons with spin $\alpha$ and $\beta$ contributions. The total ($\alpha+\beta$) spin density on the carbon atoms is 0.886.

part of the correlation energy. These symmetry breaking one-particle wave functions proved to be very important also as different zeroth-order reference functions in investigating the correlation effects in polymers by perturbation theoretical methods[4].

## Lattice Energy of 3D Polyacetylene Crystals

The polymer chains in polyacetylene crystals are closely enough packed that interchain interactions can substantially modify the conformational properties. The interaction energy of polymers in the 3D structure depends very sensitively on the setting angle ∅ which the plane of the polymer backbone makes with the (001) plane. The uncertainty of this important variable is 8-10° in experimental studies[7] which makes a more accurate calculation of the interaction energy impossible. Therefore, we optimized ∅ by summing up pairwise the interchain interaction energies and using the orthorhombic structure with experimental values for the lattice constants A and C. For the periodicity along the chain-axis B we used the theoretically obtained single-chain results which are in very good agreement with the corresponding experimental values[7]. To obtain the HF part of the interaction energy we calculated the total energies for all inequivalent chain-pairs (using a double-cell as translational unit). For the calculation of the dispersion part we used ab initio atom-atom dispersion potentials[8]. It is interesting to note that the HF contribution led in all cases to an effective

Table 4 Crystal Structure Parameters And Lattice Energy Per $C_8H_8$ Unit In Three Different Polyacetylene Crystals

| Polyacetylene crystal | A(Å)[a] | B(Å)[b] | C(Å)[a] | ∅ (degree)[b] | Energy / $C_8H_8$ Unit (hartree)[b,c] |
|---|---|---|---|---|---|
| alternating-trans | 7.410 | 2.466 | 4.08 | 46.7 | -303.853186 |
| cis-transoid | 7.610 | 4.435 | 4.39 | 45.3 | -303.838400 |
| trans-cisoid | 7.610 | 4.463 | 4.39 | 45.0 | -303.826101 |

[a] Experimental value taken from Ref. 7.

[b] Theoretical value calculated in Ref. 3.

[c] The unit cell of the trans modification contains four CH units, this energy value refers to a double cell.

repulsion which was, however, overcompensated by an attractive dispersion interaction. The binding in the polymer crystal is thus exclusively due to dispersion forces. In Table 4 we show besides the structural parameters the energy of a $C_8H_8$ unit in the three structures investigated. Comparing these values with the corresponding ones obtained for single chains we can see that the inter-polymer interaction further stabilizes the trans structure relative to the cis ones.

## Effect of Doping with Li and Na

To understand the mechanism and effect of doping in polyacetylenes we performed calculations for both cis- and trans single chains doping them by 25 per cent Li and Na atoms, respectively. In the case of the trans chains the calculations have been repeated with 33 per cent dopants. Two different types of impurity positions have been considered. In the case of position A the impurity atom lies equidistantly from atoms $C_1$, $C_2$ and $C_3$ for the trans chain and it has the same distance from atoms $C_1$, $C_2$, $C_3$ and $C_4$ in the cis chain, respectively (see Figure 1); in position B it lies above the $C_1$-$C_2$ bond in both systems.

The impurity-carbon distances as well as all intrachain carbon-carbon distances have been simultaneously optimized in all cases. Our results can be summarized as follows (for more details see Ref. 3):

i) In contrast to previous calculations performed with the FSGO method[9] the ab initio procedure yields always a definitive energy minimum with respect to the impurity-chain distance i.e. the Li and Na atoms really bind to polyacetylene. This fact insures a physically meaningful optimization of the new chain structures in the presence of the impurity atoms.

ii) The Peierls instability disappears in both cis- and trans-PA, i.e. the equidistant chains become more stable than the bond-alternating ones. Impurity position A is energetically more favourable in cis-PA while position B is preferred in trans-PA.

iii) The charge transfer from both Li and Na to the PA chains increases with decreasing bond alternation and reaches its maximum value for the equidistant structures (~0.15e for Li and ~0.7e for Na, respectively).

iv) Parallel with increasing charge transfer and decreasing bond alternation the single particle gap is diminishing and it is reduced to ~2.5eV (as compared with its value of ~9eV in the pure material).

## Calculation of Correlation Corrections by Perturbation Theory

We applied for this purpose the Møller-Plesset partitioning scheme and made use of the fact that in second order of perturbation theory the total correlation energy can be calculated as a sum of pair-correlation contributions. Obtaining in this way the correlated total energies of the N+1,N and N-1 particle systems one can calculate the positions of the new, correlation corrected conduction - and valence band states, respectively. We found[4] that the valence band is shifted upwards while the conduction band moves downwards due to the correlation correction. As a result, the new quasi-particle gap is substantially lower than the HF gap. In pure trans-PA the gap is reduced by ~50 per cent. We are repeating now this calculation also in the presence of impurities to see whether the combination of the two factors produces really a nearly zero gap in PA.

## POLYDIACETYLENES

Four typical backbones of polydiacetylene (PDA) chains have been also investigated substituting the side chains by hydrogen atoms.[10] Figure 2 shows the unit cell of these calculations. The different interatomic distances used are collected in Table 5. From the total energies per elementary

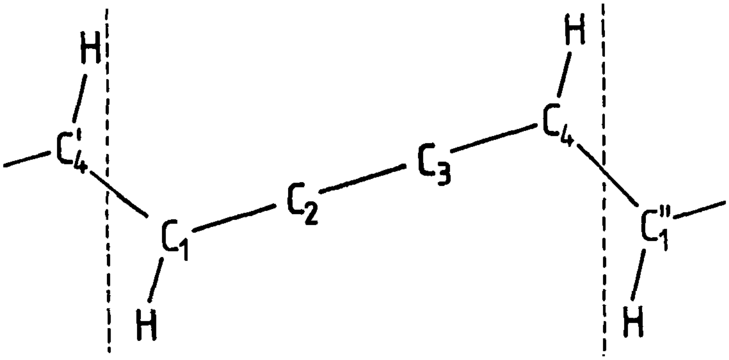

Figure 2: Segment of a typical polydiacetylene (PDA) backbone. The side chain groups are substituted by hydrogen atoms and the translationally invariant unit cell is surrounded by broken lines. The carbon-carbon bond distances are varying for different models as defined in Table 5.

Table 5 Atomic Distances (Å), Total Energies Per Diacetylene Unit (Hartree), Valence- And Conduction Band Widths ( $\delta E_V$ and $\delta E_C$, respectively, in eV). The Numbering Of The Atoms Is Defined In Figure 2.

| PDA model | $R_{1,2}$ | $R_{2,3}$ | $R_{4,1}$ | $E_{tot.}$ | $\delta E_v$ | $\delta E_c$ |
|---|---|---|---|---|---|---|
| Ideal acetylene | 1.45 | 1.20 | 1.34 | -150.5762 | 3.33 | 5.11 |
| PTS backbone | 1.43 | 1.21 | 1.36 | -150.5735 | 5.12 | 5.42 |
| TCDU backbone | 1.38 | 1.24 | 1.42 | -150.5553 | 6.18 | 6.56 |
| Ideal butatriene | 1.35 | 1.26 | 1.48 | -150.5434 | 6.20 | 6.68 |

cell we can see that the relative stability of the PDA backbone increases by ~20 kcal/mol per diacetylene unit as the bonding sequence goes over from the ideal butatriene structure to the acetylene one. The corresponding energy difference in the case of the TCDU to PTS transition is ~11 kcal/mol. Both the valence- and conduction band widths increase monotonically in going from the acetylene-like structure to the butatriene-like one. The explicite calculation of the effect of different side-chain groups on the electronic properties of these backbones is in progress.

## INFINITE STACKS OF TCNQ AND TTF MOLECULES

Ab initio HF CO calculations were performed also for stacked chains of TCNQ and TTF molecules using the geometry of the mixed crystal (3.18 Å interplain distance in TCNQ and 3.47 Å in the TTF stack, respectively. In Table 6 we show the positions and widths of the valence and conduction bands of poly(TCNQ) and poly(TTF). The most interesting result

Table 6 The Valence- and Conduction Bands of Poly(TCNQ) and Poly(TTF). For Comparison The Table Contains Also The Corresponding Single MO Levels (All Quantities in eV).

| | | $E_{MO}$ | $E_{min}^{CO}$ | $E_{max}^{CO}$ | $\delta E$ |
|---|---|---|---|---|---|
| poly(TCNQ) | Valence band | -6.838 | -7.252($\pi$)[a] | -7.157($0$) | 0.095 |
| | Conduction band | 0.438 | -0.487($0$) | 0.687($\pi$) | 1.174 |
| poly(TTF) | Valence band | -3.774 | -3.801($\pi$) | -3.498($0$) | 0.303 |
| | Conduction band | 8.466 | 8.511($\pi$) | 8.594($0$) | 0.083 |

[a] In parentheses the corresponding values of $\underline{k}\cdot\underline{a}$ are given.

obtained in this study[11] was that the valence band of poly (TTF) (from which the charge transfer [C.T.] occurs) is comparatively broad ( ~0.3 eV) and the conduction band of poly(TCNQ) (to which the charge is transferred) is broad (~1.2 eV), while both the valence band of poly(TCNQ) and the conduction band poly(TTF) (which do not take part in the CT process) have widths less than 0.1 eV. We found furthermore that the conduction and valence bands of both systsms are $\pi$-bands with opposite dispersions and the position of the conduction band in poly(TCNQ) and that of the valence band in poly(TTF) favours more CT than the corresponding single MO levels. The investigation of the CT process in the 3D crystal is in progress. These calculations will throw most probably also some light on the experimental finding that while in a mixed TCNQ-TTF aqueous solution there is no C.T. between the two components[12], in their molecular crystal there is a charge transfer of ~0.6 e per molecule pair. It is worthwhile to mention in this relation that periodic nucleotide base stacks have a geometrical structure which is very similar to the stacked columns of TCNQ with a stacking distance of 3.36 Å. As a consequence their band widths[13] are comparable to those of the TCNQ and TTF stacks and therefore one can expect that by doping them with appropriate donor or accpetor molecules highly conducting regions could be formed also in these nucleotide base stacks (which are experimentally available).

## ELECTRONIC STRUCTURE OF $(SN)_x$

In the case of metallic polymers the electronic properties are especially sensitive to the quality of the atomic basis set used in the calculations. Therefore, besides ab initio minimal basis set calculations[14] we studied single chains of $(SN)_x$ also at the double-$\zeta$ level[15]. For the width of the half-filled metallic band we obtained 4.12 eV ($E_{min.}$ = -9.854 eV, $E_{max.}$ = -5.734 eV) and the Fermi level lies at $E_F$ = -7.821 eV. The calculated effective electronic mass at $E_F$ (1.7 $m_c$), the corresponding density of states (0.14/ eV spin molecule ) and the charge transferred from the S atom to the N atom (0.4 e) are in reasonable agreement with experiment.

To understand the effect of various impurities on the transition temperature of the superconductive state in $(SN)_x$ we investigated the changes in the density of electronic states $\rho$ (E) of this polymer due to hydrogen impurities bound to the N atoms (at IBM San Jose 4-8 per mole cent hydrogen impurities were found in $(SN)_x$[16]. We applied for these calculations the coherent potential approximation

(CPA) using an energy and momentum dependent self-energy $\Sigma(E,k)^{17}$. The most interesting two conclusions of these investigations are the following:

i) The $\rho(E)$ curves of the doped system exhibit a complicated structure with spikes and dips which go to zero in many cases producing gaps in the mixed systems. Since there is no sign of such dips in the host system their occurence (already at 3 per cent impurity content) is a genuine effect of aperiodicity.

ii) The value of $\rho(E)$ at the Fermi level increases monotonously with the impurity content ( $\rho(E_F)$ = 0.10, 0.11, 0.13, 0.18 and 0.26 at 0, 3, 10, 30 and 50 per cent of H impurity, respectively). According to the BCS theory of superconductivity the critical temperature $T_c$ depends exponentially on this parameter ($T_c \sim \exp\{-1/\rho(E_F)\cdot V\}$, where V is an effective electron-electron interaction parameter). One would expect, therefore, that due to the increase of $\rho(E_F)$ with the concentration of hydrogen, the transition temperature would also increease at higher level of dopings.

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