A Comparison between Polyatecylene and Polycarbonitrile *

Michael Springborg
Fakultät für Chemie, Universität Konstanz, D-W-7750 Konstanz, Federal Republic of Germany

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Results of a theoretical, comparative study of the electronic properties of *trans*-polyacetylene and polycarbonitrile are reported. Polyacetylene consists of zigzag chains of CH units, whereas polycarbonitrile has every second CH unit replaced by an N atom. Ground-state properties (structure, electronic bonds and bands, densities of states, momentum distributions, and reciprocal form factors) of the periodic, infinite, isolated chains are studied by means of first-principles, density-functional calculations. It is demonstrated how the presence of the (nitrogen) heteroatoms in the backbone of polycarbonitrile leads to a partial localization of the electrons. In order to investigate charged chains, model calculations are subsequently performed. These indicate solitons but not polarons to be stable. In total, the analysis demonstrates how the combination of information that can be obtained from various experiments provides a detailed description of the compounds.

Key words: Conjugated polymers; Structure; Electronic structure; Momentum densities; Solitons.

1. Introduction

The discovery [1] of a large doping-induced increase in the electrical conductivity of polyacetylene has led to an enormous increase in the research in the properties of this and related so-called synthetic metals [2]. Although *trans*-polyacetylene (Fig. 1a) is often considered the prototype of these materials, this compound is special in several aspects. It has thus a particularly simple polymer backbone containing only carbon atoms, whereas the backbones of many other conjugated polymers contain heteroatoms closely connected to them. It is frequently assumed that the presence of heteroatoms does not affect the properties of the polymer in any significant way, but only few detailed studies have addressed this question. Another property, that makes *trans*-polyacetylene atypical is its high symmetry, which leads to the possibility of forming solitons, as we shall see. This symmetry is absent for most other conjugated polymers.

The interatomic bonds in *trans*-polyacetylene can be interpreted as being σ-bonds formed by sp^2 hybrids on the C atoms and s-functions on the H atoms. The last valence electron per CH unit participates in π-bonds between the C atoms. The π-electrons are those defining the orbitals closest to the Fermi level. The observed bond-length alternation, which opens up a gap at the Fermi level, is accordingly ascribed a Peierls distortion.

We notice that the compound has two energetically degenerate structures (phase A and B) only differing in the alternation. Domain walls between these two phases, solitons, may thus exist and will be able to move almost freely along the chain. However, for many other conjugated polymers the degeneracy between the A and B phases is lifted and, consequently, the existence of polarons, being local distortions between two parts of the chain with the same phase, has been proposed. It is often believed that these struc-

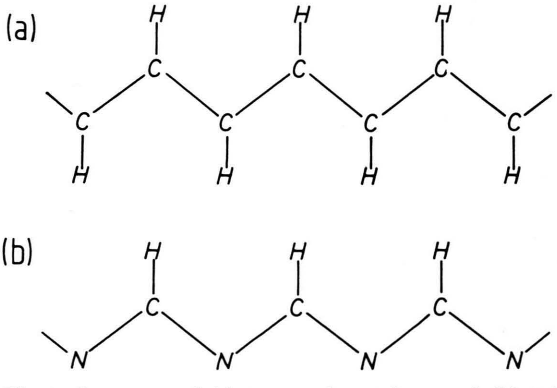

Fig. 1. Structure of (a) *trans*-polyacetylene and (b) polycarbonitrile.

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Reprint requests to Dr. M. Springborg, Fakultät für Chemie, Universität Konstanz, Postfach 55 60, D-W-7750 Konstanz, Fed. Rep. of Germany.

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tural defects are created in the doped or photo-excited materials (see, e.g., [3]).

Starting with *trans*-polyacetylene (PA) of Fig. 1 a one may arrive at the closely-related compound polycarbonitrile (PCN) by substituting every second CH group by an N atom (Fig. 1 b). As the number of electrons is the same and so is the structure, one should expect that a comparison between the two compounds of Fig. 1 will give information about the rôle of the heteroatoms. It is the purpose of the present contribution to report results of such a study. Two features are, however, immediately clear. First of all, every second of the σ-bonds between the C and the H atoms are for PCN replaced by N lone-pairs. Secondly, the presence of the nitrogen atoms lowers the symmetry such that the structure without a bond-length alternation will have a gap at the Fermi level. It is therefore not obvious that this material does have a nonvanishing bond-length alternation, indicating that solitons and polarons may not exist for PCN.

2. Theoretical Method

We have applied the first-principles, density-functional, full-potential, LMTO method for helical polymers [4] to explore the electronic ground-state properties of the isolated, infinite, periodic chains.

Assuming the Born-Oppenheimer approximation valid we make use of the density-functional formalism of Hohenberg and Kohn [5]. The eigenfunctions to the Kohn-Sham equations [6] are expanded in a basis of linear-muffin-tin orbitals as described in detail [4]. It should, however, be stressed that the potential is not assumed being of muffin-tin shape. In the present implementation of the LMTO method we make explicit use of the quasi-one-dimensional periodicity [4].

The calculations give information about the total energy, electron density in position space, and energy bands as functions of structure [4]. Recently the method has been extended to yield Mulliken populations, densities of states, photoelectron spectra, energy-loss spectra, electron densities in momentum space, and reciprocal form factors [7].

The first-principles method is specifically designed for studying neutral, periodic polymers, and is therefore not adequate for investigating solitons and polarons. In order to explore those we therefore map the results of the first-principles calculations on an appropriate model-Hamiltonian $\hat{H}_{\text{eff}}$ with which we subsequently examine the structural defects. $\hat{H}_{\text{eff}}$ contains a tight-binding part for the π-electrons (since these define the orbitals closest to the Fermi level and therefore are most important when the polymer is doped or photo-excited) and a remainder. For more details the reader is referred to [7] and [8].

3. Structure

For PA we assumed the C–H bonds to have a fixed length of 2.10 a.u. and to lie along the negative C–C–C bond angle bisectors. This resulted in the lowest total energy for C–C–C bond angles of 128° and C–C bond lengths of 2.58 and 2.76 a.u. As discussed in [7], these values compare well with experimental and other theoretical information. In particular we notice here the prediction of a C–C bond-length alternation.

Assuming all C–N bonds of PCN to have the same lengths and the C–H bonds to be perpendicular to the polymer axis, the lowest total energy was found for C–N–C and N–C–N bond angles of 122°, C–N bond lengths of 2.57 a.u., and C–H bond lengths of 2.05 a.u. As we shall see in Sect. 4, this structure – with no bond-length alternation – possesses a band gap at the Fermi level. Hence a Peierls distortion should not be expected. However, in a partially restricted geometry variation we found a lower total energy for C–N bond lengths alternating between 2.54 and 2.67 a.u. We will nevertheless ignore the effects of the bond-length alternation throughout most of the remaining part of this paper.

4. Energy Bands and Densities of States

In Fig. 2 we show the band structures of the optimized structure of PA as well as those of the optimized structure of PCN with no bond-length alternation.

For PA without bond-length alternation the bands would meet pairwise at the zone edge ($k=1$), reflecting the higher (zigzag) symmetry. In that case, and by neglecting the avoided crossings, one may form a hypothetic broad σ-band between roughly -21 and -8 eV and a narrower one between -14 and -9 eV. The former can be related to the σ-bonds between the C atoms and the latter to those between the C and the H atoms.

The bands for PCN can to some extent be interpreted according to this picture. We thus recognize the

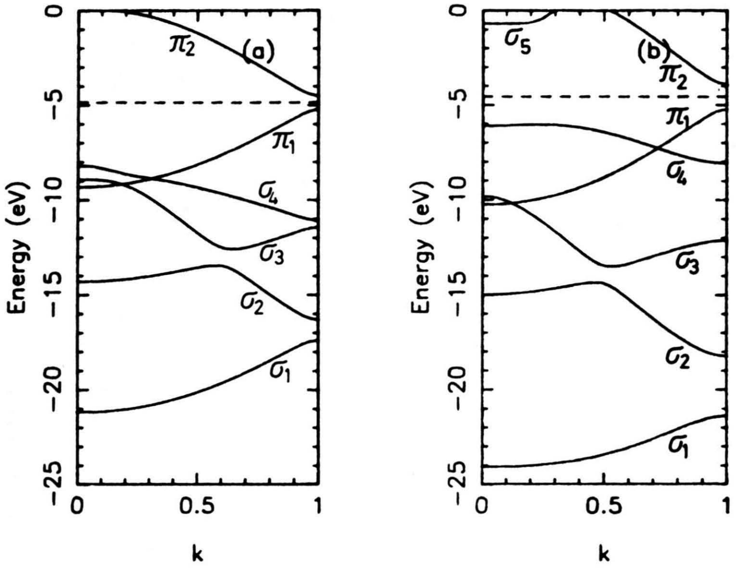

Fig. 2. The valence bands and the lowest conduction bands for (a) PA and (b) PCN. $k=0$ and $k=1$ correspond to the zone center and the zone edge, respectively, and the dashed lines mark the Fermi level.

broad σ-band between -24 and -10 eV from the C−N σ-bonds. However, the narrower hypothetic σ-band is split into a lower part at around -15 eV being due to the C−H σ-bonds and an upper part at roughly -7 eV formed by nitrogen lone-pairs.

This picture is confirmed by Figure 3c. This shows the Mulliken net populations for PCN as functions of band energy. Since the bands overlap and we only have a finite set of discrete k-points, these populations appear not as smooth functions of energy but they show nevertheless the trends. In particular, they show that both the uppermost σ valence and the π valence band have large nitrogen components, whereas the π conduction band is dominated by carbon components.

This difference in the nature of the π-bands indicates that the π-electrons, which are the most mobile electrons, are more localized for PCN than for PA. It also follows that PCN will possess a dipolar moment and that it thus may be of interest in non-linear optics.

In Figs. 3a and 3b we show the densities-of-states corresponding to the band structures of Figure 2. Comparison of these shows that the orbital energies are more spread out for PCN than for PA but that the

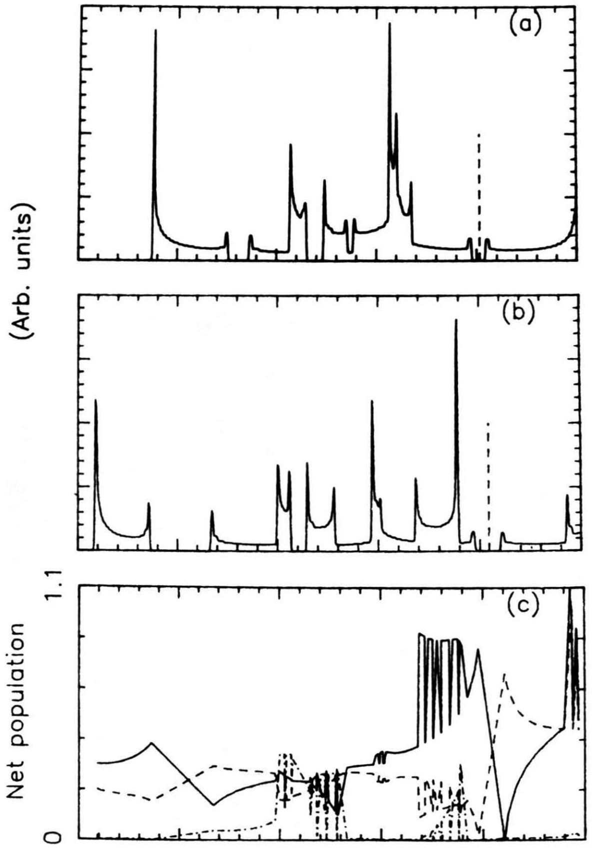

Fig. 3. a), b) Densities-of-states for the bands of Figs. 2a and 2b, respectively. c) shows the Mulliken net populations as functions of band energy for PCN. Here, the full line is that of nitrogen, the dashed line that of carbon, and the dash-dotted line that of hydrogen.

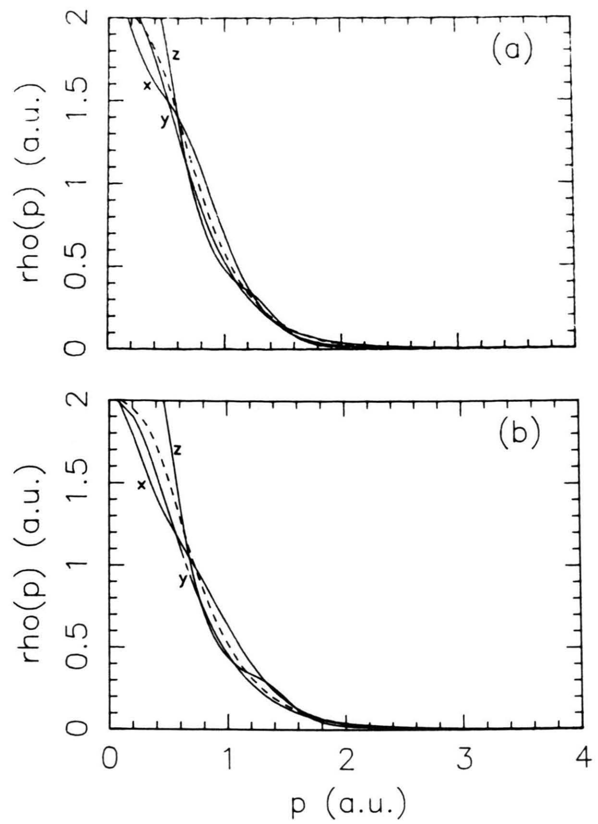

Fig. 4. Momentum densities for the valence electrons of (a) PA and (b) PCN. The polymers are assumed to be placed in the (x, z) planes with z parallel to the polymer axis. x, y, and z mark the densities along the p_x, p_y, and p_z-axis, respectively, and the dashed lines are the spherical averages.

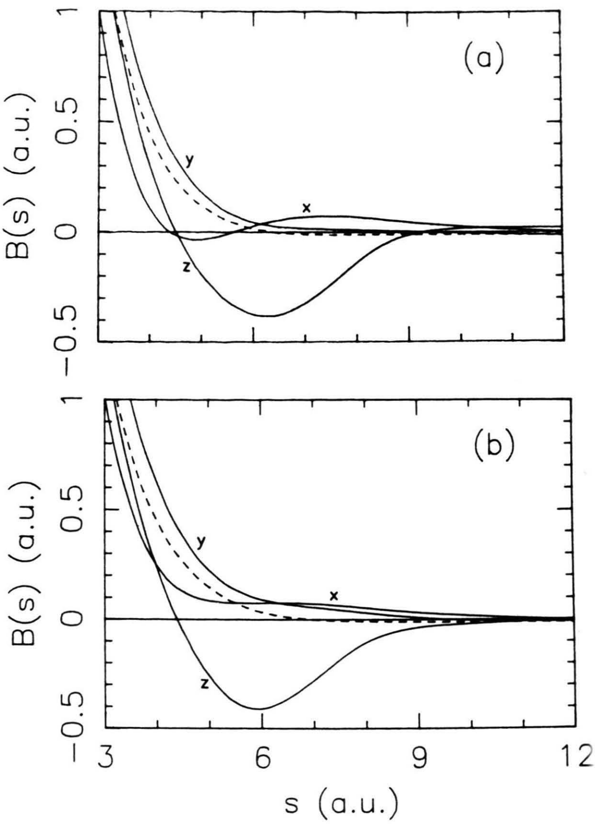

Fig. 5. Reciprocal form factor $B(s)$. The notation corresponds to that of Figure 4.

bands for PCN are split into more, narrower parts. This indicates a larger electron localization for PCN than for PA and can be related to the different single-electron energies for isolated N and C atoms. Finally, since the photoelectron spectra can be obtained as modulations of the densities-of-states, we do not show those here but refer to [7] and [8].

5. Momentum Densities

We have assumed the polymers to be placed in the (x, z) plane with the z-axis parallel to the polymer axis. The calculated electron densities in momentum space along the p_x, p_y, and p_z-axes as well as the spherical average become then as shown in Figure 4. We mention that, compared with the results of [7] and [8], the quality of the calculations has been improved, and thus that the results of Fig. 4 are more accurate.

It is seen that the momentum densities for the two compounds are relatively structureless and very similar. There is, however, one important difference: the densities for $|\boldsymbol{p}|$ in the range between 0 and 1 a.u. are larger for PA than for PCN. This localization of the electrons of PA in momentum space corresponds to the above-mentioned delocalization in position space. We furthermore recognize for both compounds some weak features for $p_z \simeq 1.4$ a.u., which can be related to standing waves along the polymer backbone.

6. Reciprocal Form Factors

The reciprocal form factor, $B(\boldsymbol{s})$, being the Fourier transform of the momentum density or, equivalently, the sum of the single-particle auto-correlation functions in position space [9], is shown in Figure 5. Here, the x and z-components contain much more structure (like nodes and extension) for PA than for PCN. This indicates that the orbitals of PCN are partially localized to either the CH units or the N atoms. On the other hand, the *y*-components, which for not too small values of *y* have major negative contributions from the π-electrons, are fairly similar for the two compounds, although slightly larger for PA than for PCN. This indicates that the negative contributions from the π-electrons of PCN are more rapidly approaching 0 than those of PA, and hence that the nitrogen *p*-functions have a smaller range than carbon *p*-functions.

7. Solitons and Polarons

In studying solitons and polarons in PCN we have to leave the assumption of constant C−N bond lengths. It turned then out that any bond-length alternation is accompanied by an increase in the gap such that it is increased from 0.88 to 2.42 eV according to our model calculations when passing from the optimized structure without bond-length alternation to that with bond-length alternation. One may hence ascribe the lowering of the total energy upon bond-length alternation to a relatively strong electron-phonon coupling of the π-electrons that dominates over the elastic energy of the lattice, as originally proposed by Rice and Mele [10] (for a further discussion of this point, see [8]).

Our model calculations showed subsequently that, when adding or removing a single electron from a long chain, the total energy could be lowered by creating a soliton compared with the total energy of the undistorted, periodic chain. This was found both for PA and for PCN.

Figure 6 offers part of an explanation for this result. We see that the occurrence of a soliton results in extra levels inside the gap. It is energetically easier to populate or depopulate these levels than band orbitals, such that the cost due to the creation of the solitons is compensated for the charged systems. We add that the shown densities-of-states in the gap are observable in optical experiments on doped or photoexcited materials.

There is one remarkable difference between PA and PCN. For PA there is only one gap level, which is placed almost exactly at the mid-gap position; for PCN two gap levels appear, placed roughly at those energies where the band edges occur for the structure with no bond-length alternation. In a more general study [11] we have argued this difference to be related to the lack (PCN) vs. existence (PA) of a band-gap closure for the structures without bond-length alternation. It turns out, moreover, that the electron densities of the two gap levels for PCN are different, such that the lower is mainly generated by nitrogen-centered functions and the upper by carbon functions. This difference is equivalent to that found for the π valence and conduction bands.

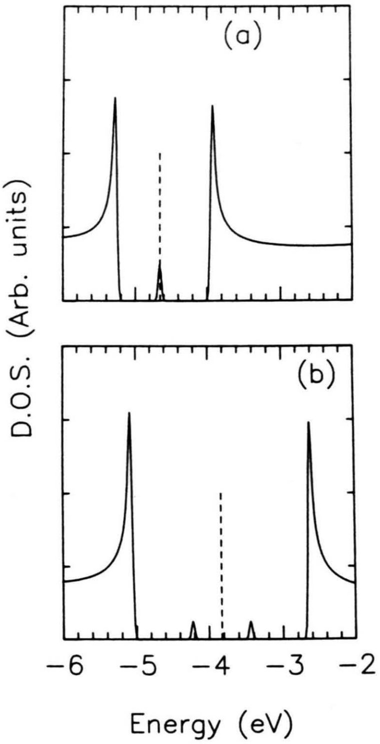

Fig. 6. Densities-of-states close to the band gap for the optimized structure of a soliton in (a) PA and (b) PCN. The vertical dashed line is the Fermi level for the neutral system.

Finally, the existence of polarons was not supported by the results of the model calculations for the present conjugated polymers, although they most likely exist for other conjugated polymers.

8. Conclusions

We have demonstrated that the presence of heteroatoms in the backbone of conjugated polymers may modify the electronic porperties in definite ways. Thus, although PA and PCN are very similar, the former as a vanishing band gap and the latter a nonzero gap for structures with no bond-length alternation. Nevertheless, for both materials the total energy is lowered for structures for which the bond lengths alternate.

The presence of the nitrogen atoms in the backbone of PCN leads to a partial localization of the electrons. This could be observed in the electronic bands and the densities-of-states as the occurrence of more, narrower bands for PCN than for PA. Moreover, the momentum density for PCN was more delocalized than that of PA. The reciprocal form factor indicated the orbitals of PCN to be localized either to the CH units or the N atoms, and those of PA in comparison to be more delocalized.

The fact that the systems showed a preference for a bond-length alternation made it possible for structural defects like solitons and polarons to exist. Our model calculations predicted, however, only solitons to be stable but polarons to be unstable. For the solitons a remarkable difference was observed: they induced two gap levels for PCN but only one for PA.

In total we have shown how a detailed description of the electronic properties of specific compounds can be obtained by combining a number of different kinds of experimentally obtainable information. This analysis demonstrated further that the effects of heteroatoms in the backbone of conjugated polymers are to be included in any accurate description of the properties of the systems of interest.

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