

Structural and Electronic Properties of Fluorinated and Chlorinated Polyacetylene

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Received July 6, 1999

Abstract: Using a density-functional method we have calculated the electronic and structural properties of infinite and periodic $(CF)_x$, $(CCl)_x$, and $(CFCCl)_x$ chains. Only for the $(CF)_x$ and $(CCl)_x$ trans isomers without a C–C bond-length alternation we have optimized the structure completely and subsequently explored whether the total energy for these isomers could be lowered upon a such alternation. Finally, we studied the electronic properties of different cis isomers with fixed structures as well as of trans and cis isomers of $(CFCCl)_x$. Special emphasis is put on whether these newly synthesized materials have properties resembling those of most other conjugated polymers, i.e., whether π orbitals from mainly carbon functions are those closest to the Fermi level and whether a bond-length alternation exists. We find that the F-substituted materials in many respects are similar to the unsubstituted ones (with, however, smaller differences), but that the Cl-substituted ones differ significantly from the unsubstituted ones. The trans isomers of the systems with mixed substitutions possess properties that are intermediate between those of the F- and the Cl-substituted ones. On the other hand, the cis isomers of $(CFCCl)_x$ have markedly different properties and are the only ones with F/Cl nearest neighbors. A comparison with the experimental information suggests that for $(CFCCl)_x$ the trans isomer is the one that is synthesized. Finally, we predict that only for $(CF)_x$ will solitons or polarons be generated upon doping.

Section 1. Introduction

In the last two decades there has been intensive activity in the research in conjugated polymers, partly in order to understand the underlying principles governing their properties and partly to improve, vary, and control these properties (see, e.g., ref 1¹). These polymers are based on a largely planar backbone of sp^2 -bonded carbon atoms with π orbitals perpendicular to this plane defining the orbitals closest to the Fermi level. The energy gap between the occupied and unoccupied π orbitals is usually small (1–3 eV) so that these materials are semiconductors and not insulators as most often is the case for carbon-based polymers. Nevertheless, they have the usual mechanical properties of plastics.

The prototype of these materials is polyacetylene, $(CH)_x$, of Figure 1. The trans isomer with constant C–C bond lengths, that is shown in Figure 1a, has a zigzag symmetry and five valence electrons per repeated unit (one CH unit). Therefore, the π band is half-filled, and by letting the C–C bond lengths alternate (i.e., allowing for a dimerization), as in Figure 1b, the unit cell is doubled, a gap appears at the Fermi level, and the total energy is lowered (a Peierls' distortion). The same is not true for the cis isomer of Figure 1c but, nevertheless, here also the C–C bond lengths may alternate giving either the cis–trans isomer of Figure 1d or the trans–cis isomer of Figure 1e. Of these, the cis–trans isomer is the stabler form (see, e.g., ref 2² and references therein). (As is common practice, we shall here refer to the systems of Figures 1a–b as trans isomers and those of Figures 1c–e as cis isomers.)

Other conjugated polymers are obtained by replacing (some of) the hydrogen atoms with other sidegroups such as alkyl or

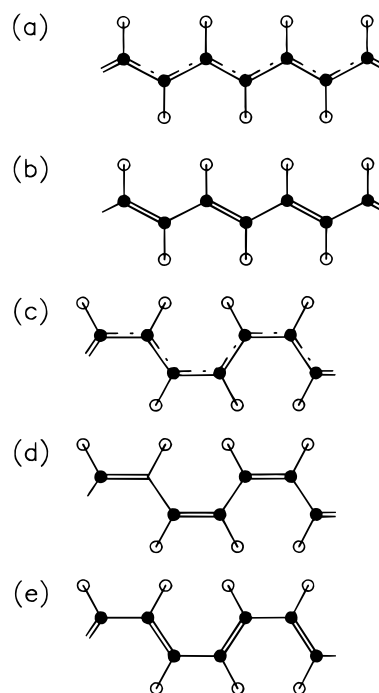


Figure 1. Structure of (a,b) trans polyacetylene and (c–e) cis polyacetylene. (a) corresponds to the undimerized form and (b) to the dimerized form, whereas (d) is the cis–trans and (e) is the trans–cis isomer. (c) will be denoted the undimerized isomer. The black circles mark the carbon atoms and the white ones represent H, F, or Cl atoms.

phenyl groups and/or incorporating five-membered heterocycles or phenyl rings into the backbone. Here, the heteroatoms of the heterocycles are most often sulfur, nitrogen, or, in some cases, oxygen. Finally, polymers containing heteroatoms directly in the backbone have also been considered. The heteroatoms

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(2) Wu, C. Q.; Miao, J.; Yu, J.-Z.; Kawazoe, Y. *Phys. Rev. B: Condens. Matter* 1998, 57, 6.

are then often sulfur or nitrogen, but also metal atoms (like Pd or Pt) have been used.

Recently Gould et al.³ reported the synthesis of polydifluoroacetylene, polydichloroacetylene, and polychlorofluoroacetylene, i.e., the synthesis of polymers of the type of Figure 1 but with all hydrogen atoms replaced with either fluorine or chlorine or with a regular 1:1 mixture of fluorine and chlorine. They reported that they observed both trans and cis forms of these new materials.

Since F and Cl are much more electronegative than other substituents that usually are considered, it is of importance to explore whether these modifications lead to materials that retain the typical properties of the conjugated polymers, i.e., whether they are semiconducting with fairly delocalized π orbitals (derived mainly from carbon-centered functions) closest to the Fermi level and whether a C–C bond-length alternation exists. To study this we have performed density-functional calculations on various infinite, periodic polymers of the trans and cis forms. For the trans forms we optimized the structure and subsequently we considered related structures in order to explore the electronic properties of the cis forms. To our knowledge there exists only one other theoretical study addressing the properties of such polymers.⁴ That work, however, considered only fluorinated trans polyacetylene, and as we shall see, there are significant differences between the fluorinated and the chlorinated materials as well as the system with mixed substitutions.

The rest of the paper is organized as follows. In Section 2 we describe our theoretical method briefly. Section 3 contains the results, and the conclusions are summarized in Section 4.

Section 2. Computational Method

Our computational method has been described in detail elsewhere^{5,6} and shall therefore be described only briefly here. We apply the Hohenberg-Kohn density-functional formalism⁷ in the single-particle formulation of Kohn and Sham.⁸ The single-particle equations

$$\hat{h}_{\text{eff}}\psi_i(\vec{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \right] \psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r}) \quad (1)$$

are solved by expanding the solutions ψ_i in a basis set of LMTOs (linearized muffin-tin orbitals)

$$\psi_i(\vec{r}) = \sum_{R,L,\kappa} \chi_{L,\kappa}(\vec{r} - \vec{R}) c_{i,R,L,\kappa} \quad (2)$$

The three-dimensional space is separated into atom-centered, non-overlapping, so-called muffin-tin spheres and the interstitial region. An LMTO centered at an atom at \vec{R} and having an angular dependence as specified through $L \equiv (l,m)$ is defined as a spherical Hankel function times a harmonic function, $h_l^{(1)}(\kappa|\vec{r} - \vec{R})Y_L(r - \vec{R})$, in the interstitial region. Inside any sphere this function is augmented continuously and differentiably with numerical functions that are obtained by replacing the potential $V(\vec{r})$ in eq 1 by its spherically symmetric part. This leads to a basis set that is of limited size but still provides accurate solutions to eq 1. It shall be stressed that the calculations consider the full potential, and the muffin-tin part is used solely in the construction of the basis functions.

In eq 1 the potential $V(\vec{r})$ is the sum of the electrostatic potential from the nuclei, that of the electrons, and the exchange-correlation

potential. For the latter we use the local-density approximation of von Barth and Hedin.⁹

The basis set we are using consists of two subsets of s , p , and d functions on all sites. The two sets differ in the decay constants κ of the Hankel functions that were chosen as 0.7i and 1.5i for the two sets, respectively. We used sphere radii of 1.2 au for carbon and fluorine, 1.7 au for chlorine, and 0.7 au for hydrogen.

We assume that the polymers are infinite, periodic, helical, isolated, and with a straight helical axis. By defining LMTOs in local atom-centered coordinate systems, we can construct symmetry-adapted Bloch functions from the equivalent basis functions of different unit cells

$$\chi_{L,\kappa}^k(\vec{r}) = \lim_{N \rightarrow \infty} \frac{1}{\sqrt{2N+1}} \sum_{n=-N}^N \chi_{L,\kappa}(\vec{r} - \vec{R}_{np}) e^{ik\pi n} \quad (3)$$

where \vec{R}_{np} is the position of the p th atom of the n th unit cell. The irreducible part of the first Brillouin zone corresponds to $k \in [0;1]$, and the k -space sampling is performed using 11 equidistant k points in this interval including the end points.

From eq 3

$$\langle \chi_{L_1,\kappa_1,p_1}^{k_1} | \chi_{L_2,\kappa_2,p_2}^{k_2} \rangle = \delta_{k_1,k_2} \lim_{N \rightarrow \infty} \sum_{n=-N}^N \langle \chi_{L_1,\kappa_1}(\vec{r} - \vec{R}_{0p_1}) | \chi_{L_2,\kappa_2}(\vec{r} - \vec{R}_{np_2}) \rangle e^{ik_1\pi n} \quad (4)$$

and

$$\langle \chi_{L_1,\kappa_1,p_1}^{k_1} | \hat{h}_{\text{eff}} | \chi_{L_2,\kappa_2,p_2}^{k_2} \rangle = \delta_{k_1,k_2} \lim_{N \rightarrow \infty} \sum_{n=-N}^N \langle \chi_{L_1,\kappa_1}(\vec{r} - \vec{R}_{0p_1}) | \hat{h}_{\text{eff}} | \chi_{L_2,\kappa_2}(\vec{r} - \vec{R}_{np_2}) \rangle e^{ik_1\pi n} \quad (5)$$

In the actual calculations, the N summations are carried through so far that they can be considered converged. Nevertheless, differences in how various summations are carried through may result in overall rigid shifts of the band structures making a direct comparison between those of, e.g., the trans and cis isomers, slightly more difficult.

To analyze our results we shall use the energy-resolved Mulliken net populations (i.e., the crystal orbital overlap populations—COOP¹⁰). These give information on the distribution of the electrons on the various atoms for the individual orbitals. However, since they cannot be considered absolute quantities, we have broadened them with Gaussians of a finite width in order to obtain smooth curves.

We optimized first the structure of the undimerized trans isomers that contain only one CF or CCl unit per unit cell when utilizing the zigzag symmetry. Subsequently, we doubled the unit cell and allowed the CF or CCl units to move rigidly parallel to the polymer axis in alternating directions, thereby leading to alternating C–C bond lengths but keeping all other structural parameters fixed. In all cases it was assumed that the C–F or C–Cl bonds were perpendicular to the polymer axis. For the cis isomers we used the bond lengths and bond angles as found for the trans isomers. However, it turned out that this led to very short F–F and Cl–Cl distances. Therefore, we rotated the C–F and C–Cl bonds about the C atoms and in the polymer plane leading to equidistantly placed F or Cl atoms.

We also considered polymers where every second H atom was replaced by an F atom and every other second by a Cl atom leading to (CFCCl)_x. For this we used the C–F and C–Cl bond lengths from the pure systems and averaged C–C bond lengths and C–C–C bond angles from those. Also here we forced the F and Cl atoms to be placed equidistant for the cis isomers.

The band structures were calculated using unit cells with four atoms, i.e., by using translational symmetry for the trans isomers and zigzag

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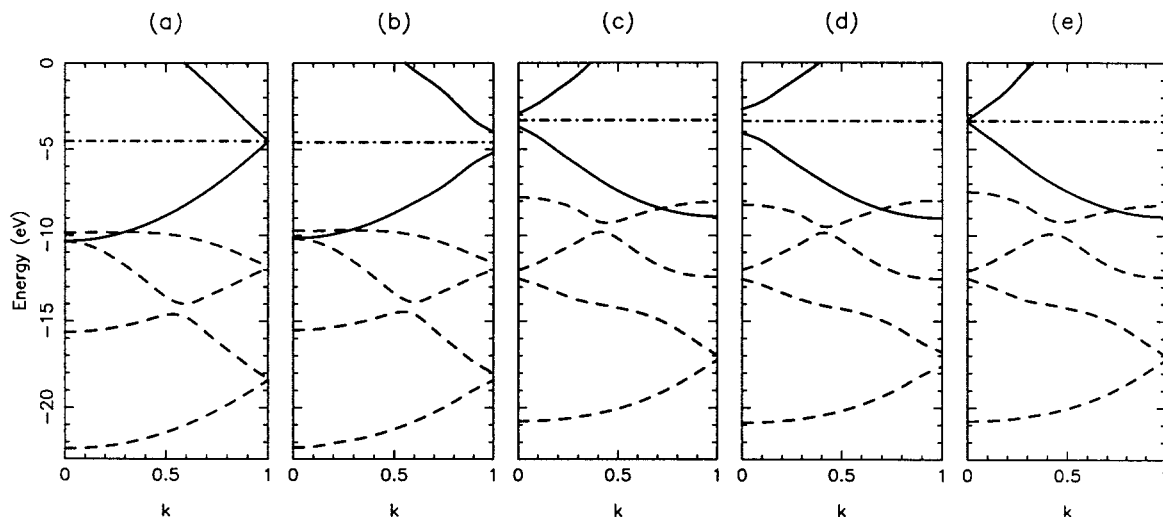


Figure 2. Band structures for unsubstituted polyacetylene, $(\text{CH})_x$, for the structures of Figure 1. The horizontal dash-dotted lines mark the Fermi level, $k = 0$ and $k = 1$ are the center and edge of the first Brillouin zone, respectively, and dashed and full curves show bands of σ and π symmetry, respectively.

Table 1. Bond Lengths (in a.u.) and Bond Angles (in Degrees) for the Different Trans Polyacetylenes $(\text{CX})_x^a$

	X = H	X = F	X = Cl
C-X	2.064	2.652	3.281
C-C (single) ^a	2.636	2.653	
C-C (undim) ^a	2.576	2.581	2.578
C-C (double) ^a	2.520	2.509	
C-C-C	123.7°	130.2°	132.8°

^a The second and fourth horizontal entry give the C-C bond lengths for the dimerized isomer of Figure 1b, whereas the third one gives those for the undimerized isomer of Figure 1a.

symmetry for the cis isomers. Thereby, the π functions of neighboring units become parallel for the trans isomers and antiparallel for the cis isomers.

Finally, for the sake of comparison, we also considered the unsubstituted polyacetylenes $(\text{CH})_x$ for which we used the structural information that we have calculated recently for the trans isomers.¹¹ Also for this we considered cis isomers with bond lengths and angles similar to those for the trans isomers, but with the hydrogen atoms placed equidistant parallel to the polymer axis.

Section 3. Results

In Table 1 we list the bond lengths and bond angles as optimized in the present work together with those we have found for unsubstituted trans polyacetylene.

The results show that the C-C bond lengths change only very little when replacing H by F or Cl. However, for the chlorinated system there was no tendency of a bond-length alternation, which can be understood from the band structures (see below). On the other hand, both the larger charge polarization and the larger sizes of F and Cl compared with H can explain why the C-C-C bond angles become larger when replacing H by F or Cl. Finally, the C-F and C-Cl bond lengths compare very well with those usually considered realistic.¹²

Figure 2 shows the band structures for the original, unsubstituted compound $(\text{CH})_x$. The bands closest to the Fermi level are of π symmetry (notice that due to the difference in the local description of the π orbitals between trans and cis isomers, the gap occurs at $k = 1$ for the trans isomers and at $k = 0$ for the cis isomers), and by comparing with the COOP curves of Figure

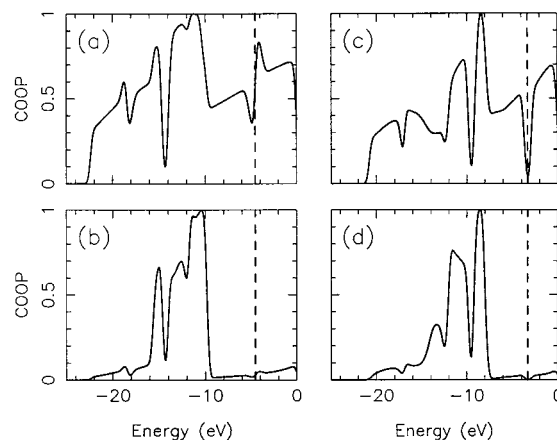


Figure 3. The crystal orbital overlap populations (COOP) on (a,c) the carbon atoms and (b,d) the hydrogen atoms for the undimerized (a,b) trans and (c,d) cis isomer of unsubstituted polyacetylene. Notice that the figures do not have a common ordinate scale and that the results have been broadened by Gaussians of a finite width in order to obtain smooth curves. The vertical dashed lines represent the Fermi energy.

3 it can be seen that these orbitals have only minor components on the hydrogen atoms and, accordingly, are localized to the carbon atoms. The band structures for the two trans isomers, Figure 2a,b, demonstrate clearly how the bond-length alternation leads to a band gap at the Fermi level. On the other hand, for the cis isomers, the trans-cis isomer (with alternating C-C bond lengths) is the one with the smallest gap and the cis-trans isomer has the largest gap. The COOP curves of Figure 3 (here, as well as below, we show those only for the structures without bond-length alternations; those for the structures with such differ only marginally from those shown) show that the hydrogen atoms have their main contributions in the region -16 to -10 eV. Finally, we notice that the band structures for the cis isomers appear to be shifted roughly 1.5 eV upward in energy compared with those of the trans isomers. This rigid shift, we believe, is due to the above-mentioned differences in the calculations and similar, but smaller, shifts are also found for the other systems of the present study.

In Table 2 we list the Mulliken gross populations on the different atoms for the various compounds. The table indicates that carbon has donated electrons to hydrogen, but we stress that the Mulliken populations are not to be considered absolute

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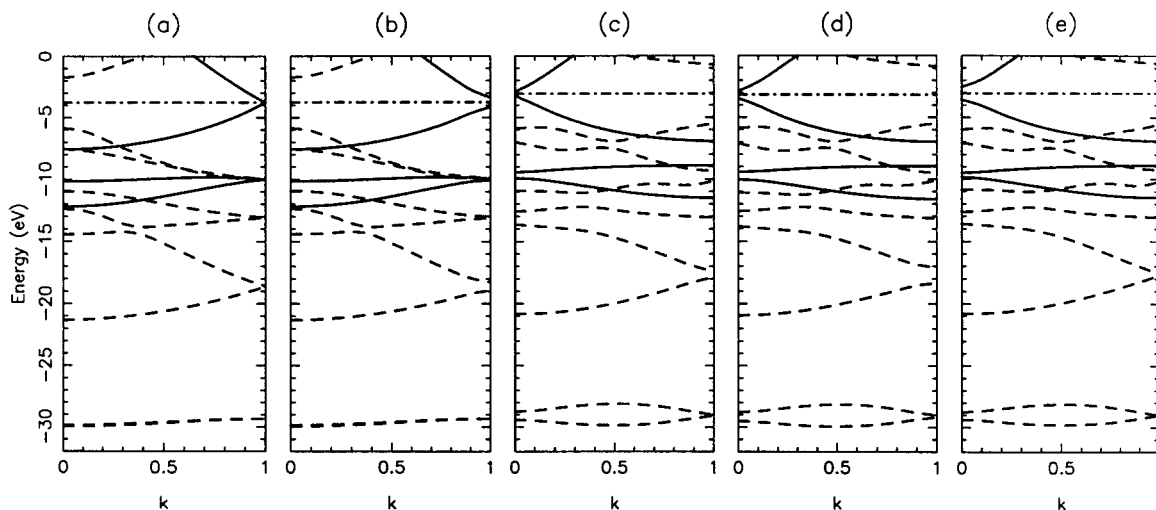


Figure 4. As Figure 2, but for the fluorinated polyacetylene.

Table 2. Mulliken Gross Populations q_Z for the Systems Studied in the Present Work^a

structure ^b	X	q_C	q_H	q_F	q_{Cl}
undim. trans	H	3.85	1.15		
dim. trans	H	3.85	1.15		
undim. cis	H	3.82	1.18		
cis-trans	H	3.82	1.18		
trans-cis	H	3.83	1.17		
undim. trans	F	3.81		7.19	
dim. trans	F	3.81		7.19	
undim. cis	F	3.84		7.16	
cis-trans	F	3.85		7.15	
trans-cis	F	3.84		7.16	
undim. trans	Cl	4.05			6.95
undim. cis	Cl	4.13			6.87
undim. trans	F/Cl	3.87/4.03		7.23	6.87
dim. trans	F/Cl	3.88/4.02		7.22	6.88
undim. cis	F/Cl	3.89/3.83		7.38	6.90
cis-trans	F/Cl	3.89/3.82		7.38	6.90
trans-cis	F/Cl	3.89/3.85		7.39	6.87

^a The structure refers to Figure 1 and X to the atoms attached to carbon atoms. ^b For the mixed systems $(CFCCl)_x$ the first population for the C atoms refers to that for the atom bonded to an F atom and the second to that for the atom bonded to a Cl atom.

numbers and, in particular, our calculations that apply s , p , and d functions on all sites, including hydrogen, will overestimate the number of electrons on hydrogen atoms. But the numbers indicate that there are only minor differences in the trans and cis isomers.

Figure 4 shows the band structures for the fluorine-substituted materials. Compared with those of the unsubstituted materials, Figure 2, we observe that many more bands appear, but despite this difference, the main characteristics of Figure 2 are recovered in Figure 4. Most notably, the bands closest to the Fermi level are of π symmetry (which is in agreement with the results of Bakhshi et al.⁴), and upon a dimerization, a band gap opens up for the trans isomers, Figure 4a,b. This explains why the structures of the trans isomers are very similar to those for the unsubstituted material. On the other hand, for the cis isomer there is a smaller difference in that here the trans-cis isomer is the one with the largest gap. Our calculations indicate actually also that this structure is that of the lowest total energy for the cis isomers, but lacking a complete structure optimization this conclusion should be taken with some caution.

The COOP curves of Figure 5 show that the lowest valence bands are centered on the fluorine atoms (i.e., they are due to the F 2s functions). But most important, here also the frontier

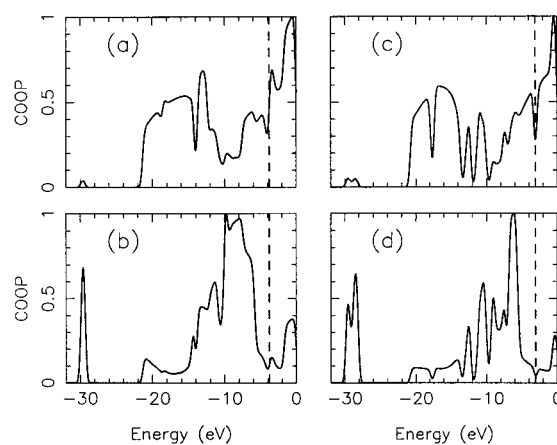


Figure 5. As Figure 3, but for the fluorinated polyacetylene. (b) and (d) show the populations on the fluorine atoms.

orbitals are formed mainly by carbon-centered functions. The Mulliken gross populations of Table 2 indicate, moreover, a smaller electron transfer from carbon to fluorine, consistent with chemical intuition.

For the chlorine-substituted systems the situation is markedly different; cf. Figure 6. Both the undimerized trans and the undimerized cis isomer have more bands crossing the Fermi level and, therefore, a bond-length alternation is not able to open up a gap at the Fermi level. This explains why we do not find such in our calculations. Moreover, the COOP curves (Figure 7) show that the chlorine-centered functions contribute to the orbitals over the complete energy range of the valence bands and the lowest conduction bands, which also is a difference from $(CH)_x$ and $(CF)_x$. Thus, the fact that the Cl 3s and 3p functions appear at higher energies than the F 2s and 2p functions and the H 1s function leads to significantly more hybridizations between the C and the Cl functions for the uppermost occupied orbitals than between C and either the F or H atoms. Therefore, the Mulliken populations of Table 2 show a trend opposite of that found for the other systems. The fact that $(CCl)_x$ is different from the other systems is in accord with the experimental results of Gould et al.,³ who reported that this compound possesses a nonplanar structure. For such, it is no longer possible to separate the orbitals into being of σ and π symmetry, and the bands are not allowed to cross. It is possible that in that case the system can have a gap at the Fermi level, but it requires dihedral angles of the backbone markedly different from 0° or 180° .

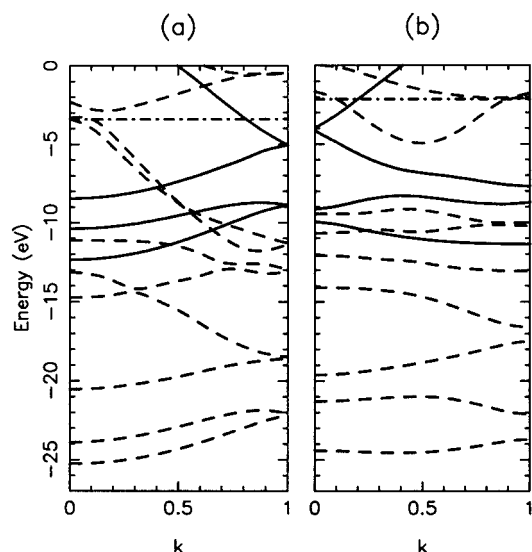


Figure 6. As Figure 2, but for the chlorinated polyacetylene. Moreover, results are shown only for the undimerized isomers, i.e., in (a) for the undimerized trans isomer and in (b) for the undimerized cis isomer.

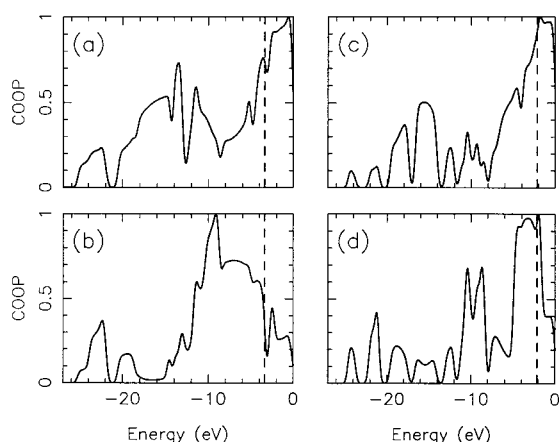


Figure 7. As Figure 3, but for the chlorinated polyacetylene. (b) and (d) show the populations on the chlorine atoms.

For the mixed substitutions, i.e., for $(CFCCl)_x$, we did not optimize the structure but used averaged parameters as described above. For the undimerized trans isomer this gave the band structures of Figure 8a which possess two bands crossing the Fermi level of which only one is of π symmetry. However,

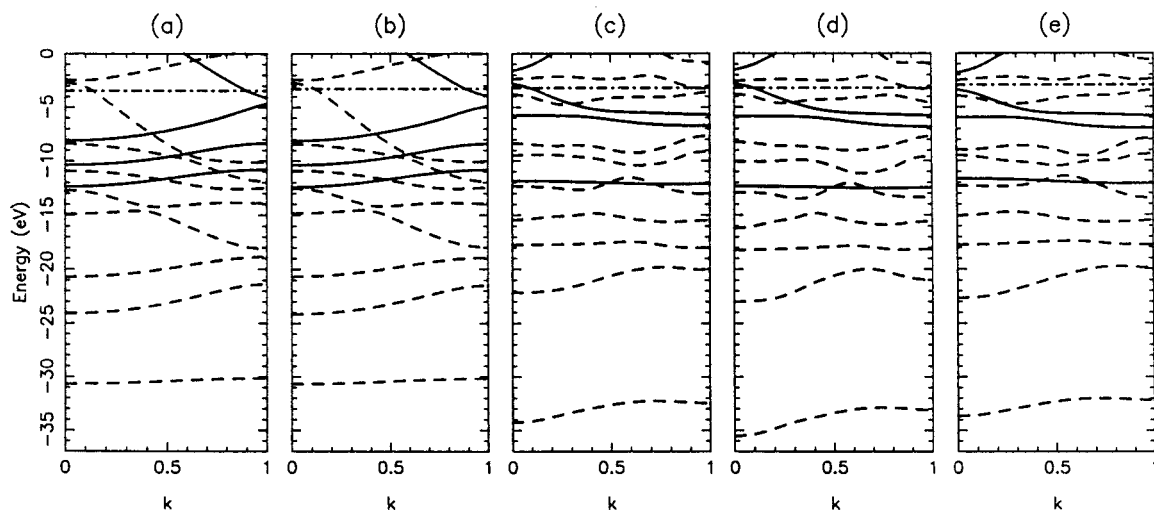


Figure 8. As Figure 2, but for $(CFCCl)_x$.

allowing the C–C bond lengths to alternate (by moving the CF and CCl units rigidly in alternating directions parallel to the chain axis) led to a lowering of the total energy, and the lowest total energy was found for C–C bond lengths of 2.497 and 2.664 au, i.e., values that are very similar to those of Table 1. Furthermore, the existence of a bond-length alternation is also consistent with the experimental proposal that the system has the structure $(-CF=CCl-)_x$. The band structures, Figure 8b, show, however, that the bond-length alternation does not lead to a gap at the Fermi energy. The stability of solitons for the unsubstituted polymer is due to the occurrence of states in the gap between occupied and unoccupied orbitals that may become populated or depopulated upon doping. A similar possibility does not exist for this polymer, and therefore, we predict that solitons are not created upon doping.

The COOP curves for the undimerized trans isomer, Figure 9a–d, are fairly similar to those of Figures 5 and 7. Also, the Mulliken gross populations of Table 2 resembles those of the $(CF)_x$ and $(CCl)_x$.

Subsequently, we studied the various cis isomers with the different C–C bond lengths. Whereas the trans isomers have Cl–Cl and F–F nearest-neighbor pairs but no Cl–F equivalents, the situation is reversed for the cis isomers. Therefore, there are significant differences in the band structures between the trans isomers and the cis isomers, as seen in Figure 8. In fact, the trans–cis isomer, which is the one with the largest unit-cell length and therefore the smallest steric interactions between the halogen atoms, has a small gap at the Fermi level with flat σ bands and broader π bands in its closest vicinity. For the other cis isomers we observe two bands just crossing the Fermi level. The existence of a band gap for the trans–cis isomer suggests that this isomer may be stable, and also, the experimental observation of a $(-CF=CCl-)_x$ structure is in accordance with this.

The COOP curves for the cis isomers, see Figure 9e–h, are markedly different from those of any other of the systems considered here. Thus, except for the absolutely lowest valence orbitals, which largely are due to fluorine functions, all atoms contribute to the complete valence band and the lowest conduction-band energy range. This difference is a direct consequence of the existence of F–Cl nearest-neighbor pairs. A further consequence of this difference is that the Mulliken gross populations of this compound (Table 2) also differ significantly from those of all other compounds considered here. Thus, whereas the chlorine atoms and the carbon atoms directly

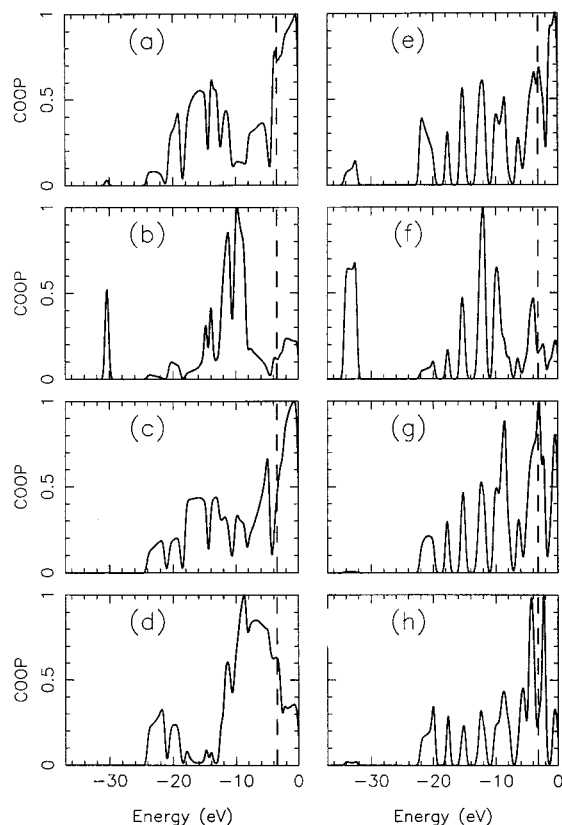


Figure 9. As Figure 3, but for $(CFCCl)_x$. Results are shown only for the undimerized isomers, and (a–d) are those for the trans isomer and (e–h) for the cis isomer. Moreover, (a,e) are the populations for the carbon atoms next to the fluorine atoms, (b,f) the populations for the fluorine atoms, (c,g) those for the carbon atoms next to the chlorine atoms, and (d,h) those populations for the chlorine atoms.

bonded to the fluorine atoms have populations not too different from those of the equivalent atoms of the other systems studied here, the gross populations on the fluorine atoms are significantly larger than those for any other system, and those on the carbon atoms bonded to the chlorine atoms are found to be strongly reduced.

This difference may be used in giving information on the structure of $(CFCCl)_x$. For an isolated, neutral carbon atom we find that the $1s$ orbital has an energy of -272.2 eV, whereas for the C^+ ion it is lowered to -286.2 eV. Although the absolute numbers may be inaccurate (usually, local-density calculations give core–electron orbital energies that are too high) the trend should be correct: the less electrons, the lower is the energy of

the $1s$ orbital. According to Gould et al.,³ the $1s$ binding energies of the carbon atoms bonded to fluorine are lower than those for the atoms bonded to chlorine. Moreover, these energies show only smaller differences between $(CF)_x$ and $(CCl)_x$, on one hand, and $(CFCCl)_x$ on the other hand. Therefore, the trans isomer seems to be the one that has been synthesized.

Section 4. Conclusions

Our theoretical study on the halogen-substituted polyacetylene has revealed that the C–C bond lengths are only insignificantly affected by these substitutions compared with the unsubstituted material. The C–C–C bond angles become slightly increased. The F-substituted compounds possess properties very similar to those of the unsubstituted system including the existence of a C–C bond-length alternation and of π bands closest to the Fermi level formed by carbon-centered functions. For the cis isomers, there is a smaller difference between the F-substituted and the unsubstituted system in that the trans–cis for the former and the cis–trans isomer for the latter is the one of the largest band gap and (maybe) the lowest total energy of the cis isomers. The fact that the F-substituted materials possess a bond-length alternation also means that structural distortions such as solitons and polarons (where the bond-length alternation locally is either reversed or disrupted, respectively) may exist and be important for transport properties as is the case for many other conjugated polymers (see, e.g., ref 1).

The Cl-substituted materials were markedly different. More bands crossed the Fermi level, and there was no indication of a C–C bond-length alternation. Furthermore, Cl-centered functions contribute significantly to the orbitals closest to the Fermi level. Therefore, for this material, solitons or polarons most likely do not exist, and it will have different transport properties than those of, e.g., $(CH)_x$.

For the materials with mixed substitutions, $(CFCCl)_x$, the trans isomers showed many similarities with the simpler ones, $(CF)_x$ and $(CCl)_x$. Interestingly, this material does possess a bond-length alternation, although this does not lead to a band gap at the Fermi level. Therefore, for this also, neither solitons nor polarons will exist. The cis isomers of $(CFCCl)_x$ are the only systems with F–Cl nearest neighbors and, accordingly, their electronic properties were markedly different from those of the other systems studied here. However, although they may have a gap at the Fermi level, their electronic properties were not in accord with the experimental information.

Acknowledgment. The author is grateful to Fonds der Chemischen Industrie for very generous support.

JA9923181