

Theoretical Analysis of Poly(difluoroacetylene) PDFA

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Abstract

Due to the π -donating ability of fluorine, fluorosubstitution has a remarkable effect on the band structure of polyacetylene (PA). Valence and conduction band edges decrease in energy, leading to narrower valence and wider conduction bands. Ionization potential and electron affinity of PDFA are predicted to be about 1.5 eV higher than those of PA. This indicates that PDFA is an excellent candidate for an n-type conductor. PDFA tends to adopt non-planar structures but the energy of planarization is only 5.44 kcal/mol. Alternating difluoroethylene and ethylene units yield planar polymers with decreased band gaps. Ionization potential and electron affinity of the mixed polymer are between those of the homopolymers.

Keywords: Density functional calculations, donor-acceptor concept, band gap, band width, conductivity

1. Introduction

Polyacetylene (PA) was the first first conducting organic polymer and has it holds the record in conductivity to this date. However, technical applications could not be realized since PA is unstable in air, insoluble and brittle. A major drawback is also that PA can not be n-doped.[1] Fluorine substitution can be expected to help overcome some of these problems.[2] Carbon fluorine bonds are very strong and the high electronegativity of fluorine should stabilize the system by lowering the energy levels. The π -donating ability of fluorine should mainly influence the conduction band. To examine whether fluorine substitution can be expected improve on the properties of PA, oligomers of tetrafluoroacetylene were investigated theoretically and compared to acetylene oligomers.

2. Methods

Oligomers of tetrafluoroacetylene, of acetylene, and of mixed oligomers with up to 12 conjugated double bonds were optimized in planar geometry. For substituted and unsubstituted octatetraenes, non-planar structures were investigated as well. Geometry optimizations were performed using density functional theory (DFT). Becke's three parameter hybrid functional was combined with Perdew and Wang's correlation functional.[3] The weight of the Hartree-Fock exchange was raised to 30%. Octatetraenes were re-optimized at MP2. For all calculations Stevens Basch Krauss pseudopotentials and split valence plus polarization basis sets were employed[3]. The calculations were performed with Gaussian 98.[4]

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3. Results and Discussion

Figures 1 and 2 show energy level diagrams of polyenes and fluoropolyenes.

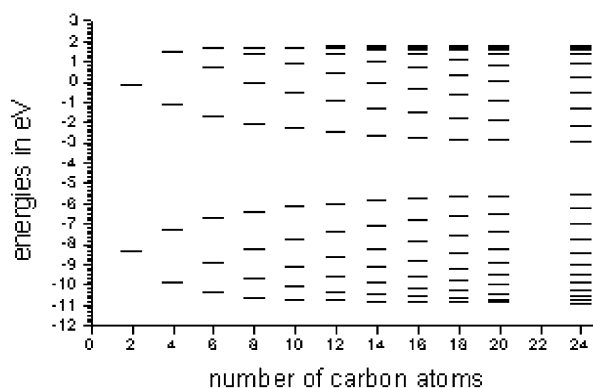


Fig. 1 Energy levels of ethylene through $C_{24}H_{26}$.

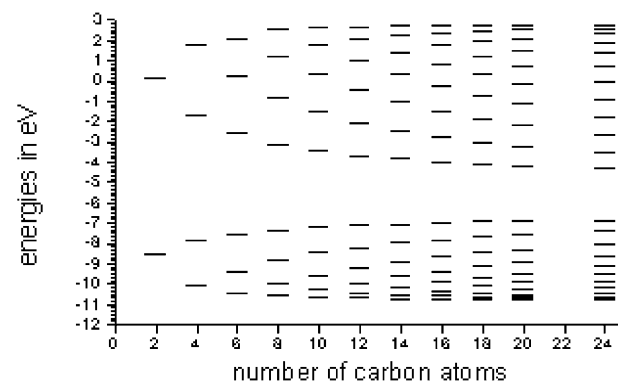


Figure 2. Energy levels of tetrafluoroethylene through $C_{24}F_{26}$.

Comparison of Figs. 1 and 2 reveals that HOMO and LUMO energy levels of ethylene and fluoroethylene are very similar. However, PDFA is predicted (by extrapolation) to have a 1.5 eV higher ionization potential (IP) and a 1.5 eV larger electron affinity (EA) than PA. The reason is that the HOMO decreases less and the LUMO decreases more upon chain lengths increase after fluorine substitution. This can be attributed to inductive and mesomeric effects of fluorine. The inductive effect leads to electron withdrawal, which is accompanied by a contraction of the occupied orbitals. The more contracted orbitals overlap less and their energies increase less upon polymerization. The mesomeric effect of fluorine, that is π -donation from one of its lone pairs, leads to injection electron density into the unoccupied π -orbitals, which become more diffuse. This increases overlap in the π -system and therefore the energies of the unoccupied orbitals decrease more upon chain length increase. The results are higher IP, higher EA, narrower valence and wider conduction bands of PDFA as compared to PA. The band gaps of PA and PDFA are almost identical (1.6 eV).

Figure 3. shows various geometries of decafluoro-octatetraene. All but the planar trans structure are minima. DFT and MP2 reveal that no planar structure exists for C_8F_{10} and that the cis-transoid conformation is more stable than the all-trans form. DFT and MP2 disagree, however, regarding the global minimum and regarding the relative energies, which are larger at MP2. MP2 places the helical form 1.27 eV below the cis-transoid conformation. Non-planar structures have energy gaps that are between 0.2 and 0.4 eV larger than that of the planar trans-form. The energy gaps of the trans-cisoid and of the helical form are more than 1 eV larger.

The helical form looks like the structure that has been found experimentally for the decacyano-octatetraene dianion.[5] Like poly(dicyanoacetylene), PDFA will not be a conductor, if the structure remains helical in the solid state. However, calculations at the same level of theory show that the energy difference between the helical and the planar trans form for $C_8(CN)_{10}$ is 23.26 kcal/mol at MP2 while that for C_8F_{10} is only 5.44 eV. Thus the tendency to adopt a helical structure is much weaker for C_8F_{10} . Therefore, crystal packing effects might shift the preference towards a more planar conformation.

If the most stable form of PDFA turns out to be helical, an alternative exists in replacing only half of the hydrogen atoms with fluorine. $C_8F_4H_6$ is planar at DFT and MP2 levels of theory. The corresponding polymer is predicted to have a 0.34 eV smaller band gap than PA and PDFA. IP, EA, valence and conduction band widths for the polymer are predicted to be average between those of the HOMO polymers. Thus properties of fluoro substituted polymers can be tuned by varying the fluorine content.

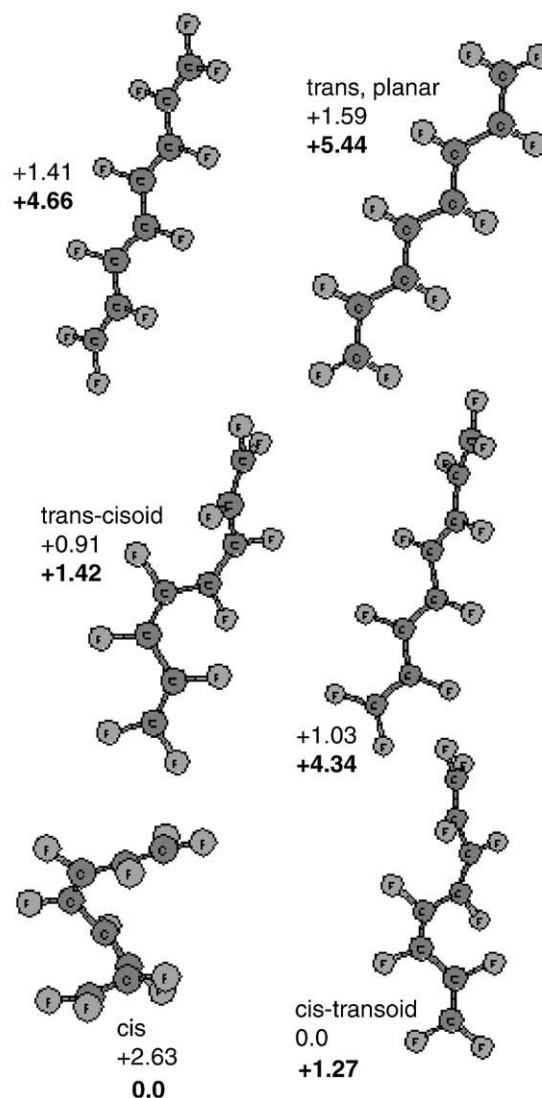


Fig. 3 Geometries of C_8F_{10} . Relative energies are given in kcal/mol. MP2 values are in bold face.

4. Conclusions

Fluorosubstitution increases IP and EA compared to PA and might therefore stabilize the neutral and the n-doped form. Moreover, fluorine increases the conduction band width and might therefore increase electron mobility. Due to electrostatic repulsion between fluorine atoms PDFA tends to be non-planar. However, alternating ethylene and difluoroethylene units lead to a planar polymer with equally promising properties.

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