

Electronic Structure of Heterocyclic Ring Chain Polymers

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Abstract

The band gaps, ionization potentials and electron affinities of conjugated chain polymers comprising heterocyclic aromatic rings are studied systematically as a function of atomic substitutions with N, O and S using first principles density functional calculations.

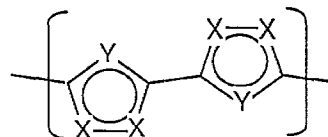
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Heterocyclic ring chain polymers such as polythiophene (PTh, **4**, cf. Fig. 1) and polypyrrole (Ppy, **2**) are among the most widely studied conjugated polymers. For practical purposes they are more stable under ambient conditions than polymers containing linear conjugated chain fragments such as poly-acetylene or poly-phenylene-vinylene. Polythiophene and its oligomer analogues are studied widely as semiconducting materials in electronic devices[1]. Polypyrrole is readily oxidized and is used in oxidized form as a conducting material. Polyfuran (Pfu, **3**) is similar to PTh and Ppy, but studied less intensively. One of the problems in applying organic semiconductors can be their relatively low ionization potential, which makes them sensitive to oxydation. Polymer electron affinities are generally low, which makes it difficult to reduce polymers (dope them n-type), and, in an actual device, to find suitable metal contacts with a low enough barrier for injecting electrons. Such problems have stimulated the interest in heterocyclic ring chain polymers which contain nitrogen atoms in the polymer backbone, such as the polydiazoles **6-8**. Molecules and polymers containing diazole moieties are expected to have higher ionization potentials compared to their all-carbon counterparts and possibly also a higher electron affinity. Oxadiazole(**7**)- and azadiazole(**8**)-containing molecules and polymers have been studied for instance as electron transport/hole blocking layer in multilayer LED's. So far such polymers include non-conjugated moieties in the main chain to enhance processability, but work is in progress to synthesize all-conjugated diazole containing polymers, aiming at increasing the electron mobility[2,3].

In this paper the electronic structure of an isoelectronic series of heterocyclic ring chain polymers (cf. Fig. 1) is studied systematically within the local density approximation to density functional theory (LDA), using Car-Parrinello techniques to simultaneously optimize both the electronic and the geometrical structure of the polymers[4]. We will focus on the systematics of oxidation/reduction potentials and optical band gaps within the series **1-8** as a function of the chemical substitution. To complete the series we include the non aromatic polymers **1** and **5**, in which the ring is closed by a methylene bridge.

The structural and electronic properties of PTh and Ppy have been studied extensively using semi-empirical Hartree-Fock, *ab*

initio Hartree-Fock and density functional methods (in order of increasing improvement of theoretical description)[5-13]. Whereas ground state properties (structures, charge densities, ionization potentials, etcetera) can be described adequately, all of these methods have problems describing excited states. For methods related to Hartree-Fock this is reflected by the fact that, for instance, band widths and semiconductor band gaps are very ill-reproduced. Such quantities are then often calculated on an ad hoc basis, using a much coarser level of theory; typically a parametrized, non self-consistent, one-electron Hückel-type Hamiltonian[5-7]. In principle, Hartree-Fock electronic structures can be improved systematically by incorporating many body effects[8,14], but this is computationally very expensive. Density functional methods yield much better results for band widths and band gaps as compared to Hartree-Fock, but band gaps are still off by 40-50%[9-13]. A simple, uniform scaling of the calculated band gaps, however, brings them into close agreement with experiment, which is the pragmatic approach followed in this paper[11-13]. A strategy for improvement, incorporating many body effects, will be discussed in Ref.[15].



| | X | Y | Gap (eV) | IP (eV) | EA (eV) |
|----------|----|-----------------|----------|---------|---------|
| 1 | CH | CH ₂ | 0.93 | 3.84 | 2.91 |
| 2 | CH | NH | 3.18 | 3.86 | 0.68 |
| 3 | CH | O | 2.36 | 4.30 | 1.95 |
| 4 | CH | S | 2.16 | 4.61 | 2.45 |
| 5 | N | CH ₂ | 2.06 | 6.14 | 4.09 |
| 6 | N | NH | 4.49 | 6.12 | 1.63 |
| 7 | N | O | 3.79 | 7.05 | 3.26 |
| 8 | N | S | 3.19 | 6.58 | 3.40 |

Fig.1 Schematic unit cell of heterocyclic ring chain polymers and calculated band gaps, ionization potentials(IP) and electron affinities(EA).

Fig. 1 gives the calculated electronic parameters for polymers (1-8) with optimized geometries. In our calculations we include only the valence electrons explicitly, using norm-conserving pseudo-potentials to represent the ion cores. The results are generally very similar to results obtained with all-electron calculations, so this represents a good approximation. The valence wave functions are then expanded in a basis set consisting of plane waves in order to solve the Kohn-Sham equations efficiently. The basis set can be improved systematically by including plane waves with smaller wave lengths. Calculating the total energy of a periodic system involves a Brillouin zone integration; in this case two sampling points along the direction of the polymer chain give sufficient accuracy. For details of the calculation, we refer to Refs. [11-13]. The calculations aim at the limit of single, isolated polymer chains. The ionization potentials (IP) are obtained by extrapolating the Hartree potential perpendicular to the polymer chain to infinity, which defines the point of zero energy for removing an electron from a single polymer chain. We do not consider a possible additional 'polarization energy' correction for the solid state[13], since relative IP's are most important and we expect these to be given correctly in Fig.1. The band gaps are obtained by dividing the calculated LDA band gaps by a factor of 0.6, a 'scissors' type of operation which has lead to good results previously[11-13]. The electron affinities (EA) are obtained by subtracting the band gaps from the IP's.

The basic idea that the IP of a polymer is increased when carbon atoms in the backbone are substituted by the more electronegative nitrogen atoms, works quite well, as can be observed by comparing the entries 1 and 5, 2 and 6, etcetera in Fig. 1. This substitution at the X position increases the IP by 2-2.7 eV. The corresponding EA is also increased, but only by 1-1.3 eV; the band gap is increased by 1-1.4 eV. The reason for the difference in change between IP and EA can be rationalized in a simple way. The generic shape of the highest occupied polymer orbital (HOPO), which determines the IP, and of the lowest unoccupied polymer orbital (LUPO), which determines the EA, are shown in Fig. 2. Projecting polymer orbitals on a localized basis ϕ_i , numbering the sites by i , denoting the expansion coefficients by c_i , and the on-site difference in potential between a carbon and a nitrogen atom as $\Delta V_i = \langle \phi_i | \Delta V | \phi_i \rangle$, the change in energy eigenvalues $\Delta \epsilon$ within first order perturbation energy if carbon atoms are substituted by nitrogen atoms at the X positions is $\Delta \epsilon = \sum_x |c_x|^2 \Delta V_x$. Since the coefficients c_x at the X positions are larger for the HOPO than for the LUPO, one expects the IP to be affected more than the EA by the substitution.

Substituting at the Y positions affects the IP to a much lesser degree, as can be observed by comparing the two series 1-4 and 5-8 in Fig. 1. This can be understood following the simple reasoning above, since the coefficient c_Y at the Y position for the HOPO is zero for reasons of symmetry, cf. Fig. 2, and thus in first order perturbation the IP is not affected by this substitution. One indeed observes in Fig. 1 that this substitution changes the IP by less than 1 eV, substitution by O or S leading to the largest IP. The band gap is strongly increased when the methylene bridge (1, 4) is substituted by NH, O, or S. This substitution makes the ring aromatic and it clearly demonstrates that the hetero-atoms are very important in describing the electronic structure around the band gap. In contrast, the methylene bridged ring 1 resembles polyacetylene. Along the series NH, O, S (2-4, 6-8) the band gap decreases. Apparently,

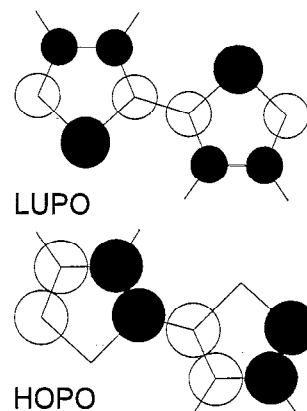


Fig.2 Generic representation of the highest occupied polymer orbital (HOPO) and the lowest unoccupied polymer orbital (LUPO). These are both π -states; the circles give the size of the coefficients c_i obtained by projecting on the atomic p_z orbitals; black for positive and white for negative sign.

the anti-bonding interaction between the hetero atom at the Y position and the rest of the ring in the LUPO, cf. Fig. 2, decreases along this series, thereby decreasing the band gap and increasing the EA.

In terms of having a small band gap and a large electron affinity the methylene bridged compounds 1 and 5 are in principle most interesting, but their properties are probably very similar to those of (substituted) polyacetylene. Within the same criteria the S substituted compounds 4 (polythiophene, PTh) and 8 (polythiadiazole, PTD) are next most interesting, the latter being suited as electron transport/hole blocking material and the NH substituted polymers 2 and 6 are least interesting.

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