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Berengere Themans [a] , Jean-Marie Andre [a] & Jean-Luc Bredas [a]
[a] Laboratoire de Chimie Théorique Appliquée, Facultés Notre-Dame de la Paix, B-5000, Namur, (Belgium)
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THEORETICAL PREDICTION OF POTENTIALLY NEW HIGHLY CONDUCTING POLYMER COMPLEXES : VEH STUDY OF NITROGEN AND OXYGEN CONTAINING CONJUGATED POLYMERS

BERENGERE THEMANS, JEAN-MARIE ANDRE, and JEAN-LUC BREDAS
Laboratoire de Chimie Théorique Appliquée,
Facultés Notre-Dame de la Paix, B-5000 Namur (Belgium).

Abstract The electronic structure of nitrogen and oxygen containing conjugated polymers is investigated by means of the Valence Effective Hamiltonian (VEH) technique. Parameters related to the conductivity properties upon doping such as ionization potentials, bandgaps, and bandwidths are discussed in detail for polyaniline, polyquinoline, polyfuran, poly(p-phenylene oxide), and polybenzofuran.

Since the discovery of high conductivity in doped polyacetylene, chemists and physicists have devoted much effort to dope other conjugated polymers.[1] Oxygen containing systems have been less thoroughly investigated. Until now, conductivities upon doping have been reported for polyfuran ($100\ \Omega^{-1}cm^{-1}$) [2] and AsF_5-doped poly(p-phenylene oxide) ($10^{-3}\Omega^{-1}cm^{-1}$).[3] In this paper, some nitrogen and oxygen containing conjugated polymers are theoretically studied by means of the Valence Effective Hamiltonian technique. This method has been demonstrated to afford excellent estimates of electronic properties such as ionization potentials (IP), bandwidths (BW), bandgaps (Eg), and electron affinities (EA).[4] These properties are important in the search for new highly conducting polymers. IP and EA (EA=IP-Eg) values indicate the ease of ionizing the polymers upon p-type and n-type doping, respectively; BW values for the highest occupied or lowest unoccupied bands are a measure of the delocalization in the system and can be roughly correlated with the mobilities of the charge carriers in these bands. Previously, we have investigated the properties of hydrocarbon, sulfur, and nitrogen containing conjugated polymers.[4] In order to extend the VEH technique to other polymers, we have recently parameterized the oxygen atom.[5]

Hereafter, we discuss the electronic properties of nitrogen containing systems such as polyquinolines and derivatives, polyaniline, and oxygen containing systems such as polyfuran, poly(p-phenylene oxide) and polybenzofuran; comparison with sulfur analogs is made (table 1).

TABLE 1. VEH results for IP, HOMO BW, Eg(π-π^*), EA of conjugated polymers. All energies in eV; conductivities (σ) in $\Omega^{-1}cm^{-1}$.

	IP	BW	E_g	EA	σ	Ref.
Polyquinoline	6.0	0.8	3.2	2.8		
Poly(4-phenyl)quinoline	6.0	0.5	3.2	2.8	$10^{(6)}$	
Poly(2,6-naphthylene)	5.3	1.1	2.8	2.5	$0.1^{(7)}$	
Polyaniline	5.1	2.3				
Polyfuran	4.9	3.7	3.1	1.8	$100^{(2)}$	
Poly(p-phenylene oxide)	6.6	0.9			$10^{-3(3)}$	
Polybenzofuran	4.9	2.2	2.7	2.2		

NITROGEN CONTAINING CONJUGATED POLYMERS

Recently, films of polyquinoline (PQ) have been reported to show conductivities of the order of $10\Omega^{-1}cm^{-1}$ upon doping with sodium. Pressed pellets of poly(2,6-naphthylene) (PN),[6] an isoelectronic compound, yield a conductivity of about $0.1\Omega^{-1}cm^{-1}$ upon SbF_5 doping.[7] The band structure of PQ is very similar to that of PN.[8] PQ, as well as its phenyl derivative, poly(4-phenyl)quinoline, has a large IP value ($\sim$6.0 eV) and a large EA value ($\sim$2.8 eV). This indicates that these systems could be p-doped only by very strong acceptors and can be easily n-doped. However, bandwidth values are small and suggest that conductivities upon doping as high as in polyacetylene or poly(p-phenylene) cannot be achieved.

Polyaniline (PAn) can be synthesized by chemical or electrochemical method. PAn presents conductivities ranging between 10^{-2} and $1\Omega^{-1}cm^{-1}$ depending on the redox level and/or preparation.[9] We discuss here the PAn form consisting of phenyl rings connected by NH units, i.e. the analog of poly(p-phenylene oxide) (PPO) and poly(p-phenylene sulfide) (PPS). We have considered a nonplanar conformation, with adjacent rings twisted by 90° with respect to one another.

The VEH band structure is displayed in figure 1a. The width of the highest occupied band (2.3 eV) is much larger than in PPS (1.2 eV) and PPO (0.9 eV). This suggests higher conductivity upon doping. Furthermore, because of its lower IP, PAn could be p-doped with weaker acceptors than PPO and PPS. PAn appears thus more attractive for p-doping than its sulfur and oxygen counterparts.

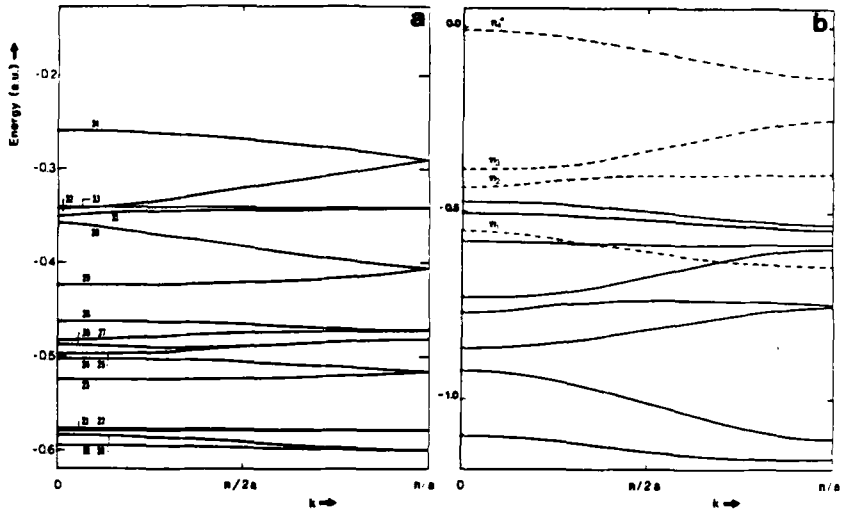

Figure 1. VEH band structure of the highest occupied orbitals of a) polyaniline and b) polyfuran (* stands for an unoccupied orbital).

OXYGEN CONTAINING CONJUGATED POLYMERS

The geometry used in the VEH calculations for polyfuran (PF) is taken from X-ray diffraction data on furan molecule.[10] The band structure (figure 1b) shows features similar to those found in polypyrrole and polythiophene; e.g., the HOMO (Highest Occupied Molecular Orbital) π orbital has no contribution coming from oxygen, whereas the LUMO (Lowest Unoccupied Molecular Orbital) π orbital does. The IP value (4.9 eV) is slightly lower than in polythiophene, but is larger by 0.9 eV with respect to polypyrrole. The HOMO BW is large(3.7 eV), in agreement with the high conductivity reported upon doping.[2]

In analogy to PPS, X-ray diffraction data on PPO show that

adjacent phenyl rings are perpendicular to each other.[11] Until now, the highest reported conductivities upon doping are about $10^{-3}\Omega^{-1}cm^{-1}$. Compared to PPS, the IP value is larger by 0.3 eV. The HOMO BW is about 0.9 eV which is, as pointed out before, much lower than in PAn and of the same order as in PPS. It is known that upon high doping, PPS undergoes chemistry leading to a coplanar fused structure: polybenzothiophene.[12] By analogy, we have also considered the equivalent compound for PF, i.e. polybenzofuran (PBF). VEH calculations indicate that with respect to polybenzothiophene, PBF has a much lower IP(4.9 eV) and a larger HOMO bandwidth (2.2 eV). As a result, PBF appears very interesting, even more so than its sulfur counterparts.

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