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STUDIES ON NITROGEN-CONTAINING POLYMERS $(-\underset{\text{R}}{\underset{|}{\text{C}}}=\text{N}-)_n$

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Abstract This paper is devoted to the theoretical investigation of the potentialities of some nitrogen-containing polymers to become electroactive. Fundamental band parameters are computed within a valence-effective hamiltonian framework.

INTRODUCTION

Compounds of the type $(\text{R}-\underset{\text{I}}{\underset{|}{\text{C}}}=\text{N})_n$ are reported in the litterature as stable to ambient atmosphere¹. They seem to offer opportunity to introduce easily a variety of substituents on a polymeric conjugated chain. Could such systems be electroactive ?

METHODOLOGY

To answer the above question we need the fundamental band parameters², ionization potential (IP), band gap (Eg) and bandwidth (BW). They are computed within the framework of a valence-effective hamiltonian (V.E.H.) technique^{3,4}. This methodology has been established as a very useful tool to provide theoretical band parameters of ab initio quality without the consumption of large computational time. These theoretical results generally match very well the experimental estimates⁵ except for the necessity of subtracting 1.9 eV to I.P. to account for the polarization energy. Such a correction has been made throughout the present paper. We are mainly concerned with three polymers : poly-acetonitrile (R is CH₃), poly-benzonitrile (R is C₆H₅) and poly-pyridine

$(-\text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{N}-)_n$ which is not exactly a term of the $(\text{RCN})_n$ series but offers a total similarity of genesis to the true members of the family⁶.

POLY-ACETONITRILE

Basic assumptions

Several attempts of geometries have been made. Starting from a trans configuration we have twisted the chain into an helix, using either standard bond lengths⁷ or the C = N and C - N lengths optimized by Karpfen⁸ for polymethinimine, the first term of the series (R is H).

Results

They are summarized in table I. All energies are given in e.V.

TABLE I Band parameters of $(\text{CH}_3\text{CN})_n$ versus geometry

Torsional angle θ	Standard lengths			Karpfen lengths		
	IP	Eg	BW	IP	Eg	BW
0°	6.3	3.7	2.6	5.1	3.1	2.9
30°	6.6	4.6	4.5			
45°	8.0	6.5	1.6			
60°	8.0	7.2	1.6			
90°	8.0	8.3	1.6	6.7	4.8	0.9
180° (cis)	7.3	5	1	7.7	8.5	1.7

Attempt to optimize the geometry

Non-bonded interatomic interactions are represented by an exp-6 dispersive-repulsive potential^{9,10,11} and Coulomb interactions. Partial charges are obtained from the VEH-LCAO coefficients. Optimal situation occurs for $\theta = 60^\circ$ with standard lengths, $\theta = 90^\circ$ with Karpfen lengths, i.e. for an interdistance $\text{CH}_3 - \text{CH}_3$ close to the sum of Van der Waals' radii.

POLY-BENZONITRILEBasic assumptions

Standard bond lengths are used. We start from a trans geometry in which aromatic rings are orthogonal to the plane of the ... - C = N - C = N - ... skeleton. The conjugated chain is in turn twisted into an helix.

Results

They are packed in table II (energies in eV)

attempts to optimize the geometry

Actually we have not yet performed any attempt in this sense.

Nevertheless let us observe that the distance between two aromatic

TABLE II Band parameters of $(C_6H_5CN)_n$ versus geometry

	IP(eV)	Eg(eV)	BW(eV)
15° semi-metal but quite hypothetical			
30°	5.0	0.8	1.5
45°	5.4	1.2	1.2
60°	6.0	1.9	0.65
90°	7.15	3.1	0.05
180°	6.6	2.6	0.3

rings is less than the thickness of a ring for $\theta < 45^\circ$, larger for $\theta > 45^\circ$ and roughly equal to the thickness of a ring for $\theta = 45^\circ$. Despite the vanity of assuming the geometry of a molecule only from Van der Waals-like data⁹, this value $\theta = 45^\circ$ can be regarded as a rough indication of what could be a plausible geometry of polybenzonitrile.

$(C_6H_5CN)_n$ has then an I.P. consistent with the possibility of doping by strong electron acceptors but the B.W. appears too small to generate a good electrical conductivity upon this doping.

POLY-PYRIDINE

We assume a trans planar configuration. $N = C$ and $N - C$ bond length values are chosen identical to the optimal ones of polymethinimine while $CH = CH$ and $CH - CH$ lengths are taken equal to those of polyacetylene. Table III lists the results obtained. The polymer might offer some interest as a potentially electroactive material.

TABLE III Band parameters of polypyridine

IP(eV)	Eg(eV)	BW(eV)
5.4	2.1	2.3

CONCLUSION

Whilst $(CH_3CN)_n$ does not seem capable to be electroactive, $(C_6H_5CN)_n$ and polypyridine might present some interest.

The synthesis and characterization of these polymers are in progress in our laboratory.

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