Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 05 Dec 2006.

To cite this article: M. C. Piqueras , R. Crespo , E. Ortí & F. Tomás (1993): Structural and Electronic Properties of Oligomeric Heteroarylene Vinylenes: A Theoretical Approach, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 236:1, 219-224

To link to this article: http://dx.doi.org/10.1080/10587259308055231

Mol. Cryst. Liq. Cryst. 1993, Vol. 236, pp. 219–224
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Printed in the United States of America

STRUCTURAL AND ELECTRONIC PROPERTIES OF OLIGOMERIC HETEROARYLENE VINYLENES: A THEORETICAL APPROACH

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Abstract The structural and electronic properties of trans-bis (2-thienyl)ethylene, trans-bis(2-furyl)ethylene and trans-bis(2-pyrryl) ethylene have been investigated from a theoretical standpoint. Ab initio methods have been employed to calculate the geometric structures and ionization potentials. Furthermore, VEH ionization potentials and π-π^* electronic transitions are reported. A progressive decrease of the ionization potential occurs when exchanging sulfur by oxygen and when replacing oxygen by a NH group. An increase of the energy of the first electronic transition is observed in going from trans-bis(2-thienyl)ethylene to trans-bis(2-furyl)ethylene but not when passing to trans-bis(2-pyrryl)ethylene. These trends are correlated with available theoretical and experimental data on polymers. The adequacy of ab initio and VEH methods to predict correctly the electronic properties of trans-bis(2-furyl)ethylene is discussed.

INTRODUCTION

Poly(heteroarylene vinylenes) are being extensively investigated in view of their potential use as molecular materials in highly specific applications such as modified electrodes and electronic devices[1]. This interest is rooted in the fact that these polymers are synthesized via a high molecular weight, soluble precursor yielding high quality materials which can be easily formed into films of controlled thickness and oriented to a high degree[2]. Furthermore, they exhibit superior chemical stability against oxygen and moisture at room temperature compared to early developped polymers. These studies show that the incorporation of electron donating groups improve the electronic properties of the unsubstituted polymers[3]. However, the influence of the heteroatom composition is a matter of controversy because the role played by the heteroatom in the electronic properties of

poly(heterocycles) has been questioned in several papers. For some authors, the influence of the heteroatoms is negligible[4,5], whereas for other, there is a dominant effect of the heteroatom because of the direct interaction of its p-orbital lone pair with the carbon backbone π-band structure[6]. Besides other processes, the control of the structure and properties of conducting polymers has been addressed through the modification of the monomer structure[7]. Experimental results evidence that monomeric structures remain the most appropriate for efficient electrosynthesis of extensively conjugated and highly conducting polymers[8]. Owing to the simplicity of their structure, oligomers constitute interesting models to study the electronic properties of polymers[9]. This has determined a renewal of interest in the theoretical and experimental study of oligomeric systems[10].

In this paper we focus on trans-bis(2-thienyl)ethylene, trans-bis(2-furyl) ethylene and trans-bis(2-pyrryl)ethylene which, respectively, correspond to the monomers of poly(thienylene vinylene) (PTV), poly(furylene vinylene) (PFV) and poly(pyrrylene vinylene) (PPyV). We report a theoretical investigation on the structural and electronic properties of these materials. We have performed geometry optimizations using ab initio SCF-LCAO-MO methods as implemented in the MONSTERGAUSS-90[11] to obtain reliable geometric structures for the monomers. The calculated geometries have been used as inputs for electronic structure calculations employing the valence effective Hamiltonian (VEH) technique[12]. This method has been widely used in the past to predict electronic properties of both molecules and polymers giving excellent agreement with experimental data[13].

RESULTS AND DISCUSSION

Geometric Structures

Except for trans-bis(2-thienyl)ethylene no structural data are available in the literature, and we have used a theoretical approach to obtain reliable geometries for the monomers. The geometries of trans-bis(2-furyl)ethylene and trans-bis(2-pyrryl)ethylene have been fully optimized using he 3-21G basis set while that of trans-bis(2-thienyl)ethylene has been obtained at the 3-21G* level. The molecules were kept planar and subjected to a C_{2h} symmetry constraint. As it is displayed in Fig. 1, the rings in the monomer unit are alternated in such way that the heteroatoms in adjacent rings point to opposite directions in order to accomplish that all the vinyl groups are trans with respect to the double bonds on adjacent rings. This assumption has been taken on the basis of accurate ab initio calculations performed to investigate the conformational properties of 2-vinylpentaheterocycles, for which the trans rotamer is always predicted as the most stable conformation[14]. Furthermore, the restriction to coplanarity is justified by the slight dependence of the electronic properties on the torsion angles

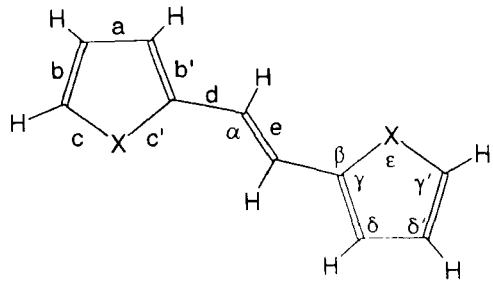

FIGURE 1 Geometry of trans-bis(2-heteroaryl)ethylene. See Table I for values of bond lengths and bond angles.

at least for values smaller than 20°[15]. It is further justified by the fact that we are mainly interested in the relative changes that the electronic properties undergo upon exchange of the heteroatoms and not in their absolute values.

Table I summarizes the main geometrical parameters obtained from ab initio optimizations together with experimental X-ray[16] and MNDO values[17] reported for trans-bis(2-thienyl)ethylene. The geometries optimized for trans-bis(2-thienyl)ethylene and trans-bis(2-furyl)ethylene are very similar and show a clear alternation of single and double bonds. Trans-bis(2-pyrryl) ethylene shows smaller differences between the lengths of the C-C bonds constituting the pyrrole rings and displays a more delocalized structure. The

TABLE I Geometries of trans-bis(2-furyl)ethylene (A), trans-bis (2-pyrryl)ethylene (B) and trans-bis(2-thienyl)ethylene (C) calculated at the ab initio double-zeta level. Also listed are the experimental[16] and MNDO[17] geometries of trans-bis(2-thienyl)ethylene. Bond lengths are in angstroms. Bond angles are in degrees. See Fig. 1 for the labeling of bond lengths and bond angles.

	A	B	C	C(expt.)	C(MNDO)
bond lengths					
a	1.445	1.425	1.433	1.44	1.447
b	1.340	1.360	1.347	1.351	1.375
b'	1.348	1.369	1.355	1.40	1.380
c	1.382	1.376	1.723	1.701	1.673
c'	1.380	1.377	1.738	1.701	1.694
d	1.441	1.450	1.456	1.457	1.455
e	1.326	1.328	1.327	1.309	1.358
bond angles					
α	123.4	126.5	126.1	125.8	126.4
β	118.6	124.9	123.9	124.2	119.6
γ	109.1	107.1	110.6	111.3	110.1
γ'	109.6	108.0	112.0	111.0	111.8
δ	106.8	107.1	112.4	110.5	112.3
δ'	107.1	108.0	113.3	114.4	111.3
ε	107.5	109.7	91.7	93.2	94.5

bond lengths and bond angles calculated for trans-bis(2-thienyl) ethylene are in very good agreement with X-ray reported data[16]. Our ab initio parameters are in better agreement with experimental values than the MNDO results which always underestimate the C-S bond lenght[18]. There are slight differences between the experimental and calculated lengths of the two double bonds inside the ring. In the X-ray structure the inner double bond is weakened and the outer double bond is strengthened while the ab initio results show similar values for both bond lengths. MNDO results also predict similar lengths for these bonds[17]. The 3-21G* bond length calculated for the central vinylene double bond is in very good agreement with the experimental value which is overestimated by the MNDO method. The experimental and calculated values for the single bond joining the vinyl group to the ring are almost the same in all the structures. Very slight differences between experimental and ab initio bond angles are observed.

Electronic Properties

The VEH values calculated for the first ionization potentials (IP) and the lowest-energy π-π^* electronic transitions (HOMO-LUMO energy gap, E_g) of trans-bis(2-heteroaryl)ethylenes together with those obtained for the IP at the ab initio double-zeta level are collected in Table II (for convenience we have maintained the term E_g when referring to the monomers). For the sake of comparison we have included the IP and Eg values previously reported for poly(thienylene vinylene) (PTV) and poly(furylene vinylene) (PFV)[20] and for poly(pyrrylene vinylene) (PPyV)[21]. Table II also reports the experimental values for PTV and PFV[19]. As can be seen, the VEH ionization potentials calculated for the monomers are higher than those from ab initio calculations. The evolution computed for the IPs is in accord with the optimized geometries since the IP decreases as the delocalization in the monomers increases. Both ab initio and VEH calculations predict a lowering of the IP when passing from trans-bis(2-thienyl)ethylene to trans-bis(2-furyl) ethylene and from this to trans-bis(2-pyrryl)ethylene. Unfortunatelly, there is no experimental gas phase data to compare with. Nevertheless, these trends are similar to those observed for PTV, PFV and PPyV at the theoretical level[20,21] and with those obtained from electrochemical potential spectroscopy data[17,19]. There is also a good accord with the IP reported by Jen et al.[22] for PFV which is measured to be 0.25 eV smaller than that of PTV.

Ab initio electronic transition energies are not given in Table II since it is well known that standard ab initio Hartree-Fock methods provide too diffuse virtual orbitals and, as a consequence, too large transition energies. In contrast, the VEH method has been shown to provide accurate estimates of π-π^* transitions since it is not contamined by any information coming from the unoccupied Hartree-Fock molecular orbitals[23]. The VEH value calculated for the π-π^* electronic transition (E_g) of trans-bis(2-thienyl)ethylene (3.29 eV) correlates with the experimental value (3.49 eV)[17]. The calculated E_g values

TABLE II Ab initio and VEH ionization potentials and VEH π-π^* electronic transition of trans-bis(2-thienyl)ethylene (A), trans-bis (2-furyl)ethylene (B) and trans-bis(2-pyrryl)ethylene (C). Also listed are VEH[20,21] and experimental[19] ionization potentials and band gaps of poly(thienylene vinylene), (PTV)poly(furylene vinylene) (PFV) and poly(pyrrylene vinylene) (PPyV). All the values are in eV.

System	IP(ab initio)	IP(VEH)	IP(expt.)	E_g[a](VEH)	E_g[a](expt.)
A	7.53	8.04		3.29	3.49
B	7.39	7.79		3.81	
C	6.79	7.20		3.86	
PTV		4.89	4.76	1.75	1.64
PFV		4.52	4.52	1.92	1.76
PPyV		4.01		2.11	

[a]E_g in the monomer case is the energy difference between the HOMO and LUMO levels.

increase in going from trans-bis(2-thienyl)ethylene to trans-bis(2-furyl) ethylene, but remains almost constant in going from trans-bis(2-furyl) ethylene to trans-bis(2-pyrryl)ethylene. This fact disagrees with the theoretical and experimental data observed for PTV, PFV and PPyV[17,19-21] since a progressive increase of about 0.2 eV in each step is predicted in going from PTV to PPyV. In contrast, the increase of 0.52 eV is calculated in going from trans-bis(2-thienyl)ethylene to trans-bis(2-furyl)ethylene and of 0.05 eV when passing to trans-bis(2-pyrryl)ethylene. These results seem to suggest that there is not a good theoretical description of the trans-bis(2-furyl)ethylene at this level. This disagreement in determining the electronic properties of compounds containing oxygen atoms was previously observed in VEH calculations of methoxy derivatives of PTV and PPV and their monomers[17], and was assigned to a not very good parameterization of the oxygen atom in the VEH methodology. However, as can be observed from Table II, the differences between the electronic properties calculated for the monomers using both ab initio and VEH methods are similar. The most likely explanation for this discordance seems to be that the results obtained at the ab initio double-zeta level are not enought accurate for a good description of trans-bis(2-furyl)ethylene. We are performing accurate ab initio calculation with more extended basis sets including polarization functions in order to clarify and ascertain this disagreement.

ACKNOWLEDGEMENTS

We thank the Servei d'Informàtica de la Universitat de València for the use of their computing facilities. M.C.P. and R.C. are grateful to the Ministerio de Educación y Ciencia of Spain for a Doctoral Grant. This work has been supported by the Generalitat Valenciana and the DGYCIT Projects PS88-0112 and OP90-0042.

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