

## Electronic Structure of Ethynylthiophenes

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He I and He II photoelectron spectra of all isomeric mono- and diethynylthiophenes were recorded. The electronic structure was analyzed and spectra assigned on the basis of empirical considerations and semiempirical MO calculations. The spectra indicate various interactions taking place between thiophene  $\pi$  and ethynyl  $\pi$  orbitals. The relationship between deduced electronic structure and formation of novel polymer materials is discussed.

### Introduction

Conjugated polymers (CP), i.e., those with delocalized  $\pi$  states, have been studied extensively over the last 2 decades primarily because they are a basis of new materials with technological applications in the fields of electrochemical energy storage (rechargeable batteries), electrochromic devices (displays), photovoltaic cells, and various sensors. The applicability is a direct consequence of their physicochemical properties in particular nonlinear optical response and highly anisotropic electrical conductivity.<sup>1</sup> Two main types of CPs can be distinguished: CPs with degenerate ground state (e.g. polyacetylene) and CPs with nondegenerate ground state (e.g. polythiophene).<sup>2</sup> The mechanism of electrical conduction is different in the two types being based on solitons in the former and on polarons (or bipolarons) in the latter.

Charge carrying excitations (resembling geometrical defects) introduced by doping with suitable electron donors or acceptors are responsible for electrical conductivity. Doping process introduces geometrical and electronic structure changes into the polymer backbone creating new self-localized energy states in the forbidden energy gap between valence and conduction bands. The above mentioned processes are rather complex and remain unclear in detail. The electronic structure of the polymer ground state must play an important role. It is difficult to study the electronic structure of a polymer sample (both experimentally and theoretically) on the account of its wide distribution in molecular sizes, conformational, and isomeric flexibilities. Instead, a carefully prepared monomer or oligomer "building blocks" are selected and the real polymer properties inferred by extrapolation or analogy.<sup>3</sup>

We follow the same approach in this work by attempting to analyze the electronic structure of ethynylthiophenes, "building blocks" for a polymer consisting of (-thiophene-C $\equiv$ C-) repeating units. This new polymer would be a combination of the two CP types previously mentioned.

Relevance of such "building block" studies can be illustrated on the example of polythiophene and its "building block" bithiophene. UV photoelectron spectroscopy (UPS) studies have shown<sup>3,4</sup> that substituted bithiophenes have low inter-ring torsional energy barrier and are prone to significant electronic structure variations as a result. Polythiophenes have the advantage of processability (solubility in organic solvents) but at the cost of poorly defined electronic and molecular structures. A secondary interest in the electronic structure of ethynylthiophenes stems from possible but yet unexplored interactions between thiophene ring and substituents with  $\pi$  moiety.

### Experimental Section

**Ultraviolet Photoelectron Spectroscopy (UPS).** The He I and He II UPS spectra were recorded on a UPG-200 Leybold-Heraeus spectrometer using Ar<sup>+</sup> <sup>2</sup>P<sub>3/2</sub> and <sup>2</sup>P<sub>1/2</sub> calibration lines and achieving resolution of 25–30 meV. The sample inlet temperatures were in the range 20–30 °C. The ionization energies ( $E_i$ ) quoted in Figures 1–3 and Table 1 refer to adiabatic or vertical energies, whichever could be measured more accurately. Strong band overlap and pronounced vibrational fine structure made in some cases accurate measurement of adiabatic  $E_i$  preferable to an unreliable estimate of vertical  $E_i$ s. Narrow range scans (4 eV wide, not presented in Figures 1–3) were used for accurate measurements of vibrational fine structures. Vibrational normal mode assignments given in Table 1 are based on thiophene molecular frequencies<sup>5</sup> and ethyne ion frequencies.<sup>6</sup> UV spectra were also recorded (in hexane and methanol) and the following values measured for lowest energy band maxima, which correspond to  $\pi$ - $\pi^*$  electronic transitions (compound,  $\lambda$ /nm ( $E_g$ /eV): 2-, 256 (4.8); 3-, 250 (5.0); 2,5-, 290 (4.3); 2,4-, 260 (4.8); 3,4-, 222 (5.6); 2,3-, 274 (4.5).

**Theoretical Calculations.** MO eigenvalues and eigenvectors were calculated at the semiempirical level (AM1 and PM3 Hamiltonians) with MOPAC 6.0 package. Experimental bond lengths for thiophene and ethyne moieties were used as initial guess after which all geometries were fully optimized.

**Synthesis.** The synthetic route to ethynylthiophenes is depicted in Scheme 1. The regioselective ethynyl cross-coupling procedures of Sarkar et al.<sup>7</sup> and Neenan et al.<sup>8</sup> were used. Compounds **1a**, **1b**, and **2a** were prepared according to the first procedure, while higher yields were obtained with the latter methodology for compounds **2b–2d**. Compounds **2b–2d** are hitherto unknown. All compounds were characterized by 300-MHz <sup>1</sup>H NMR, mass spectrometry and C,H elemental analysis.

### Results and Discussion

The electronic structure of substituted thiophenes has been studied previously using UPS.<sup>9–11</sup> The main effort was directed toward spectral assignments and unraveling of many interactions between substituent and the five-member ring  $\pi$  orbitals. The picture which emerged from analysis indicated that considerable electronic structure variations occur depending on the substituent's position ( $\alpha$  or  $\beta$ ) and type. Some substituents had  $\pi$  orbitals which could be expected to interact with ring  $\pi$  systems (-CN, -COCH<sub>3</sub>, -NO<sub>2</sub> groups) but their spectral bands were either not sharp or were embedded within a cluster of  $\sigma$  ionizations making monitoring of such  $\pi$ - $\pi$  interactions difficult.

In order to get a better insight into ring-substituent  $\pi$ - $\pi$  interactions we have recorded spectra of two isomeric ethynyl and four isomeric diethynylthiophenes.

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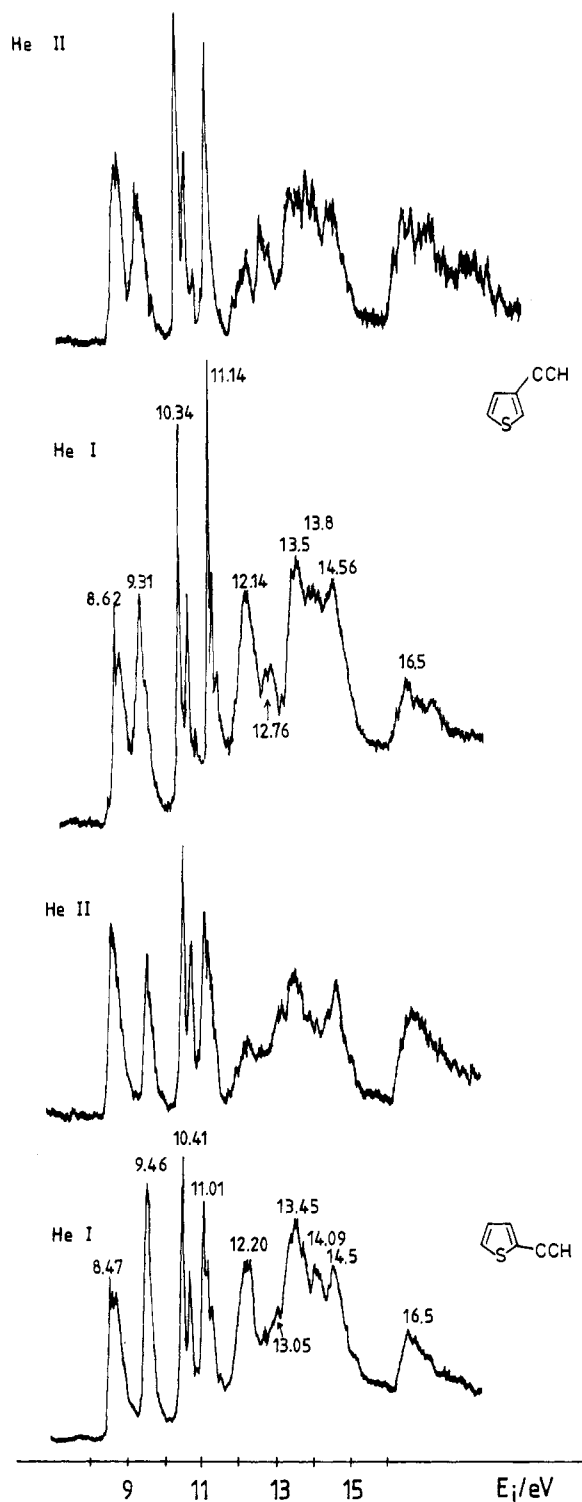


Figure 1. Photoelectron spectra of ethynylthiophenes.

Overall spectral assignments follow readily from correlations with unambiguously assigned UPS of thiophene and ethyne (Figure 4). They indicate that ionic systems  $\tilde{X}$  and  $\tilde{A}$  originate from thiophene  $\pi$  orbitals while systems  $\tilde{B}$ – $\tilde{E}$  ( $\tilde{B}$ – $\tilde{C}$  in the case of monoethynylthiophenes) comprise ethyne  $\pi$  ionizations ( $\pi_{CC}$ ). Vibrational fine structure observed in  $\tilde{B}$ – $\tilde{E}$  systems being similar to ethyne molecular ion further supports the assignment. Ring  $\pi$  ionizations ( $\tilde{X}$  and  $\tilde{A}$ ) show the same He I/He II intensity variations as in thiophene<sup>12</sup> indicating similar character and localization properties of corresponding orbitals.

The most difficult part of the assignment concerns the relative order of  $\pi_{CC}$  ionizations and is due in part to overlapping bands and extensive vibrational fine structure which precludes in some

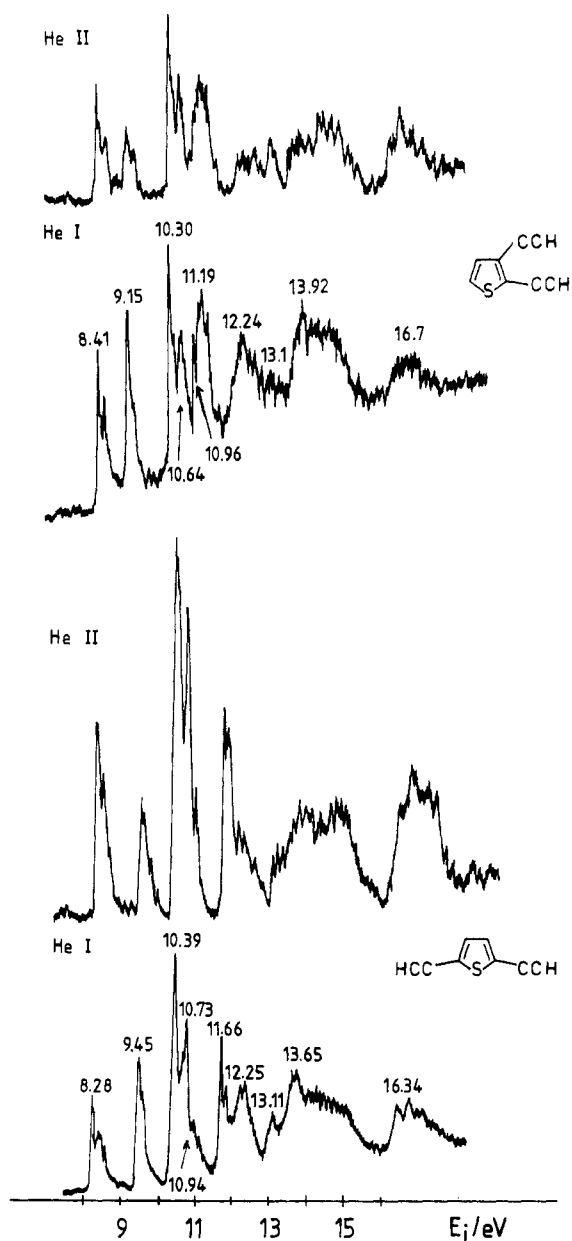


Figure 2. Photoelectron spectra of diethynylthiophenes I.

cases measurements of vertical  $E_{is}$ .  $\pi_{CC}$  ionizations can be classified into two distinct symmetry types by making a reasonable assumption that the molecule is planar: symmetric ( $a'$ ,  $a_1 + b_2$ ) and antisymmetric ( $a''$ ,  $a_2 + b_1$ ). In fact we observed distinct  $\pi_{CC}$  ionizations in all ethynylthiophenes (Figures 1–3) which by itself suggests planarity.  $\pi_{CC}$  orbitals of different symmetry types having different MO characters can be expected to show different photoionization cross-section variations in He I/He II experiments. Furthermore, antisymmetric  $\pi_{CC}$  orbitals can be expected to interact more strongly with ring  $\pi$  orbitals than symmetric ones which will modify geometries of respective ionic states. This will in turn be reflected in different Franck–Condon profiles: sharper for symmetric (more localized) and broader for antisymmetric (more delocalized)  $\pi_{CC}$ . These effects are observable in the spectra of ethynylthiophenes although in some molecules they are more pronounced than in others. In monoethynyl derivatives (Figure 1) symmetric and antisymmetric  $\pi_{CC}$  bands ( $\tilde{B}$  and  $\tilde{C}$ , respectively) have similar shapes and exhibit little He I/He II intensity variation. This is characteristic of weak  $\pi$ – $\pi$  ring–C≡C interactions. However,  $\pi_{CC}$  splitting is slightly larger in 3-ethynyl- than in 2-ethynylthiophene with consequently stronger  $\pi$ – $\pi$  interaction in the former. In diethynylthiophenes  $\pi_{CC}$  splitting is more pronounced and four bands have different

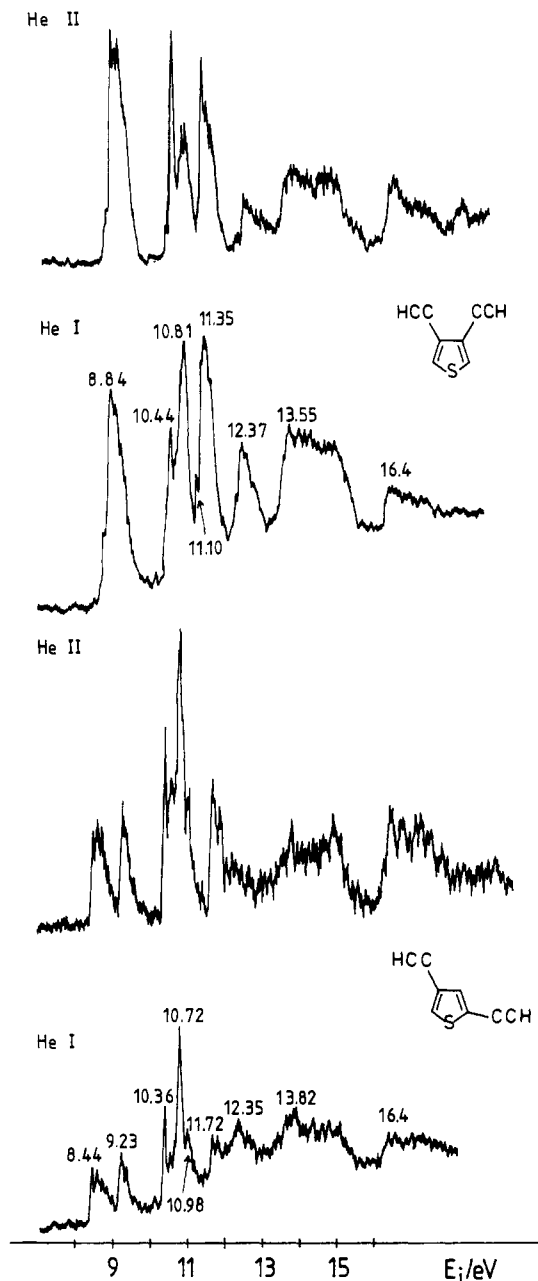
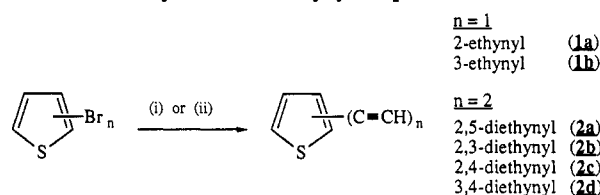


Figure 3. Photoelectron spectra of diethynylthiophenes II.

shapes as well as He I/He II intensities. The effect is best seen in 3,4-ethynylthiophene He I spectrum (Figure 3) where bands at 10.44 and 11.10 eV are sharp while those at 10.81 and 11.35 eV are broad. In spite of some band overlap the interpretation is confirmed when one examines the He II spectrum with its band contours and distinct intensity changes. It would be desirable to confirm the (anti)symmetric character of  $\pi_{CC}$  ionizations independently of Franck–Condon profiles since in some spectra they may be distorted by band overlap.

One way of doing so is to study He I/He II intensity changes. Symmetric (in-plane)  $\pi_{CC}$  orbitals may interact with ring  $\sigma$  orbitals and thus acquire some C 2s character while this is not possible for antisymmetric (out-of-plane)  $\pi_{CC}$  orbitals which will retain C 2p only character. The C 2p atomic subshell photoionization cross-section decreases (on going from He I to He II) from 6.128 to 1.875 Mb, while for C 2s the change is marginal, from 1.23 to 1.17 Mb.<sup>13</sup> The changes for S 3p and H 1s are even more pronounced: 4.33  $\Rightarrow$  0.603 Mb and 1.89  $\Rightarrow$  0.3 Mb, respectively. This provides a convenient way of distinguishing  $\sigma/\pi$  ionizations in general and  $\pi_{CC}(a')$ / $\pi_{CC}(a'')$  ionizations in particular. Any quantification of frequency-dependent intensity changes will,

#### SCHEME 1: Synthesis of Ethynylthiophenes<sup>a</sup>



<sup>a</sup> Reagents and conditions: (i)  $\text{HC}\equiv\text{CC}(\text{Me})_2\text{OH}/(\text{Ph}_3\text{P})_2\text{PdCl}_2(\text{cat.})/\text{CuI}(\text{cat.})/\text{Et}_2\text{NH}$ , then  $\text{MeOH}/\text{KOH}/\text{reflux}$ ; (ii)  $\text{HC}\equiv\text{CTMS}/^1\text{Pr}_2\text{NH}/(\text{PhCN})_2\text{PdCl}_2(\text{cat.})/\text{Ph}_3\text{P}/\text{CuI}(\text{cat.})$ , then  $\text{MeOH}/30^\circ\text{C}$ .

however, be strongly influenced by the level of theory used, i.e. semiempirical or ab initio values of semiempirical parameters, ab initio basis sets, etc. Nonetheless, MOPAC AM1 results are helpful by showing that  $\pi_{CC}(a'')$  orbitals have 10–15% S 3p and 0% C 2s character while  $\pi_{CC}(a')$  orbitals have 5–10% S 3p and 3–4% C 2s character.

The conclusion then is that antisymmetric  $\pi_{CC}$  ionizations should show a decrease in band intensity (relative to symmetric  $\pi_{CC}$ ) on going from He I to He II radiation. Using this criterion, it is easy to complete the assignment of  $\pi_{CC}$  bands; an assignment which is consistent with the one obtained when examining Franck–Condon profiles (Table 1).

The assignment of sulfur lone pair ( $n_S$ ) and totally symmetric ring  $\pi_1$  orbital ionizations also requires analysis of He I/He II intensity variations.  $n_S$  and  $\pi_1$  ionization intensities of thiophene show opposite trends;  $n_S$  decreases while  $\pi_1$  increases on going from He I to He II radiation.<sup>12</sup> We used this empirical observation for assignment of  $n_S$  and  $\pi_1$  ionizations in ethynylthiophene spectra although the effect is more obvious for  $n_S$  than for  $\pi_1$  bands. The relative order of  $n_S$  and  $\pi_1$  ionizations has been recently confirmed by synchrotron photoelectron spectroscopy of thiophene.<sup>14</sup>

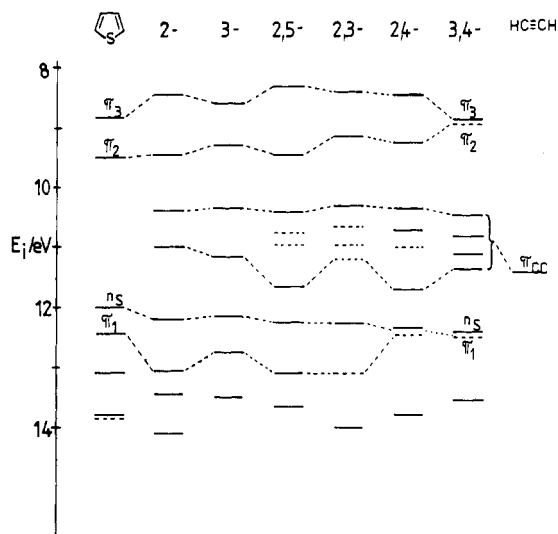
MOPAC calculations support the empirically derived assignment of  $\bar{X}$  and  $\bar{A}$  systems as arising from ring  $\pi_3$  and  $\pi_2$  orbitals and  $\bar{B}$ – $\bar{E}$  systems representing  $\pi_{CC}$  ionizations. AM1 calculations are in slightly better agreement with empirical assignment: for instance the wrong order of  $\pi_3$  and  $\pi_2$  ionizations is predicted only in 3,4-derivative while PM3 calculations give the wrong order in 3,4-, 2,3-, and 3-derivatives.  $\pi_{CC}$  sequences are also different in empirical, AM1, and PM3 assignments. In this instance however ionizations span a narrow  $E_i$  range, thus making any Koopmans' approximation based assignment unreliable. We believe empirical assignment to be more reliable (Table 1) which is why the MO eigenvalues have not been reported explicitly. Another common feature of the calculations is that they place  $n_S$  at lower  $E_i$  than the lowest  $\pi_{CC}$  ionization (in 2,5-derivative) which is manifestly wrong. Finally we must add that since the assignment of the  $\pi_1$  ionization band in thiophene<sup>14</sup> has not been unambiguously confirmed, it makes our  $\pi_1$  assignments only tentative.

#### Relation to Polymer Properties

The electrical conductivity of CPs is governed jointly by several important electronic structure parameters: ionization energy and electron affinity (related to ease of doping), widths of HOMO and LUMO solid state bands (influence mobility of charge carriers), and bandgap ( $E_g$ , determines intrinsic electrical conductivity). In some CPs electron transport is almost "metallic" (polyacetylene) but in most it can be achieved via "electron tunneling" between localized electronic states which are close in energy or space. To achieve this condition the electronic structure of "building blocks" should (among other requirements) have good conjugation allowing spread of charge-carrying states (solitons, polarons) over several monomer units. The ethynylthiophenes with strongest ring– $\text{C}\equiv\text{C}$   $\pi$  interactions would satisfy this criterion. Figure 4 shows that 2,5- and 3,4-ethynylthiophenes

**TABLE 1: Ionization Energies ( $E_i$ /eV), Vibrational Fine Structure, and Assignments of Photoelectron Spectra of Ethynylthiophenes**

compound	state	$E_i$ /eV	MO (symmetry)	$\tilde{\nu}(\approx 50)/\text{cm}^{-1}$	mode
2-	$\tilde{X}$	8.47	$\pi_3$ ( $a''$ )	650	ring deform
	$\tilde{A}$	9.46	$\pi_2$ ( $a''$ )	810	ring stretch
	$\tilde{B}$	10.41	$\pi_{CC}$ ( $a'$ )	2020	CC stretch
	$\tilde{C}$	11.01	$\pi_{CC}(a'')$	1050	deform
	$\tilde{D}$	12.20	$n_S$ ( $a'$ )		
3-	$\tilde{X}$	13.05	$\pi_1$ ( $a''$ )		
	$\tilde{A}$	8.62	$\pi_3$ ( $a''$ )		
	$\tilde{B}$	9.31	$\pi_2$ ( $a''$ )	1940	CC-stretch
		10.34	$\pi_{CC}$ ( $a'$ )	480	bending
				810	deform
2,5-	$\tilde{C}$	11.14	$\pi_{CC}$ ( $a''$ )		
	$\tilde{D}$	12.14	$n_S$ ( $a'$ )		
	$\tilde{E}$	12.76	$\pi_1(a'')$		
	$\tilde{X}$	8.28	$\pi_3$ ( $a_2$ )	1290	ring stretch
	$\tilde{A}$	9.45	$\pi_2$ ( $b_1$ )		
2,3-	$\tilde{B}$	10.39, 10.73, 10.94	$\pi_{CC}(a_1, a_2, b_2)$	2660	CH-stretch
				1130	deform
	$\tilde{E}$	11.66	$\pi_{CC}$ ( $b_1$ )		
	$\tilde{F}$	12.25	$n_S$ ( $a_1$ )		
	$\tilde{G}$	13.11	$\pi_1$ ( $b_1$ )		
2,4-	$\tilde{X}$	8.41	$\pi_3$ ( $a''$ )	1290	ring stretch
	$\tilde{A}$	9.15	$\pi_2$ ( $a''$ )		
	$\tilde{B}$	10.30, 10.64	$\pi_{CC}$ ( $a' + a''$ )	1210	deform
	$\tilde{D}$	10.96, 11.19	$\pi_{CC}$ ( $a' + a''$ )	1530	CC-stretch
	$\tilde{E}$	12.24, 13.1	$n_S + \pi_1$ ( $a' + a''$ )		
3,4-	$\tilde{X}$	8.44	$\pi_3$ ( $a''$ )		
	$\tilde{A}$	9.23	$\pi_2$ ( $a''$ )		
	$\tilde{B}$	10.36, 10.72, 10.98	$\pi_{CC}$ ( $a' + a' + a''$ )	1050	deform
	$\tilde{E}$	11.72	$\pi_{CC}$ ( $a''$ )		
	$\tilde{F}$	12.35	$n_S + \pi_1$ ( $a' + a''$ )		
3,4-	$\tilde{X}$	8.84	$\pi_3 + \pi_2$ ( $a_2 + b_1$ )	1130	in-plane CH deform
	$\tilde{A}$	10.44	$\pi_{CC}$ ( $b_2$ )	1050	deform
	$\tilde{B}$	10.81	$\pi_{CC}$ ( $a_2$ )		
	$\tilde{D}$	11.10	$\pi_{CC}$ ( $a_1$ )	880	deform
	$\tilde{E}$	11.35	$\pi_{CC}$ ( $b_1$ )		
	$\tilde{F}$	12.37	$n_S + \pi_1$ ( $a_1 + b_1$ )		

**Figure 4.** Energy level diagram for ethynylthiophenes (based on Koopmans' approximation).

are suitable models of corresponding poly(ethynylthiophenes). The 2,5-derivative can be expected to have the smallest bandgap ( $E_g$ ) (see Experimental Section). The 3,4-derivative is an unusual "building block" since when polymerized it would form a two-dimensional structure with high fractal dimension as opposed to a nominally one-dimensional (low fractal dimension) 2,5-derivative. Additional experimental work is of course required to prove this hypothesis and also to determine another

important CP parameter: forbidden energy gap between valence and conduction bands. In electron spectroscopic terms electron attachment energy should be measured (LUMO energy).

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