Determination of the Electronic Structure of Oligo(2-thienyl ketones) and Extrapolation to Poly(thienylene ketone)

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Gas-phase ionization and attachment energy (IE and AE) values of the first few oligomers of 2-thienyl ketone have been determined experimentally. The assignments of the ultraviolet photoelectron spectra agree with the results of theoretical HF/6-31G** calculations. The constant value of the HOMO energy allows extrapolation to the corresponding polymer. A combined analysis of the AE values, the electrochemical reduction data, and the results of ab initio 6-31G** and semiempirical calculations allows one to obtain the LUMO energy for the oligomers and for an ideal gas-phase poly(thienylene ketone). The narrow valence band and the high IE value of the polymer are not propitious to p-doping. On the other hand, the high electron affinity of the oligomers and the polymer, the reversibility of the oligomer electrochemical reduction, and the large conduction band of the polymer indicate that the oligomers, and likely the polymer, could give rise to n-doped materials having high electrical conductivity.

Introduction

Polymers deriving from aromatic and heteroaromatic compounds such as benzene, thiophene, and pyrrole increase their electrical conductivity by several orders of magnitude when properly p- or n-doped. The insertion of ring substituents improves the polymer properties (solubility in common organic solvents, processability, electrical conductivity) and provides an opportunity for modulating these properties by modifying the stereoelectronic effects of substituents.[1−6]

Most reported work deals with p-doped polythiophenes because of their chemical stability both in their neutral and oxidized states, while scant information is available on the corresponding n-doped compounds, probably because of the smaller increase in electrical conductivity upon reduction than upon oxidation.[7]

The introduction of electron-withdrawing groups such as carbonyl,[8] dicyanomethylene,[9] or 1,3-dioxalane[10] to bridge the 4,4′-position of a bithienyl precursor allowed the preparation of polymers having a significantly reduced band gap with respect to poly(bithiophene). In particular, in the case of cyclopenta-[2,1-*b*:3′,4′-*b*′]dithiophen-4-one such reduction results from a strong stabilization of the LUMO, while the carbonyl group seems to have only a moderate effect on the energy level of the HOMO of the monomer and the polymer.[11,13]

The chemical synthesis of poly(3-alkylthienylene ketones) has been recently reported, and the possibility than they could give rise to n-doped conducting polymers has been advanced.[11] Later the same authors reported, however, that the voltammetric reduction of poly(3-alkylthienylene ketones) was irreversible and that, therefore, the compounds were useless for practical applications.[12]

An analysis of literature data indicates that the determination of the physicochemical properties of raw polymers is highly uncertain because of the nonuniformity and low level of reproducibility of the materials and the presence of impurities. Oligomers, on the other hand, can be prepared with high purity, and their properties, determined experimentally and computationally with high accuracy, can be extrapolated to the polymer. In addition, oligomers can be used successfully in molecular devices[13] even though the corresponding polymer is too impure to obtain satisfactory results.

We have undertaken a multidisciplinary study of methylthienyl ketone (THCO), of dithienyl ketone (2THCO), and of the longer oligomers 3THCO and 4THCO (see Chart 1) to determine with accuracy and reproducibility their geometric and electronic structures and to verify the possibility that such oligomers (and the polymer) could be precursors of materials possessing high electrical conductivity.

The geometric parameters, the most probable conformation, and the analysis of the steric and electrostatic intramolecular interactions for the *n*THCO ($n = 1-4$) derivatives have been

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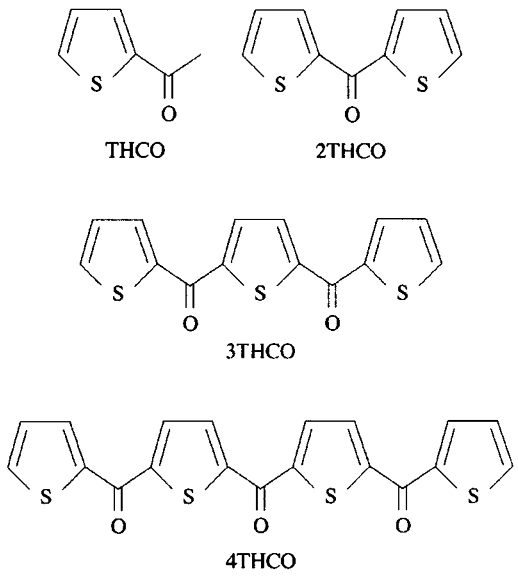
CHART 1



determined[14] by ab initio calculations at the HF/6-31G** (or higher) level, keeping the thiophene rings planar for $n \geq 2$. The most probable conformation is rodlike (prevailing S,O-*cis* orientation) with a ring deviation from the main molecular plane of about 20°.

In this paper we present the analysis of the electronic structure of these oligomers using thiophene (TH) and acetone as reference compounds. Ionization energy (IE) and attachment energy (AE, which is the negative of the electron affinity) values were obtained by ultraviolet photoelectron (UP) and electron transmission (ET) spectroscopies, respectively, and the electrochemical reduction (E_{cp}) potentials by cyclic voltammetry (CV). The assignment of the spectral features to the corresponding MO's has been assisted by ab initio and semiempirical calculations.

Experimental Section

Photoelectron (PE) Spectra. The He I spectra were recorded on a Perkin-Elmer PS-18 photoelectron spectrometer connected to a Datalab DL4000 signal analysis system. The bands, calibrated against rare-gas lines, were located using the position of their maxima, which were taken as corresponding to the vertical IE values. The accuracy of the IE values was estimated to be ±0.05 eV for peak maxima and 0.1 eV for shoulders. The assignment of PE spectra is based on the composite-molecule approach and the substituent effect, using as reference compounds thiophene (TH) and acetone.

Electron Transmission (ET) Spectra. Our electron transmission apparatus is in the format devised by Sanche and Schulz[15] and has been previously described.[16] To enhance the visibility of the sharp resonance structures, the impact energy of the electron beam is modulated with a small ac voltage, and the derivative of the electron current transmitted through the gas sample is measured directly by a synchronous lock-in amplifier. The present spectra have been obtained by using the apparatus in the "high-rejection" mode,[17] unless otherwise stated, and are, therefore, related to the nearly total scattering cross section. The electron beam resolution was about 50 meV (fwhm). The energy scales were calibrated with reference to the $(1s^1 2s^2)^2S$ anion state of He. The estimated accuracy is ±0.05 or ±0.1 eV, depending on the number of decimal digits reported.

Cyclic Voltammetry (CV). Electrochemical measurements were performed in DMF with 0.1 M tetrabutylammonium perchlorate (TBAP) as background electrolyte; DMF was dried by storage for at least 1 week over molecular sieves and distilled at 30 °C under vacuum immediately before use. A compartmented cell was employed: the reference electrode was silver wire, and the counter electrode was a platinum sheet. The working electrode was made from a gold wire sealed inside a glass tube so as to obtain a disk electrode with an area of 7.8×10^{-3} cm^2. Before each run the gold surface was amalgamated with Hg. Azobenzene was used as internal standard for the peak current and potential.[18] All potentials are vs SCE.

Calculations. The valence orbital energy and localization properties for TH, THCO, 2THCO, 3THCO, 4THCO, and acetone were obtained at the HF/6-31G** level using the Gaussian 94[19] series of programs and allowing complete relaxation of all internal parameters. The conformations to be optimized were chosen on the basis of previous[14] HF/6-31G** frozen ring calculations. Namely, S,O-*cis* (*c*) and S,O-*trans* (*t*) for THCO, *cc*, *ct*, and *tt* for 2THCO, the four lowermost (two *cc*-*cc* and two *ct*-*cc*) conformations for 3THCO, and the "all-cis" conformation for 4THCO. On the basis of literature results,[20] acetone was optimized in the keto form with the methyl groups in an eclipsed position and a C−H bond in the C−C−C plane (C_{2v} symmetry). The vertical ionization energy value related to the HOMO of acetone was computed with the ΔSCF and ΔMP2 procedures at the MP2/6-31G** optimized geometry. In the other cases, the filled and empty orbital energies (HF/6-31G**) for the neutral ground state were compared with experimental IE and AE values using Koopmans' theorem (KT) approximation.[21]

The samples were prepared according to literature methods[22−24] except for THCO which was commercially available.

Results and Discussion

Filled Orbitals. The He I UP spectra of compounds 1−4 are shown in Figure 1. The IE values lower than 11 eV are presented in the partial energy level diagrams of Figure 2 together with the relevant data for the reference compounds thiophene[25,26] and acetone[27] and the corresponding computed data (HF/6-31G**). The number of ionization events attributed to the experimental bands (see below) is reported in parentheses.

The low IE region (IE < 11.5 eV) of the spectrum of thiophene exhibits two bands of similar intensity deriving from electron ejection from the π_{1a2} (8.88 eV) and π_{2b1} (9.52 eV) MO's,[25,26] while, in the corresponding region of the spectrum of acetone, there is an isolated band ascribed[27] to the lone pair orbital of the carbonyl group (n_{CO}, 9.70 eV). In the KT approximation[21] the HF/6-31G** calculations (8.97 and 9.26 eV) reproduce the experimental π-IE values for TH, although the energy splitting (0.64 eV experimentally) is underestimated (0.29 eV). The experimental geometry of TH[28] is better reproduced by MP2/6-31G** than HF/6-31G** calculations.[29] When the optimized MP2 geometry is used in the HF calculations, the agreement between the π-energy levels ($\pi_{1a2} = 8.71$, $\pi_{2b1} = 9.30$, $\Delta IE = 0.59$ eV) and the experimental data improves.

On the other hand, the n_{CO} KT value for acetone depends slightly on the molecular geometry (MP2, HF, or experimentally determined[30−33]) and the computed IE value (11.1 ± 0.05 eV) is about 1.4 eV higher than the experimental one. However, when the ΔMP2 procedure between the neutral and the cation states is used, the n_{CO} IE value is nicely reproduced ($IE_{exp} = 9.70$, $IE_{\Delta MP2} = 9.73$ eV). The analysis of the electron correlation

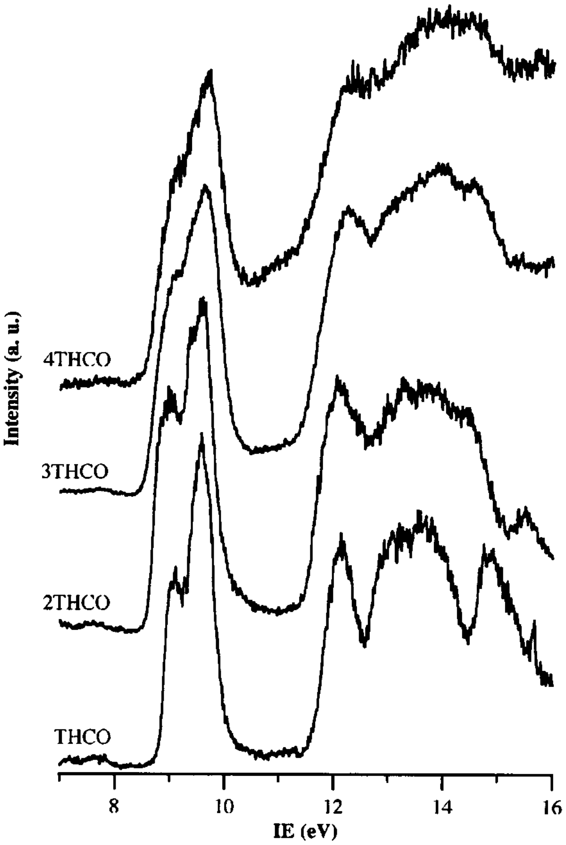


Figure 1. He I UV-photoelectron spectra for compounds THCO, 2THCO, 3THCO, and 4THCO.

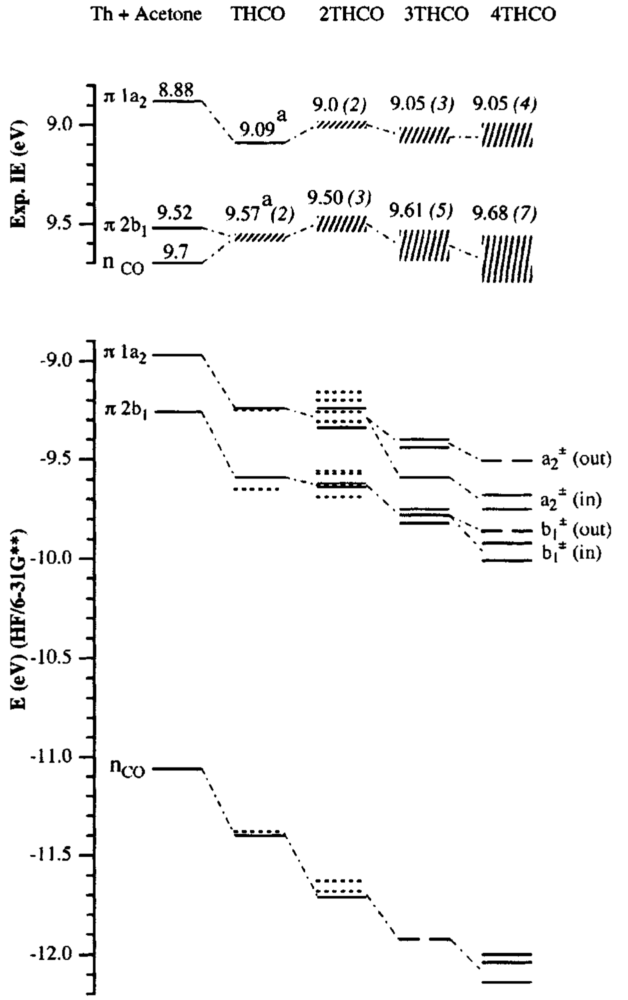


Figure 2. Top part: correlation of experimental π and n_{CO} ionization energies (IE's) for thiophene (TH), acetone, and thienyl ketones *n*THCO ($n = 1-4$). Bottom part: Correlation of the corresponding HF/6-31G** energies. The values quoted refer to the most stable (S,O-*cis*) conformers, and the dotted levels, to rotamers containing the heteroatoms in the S,O-*trans* orientation. For values with superscript a, the corresponding experimental values for 2-thiophenecarboxyaldehyde are 9.37 and 9.87 eV.[26]

($\Delta E_{corr} = \Delta MP2 - \Delta SCF = 1.5$ eV) and relaxation ($E_{relax} = KT - \Delta SCF = 2.9$ eV) energy associated with the first ionization process of acetone indicates that the large n_{CO} IE value computed in the KT approximation derives from the large relaxation energy which accompanies electron extraction from an MO mainly localized at a "hard" heteroatom.[34] On the other hand, the relaxation energy accompanying ionization from a delocalized π-MO of TH is comparable to the decrease of correlation energy, so that the experimental π-IE values are reproduced in the KT approximation.[34]

The spectrum of THCO can be considered to derive from those of TH and acetone. In the most probable (planar, S,O-*cis*) conformation of THCO, the n_{CO} and the π-ring orbitals cannot interact for symmetry reasons. We, therefore, expect three bands in the energy region below 11 eV of the UP spectrum of THCO. In fact, only two partially resolved bands centered at 9.09 and 9.57 eV are observed. Their intensity ratio, about 1:2, indicates that the π_{2b1} and n_{CO} ionizations are accidentally degenerate (see Figures 1 and 2).[35] The π-MO's are stabilized with respect to the corresponding orbitals of TH by the inductive effect of the acetyl group, while the n_{CO} MO is destabilized in THCO with respect to acetone by through-bond and through-space[36] mixing with σ_{ring} orbitals mainly localized at the sulfur atom, in agreement with the short S---O contact.[14] There is no evidence in the spectrum for the presence of two rotamers. The presence of the S,O-*trans* rotamer however, cannot be excluded because the calculations predict IE values nearly coincident with those of the most stable S,O-*cis* rotamer[14] (see Figure 2). It is to be noticed that the two rotamers also have almost indistinguishable ^{1}H NMR spectra.[37]

On passage from THCO to the higher oligomers, no new bands appear in the low-IE region of the UP spectra. At variance, in dithiophene the splitting between the MO's resulting from the HOMO of the monomer is of the order of 1.8 eV and increases with chain length.[38,39] The two bands observed around 9 and 9.6 eV in the present series (see Figures 1 and 2) become increasingly broader, indicating a slight interaction among the thienocarbonyl units. The relative intensity of the two partially overlapped bands goes from 1:2 (THCO) to approximately 2:3 (2THCO), 3:5 (3THCO), and 4:7 (4THCO), in accordance with the number of π_{1a2}, and π_{2b1} plus n_{CO} MO's in the various oligomers (see the upper part of Figure 2) The results of the calculations, shown in the lower part of the same figure, confirm this assignment when the neglect by KT calculations of the large relaxation energy accompanying the n_{CO} ionizations is taken into account.

Part of the observed band broadening could derive from the presence in the analyzed samples of conformers containing the heteroatoms in the S,O-*trans* orientation. However, their relative intensity with respect to the most stable cis conformers is predicted by the calculations to be quite small (THCO, $c = 89$, $t = 11\%$; 2THCO, $cc = 84$, $ct = 15.1$, $tt = 0.9\%$), or when the conformers have comparable energy as for the *cc*-*cc* and *ct*-*cc* species for 3THCO,[14] corresponding ionizations have quite close values. In both cases, therefore, conformers different from the "all-cis" one are not expected to contribute significantly to the band envelope shape.

The small conjugation among the occupied π-orbitals of the thienocarbonyl units is clearly indicated also by the presence of (quasi) nodes at the carbonyl carbon atoms in the π-MO's. The eigenvector analysis of the filled π-orbitals of 4THCO can be used as an example to understand the origin of the observed small energy splitting and peak broadening. The uppermost eight π-MO's can be divided into two sets of a_2 and b_1 parentage, respectively, each contributing to one of the two maxima present in the low-energy region of the spectrum (see Figure 2). The π-MO's are mainly localized at two rings only. The combinations resulting from group orbitals localized at the outer rings lie at higher energy than those localized at the inner ones, because of a larger stabilizing inductive effect from the carbonyl groups experienced by the latter. Finally, the in-phase combinations at the inner rings are slightly (0.09 eV) destabilized with respect to the corresponding out-of-phase combinations due to a small mixing with the π_{CO} and σ_{SC2} orbitals.

At variance with oligothiophenes[38,39] and oligofurans,[40] the valence band of oligo(thienyl ketones) (and, therefore, of the corresponding polymer) is rather narrow and the ionization threshold does not move toward lower energy values with increasing length of the chain but remains at nearly 9.0 eV. These oligomers, therefore lack the basic properties to acquire high electrical conductivity upon p-doping.

Empty Orbitals. Whereas the first IE value remains constant when the oligomer length increases, the energy of the maximum of the band related to the first $\pi^* \leftarrow \pi$ optical transition decreases in the series THCO 4.40 eV ($\lambda_{max} = 282$ nm)[41] > 2THCO 3.95 eV ($\lambda_{max} = 313$ nm)[41] > 4THCO 3.61 eV ($\lambda_{max} = 344$ nm).[42] This trend suggests that the LUMO energy decreases significantly in the same direction and, therefore, also the occurrence of large interactions among the π^* orbitals of the rings and the carbonyl groups, at variance with the behavior of the corresponding filled π-MO's. On that account, we have determined the gas-phase AE values by means of ETS and the reduction potentials in solution by means of CV to ascertain whether the present oligomers could be precursors of n-doped materials.

The ET spectra of compounds THCO, 2THCO, and 3THCO are shown in Figure 3, and the AE values are reported in the partial energy level diagram of Figure 4 together with those of the reference molecules TH[43] and acetone[44] and the LUMO energy values extrapolated from electrochemical data; see below. Table 1 collects the experimental AE values and the corresponding computed data for acetone, TH, and the most stable conformer of the nTHCO ($n = 1-4$) derivatives. The MINDO/3 values, for all the compounds, and the LCBO[45,46] values for the nTHCO ($n = 1-3$) derivatives are also included in Table 1 because these semiempirical methods have proved to closely reproduce, in Koopmans' approximation, the experimental AE values for oligothiophenes.[38,39] In addition, the most stable conformation of the thienyl ketones is planar at the MINDO/3 level, making the eigenvector analysis of π-MO's quite simple.

The ET spectrum of TH exhibits two resonances, ascribed[43] to electron capture into the π^*-MO's, at 1.15 ($3b_1$) and 2.63 ($2a_2$) eV, while the resonance related to the π^*_{CO} orbital of acetone occurs at 1.31 eV.[44] The corresponding group orbitals of THCO are expected to mix strongly because of energy proximity and large wave function coefficients at the interacting atoms. As a consequence of the strong $\pi^*_{ring}-\pi^*_{CO}$ mesomeric interaction, the separation between the orbitals of $2a_2$ and $3b_1$ parentage in THCO is expected to increase with respect to the reference compounds. In addition, the inductive electron-attracting effect of the carbonyl group stabilizes the ring π^*-MO's. However, in the spectrum of THCO there are only two resonances, at 1.68 and 2.93 eV, suggesting that electron capture into the LUMO, deriving from ring π^*_{3b1}/π^*_{CO} mixing, occurs at an energy close or lower than 0 eV. In agreement with this hypothesis, an analogous strong π^*_{ring}/π^*_{CO} mixing causes the first anion state of benzophenone and benzaldehyde to be slightly stable.[47] It is to be noticed that while π-conjugation and the inductive effect of the carbonyl group perturb the energy of the HOMO in opposite directions, the two effects are concomitant in stabilizing the LUMO.

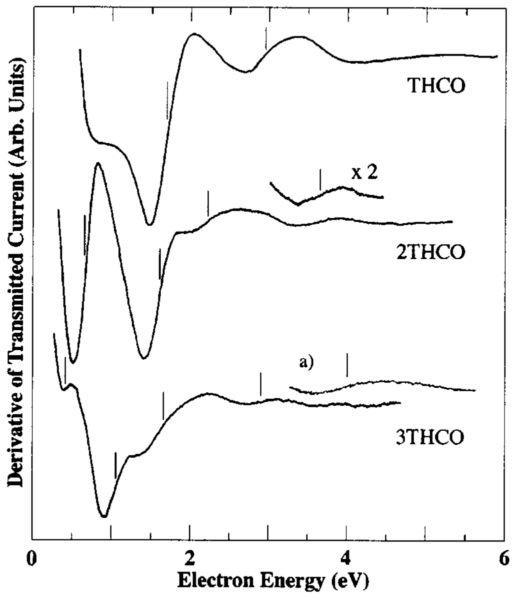


Figure 3. Derivative of the transmitted electron current for the gas-phase thienyl ketones THCO, 2THCO, and 3THCO (see Chart 1).

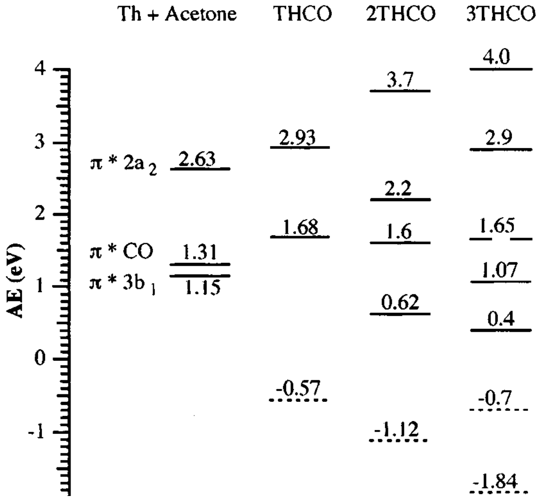


Figure 4. Full lines: Correlation between experimental π^*-AE values for acetone, TH, THCO, 2THCO, and 3THCO (see Chart 1). Dotted lines: Extrapolated values from the E_{cp}/LUMO energy correlation (see text and Table 2).

The HF/6-31G** calculations predict the lowest σ^*_{SC2} orbital of TH (in agreement with MS-Xα calculations[43]) and THCO to lie below the highest π^* MO (see Table 1). However, as expected,[38,39,43,48] the corresponding signal is not detected in the ET spectra, probably being obscured by the more intense π^* resonances.

We can analyze the spectrum of 2THCO by first considering that the π^*_{2a2} and π^*_{3b1} group orbitals generate the in-phase

TABLE 1: Experimental AE Values and Computed Energy Levels (eV) for Acetone, Thiophene (TH), and Thienyl Ketones (*n*THCO, *n* = 1−4)

	expt	HF/6-31G**	MINDO/3	LCBO
Acetone	1.31[a]	4.60 π^*_{CO}	1.10	
TH[b]	2.63	6.45 $\pi^*_{2a_2}$ (5.15 $\sigma^*_{\mathrm{SC}_2}$)	2.84	
	1.15	3.74 $\pi^*_{3b_1}$	1.29	
THCO	2.93	7.07 a_2[c] (5.19 $\sigma^*_{\mathrm{SC}_2}$)	2.69	2.92
	1.68	5.14 π^*	1.82	1.66
	<0.0	2.27 b_1[c]	0.20	−0.67
2THCO	3.7	7.76 a_2^+	3.30	3.51
	2.2	5.75 a_2^- (5.42 $\sigma^+ + \pi$)	2.52	2.2[d]
	1.6	5.07 $\pi + \sigma^+$ (4.99 σ^-)	2.07	1.72
	0.62	3.24 b_1^-	0.89	0.62[d]
	<0.0	1.76 b_1^+	−0.10	−1.32
3THCO	4.0[e]	7.26	3.26	3.97
	2.9	7.08 (4 σ^* MO's)	3.12	2.92
	1.65	5.45	2.41	2.2
	1.65	5.34 $\pi + \sigma$[f] (5.04 σ, 4.88 σ)	2.20	1.74
	1.07	4.45	1.60	1.66
	0.4	3.01 b_1	0.76	0.62
	<0.0	2.11 b_1	0.16	−0.67
	<0.0	1.13 b_1	−0.52	−1.79
4THCO			3.22	
			3.16	
			3.00	
		5.37	2.34	
		5.23 (3 σ^* MO's)	2.24	
		4.62	1.83	
		4.10	1.36	
		2.86 b_1	0.68	
		2.30 b_1	0.28	
		1.45 b_1	−0.27	
		0.76 b_1	−0.70	

[a] From ref 44. [b] From ref 43. [c] See ref 35. [d] Experimental AE values used as Coulomb integrals in the LCBO calculations; see text. [e] Resonance observed in the "open spectra" related to the back-scattering cross section.[17] [f] Average value of two MO's of very similar parentage computed at 5.49 and 5.18 eV.

(a_2^+ and b_1^+) and out-of-phase (a_2^- and b_1^-) combinations stabilized (0.4−0.5 eV) with respect to the corresponding orbitals of TH by the inductive effect of the carbonyl group. Only the in-phase combinations can interact with the π^*_{CO} orbital, with consequent destabilization (a_2) and stabilization (b_1), respectively. As observed for THCO, the feature related to the LUMO is not present in the spectrum. This analysis is in agreement with the theoretical results; see Table 1. The HF calculations predict, in addition, that the σ^*_{SC2} orbitals give rise to the in-phase (σ^+) and out-of-phase (σ^-) combinations and that the former mixes with the central π^* orbital with which it is nearly degenerate. The resulting energy splitting, however, is quite small (see Table 1) owing to the small deviation from planarity[14] (about 20°) and the small σ/π mixing.

The agreement between experimental and computed data for TH, THCO, and 2THCO is quite satisfactory as far as the nature and the ordering of the π^*-MO's are concerned. This allows one to assign the ET spectrum of 3THCO as shown in Table 1. In particular, only five π^*-resonances out of the eight expected are present. The LUMO and the second LUMO likely give rise to stable anions not observed by ETS, the computed orbital energies being smaller than that of the LUMO for THCO. In addition, the third experimentally observed resonance (fwhm $\approx$ 0.8 eV) appears to correspond to two computed energy levels.

The low vapor pressure of 4THCO does not allow its ET spectrum to be obtained. The computed π^*-MO energies are included in Table 1. The strong σ/π mixing renders recognition of the highermost π^*-MO's at the HF/6-31G** level rather difficult.

TABLE 2: LUMO Energies (eV) for Oligo(thienyl ketones) (*n*THCO) from Theoretical Calculations and E_{cp} Values

	HF/6-31G**	MINDO/3	LCBO (from Table 1)	E_{cp} (see text)	E_{cp} (oligothiophenes[a])
THCO	−0.32	−0.45	−0.67	−0.57	0.0 (2TH)
2THCO	−0.69	−0.84	−1.32	−1.12	−0.5 (3TH)
3THCO	−1.16	−1.39	−1.79	−1.84	−0.74 (4TH)
	−0.44[b]	−0.51[b]	−0.67[b]	(−0.7)[b,c]	
4THCO	−1.43	−1.62		−2.09	
polymer				(−2.67)[d]	−1.1 (poly-TH)

[a] From ref 39. [b] 2nd LUMO. [c] Extrapolated value from the correlations between the theoretical and the E_{cp} data. [d] Extrapolated value; see text.

Unfortunately, the resonance related to the LUMO is never present in the spectra because of the high electron affinity of the present compounds. For an evaluation of its energy, we have therefore used an LCBO approach which is a Hückel-type calculation with internal parametrization able to reproduce with good accuracy AE values for related molecules. When the LCBO method is applied to empty orbitals, all the filled MO's are neglected.[46] In the present case the AE values of THCO, 2THCO, and 3THCO have been computed taking as Coulomb integrals the experimental AE values of the noninteracting a_2^- (2.2 eV) and b_1^- (0.62 eV) orbitals in 2THCO and a value (1.1 eV) intermediate between the π^*_{CO} AE measured in acetone and formaldehyde.[49] The interaction parameter, β, has been chosen to reproduce the THCO data taking into account the different values of the $2a_2$ and $3b_1$ wave function coefficients at the substituted carbon atom of TH obtained by semiempirical calculations. The LCBO data reported in the last column of Table 1 are in good agreement with available experimental AE values. The predicted LUMO energies, −1.79 (3THCO), −1.32 (2THCO), and −0.67 (THCO) eV, might be too low because they neglect interaction with the filled MO's,[46] which is expected to influence mainly the lowermost empty orbitals.

Different and probably less accurate estimations of the LUMO AE values are provided by the correlation of the HF/6-31G** and MINDO/3 energy levels with the experimental AE data. The extrapolated LUMO AE values are reported in columns 2 and 3 of Table 2. All the values are negative, confirming that stable anions are formed in the lowermost electron capture processes.

It can be observed that the energy of the LUMO sharply decreases with increasing oligomer length and that, at the same time, the number of π^*-levels lying below the first σ^*-level increases in the order 2THCO (2) < 3THCO (4) < 4THCO (6). That is, on increase of the chain length, the conduction band expands toward higher electron affinity values and includes an increasing number of closely spaced energy levels (mainly of π^*_{b1} parentage) indicating that ketothienyl chains have propitious properties to be n-doped. In agreement, eigenvector analysis shows that the conjugation among empty orbitals extends throughout the rings and the carbonyl groups.

The localization properties of the HOMO and the LUMO of 4THCO obtained at the MINDO/3 level are shown in Chart 2. The sketch of the HOMO clearly shows the interruption of conjugation at every carbonyl carbon atom, whereas an extra electron in the LUMO is delocalized along all the chain. For the corresponding poly-THCO electrical conductivity along the chain does not seem to be favored by quinoid structure formation upon doping. On the other hand, it has been shown[50] that terthiophene radical cations dimerize easily in solution to give rise to face-to-face π-dimers which have spectroscopic and ESR properties analogous to those reported for bipolarons. Such

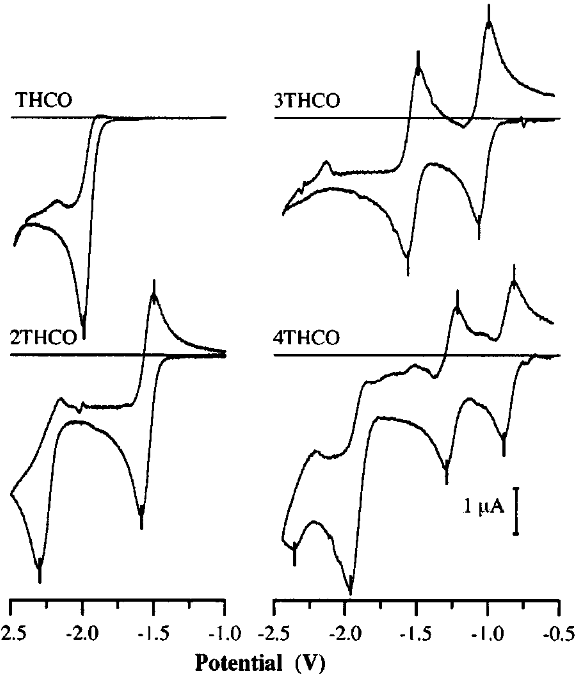
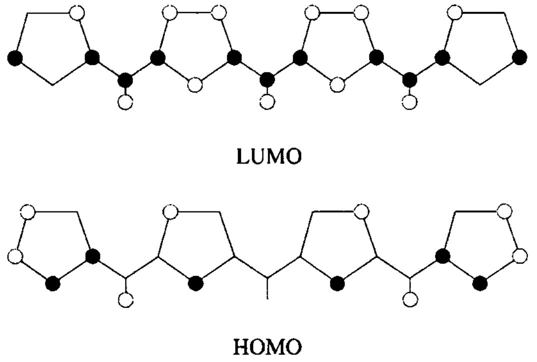


Figure 5. Cathodic CV pattern (at 100 mV s^{-1}) for 1.8, 1.9, 1.4, and 1.2 mM *n*THCO ($n = 1-4$) derivatives in DMF/0.1 M TBAP at a stationary amalgamated Au electrode, using as reference electrode a silver wire. All potentials are vs SCE.

CHART 2



interactions should lead to the formation of π-stacks in the solid phase where intermolecular interactions are even stronger.[50] Poly-THCO possesss suitable geometrical requirements to form face-to-face stacks.[14] It has been shown[13] that the electrical conductivity of sexithiophenes is 120 times larger along the stacking axis than along the oligomer chains. Therefore, on the basis of their geometrical and electronic properties, the n-doped poly-THCO are expected to be suitable candidates for molecular devices.

Cyclic Voltammetry. The cathodic CV patterns at the gold electrode for the various *n*THCO derivatives are presented in Figure 5. The relevant data therefrom are collected in Table 3, where E_{cp} and E_{ap} are the cathodic and associated anodic peak potentials, respectively, and *n* is the number of exchanged electrons.

The cathodic CV pattern of THCO shows the presence of a bielectronic irreversible process ($E_{cp} = -1.966$ V vs SCE). In aprotic solvents the reduction of aldehydes and ketones proceeds through the formation of a radical anion, which gives rise to the dianion by further reduction.[51] Fast chemical reactions of this highly reactive species with impurities present in the solution or with mercury could account for the absence of the anodic wave associated with the reduction. The anodic wave does, however, appear at higher scan rates. The uptake of a second electron may slightly shift the potential toward the anodic direction,[51] and therefore, the measured E_{cp} value for THCO should be considered as an upper limit to the thermodynamic value.

TABLE 3: Cathodic Peak Potentials (E_{cp}) and Associated Anodic Peak Potentials (E_{Ap}) vs SCE (V) for Oligo(thienyl ketones) *n*THCO, $n = 1-4$

	E_{cp}	E_{ap}	n^a	
THCO	−1.966		2	irrev
2THCO	−1.582	−1.501	1	rev
	−2.278		1	irrev
3THCO	−1.063	−0.996	1	rev
	−1.562	−1.490	1	rev
4THCO	−0.884	−0.808	1	rev
	−1.278	−1.201	1	rev
	−1.960		2	irrev
	−2.356		(1)	irrev
polymer	(−0.47)^b			

[a] Number of exchanged electrons. [b] Extrapolated value; see text.

For $n = 2-4$, the voltammogram shows one (2THCO) or two cathodic peaks related to reversible monoelectronic processes. The value of the first cathodic peak potential decreases with increasing oligomer length (2THCO, −1.582; 3THCO, −1.063; 4THCO, −0.884 V vs SCE) following the increasing delocalization of the LUMO. It can also be noted that this effect progressively facilitates dianion formation along the oligomer series. In fact, the energy difference between the first two peak potentials decreases from 696 mV (2THCO) to 499 mV (3THCO) and to 394 mV (4THCO) with increasing charge delocalization capability.

An independent estimate of the LUMO energy can be obtained by inserting the first cathodic peak potentials in the E_{cp}/LUMO correlation previously obtained for oligothiophenes on an experimental basis.[39] The resulting LUMO energies, reported in the fifth column of Table 2, are close to the LCBO values. They clearly indicate that the stabilization is larger than that expected only on the basis of the electron-withdrawing inductive effect of the carbonyl group and in agreement with the presence of a strong ring/carbonyl π^*-orbital mixing. The electron affinity of the present compounds is much higher than that of oligothiophenes containing the same number of TH fragments: ca. 0.0, −0.5, and −0.88 eV for dimer, trimer, and pentamer, respectively;[39] see Table 2.

The literature E_{cp} value for poly-THCO is related to an irreversible process and is nearly coincident with that of 4THCO (about −1.0 and −0.96 V vs SCE, respectively).[11,12] The present data for the first reduction process of the various oligomers with $n \geq 2$ are, on the other hand, reversible and do not seem to have reached an asymptotic limit for $n = 4$. When the E_{cp} values for the *n*THCO derivatives are plotted against $1/n$, where *n* is the number of rings and carbonyl groups present in the oligomer, the value extrapolated for the polymer ($1/n = 0$) is −0.47 V vs SCE. Using the E_{cp}/LUMO correlation cited above, this value gives −2.67 eV for the LUMO energy of an isolated gas-phase chain of poly(thienylene ketone). Thus, the electron affinity of poly-THCO (2.67 eV) is much higher than that of polythiophene, poly-TH (1.1 eV).[39]

From the lowest IE and AE values it is possible to compute the energy gap between the HOMO and the LUMO (E_{GAP}) for the various oligomers and the polymer. The results obtained are reported in Table 4 together with the data for the corresponding thiophenes (TH)[39] and furanes (FU).[40] The E_{GAP} for poly-THCO, ca. 6.4 eV, is close to that of poly-TH and poly-

TABLE 4: HOMO−LUMO Energy Gap (eV) for Poly(thienylene ketone) (THCO), Polythiophene (TH), and Polyfuran (FU) and the Various Oligomers

no. of fragments	THCO	TH[a]	FU[a]
2	8.52	7.90	8.59
3	7.88	7.04	7.67
4		6.65	7.24
5	7.21	6.43	
7	6.98		
polymer	6.38	5.97	6.5

[a] From ref 40.

FU (ca. 6.0 and 6.5 eV, respectively).[39,40] The similarity of the E_{GAP} trends for the three series of oligomers confirms the E_{cp} extrapolated value for poly(thienylene ketone) (ca. −0.47 eV).

Conclusions

The electronic structure of the thienocarbonyl derivatives *n*THCO ($n = 1-4$) has been investigated by means of UP and ET spectroscopies. The assignment of the spectra is based on those of thiophene and acetone and the results of theoretical calculations. The π-IE values are reproduced in the KT approximation, while the n_{CO} IE of acetone is reproduced only when the Δ*M*P2 procedure between the cation and neutral states is used because of the large relaxation energy which accompanies electron ejection from the oxygen lone pair orbital. In the planar THCO the π-ring and the n_{CO} orbitals do not interact and the latter is nearly degenerate with the orbital of prevailing π_{2b1} parentage. In the longer oligomers ($n = 2-4$), σ/π conjugation is slightly allowed. New π-bands, however, do not appear in the low-IE region of the spectra, but rather, the two bands corresponding to those present in the THCO spectrum become broader and change their relative intensity according to the number of nearly degenerate ionization events. In the spectra there is no evidence for the presence of rotamers different from the "all-cis" one. The first IE value is nearly constant with increasing oligomer length, so that the polymer is not expected to have the required properties to be successfully p-doped.

On the other hand, the π^*_{ring} and π^*_{CO} orbitals of the TH and acetone fragments interact strongly in the *n*THCO derivatives, so that the LUMO is stable and thus inaccessible by ETS. The ET spectra of THCO and 2THCO can be easily assigned on an experimental basis. The AE trends parallel the results of the calculations, allowing the assignment of the spectrum of 3THCO. The experimental AE values of THCO, 2THCO, and 3THCO are accurately reproduced by LCBO calculations which provide, in addition, an upper limit to the LUMO electron affinity for these compounds. Less accurate estimates of the LUMO electron affinity of the *n*THCO derivatives ($n = 1-3$) are provided by linear correlations between the experimental AE values and the empty level computed (HF/6-31G** and MINDO/3) energies.

In all cases, with increasing oligomer length, the energy of the LUMO sharply decreases, the number of π^*-levels lying below the first σ^*-level increases, and the energy separation among π^*-levels decreases. The enlargement of the conduction band toward higher electron affinity values for longer oligomers indicates the possibility for these compounds to be successfully n-doped.

The opposite behavior of the HOMO and LUMO energies and localization properties, with increasing oligomer length, can be explained by considering that (i) π-conjugation and the inductive effect of the carbonyl group perturb the energy of the HOMO in opposite directions, while the two effects reinforce each other in stabilizing the LUMO, (ii) the filled π_{ring} (8.88 eV in TH) and π_{CO} (12.59 eV[27] in acetone) orbital energy of the reference compounds are quite different, while their corresponding virtual orbitals have similar energy, and (iii) the π^*_{3b1} and π^*_{CO} wave function coefficients at the interacting atoms are larger than those of the corresponding filled orbitals.

The electrochemical reduction of THCO occurs via a bielectronic irreversible process whereas the first reduction of the longer oligomers is reversible and monoelectronic. The E_{cp} values decrease when the size of the oligomer increases. When these data are inserted into the experimental E_{cp}/LUMO correlation previously obtained for oligothiophenes, the resulting LUMO energies are close to those obtained by the LCBO approach. The extrapolated E_{cp} value for the polymer (−0.47 V vs SCE) corresponds to a LUMO energy of −2.67 eV. Thus, the electron affinity of poly(thienylene ketone) is much higher than that of polythiophene (LUMO = −1.1 eV). The high electron affinity of poly-THCO counteracts the high IE value, so that the HOMO−LUMO energy gap (ca. 6.4 eV) is close to that of poly-TH (6.0 eV) and poly-FU (6.5 eV).

The geometrical and electronic properties of poly-THCO seem to be suitable for electrical conductivity along the stacking axis in the solid phase, that is perpendicularly to the chain axis, upon n-doping.

References and Notes

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