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Note

Substituent Effects in Thiophenes

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He I and He II photoelectron spectra (UPS) of 2-acetyl and 2-cyano thiophene have been measured. The electronic strucutre of the title compounds and, in particular, the effect of substituents on the thiophene π orbitals is discussed on the basis of band widths, He I/He II intensities and semi-empirical MO calculations. Definite assignments are given for the two molecules, thus completing the previous work. The available results on 2- and 3-monosubstituted thiophenes have been compiled and rationalized.

INTRODUCTION

The electronic structure of thiophene and substituted thiophenes have been studied in considerable detail by photoelectron spectroscopy (UPS) and quantum chemical methods.[1,2] In this article, we shall present new data on the recently studied[3] 2-acetyl and 2-cyano thiophenes, which will allow definitive assignments to be made. Also, we wish to analyze the effects of 2- and 3-monosubstitution on the ring π_3 and π_2 ionizations (HOMO and SHOMO).

EXPERIMENTAL

The commercial sample compounds, obtained from MTM Research Chemicals were recrystallized before use and their UPS spectra recorded on a UPG-200 Leybold-Heraeus spectrometer. Ar^+ $^2P_{3/2}$ and $^2P_{1/2}$ lines were used for calibration and resolution measurement. The resolution achieved was approximately 20 meV. The semi-empirical MO calculations with full geometry optimization were performed using AM1 Hamiltonian and HyperChem software.[4]

RESULTS AND DISCUSSION

The UPS spectra of the molecules studied are shown in Figure 1. The He I spectra have better resolution than those reported earlier,[3] although in other respects they are the same.

We shall first try to obtain an assignment for bands at 9.10 and 9.65 eV in the UPS of 2-acetylthiophene. The intensity ratio for the two bands is 1 : 1.63 (in HeI) and 1 : 1,65 (in HeII). It is obvious that the 9.65 eV band may contain two ionizations. The intensity ratio between 9.10 and 9.65 eV bands hardly changes with pho-

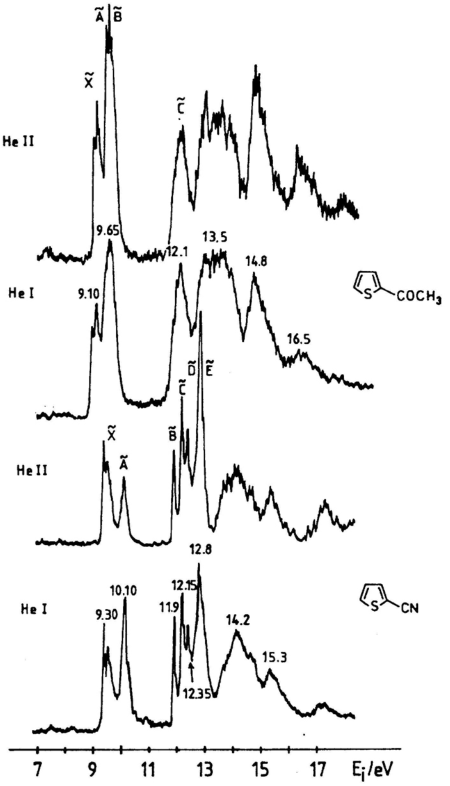

Figure 1. HeI and HeII UPS of 2-cyano and 2-acetylthiophene

ton energy. HeII/HeI atomic photoionization cross-section ratios for C2p, N2p, O2p and S3p orbitals are: 0.31, 0.45, 0.64 and 0.14, respectively.[5]

The ratios indicate that the π_S orbital band would show a significant relative intensity decrease on going from HeI to HeII excitation. The oxygen lone pair (carbonyl group) n_O band, on the other hand, should show a relative increase, compared to C2p and S3p localized MO ionizations. The two effects nearly cancel each other and lead to the 9.10/9.65 eV band ratio, being the same in HeI and HeII spectra. This is possible only if the 9.10 eV band corresponds to the ionization of π_3 and 9.65 eV band to π_S and n_O ionizations, respectively. HeII and HeI spectra thus confirm the assignment suggested previously.[3] The 12.1 eV band decreases in intensity on going from HeI to HeII (Figure 1). One should assign it to the n_S orbital rather than to σ and π_{CO}, as it has been suggested previously.[3] AM1 calculated orbital energies for π_3, π_S and n_O orbitals are: 9.86, 9.53 and 10.8 eV, respectively. There is no agreement between UPS and AM1 results, the experimentally deduced assignment being the preferred one.

The AM1 calculated energy difference between *Z* (*cis*) and *E* (*trans*) conformers (carbonyl group O atom *vs.* sulfur atom) is < 1 kJ mol^{-1} and one can expect the spectrum to represent a mixture of conformers. This is another example of the wellknown *cis* effect and was implicitly mentioned in the related UPS study of 2-furanaldehyde.[6] The calculated AM1 MO energies for Z and E isomers differ by $\leq$ 0.1 eV, which indicates that their distinction from UPS is virtually impossible.

The assignment of UPS of 2-cyanothiophene is more complicated. The 9.30 and 10.10 eV bands can, on the basis of the observed HeII/HeI intensities, AM1 calculations and arguments mentioned above, be readily assigned to π_3 and π_S ionizations, respectively. The assignment of 11.9, 12.15 and 12.8 eV bands is not so straightforward and remains tentative. (The 12.35 eV peak is part of a vibrational progression of the 12.15 eV band).

One can expect the following five ionizations to occur in the 11 – 13.5 eV region: n_S (sulfur lone pair), π_{CN} (two ionizations of a' and a" symmetry), σ_{CN}(a') and ring π_1(a") ionization. The expectation is based on the UPS of CH_3CN and thiophene.[1] The sharper bands (B and C) correspond to CN-localized π orbitals *i.e.* π_{CN}(a') and π_{CN}(a"), respectively. The n_S band (σ MO, localized on sulfur) may be attributed to the broad underlying band (D) at 12.0 eV. The 12.8 eV band is of large intensity and corresponds to two ionizations. Besides, it shows a change in profile and intensity increase on going from HeI to HeII radiation. σ_{CN}(a') and ring π_1(a") orbitals satisfy these requirements and should be assigned to the 12.8 eV band. The profile changes with photon energy because the σ_{CN} intensity increases (N2p character) while the π_1 intensity simultaneously decreases (C2p and S3p character).

The AM1 eigenvalues (assignments) were: 12.12 eV (n_S), 12.83 eV (π_{CN}, a'), 13.28 eV (π_{CN}, a"), 13.75 eV (σ_{CN}) and 14.03 eV (σ ring). Once again, it appears that the MO calculations do not wholy support the empirically derived assignment by overestimating the binding energy of the π_1 orbital.

Analysis of substituent effects has often utilized a combination of UPS and MO calculations in order to define and justify concepts like inductive and resonance effects. The simplistic correlations between experimental and calculated ionization energies (E_i) can be invalid[7] and we have decided to investigate the correlation between two experimental sets of E_i: π_3 and π_S shifts upon substitution (Table I). The wide

TABLE I

Shifts of thiophene π-ionization energies on monosubstitution
$\Delta = \pi_3 - \pi_3$ (subst) $\delta = \pi_2 - \pi_2$ (subst)

Substituent	2-position		3-position		Ref.
	Δ	δ	D	δ	
$-CCH$	0.38	0.03	0.23	0.18	8
$-COCH_3$	−0.25	−0.16	−0.85	−0.21	3
$-CN$	−0.45	−0.61			3
$-NO_2$	−0.86	−0.70	−0.93	−0.76	9
$-OCH_3$	0.67	0.27	0.48	0.30	9
$-Cl$	−0.05	−0.13	−0.20	0.04	10
$-Br$	0.25	−0.03	−0.12	0.02	11
$-I$	0.39	0.07	0.24	0.19	11
$-CH_3$	0.42	0.26			1
$-SCH_3$	0.22	0.12			1
$-CHO$	−0.52	−0.38			1
$-CH_2Cl$	−0.04	0.00			1
$-CH_2CN$	−0.35	−0.26	−0.50	−0.21	3

range of substituent types, and uncertainties in the E_i for some molecules means that the analysis can only be of qualitative value. Nonetheless, it's conclusion may prove interesting because it does not involve any reference to particular models of substitution or MO calculations. The non-linear regression analysis relating Δ and δ ($\Delta = a_o + a_1\delta + a_2\delta^2$) gave the correlation coeficients of 0.95 (for 2-substitution) and 0.98 (for 3-substitution). In both cases of substitution, the second order polynomial fits the data better than the first. The result demonstrates that the substitutent affects both π_3 and π_S ionizations albeit not to the same extent (hence nonlinear correlation is preferred to the linear one). 3-substitution influences the ring π_3 orbitals more evenly (hence a larger correlation coefficient). The different effects of α and β substitutions have been discussed previously in some detail.[12]

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SAŽETAK

Utjecaj supstituenata u tiofenima

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Snimljeni su fotoelektronski spektri (HeI i HeII) 2-ciano- i 2-acetiltiofena. Elektronska struktura, a posebno utjecaj supstituenata na π-orbitale tiofena proučen je na temelju razmatranja širine spektralnih vrpci, njihovih HeI/HeII intenziteta i semi-empirijskih MO računa. Predložena je konačna asignacija spektara dviju molekula. Dobiveni rezultati povezani su s podatcima o drugim supstituiranim tiofenima.