The Photoelectron Spectrum of 2,2′-Bitellurophene†

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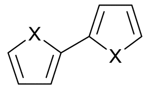
Igor Novak,*[a] Siu Choon Ng,[a] Li Wang[a] and Wei Huang[b]

[a]Department of Chemistry and [b]Institute of Materials Research and Engineering, National University of Singapore, Singapore 119260

He I and He II photoelectron spectra of 2,2′-bitellurophene were recorded and analysed on the basis of empirical arguments.

The electronic structures of 2,2′-bisheteroarylenes are interesting because they are precursors for electrically conducting polyheteroarylene polymers (*e.g.* polythiophene). The high electrical conductivity of doped polythiophene and its applications have been discussed at great length.[1,2] One of the prerequisites for high electrical conductivity (although not the only one), is the existence of delocalized electrons and bond length alternations along the π-conjugated polymer backbone.[2] The higher the degree of π-electron delocalization the more mobile the π electrons will be as charge carriers. In this work, we discuss the variation of electronic structure along the series, and especially the degree of inter-ring π-conjugation.



X = O, S, Se, Te

Experimental

The He I and He II photoelectron spectra (UPS) of 2,2′-bitellurophene and 2,2′-bithiophene were recorded on a Leybold-Heraeus UPG-200 spectrometer with a spectral resolution of 18–25 meV (measured at Ar^+ $^2P_{3/2}$ and $^2P_{1/2}$ lines). Elevated sample inlet temperatures (100–150 °C) were used during measurements in order to obtain sufficient sample vapour pressures. The measured UPS band intensities were obtained from deconvoluted band areas.

Tellurophene (1.8 g, 10 mmol) in dried diethyl ether (10 ml) was added at –20 °C to *n*-butyllithium (1.6 M in hexane, 6.90 ml, 11 mmol). After the reaction mixture was stirred at room temperature for 45 min, and cooled to –78 °C, CuCl (0.95 g, 10 mmol) was added in one portion. The reaction mixture was stirred at room temperature overnight. The black solid was filtered off, diethyl ether (20 ml) added to the solution which was then washed with water. After removal of diethyl ether, the residue was recrystallized from $CHCl_3$ to afford 2,2′-bitellurophene. Yield, 0.36 g, 10%, mp 179–180 °C ^1H NMR δ 8.68 (2H, dd, $J = 1.11$, 6.85 Hz), 7.65 (2H, dd, $J = 4.07$, 6.93 Hz), 7.44 (2H, dd, $J = 1.03$, 4.08 Hz); IR (KBr) ν_{max}/cm^{-1} 3075, 2999, 2916, 2365, 1442, 1209, 1016 and 817 cm^{-1}; MS: m/z 362 (M^+, 80%), 232 (57%), 129.9 (20%).

Results and Discussion

The He I and He II spectra are shown in Fig. 1, while the energy level scheme is depicted in Fig. 2. The assignments indicated in Fig. 2 and Table 1 can be readily obtained on the basis of considerations of band shapes and comparison with the spectra of other 2,2′-bichalcophenes.[3–5] The four bands at lowest ionization energies have markedly different bandwidths. The bands at 7.58 and 9.39 eV have broad profiles while the 8.10 and 8.36 eV bands are distinctly sharper. This observation strongly suggests that the former pair of bands correspond to ionizations from π orbitals delocalized over both rings and the latter to orbitals localized on a single ring and related to π_2 in parent tellurophene.[6] The delocalized orbitals are designated π_- and π_+ to indicate that they are the out-of-phase and in-phase linear combinations, respectively of π orbitals on tellurophene fragments. The orbitals localized on a single ring are designated π_n to emphasize their pronounced Te 5p character. Fig. 2 also indicates that π_n orbitals show a decrease in ionization energies on going from 2,2′-bifuran to 2,2′-bitellurophene, as can be expected from electronegativity trends for chalcogens in Group 16 (π_n orbitals have large heteroatom np character).

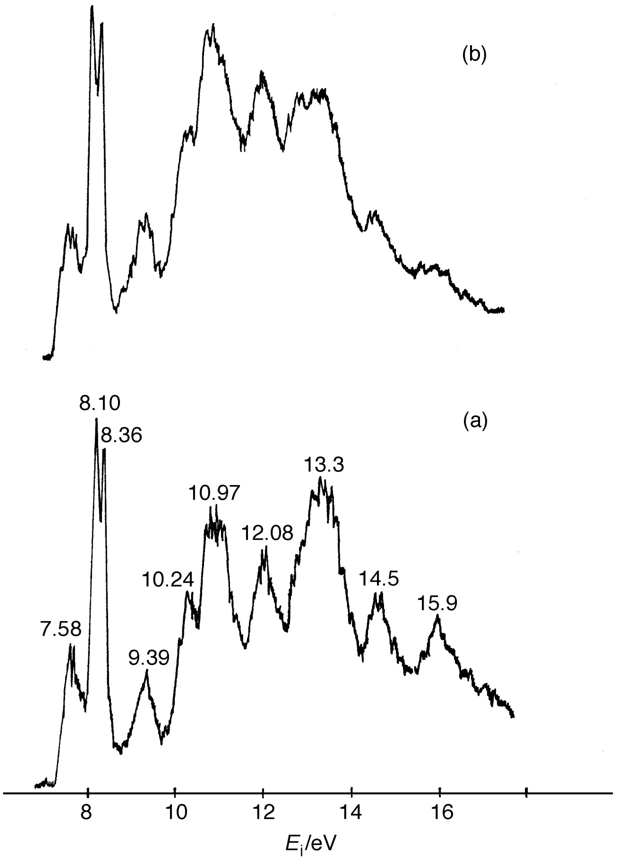


Fig. 1 Photoelectron spectra of 2,2′-bitellurophene; (a) He I and (b) He II

Theoretical assignments based on *ab initio* results (Table 1) and Koopmans theorem (KT) are at variance with the experimental results. We prefer the experimental results (Table 1) in view of the known deficiencies of KT. Relative

Table 1 Vertical ionization energies ($E_i \pm 0.05$ eV) and HF-SCF energy levels (ε/eV) in 2,2′-bitellurophene[a]

Band	E_i/eV	ε/eV	Assignment
$\tilde{X}$	7.58	7.36	π_-
$\tilde{A}$	8.10	7.84	π_n
$\tilde{B}$	8.36	7.99	π_n
$\tilde{C}$	9.39	9.83	π_+
$\tilde{D}$	10.24	9.58	σ

[a] *ab initio* calculations were performed with the Gaussian 94 program package and LanL2MB basis set which contains ECP for Te. Full geometry optimization was included.

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*To receive any correspondence (*e-mail:* chmigorn@nus.edu.sg).

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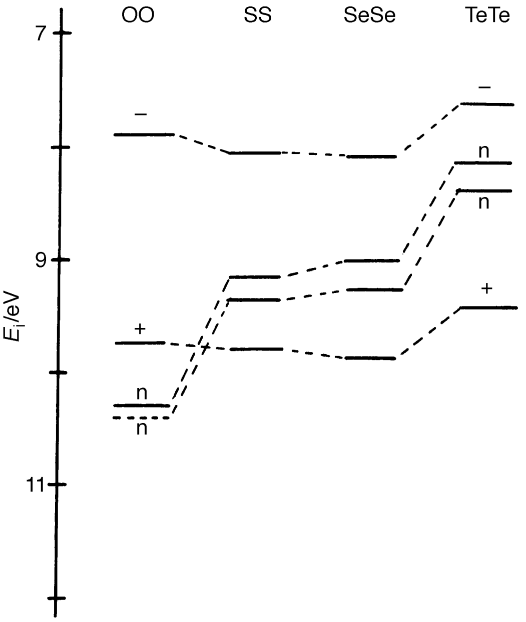

Fig. 2 Energy level diagram for 2,2′-bichalcophenes; atomic symbols designate different 2,2′-bichalcophenes

band intensities at different photon energies can be described within the framework of the Gelius model.[7] This model suggests that the MO photoionization cross-section (and the corresponding band intensity) σ_i^{MO} can be expressed as

$$\sigma_i^{\mathrm{MO}} = \sum_i P_{ij}\sigma_i^{\mathrm{AO}}$$

where P_{ij} is the electron population of the ith AO. Atomic orbital cross-sections σ_i^{AO} have been tabulated for all elements.[8] HeII/HeI AO cross-section ratios for O, S, Se and Te np ionizations are 0.638, 0.138, 0.069 and 0.106, respectively.[8] The values indicate that, amongst π_n orbitals, the largest decrease in relative band intensity can be expected in 2,2′-biselenophene and the smallest in 2,2′-bifuran. This is indeed the case as can be seen from relative band intensities given in Table 2. The C 2p cross-section will, of course, also influence MO cross-sections, but C 2p HeI/HeII cross-section variations can be assumed to be constant throughout the bichalcophene series. Two important characteristics of 2,2′-bichalcophenes should be considered: planarity (torsion barrier) and the strength of inter-ring π conjugation. The inter-ring torsion barriers and relative stabilities for *syn* and *anti* conformers of 2,2′-bichalcophenes have been studied previously by experimental and theoretical methods.[9] The results suggest that the barrier heights are of the order of a few kcal mol^{-1} while the *syn–anti* conformer difference is *ca.* 1 kcal mol^{-1}. This makes the molecules rather flexible and raises the possibility that our spectra refer to the mixture of conformers. The strength of inter-ring conjugation in 2,2′-bichalcophenes can be deduced from MO calculations, but the reliability of such results depends on the basis sets used in the *ab initio* methods and on parametrizations in semi-empirical MO methods.

We have used two experimental parameters as indicators of inter-ring conjugation: inter-ring C—C bond lengths and ionization energy difference (ΔE) between π_- and π_+ orbitals. The inter-ring C—C bond length in 2,2′-bitellurophene was measured as 1.46(3) Å by X-ray diffraction in the solid.[10] This value is intermediate between values for 2,2′-bithiophene (1.49 Å) and 2,2′-biselenophene (1.439 Å)[11] and is thus not very informative, except perhaps to suggest a marginally stronger π-conjugation in 2,2′-biselenophene. ΔE can also be used as an indicator of the strength of inter-ring π-interactions. ΔE values are 1.83, 1.72, 1.80 and 1.81 eV on going from 2,2′-bifuran to 2,2′-bitellurophene and suggest that the inter-ring interactions in 2,2′-bichalcophenes are similar as do X-ray data. We can conclude that variations of electrical conductivity observed in polychalcophenes are not due to the π electronic structure, but rather to other factors, *e.g.* inter-chain coupling or aromatic resonance energy.[2]

Table 2 The relative band intensities[3–5] in 2,2′-bichalcophenes (normalized to π_+ band intensity); n designates π_n and +/− π_+ or π_- orbitals

Compound	Band	He I	He II
2,2′-bifuran	π_-	1	1
	π_+	0.63	0.82
	π_n	1.07	1.58
2,2′-thiophene	π_-	1	1
	π_n	2.44	2.63
	π_+	0.86	0.87
2,2′-biselenophene	π_-	1	1
	π_n	3.02	1.30
	π_+	0.93	0.82
2,2′-bitellurophene	π_-	1	1
	π_n	2.41	2.66
	π_+	0.65	0.87

The caveat when discussing inter-ring interactions is that two conjugated π systems need not necessarily be delocalized into one global π system.[12] Experimental evidence is required to verify delocalization. This point is important in the discussion of electrical conductivity of polychalcophenes where global π delocalization has always been tacitly assumed.[1,2] Our spectra suggest that delocalization takes place in all 2,2′-bichalcophenes as is evident from the splitting of π_+ and π_- ionization bands.

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