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Photoelectron Spectroscopy Study of Orbital Interactions. Ethynylfurans

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He I and He II photoelectron spectra (UPS) of isomeric mono- and bis(ethynyl)furans were recorded. The assignment of spectra was based on empirical considerations (bandwidths, He II/He I intensity variations, comparison with spectra of related molecules) and *ab initio* calculations. The details of orbital interactions between the ring and ethynyl π orbitals were deduced solely on the basis of experimental data. These interactions were studied for several classes of π isoelectronic molecules.

Introduction

Ethynylfurans are heterocyclic compounds whose electronic structure is interesting for two reasons:

(1) These molecules are building blocks (monomers) in the formation of conjugated polymers. The polymers are prime targets of recent research into properties of new materials which may be suitable for nonlinear optics and as electrical conductors.[1,2] The electronic structure of these materials can be studied experimentally by photoelectron spectroscopy (UPS) in the condensed phase (as polymers)[3] or in the gas phase (as monomer building blocks).[4] Theoretical studies of oligomeric and polymeric materials can be performed by semiempirical[5] and *ab initio* methods.[6] The combined results of these studies suggest that electrical conductivity is determined by two factors: electronic structure of (monomeric) building blocks and arrangements of polymeric chains in the bulk material.

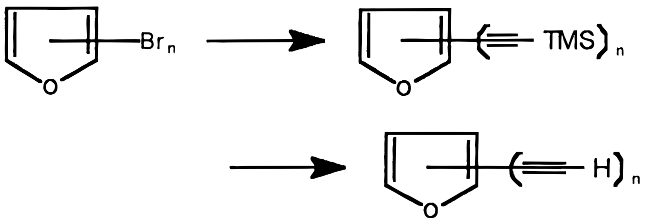
(2) Ethynylfurans provide an example where the nature and extent of intramolecular 1,4-π,π, 1,5-π,π, and 1,6-π,π interactions[7] can be studied. The interactions take place between π orbitals on substituents attached to the heteroaromatic ring which serves as a relay. Studies of interactions between the ethyne moiety and aromatic systems have been reported,[8,9] but few investigations of ethynyl−heteroaromatic interactions exist. The electronic structures of ethynylthiophenes[4] and some isomeric ethynylpyridines[10] have been reported. We wish to extend the study to ethynylfurans which are π isoelectronic with ethynylthiophenes and ethynylpyridines.

Experimental and Theoretical Methods

General. Mass spectra were recorded using a Micromass VG 7035E mass spectrometer at a source temperature of 200 °C and an ionizing voltage of 70 V. NMR spectra were obtained on a Bruker ACF300 spectrometer using $CDCl_3$ as solvent and TMS as internal reference. IR spectra of all ethynylfurans were measured on a Perkin Elmer 1600 with KBr salt plate. UV spectra were recorded by a Hewlett Packard 8452A Diode Array Spectrophotometer.

Synthesis. The synthetic route to ethynylfurans is depicted in Scheme 1. The modified regioselective ethynyl cross-coupling procedures of Neenan et al.[11] and Brandsma et al.[12] were used. Compounds **1a**−**2a** are known,[13−15] while the synthesis of **2b, 2c** has not been reported yet. All compounds were characterized by 300-MHz NMR, FTIR, and mass spectrometry. The 3,4-ethynylfuran was not prepared because the overall yield of the product was lower than 1%.[16]

SCHEME 1: Synthesis of Ethynylfurans[a]



n=1
2-ethynylfuran (1a)
3-ethynylfuran (1b)

n=2
2,5-diethynylfuran (2a)
2,3-diethynylfuran (2b)
2,4-diethynylfuran (2c)

[a] Reagents and conditions: $HC{\equiv}CTMS/Et_3N/Pd(Ph_3)_2Cl_2$(cat.)/$Ph_3P$(cat.)/CuI(cat.), then Et_2O/MeOH/KOH/30 °C.

2,3-Ethynylfuran: Yield 68%; bp 70 °C/30 mmHg; UV/vis (hexane) 217 (ϵ 4500) and 263 (12 000) nm; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 3.30 (s, 1H), 3.65 (s, 1H), 6.45 (d, 1H, J = 2 Hz), 7.30 (d, 1H, J = 2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ_c 72.3, 74.3, 82.8, 85.6, 112.5, 113.4, 140.0, and 143.3; IR (neat) 3297, 3156, 2958, 2349, 2122, 1490, 1252, 1067, 843, and 756 cm^{-1}; MS *m/z* (high resolution) 116.0271; required, 116.0262.

2,4-Ethynylfuran: Yield 72%; bp 65 °C/30 mmHg; UV/vis (hexane) 218 (ϵ 10 100) and 250 (7300) nm; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 3.04 (s, 1H), 3.38 (s, 1H), 6.68 (s, 1H), 7.57 (s, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ_c 72.8, 73.9, 79.7, 82.4, 107.8, 118.4, 136.6, and 147.2; IR (neat) 3295, 3143, 2958, 2348, 2123, 1507, 1190, 976, 825, and 665 cm^{-1}; MS *m/z* (high resolution) 116.0259; required, 116.0262.

The He I and He II UPS spectra were recorded on a UPG-200 Leybold-Heraeus spectrometer at a resolution of 18−25 meV (fwhm) in He I and 32−40 meV in He II excitation. Ar^+ $^2P_{3/2}$ and $^2P_{1/2}$ lines were used for calibration. The *ab initio* calculations at the HF/6-31G(d,p) level (full optimization) were performed with the SPARTAN program package.[17] The optimized geometries were genuine minima on the potential energy surface as indicated by the absence of imaginary vibrational frequencies. The calculations suggest that all molecules are planar in their ground states. The band intensities were deduced from the measurement of deconvoluted band areas where possible.

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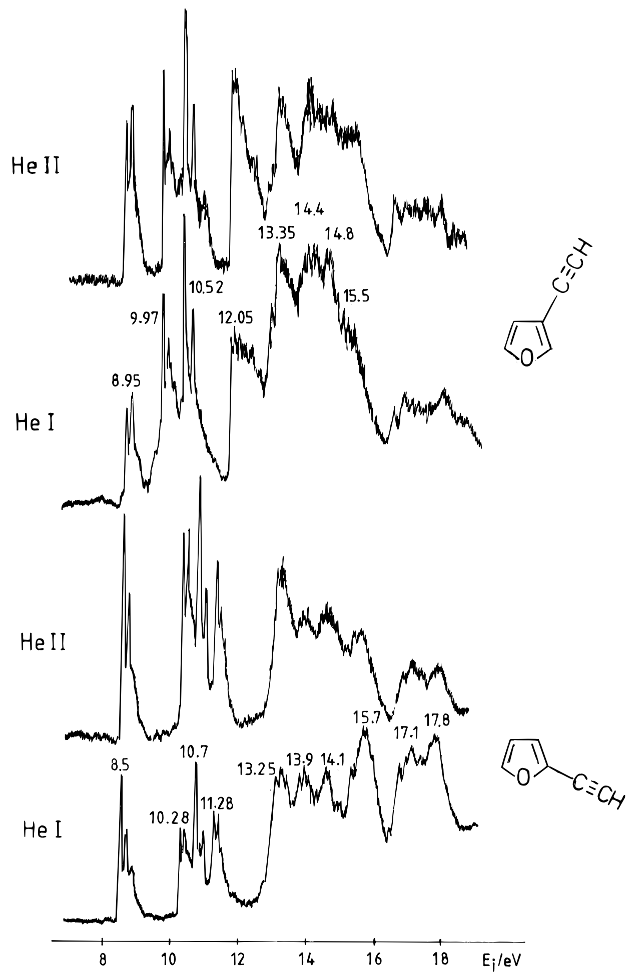

Figure 1. He I and He II UPS of monoethynylfurans.

Results and Discussion

The He I and He II spectra are shown in Figures 1−3. Table 1 summarizes measured vertical ionization energies, orbital energies and assignments, and vibrational fine structures. The MO characters given in Table 1 show only the most important fragment orbital contributions and are of *ab initio* origin. The signs in these MO descriptions refer to relative phases in the linear combinations of fragment orbitals. The energy levels in ethynylfurans and ethynylthiophenes show two salient features[4] (Figure 4):

(1) reduction of splitting between π_2 and π_3 levels in 3-substituted derivatives;

(2) greater proximity of π_2 and π_{CC} levels in ethynylfurans than in ethynylthiophenes, which is an indication of the degree of interactions between ring and substituent π orbitals.

The reduced $\pi_2 - \pi_3$ level splitting is due to different symmetries of π_2 and π_3 orbitals. Different symmetries lead to different interactions with α- and β-ethynyl substituents. Finally, different interactions induce shifts in π_2, π_3 energies and alter $\pi_2 - \pi_3$ orbital splitting.

We have established the detailed ordering of levels (ionic states), using empirical arguments (He I/He II intensity variations, comparison with spectra of related molecules, band contours, and vibrational fine structures) rather than MO calculations. The reason for this preference is that, in some spectral regions, the high density of ionic states and overlapping bands tend to make assignments based on Koopmans' approximation unreliable. Furthermore, the calculated MO characters depend to some extent on the basis set size and level of theory employed (electron correlation).

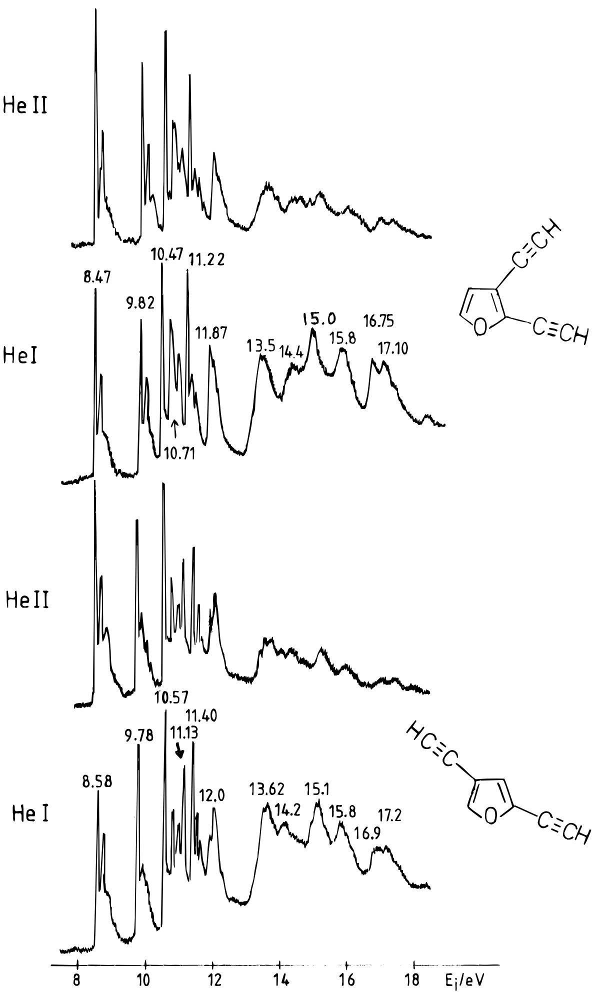

Figure 2. He I and He II UPS of bis(ethynyl)furans I.

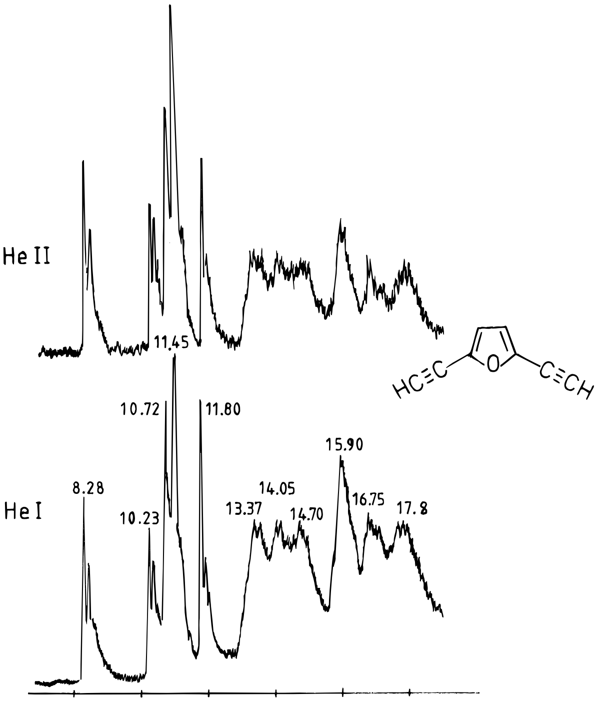

Figure 3. He I and He II UPS of bis(ethynyl)furans II.

The bands $\tilde{X}-\tilde{C}$ (in case of monoethynyl isomers) and $\tilde{X}-\tilde{E}$ (in case of bis(ethynyl) isomers) can be attributed to π orbital ionizations. (We are using IUPAC notation for the bands.) This

TABLE 1: Ionization Energies (E_i/eV), MO Energies (ϵ_i/eV), Assignments, and Vibrational Fine Structure for Ethynylfurans. IUPAC Notation[a] Is Used To Designate Ionic States ($\tilde{X}-\tilde{E}$)

molecule	ion state	E_i	ϵ_I	MO	$\nu \pm 80$/cm^{-1} (ion)	ν/cm^{-1} (molecule)
2-	$\tilde{X}$	8.5	8.37	$\pi_3 - \pi_{CC}''$	1410 ring deform	1478.1
	$\tilde{A}$	10.28	10.79	$\pi_2 + \pi_{CC}''$	1000 ring deform	1014.0
	$\tilde{B}$	10.70	11.04	π_{CC}'	2020 C≡C stretch	2111.8
	$\tilde{C}$	11.28	12.02	$\pi_3 + \pi_{CC}''$	1130 ring deform	1204.8
	$\tilde{D}$	13.25	14.98	σ_O		
	$\tilde{E}$	13.9	15.53	σ		
3-	$\tilde{X}$	8.95	8.63	$\pi_3 - \pi_{CC}''$	1210 ring deform	1162.8
	$\tilde{A}$, $\tilde{B}$	9.97	10.07	$\pi_2 - \pi_{CC}''$	1610 ring deform	1488.1
			10.73	π_{CC}'		
	$\tilde{C}$	10.52	12.51	π_{CC}''	2020 C≡C stretch	2360.5
	$\tilde{D}$, $\tilde{E}$	12.05	15.13	σ_O		
			15.72	σ		
2,5-	$\tilde{X}$	8.28	8.18	$\pi_{CC}'' - \pi_3 - \pi_{CC}''$	1410 ring deform	1496.1
	$\tilde{A}$	10.23	10.71	$\pi_{CC}'' - \pi_2 - \pi_{CC}''$	1170 ring deform	1212.4
	$\tilde{B}$		11.11	$\pi_{CC}' - \pi_{CC}'$		
	$\tilde{C}$, $\tilde{D}$	11.45	11.81	$\pi_{CC}'' + \pi_2 + \pi_{CC}''$		
			12.59	$\pi_{CC}'' - \pi_{CC}''$		
	$\tilde{E}$	11.80	11.28	$\pi_{CC}' + \pi_{CC}'$	1010 ring deform	962.3
2,3-	$\tilde{X}$	8.47	8.33	$\pi_{CC}'' - \pi_3 - \pi_{CC}''$	1410 ring deform	1491.3
	$\tilde{A}$	9.82	10.17	$\pi_2 - \pi_{CC}''$	1410 ring deform	1491.3
	$\tilde{B}$	10.47	10.83	π_{CC}'		
	$\tilde{C}$	10.71	11.82	$\pi_{CC}'' + \pi_3 + \pi_{CC}''$		
	$\tilde{D}$	11.22	11.17	π_{CC}'	1010 ring deform	1066.9
	$\tilde{E}$	11.87	12.84	$\pi_{CC}'' + \pi_2 + \pi_{CC}''$		
2,4-	$\tilde{X}$	8.58	8.44	$\pi_{CC}'' - \pi_3 - \pi_{CC}''$	1410 ring deform	1497.1
	$\tilde{A}$	9.78	9.97	$\pi_{CC}'' - \pi_2 - \pi_{CC}''$	1410 ring deform	1497.1
	$\tilde{B}$	10.57	10.85	$\pi_{CC}' - \pi_{CC}'$	2020 C≡C stretch	2120.3
	$\tilde{C}$	11.13	12.24	π_{CC}''		
	$\tilde{D}$	11.40	11.26	$\pi_{CC}' + \pi_{CC}'$	1130 ring deform	1153.7
	$\tilde{E}$	12.0	12.71	π_{CC}''		

[a] Mills, I.; Cvitaš, T.; Kallay, N.; Homann, K.; Kuchitsu, K. *Quantities, Units and Symbols in Physical Chemistry*; Blackwell: Oxford, 1993; p 28.

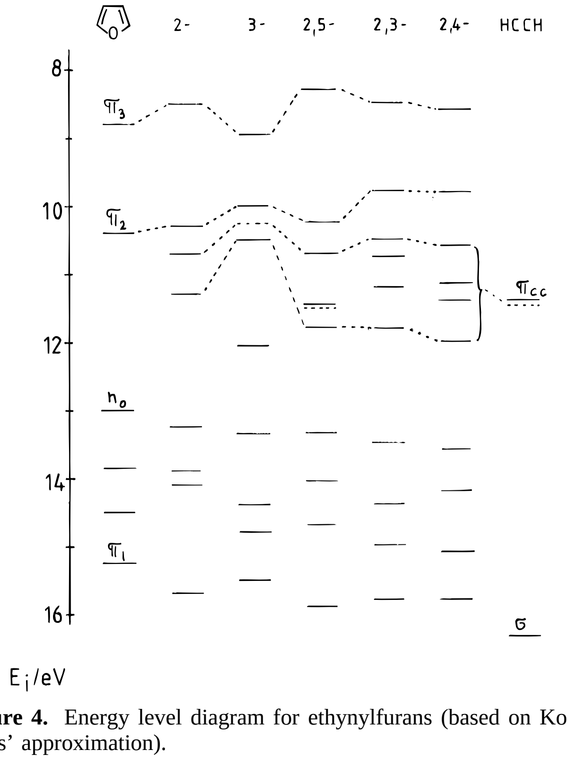

Figure 4. Energy level diagram for ethynylfurans (based on Koopmans' approximation).

conclusion is supported by correlation with spectra of furan and ethyne (Figure 4) and by *ab initio* results (Table 1).

$\tilde{X}$ and $\tilde{A}$ bands correspond to π_2 and π_3 orbitals which have substantial furan ring character, as can be deduced from the correlation diagram (Figure 4). In the spectrum of furan itself, the relative intensity of the $\tilde{X}$ band decreases compared to that of $\tilde{A}$ on going from He I to He II radiation.[18] This effect has been well established, and it reflects the difference of He II/He I photoionization cross-sectional ratios for C2p and O2p orbitals, the ratios being 0.306 and 0.639, respectively.[19] Substitution of furan may modify the intensity changes, because HOMO and HOMO − 1 orbitals (a_2 and b_1 symmetries) will alter their MO compositions by "mixing in" substituent localized orbitals of suitable symmetry. We can compare our spectra with the He I/He II spectra of iodofurans,[20] bifurans, and thienylfurans.[21] In 2-iodofuran, the intensity changes are the same as in unsubstituted furan, but in 2,5-diiodofuran the relative intensity of the $\tilde{X}$ band does not decrease significantly when compared to that of $\tilde{A}$. In the spectra of bifurans and thienylfurans any discernible trends in $\tilde{X}$ and $\tilde{A}$ intensities are lost. These two examples show that substituents can significantly modify MO character of π_2, π_3 orbitals through substituent−ring orbital interactions.

2-Ethynylfuran is the only ethynylfuran whose spectra clearly show the relative decrease of intensity of the $\tilde{X}$ band compared to the $\tilde{A}$ band on going from He I to He II. In the spectra of other ethynylfurans, either the $\tilde{X}$ and $\tilde{A}$ band intensities show no significant difference or the $\tilde{X}$ band intensity actually increases slightly compared to $\tilde{A}$ (Table 2). In the UPS of ethynylthiophenes,[4] on the other hand, the $\tilde{X}$ and $\tilde{A}$ band intensity variations are consistently similar to those in unsubstituted thiophene. The conclusion is that π orbital interactions between ethynyl and heterocyclic moieties are stronger in ethynylfurans than in ethynylthiophenes. This conclusion is difficult to reach on the basis of quantum chemical calculations or energy level diagrams.

The $\tilde{B}-\tilde{C}$ (in monoisomers) and $\tilde{B}-\tilde{E}$ bands (in disubstituted isomers) correspond to ionizations from orbitals with substantial ethynyl group character (π_{CC}). This is indicated by *ab initio* results and by the correlation diagram (Figure 4). In order to deduce MO characters, we have measured He II spectra at high

TABLE 2: Relative Intensities (Deduced from Band Areas) of Some UPS Bands. The Band Designation Is Given in Brackets, following the Intensity Value

compound	radiation	intensities			
2-	He I	1.0 ($\tilde{X}$)	0.54 ($\tilde{A}$)	0.76 ($\tilde{B}$)	0.76 ($\tilde{C}$)
	He II	1.0 ($\tilde{X}$)	0.98 ($\tilde{A}$)	0.90 ($\tilde{B}$)	0.87 ($\tilde{C}$)
2,4-	He I	1.0 ($\tilde{X}$)	0.96 ($\tilde{A}$)		
	He II	1.0 ($\tilde{X}$)	0.74 ($\tilde{A}$)		
2,3-	He I	1.0 ($\tilde{X}$)	0.93 ($\tilde{A}$)		0.84 ($\tilde{E}$)
	He II	1.0 ($\tilde{X}$)	0.73 ($\tilde{A}$)		0.45 ($\tilde{E}$)
2,5-	He I	1.0 ($\tilde{X}$)	0.76 ($\tilde{A}$)	2.23 ($\tilde{B} + \tilde{C} + \tilde{D}$)	1.08 ($\tilde{E}$)
	He II	1.0 ($\tilde{X}$)	0.79 ($\tilde{A}$)	2.38 ($\tilde{B} + \tilde{C} + \tilde{D}$)	0.77 ($\tilde{E}$)

resolution (see experimental section), which allowed us to observe intensity changes and vibrational fine structure even in the spectral regions which have high state densities.

Every ethynyl group contains two π orbitals: in-plane (π_{CC}') and out-of-plane (π_{CC}''). Due to symmetry restrictions, only the π_{CC}'' can interact with ring π orbitals and is expected to show a broad profile with long vibrational progression. The π_{CC}' band on the other hand, is expected to have an asymmetric, sharp contour, short progression, and strong 0−0 vibrational transition. Molecular frequencies for aromatic vibrational modes are in the vicinity of 900 cm^{-1}, while $-C{\equiv}C-$ stretching modes are close to 2000 cm^{-1}. The vibrational frequencies will of course be different in the ion, but the difference in wavenumbers should remain sufficient to distinguish the two modes. The excitations of the two modes will indicate ionizations from ring-localized (π_{ring}) or π_{CC} orbitals, respectively.

Analysis of UPS of ethynylfurans shows that the relative intensity of broad bands (π_{CC}'') increases more than the sharp ones (π_{CC}'). The spectrum of 2,5-bis(ethynyl)furan is a good example. The broad band at 11.45 eV increases in relative intensity when compared with the sharp one at 11.80 eV. The ethynylthiophenes exhibit the opposite trend[4] with sharp π_{CC} bands increasing more than the broad ones. The rationalization can be sought in the mixing of π_{CC} and predominantly heteroatom np orbitals (in-plane σ_X or out-of-plane π_2). S3p orbitals have a He II/He I cross-sectional ratio of 0.139 compared to 0.639 for O2p. π_{CC}' and π_{CC}'' can both gain heteroatom character, but the $\sigma_X - \pi_{CC}'$ interactions are weak, as had been demonstrated recently for ethynylpyridines.[10] The analysis of vibrational fine structure in the relevant bands of ethynylpyridines,[10] ethynylbenzene,[22] ethynylthiophenes,[4] and ethynylfurans (this work) supports this conclusion. In all these molecules sharper π_{CC} bands have high vibrational frequencies ($-C{\equiv}C-$ stretching modes).

It is interesting to compare π_{CC} bands in ethynylbenzenes,[8,22] ethynylpyridines,[10] and ethynylchalcophenes;[4] the comparison is made between isomers which are π isoelectronic.

In monoethynyl derivatives the sharp band (π_{CC}') always appears at lower ionization energy than its broad counterpart, which signifies that $\pi_{CC}'' - \pi_1$ interactions are weaker (π_1 is the ring π orbital with the highest ionization energy) than (π_3, π_2)$-\pi_{CC}''$ interactions. In bis(ethynyl) derivatives four π_{CC} bands are present, but the order of sharp and broad π_{CC} bands follows no definite trend. This reflects the plethora of possible orbital interactions.

In this work we tacitly assume the validity of the Gelius model[23] according to which the MO photoionization cross section can be expressed as a weighted sum of atomic cross sections (the weighting being proportional to electron populations of composite atomic orbitals).

Conclusion

Our discussion of substituent effects and the extent of orbital interactions is based on band contours and intensities rather than ionization energy shifts or MO calculations, as is the usual practice. Palmer et al.[22b] have commented on the problems pertaining to the use of ionization energy shifts in the analysis of electronic structure. The analysis of shifts suffers from the inherent problem of choosing a suitable reference energy level against which a shift can be measured. MO calculations suffer from "level-of-theory" problems (i.e., one can get different answers at different levels of theoretical sophistication). In order to circumvent these difficulties we suggest that measurements be performed at different photon energies with concomitant analysis of vibrational fine structure. This approach gives a more reliable picture of the interactions at hand, especially if (as in our work) the variable photon energy measurements can be performed at high resolution.

We have also shown that the interaction between ethynyl group(s) and the heterocyclic moiety is stronger in furans than in thiophenes. This suggests the possibility that 1,2-bis-(furylethynes) may be better precursors for the preparation of conducting polymers than 1,2-bis(thienylethynes) (at least according to the electronic structure criterion).

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