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Electron Attachment to the Aza-Derivatives of Furan, Pyrrole, and Thiophene

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The temporary anion states of gas-phase furan, isoxazole, oxazole, pyrrole, pyrazole, imidazole, thiophene, isothiazole, and thiazole are characterized by means of electron transmission spectroscopy. The measured energies of vertical electron attachment are compared with the virtual orbital energies of the neutral state molecules supplied by MP2 and B3LYP calculations with the 6-31G* basis set. The calculated energies, scaled with empirical equations, reproduce satisfactorily the experimental attachment energies. Replacement of a ring CH group with a nitrogen atom increases the electron-acceptor properties, although the stabilization of the π^* anion states is not as large as that of the π cation states, in line with the bond length variations caused by aza-substitution. In the spectra of thiophene and isothiazole the first π^* resonances display sharp vibrational structure with energy spacing of about 80 meV. The spectrum of isothiazole presents clear evidence for a low-energy (1.61 eV) resonance ascribed to the lowest σ^* anion state.

Introduction

Heterocyclic compounds play a very important role in chemistry as mediators for synthetic reactions, primarily as a means for preparing functionalized materials.[1] Furthermore, many molecular systems present in nature possess heterocyclic constituents. Among the simplest heterocycles are the five-membered aromatic rings, containing one or two heteroatoms. These compounds can undergo a variety of classical reactions, such as oxidative ring openings, Diels−Alder constructions, cycloadditions, and photocycloadditions. In particular, an important branch of their chemistry is directed toward compounds of natural origin as, for instance, in the case of oxidative conversion of imidazoles to optically active amino acid derivatives, the synthesis of antibiotics incorporating the oxazole ring,[1] and new preparative strategies for the construction of 2,4-disubstituted oxazoles.[2] In addition, heterocycles have recently attracted much interest[3−5] for the development of ionophores and receptors for recognition of neutral or charged species, with possible important applications in the fields of environmental, biological, and supramolecular chemistry.

Photoelectron spectroscopy and theoretical studies have provided detailed information on the energies and nature of the filled frontier molecular orbitals (MOs) in pentacyclo-heteroaromatics. Knowledge of the *empty* frontier levels is as important as that of the filled counterparts from the reactivity point of view; however, measurements of the complementary electron affinity data in this class of compounds have been reported only for pyrrole, furan, thiophene, selenophene, and tellurophene.[6,7]

In gas-phase collisions, an isolated molecule can temporarily attach an electron of proper energy and angular momentum into a vacant MO, the process being referred to as a shape resonance.[8] Electron transmission spectroscopy (ETS)[9] is one of the most suitable means for detecting the formation of these short-lived anions and elucidating the empty level electronic structure. Because electron attachment is rapid with respect to nuclear motion, temporary anions are formed in the equilibrium geometry of the neutral molecule. The impact electron energies at which electron attachment occurs are properly denoted as vertical attachment energies (VAEs) and are the negative of the vertical electron affinities. Within the Koopmans' theorem (KT)[10] approximation, VAEs are equal to the empty MO energies, just as the complementary ionization energies (IEs) supplied by photoelectron spectroscopy are equal to the negative of the energies of the filled MOs.

A theoretical approach adequate for describing the energetics of the unstable anion states observed in ETS involves difficulties not encountered for neutral or cation states. The first VAE can in principle be obtained as the energy difference between the lowest lying anion and the neutral state (both with the optimized geometry of the neutral species). A proper description of spatially diffuse species requires a basis set with diffuse functions. However, as the basis set is expanded, a self-consistent field (SCF) calculation ultimately describes a neutral molecule and an unbound electron in the continuum. Stabilization procedures are then needed to distinguish the virtual orbitals that give rise to temporary anion states from those low-energy solutions having no physical significance with regard to the resonance process.[11−15]

For instance, it has been shown[16] that the VAE (1.16 eV) supplied for benzene by B3LYP/6-311+G* calculations (i.e., with diffuse functions) is very close to experiment, but the singly occupied MO (SOMO) of the anion is described as a spatially diffuse σ^* (a_{1g}) MO rather than the valence π^* (e_{2u}) MO. For ethyne (where the first anion state is even more unstable than that of benzene), not only is the extra electron predicted to reside on a diffuse σ^* orbital but also the calculated VAE is about 1.3

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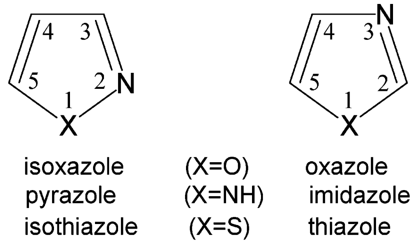
TABLE 1: Geometrical Parameters (Bond Distances in angstroms) Supplied by MP2/6-31G* (Top Entry) and B3LYP/6-31G* Calculations (Middle Entry) and Experimental (Microwave) Values in Parentheses (Lower Entry)

	d(1−2)	*d*(2−3)	*d*(3−4)	*d*(4−5)	*d*(1−5)	∠5−1−2 (deg)
furan[a]	1.3666	1.3661	1.4281			106.62
	1.3639	1.3605	1.4355			106.73
	(1.362)	(1.361)	(1.431)			(106.55)
isoxazole	1.3913	1.3285	1.4143	1.3640	1.3540	109.15
	1.3990	1.3122	1.4241	1.3599	1.3450	109.00
oxazole	1.3619	1.3037	1.3900	1.3618	1.3706	104.00
	1.3575	1.2942	1.3919	1.3559	1.3711	104.13
pyrrole[b]	1.3730	1.3829	1.4185			110.16
	1.3755	1.3782	1.4253			109.80
	(1.370)	(1.382)	(1.417)			(109.8)
pyrazole	1.3481	1.3478	1.4058	1.3853	1.3601	113.94
	1.3504	1.3328	1.4141	1.3816	1.3587	113.33
imidazole	1.3660	1.3251	1.3769	1.3778	1.3756	107.59
	1.3672	1.3149	1.3784	1.3722	1.3809	107.17
thiophene[c]	1.7176	1.3763	1.4201			91.97
	1.7361	1.3673	1.4300			91.52
	(1.714)	(1.3696)	(1.423)			(92.2)
isothiazole	1.6656	1.3378	1.4133	1.3796	1.7044	96.64
	1.6809	1.3174	1.4268	1.3694	1.7233	94.93
thiazole[d]	1.7265	1.3168	1.3733	1.3746	1.7138	89.21
	1.7497	1.3000	1.3775	1.3653	1.7347	88.54
	(1.724)	(1.304)	(1.372)	(1.367)	(1.713)	(89.3)

[a] Experimental values from ref 19. [b] Experimental values from ref 20. [c] Experimental values from ref 21. [d] Experimental values from ref 22.

CHART 1



eV lower than experiment. On the other hand, B3LYP/6-31G* calculations (without diffuse functions) correctly predict the SOMO π^* nature, but the calculated VAEs are too high.[16]

In the case of the present compounds, preliminary B3LYP calculations showed that the SOMO of the ground-state anion of imidazole is predicted to be a diffuse σ^* MO even using the smallest basis set (6-31+G*) containing diffuse functions, in contrast with the 6-31G* basis set.

Chen and Gallup[11] found a good linear correlation between the virtual orbital energies (VOEs) supplied by simple HF/6-31G calculations and the corresponding experimental VAEs. In a more extended study of the use of KT calculations for the evaluation of VAEs, Staley and Strnad[12] demonstrated the occurrence of good linear correlations between the $\pi^*_{\mathrm{C=C}}$ VAEs measured in a large number of alkenes and benzenoid hydrocarbons and the corresponding VOEs obtained with HF or MP2 calculations, using basis sets which do not include diffuse functions. More recently an analogous linear correlation has been found between π^* VAEs and the corresponding VOEs supplied by B3LYP/6-31G* calculations.[16]

Here we report the ET spectra of furan, pyrrole, thiophene, and their 2-aza and 3-aza derivatives isoxazole, oxazole, pyrazole, imidazole, isothiazole, and thiazole. The molecular structures of the latter are represented in Chart 1, together with atomic numbering. KT MP2/6-31G* and B3LYP/6-31G* calculations are carried out to support the association of the resonances observed in the ET spectra with the corresponding empty MOs and, in turn, to check their reliability in reproducing the measured π^* VAEs in heteroaromatic π-systems.

Experimental Section

Our electron transmission apparatus is in the format devised by Sanche and Schulz.[9] 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. Each resonance is characterized by a minimum and a maximum in the derivative signal. The energy of the midpoint between these features is assigned to the VAE. The present spectra were obtained by using the apparatus in the “high-rejection” mode[17] and are, therefore, related to the nearly total scattering cross-section. The electron beam resolution was about 50 meV (full width at half-maximum, fwhm). The energy scale was 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.

The calculations were performed with the Gaussian 98 suite of programs.[18] Geometry optimizations on the neutral molecules and evaluation of the virtual orbital energies are obtained at the MP2 and B3LYP level, using the 6-31G* basis set.

Results and Discussion

Molecular Geometries. The geometries of the neutral molecules were optimized with MP2 and B3LYP calculations, using the 6-31G* basis set. Table 1 reports selected geometrical parameters. The two sets of calculated bond distances are often equal within ±0.004 Å. When the difference is larger, the MP2 results are generally in better agreement with the available experimental (microwave) data,[19−22] reported in parentheses in Table 1.

Figure 1 displays a representation of the two lowest unoccupied π^* MOs of furan (C_{2v} point group) supplied by the B3LYP calculations. Similar localization properties are displayed by the π^* MOs of pyrrole and thiophene, and their aza derivatives, although in the latter the molecular symmetry is lowered to C_s.

The geometrical parameters which most directly affect the energies of the empty π^* MOs are the distances (2−3 and 4−5) between the atoms involved in the double bonds. In particular, the significant decrease of the 2−3 distance upon replacement

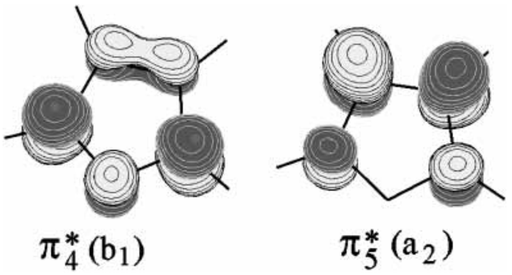


Figure 1. Representation of the two lower lying empty π^* MOs of furan, as supplied by B3LYP/6-31G* calculations.

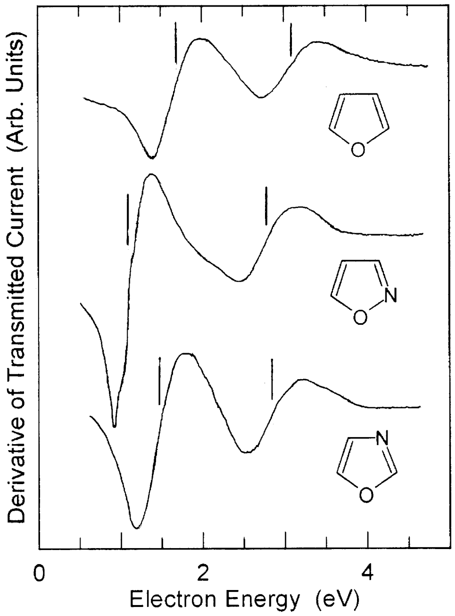


Figure 2. Derivative of transmitted current, as a function of electron energy, in furan, isoxazole, and oxazole. Vertical lines locate the VAEs.

of a CH group with a nitrogen atom (see Table 1) results in a destabilization of the two empty π^* MOs, owing to their antibonding character (see Figure 1). The 3−4 distance is also expected to play a role, but in opposite directions for the π_4^* and π_5^* MOs, due to their bonding and antibonding character, respectively, between these two atoms.

Inspection of Table 1 shows, according to both sets of calculated results, that on going from the 2-aza to the corresponding 3-aza derivatives the 2−3 and 3−4 bond distances decrease. Both geometrical variations result in a destabilization of the second empty π^* MO (π_5^*), whereas, for the LUMO (π_4^*), the two effects tend to compensate because of the bonding character between atoms 3 and 4.

ET Spectra and Calculated VOEs. Figures 2−4 report the ET spectra of the aza derivatives of furan, pyrrole and thiophene, respectively, as well as the parent compounds. The measured VAEs are given in Table 2 and in the diagram of Figure 5. The ET spectra of furan, pyrrole, and thiophene display two intense resonances associated with electron capture into the empty π_4^* and π_5^* MOs, of b$_1$ and a$_2$ symmetry (C_{2v} point group), respectively, represented in Figure 1. The present VAEs are equal, within experimental limits, to those previously measured by van Veen.[6] The first resonance of thiophene, however, displays a clear sequence of vibrational structures, with an energy spacing of about 80 meV, barely observable in the spectrum previously reported.[6] This vibrational progression of the anion most likely corresponds to the totally symmetric mode observed in the infrared spectrum of gas-phase thiophene at 839 cm^{-1} (0.104 eV).[23] The ET spectrum of isothiazole (see Figure 4) displays a vibrational progression in the first resonance even sharper than that observed in thiophene, the energy spacing being about the same (80 meV). The first resonances of the 2-aza derivatives of furan and pyrrole also show evidence

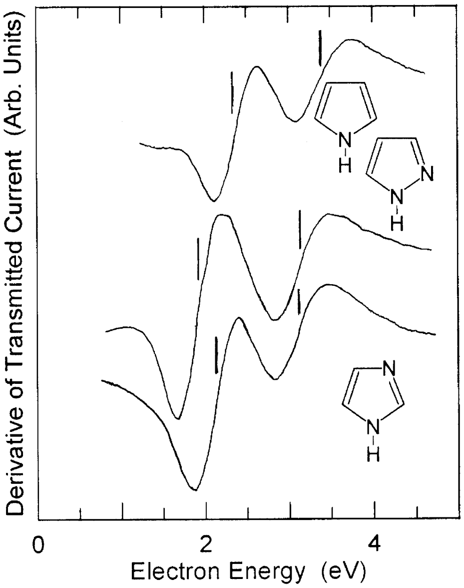


Figure 3. Derivative of transmitted current, as a function of electron energy, in pyrrole, pyrazole, and imidazole. Vertical lines locate the VAEs.

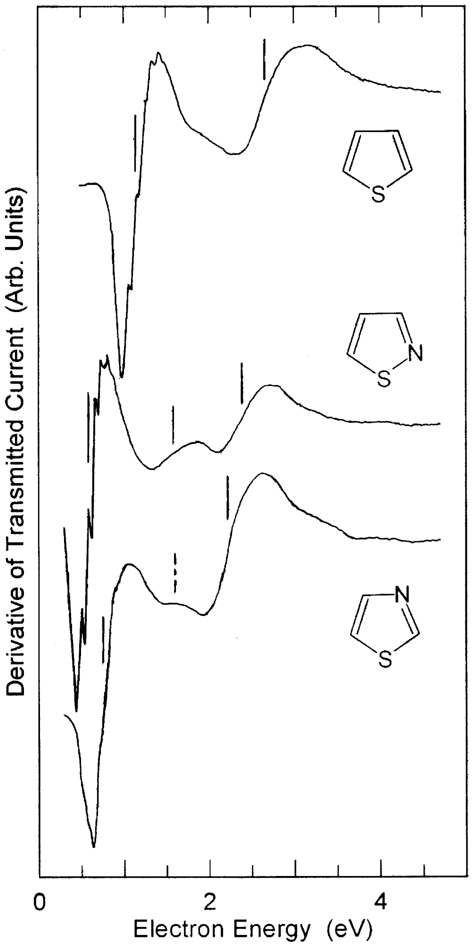


Figure 4. Derivative of transmitted current, as a function of electron energy, in thiophene, isothiazole, and thiazole. Vertical lines locate the VAEs.

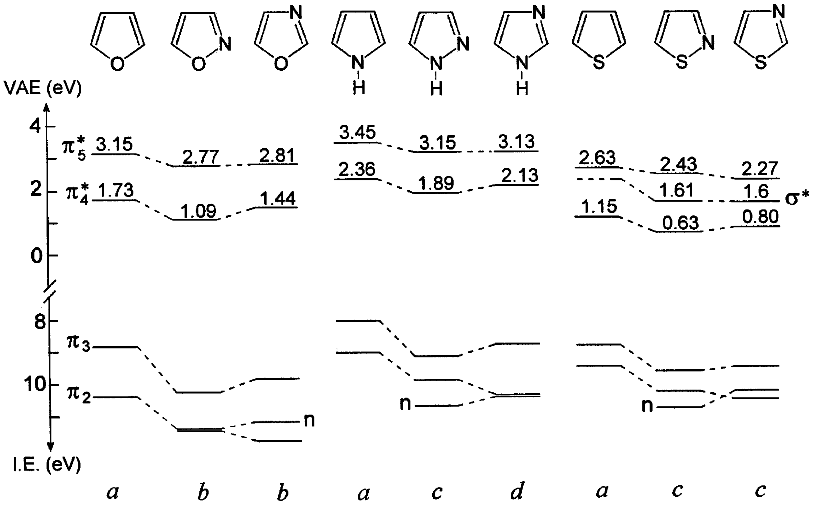


Figure 5. Diagram of the VAEs and IEs measured in furan, pyrrole, and thiophene and their 2- and 3-aza derivatives. IE values taken from the following references: (a) 3, (b) 4, (c) 25, and (d) 26.

TABLE 2: Virtual Orbital Energies (VOEs) Supplied by MP2/6-31G* and B3LYP/6-31G* Calculations and Experimental VAEs (Scaled VOEs (See Text) in Parentheses; All Values in eV)

compound	orbital	MP2/6-31G* VOE	B3LYP/6-31G* VOE	expt. VAE
furan	σ^*_{ring}	7.170	3.197	
	π^* (a_2)	6.694 (2.91)	2.139 (2.93)	3.15
	π^* (b_1)	4.566 (1.53)	0.537 (1.64)	1.73
isoxazole (2-azafuran)	σ^*_{ring}	6.907	2.687	
	π^*	6.175 (2.57)	1.553 (2.46)	2.77
	π^*	3.568 (0.94)	-0.412 (0.88)	1.09
oxazole (3-azafuran)	σ^*_{ring}	7.207	3.209	
	π^*	6.137 (2.55)	1.497 (2.42)	2.81
	π^*	4.161 (1.27)	-0.10 (1.20)	1.44
pyrrole	σ^*_{ring}	7.852	3.846	
	π^* (a_2)	7.093 (3.17)	2.636 (3.33)	3.45
	σ^*_{NH}	6.091	2.158	
	π^* (b_1)	5.462 (2.11)	1.386 (2.33)	2.36
pyrazole (2-azapyrrole)	σ^*_{ring}	7.595	3.637	
	π^*	6.618 (2.86)	2.104 (2.91)	3.15
	σ^*_{NH}	6.100	2.145	
	π^*	4.723 (1.63)	0.658 (1.74)	1.89
imidazole (3-azapyrrole)	σ^*_{ring}	7.634	3.641	
	π^*	6.592 (2.84)	2.053 (2.86)	3.12
	σ^*_{NH}	5.871	1.961	
	π^*	5.106 (1.88)	0.906 (1.94)	2.12
thiophene	σ^*_{ring}	6.618	2.769	
	π^* (a_2)	6.371 (2.70)	1.945 (2.78)	2.63
	σ^*_{SC}	5.172	0.966	
	π^* (b_1)	3.566 (0.88)	-0.207 (1.04)	1.15
isothiazole (2-azathiophene)	σ^*_{ring}	6.652	2.409	
	π^*	5.995 (2.45)	1.486 (2.41)	2.43
	σ^*_{SC}	4.764	0.378	1.61
	π^*	2.849 (0.42)	-0.882 (0.50)	0.63
thiazole (3-azathiophene)	σ^*_{ring}	6.742	2.533	
	π^*	5.864 (2.37)	1.353 (2.30)	2.27
	σ^*_{SC}	4.588	0.450	1.6
	π^*	3.128 (0.60)	-0.746 (0.61)	0.80

(although much weaker) of vibrational features not observed in the parent compounds, in line with the lower energy and consequently longer lifetime.

Figure 5, which for completeness also gives the outermost ionization energies,[24−27] shows that the two π^* anion states are stabilized on going from the unsubstituted compounds to the corresponding aza derivatives. This result is explainable in terms of the effect caused by replacement of a CH group with a more electronegative nitrogen atom, in line with the analogous increase of the electron-acceptor properties of pyridine relative to benzene.[28,29]

The stabilization caused by 2-aza substitution in furan (to give isoxazole) is 0.64 and 0.38 eV, respectively, for the first and second anion states. This difference is accounted for by the different atomic wave function coefficients of the corresponding π_4* and π_5* MOs at position 2, as shown in Figure 1. On this basis, on going from the 2-aza to the 3-aza derivative the π_4* and π_5* anions should be destabilized and stabilized, respectively. In fact, the VAE of π_4* is found to increase by 0.35 eV (in line with expectation), whereas the VAE of π_5* increases by 0.04 eV (in contrast with an expected decrease). However, this finding can be easily explained once the above-mentioned geometrical variations are accounted for. The shortening of the 2−3 and 3−4 distances acts in opposite directions for the π_4* anion state, so that the net energy perturbation is governed by the different wave function coefficients; in contrast, both geometrical changes are destabilizing for the π_5* anion state, thus balancing the opposite effect caused by a larger wave function coefficient at position 3.

The π* VAE trends observed in the pyrrole and thiophene series are qualitatively equal to that of the furan derivatives. It can be noted that the stabilizing effect brought by aza substitution on the π positive ions is even larger than on the anions and that their energy trends can be predicted using only the wave function coefficients.

As mentioned above, it has been demonstrated that measured π* VAEs are well-correlated with the corresponding virtual orbital energies (VOEs) of the neutral states calculated with basis sets which do not include diffuse functions. We have thus computed the HF/6-31G* (geometries optimized at the MP2 level) and the B3LYP/6-31G* VOEs to support the assignment of the spectral features to the corresponding empty π* MOs. The VOEs and the π* VOEs scaled according to equations given in the literature are reported in Table 2. For HF/6-31G* and MP2 geometries, we use, from ref 12, VAE = 0.64795VOE − 1.4298 (all quantities in eV). For B3LYP/6-31G*, we scale, as in ref 16, VAE = 0.80543VOE + 1.21099. Scaling of the π* VOEs leads to VAEs (in parentheses in Table 2) in good agreement with experiment with both methods, although somewhat too low (0.2−0.3 eV) in most cases. This could be due to the fact that heteroaromatics were not considered (MP2/6-31G*) or scarcely represented (B3LYP/6-31G*) in the calibration of the linear equations.

Most interestingly, the spectrum of isothiazole displays a less intense, but distinct, additional resonance (VAE = 1.61 eV) located between the two π* resonances. A similar feature, although less pronounced, is also observed at about the same energy in the 3-aza derivative thiazole. These findings confirm the prediction,[30] based on the results of MS-Xα calculations, that the lowest-lying σ* anion state of thiophene (with mainly sulfur character) lies below the second π* anion state, in contrast to furan. (The σ* resonance of thiophene is probably overlapped by the high-energy side of the lower π* resonance.) Consistently, systematic investigations[31] have demonstrated that substituents containing third-row (or heavier) elements give rise to low-energy σ* resonances not observed in the ET spectra of the corresponding second-row derivatives. In particular, in saturated thio-hydrocarbons such as diethyl sulfide, the first ($\sigma^*_{\mathrm{S-C}}$) VAE is 2.8 eV,[32] while in the three- to six-membered cyclic analogues the VAE ranges from 1.9 to 2.5 eV.[33]

In agreement with the above-mentioned MS-Xα calculations and the present experimental data, at both the MP2 and B3LYP levels (see Table 2) in thiophene and its aza derivatives, the first σ* MO (of b_2 symmetry in the C_{2v} point group notation) is predicted to lie at an energy intermediate between those of the two π* MOs and to be mainly localized on the sulfur atom and the two adjacent atoms, in an antibonding manner. By contrast, in the furan series the first σ* MO is predicted to lie well above the second π* MO and to possess different localization properties (mainly CH character, with small contributions from the heteroatoms).

Scaling of σ* VOEs to match measured resonance energies has not been extensively investigated. A study[34] of C−Cl σ* resonances in a series of chloroalkanes yielded the relation, VAE = 0.90VOE − 2.55. Applying this to the σ* resonances in the 2- and 3-azathiophenes yields 1.74 and 1.58 eV, in quite good agreement with the experimental values of 1.61 and 1.6 eV, respectively. For thiophene, the same relation predicts 2.10 eV. Interestingly, scaling of the σ* VOEs (either MP2 or B3LYP) using the earlier expressions benchmarked to π* resonances leads to VAEs of about 2.0 eV for thiophene and 1.6 eV for the two aza derivatives.

The ET spectra of pyrrole and its aza derivatives, like the furan analogues, do not display evidence for σ* resonances in the 0−5 eV energy range. According to both theoretical methods, however, the energy of their lowest lying σ* MO is about equal to or lower than that of the second π* MO (see Table 2). Using the C−Cl σ* scaling above, the MP2/6-31G* VOEs predict VAEs of 2.95−2.74 eV for these resonances. Inspection of the localization properties shows that, at variance with the thiophene counterpart (heteroatom-C antibonding of b_2 symmetry) the lowest σ* MO of pyrrole possesses a_1 symmetry and is essentially localized on the N−H bond.

The calculations thus indicate the presence of a σ^*_{NH} resonance at slightly lower energy than the second π* resonance, which is masked by the more intense signal of the latter. It is to be noted, however, that σ^*_{NH} resonances are not observed in the ET spectra of π-systems such as aniline[28] and $(C(CH_3)_3)_2C{=}NH$,[35] where π* signals are not present in the 2−4 eV energy range to obscure the spectrum. We note also that in the ET spectrum of ammonia the first feature is detected at 5.6 eV.[36] However, it was recently found that the spectrum of the saturated five-membered ring pyrrolidine seems to show a (relatively weak) resonance at 1.8 eV.[37] This prompted us to calculate the VOEs of ammonia and pyrrolidine, which turned out to be 5.970 and 6.054 eV (MP2) or 2.135 and 2.242 eV (B3LYP), respectively. These values are not only very close to each other, but also to the corresponding σ* VOE of pyrrole (6.091 and 2.158 eV; see Table 2). According to the calculations, the LUMO of NH_3 is a totally symmetric (a_1) MO. In pyrrolidine (where the N−H bond lies out of the C−N−C plane) the LUMO is localized on the N−H bond but, in contrast with pyrrole, large contributions also come from the ring carbon atoms.

These results could be interpreted in terms of a large s-wave ($l = 0$) contribution to the totally symmetric a_1 σ* resonances (ammonia and pyrrole) and consequently too great a width to show up in the total scattering cross-section, whereas the asymmetric LUMO of pyrrolidine is likely coupled to a higher partial wave. Consistently, electron energy loss measurements[38] on cyclopropane revealed the occurrence of vibrational excitation at 2.6 and 5.5 eV, the first weaker signal being associated with electron attachment to the LUMO of $a_{1'}$ symmetry, whereas only the second resonance was observed in the ET spectrum.[39]

Recent trapped electron[40] measurements on pyrazole,[41] observing electrons with final energies below 0.2 eV, showed peaks at impact energies of 0.75 and 2 eV that were ascribed to vibrational excitation via the formation of temporary anion states. The peak at 2 eV is consistent with excitation through the first π* resonance located here at 1.89 eV. However, the origin of the 0.75 eV feature has yet to be clarified, as there is no evidence for anion formation in the 0−1 eV range in the ET spectrum and, according to the present calculations, the first σ* resonance should lie well above the first π* resonance (associated with the 2 eV peak of the trapped electron spectrum). In particular, the claim based on theoretical calculations[42] that the lowest anion state in pyrazole (as well as those of pyrrole, furan, and isoxazole) is a σ* resonance is not credible because the basis functions used in the study are too diffuse. Because anion states are appropriately recognized as being diffuse in character, it is perhaps natural to increase the diffuseness of the basis sets in an attempt to permit more accurate calculations of anion energies. However, in the case of temporary negative ions, this procedure leads to a degree of variational collapse as the wave functions begin to emulate those of the continuum.[11−15]

This typically leads to σ^* anion state energies shifting to much lower values relative to those of π^* states. Thus, we consider that the 0.75 eV peak observed by Walker et al. must have another source. In work in progress, ETS measurements with greater scattered electron rejection than those used in the present study have revealed a sharp feature near the threshold for excitation of the N−H vibrational stretch in pyrazole at 0.43 eV.[43] Model calculations suggest that a dipole supported anion state at this energy could considerably enhance the vibrational excitation cross-section above its threshold, possibly accounting for the peak in trapped electron current observed by Walker et al.

Walker et al.[44] have also presented trapped electron data for isoxazole, finding peaks associated with resonance processes at approximately 1.5, 3, 4.5, and 6.6 eV. The first two of these are in reasonable agreement with the ETS values of 1.09 and 2.77 eV. No evidence was found of a peak analogous to that at 0.75 eV in pyrazole.

Conclusions

The present electron transmission spectroscopy study, in agreement with the results of MP2 and B3LYP calculations, demonstrates that replacement of a CH group with a nitrogen atom stabilizes the empty π^* MOs of the prototypical pentaheterocycles furan, pyrrole, and thiophene, mainly when aza substitution takes place at the position adjacent to the heteroatom. The effect is even larger for the filled π counterparts. Aza substitution is thus expected to enhance the reactivity of the pentaheterocycles when they act as electron acceptors or to inhibit it when they act as electron donors.

The ET spectra of isothiazole and thiazole also display an additional resonance, ascribed to electron capture into a σ^* MO with mainly sulfur character, at energy (1.6 eV) intermediate between the two π^* resonances. The corresponding signal in thiophene is masked by overlap with the more intense π^*signal.

The virtual orbital energies supplied by MP2 and B3LYP calculations for the neutral molecules and scaled with empirical linear equations closely reproduce the measured VAEs, including the σ^* VAEs in the thiophene derivatives. The calculations also predict the occurrence of a σ^* resonance localized at the N−H bond in the 2.5−3 eV energy range in pyrrole and its aza derivatives, for which no evidence is found in the ET spectra. In this case, in addition to probable overlap with the second π^* resonance, it is to be noted that because of its high symmetry (a_1 in pyrrole) and consequent large coupling with the $l = 0$ partial wave, the $\sigma^*_{\mathrm{N-H}}$ resonance could be too broad and weak to be detected in the total scattering cross-section.

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