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Temporary Anion States and Dissociative Electron Attachment to Isothiocyanates

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The temporary anion states of isothiocyanates $CH_3CH_2N{=}C{=}S$ (and $CH_3CH_2N{=}C{=}O$ for comparison), $C_6H_5CH_2N{=}C{=}S$, and $C_6H_5N{=}C{=}S$ are characterized experimentally in the gas phase for the first time by means of electron transmission spectroscopy (ETS). The measured vertical electron attachment energies (VAEs) 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 VAEs. The first VAE is also closely reproduced as the total energy difference between the anion and neutral states calculated at the B3LYP/6-31+G* level. Due to mixing between the ring and $N{=}C{=}S$ π-systems, $C_6H_5N{=}C{=}S$ possesses the best electron-acceptor properties, and its lowest-lying anion state is largely localized at the benzene ring. The anion states with mainly $\pi^*_{C=S}$ and $\pi^*_{N=C}$ character lie at higher energy than the corresponding anion states of noncumulated π-systems. However, the electron-acceptor properties of isothiocyanates are found to be notably larger than those of the corresponding oxygen analogues (isocyanates). The dissociative electron attachment (DEA) spectra show peaks close to zero energy and at 0.6 eV, essentially due to NCS^- negative fragments. In spite of the energy proximity of the first anion state in phenyl isothiocyanate to the DEA peak, the zero-energy anion current in the benzyl derivative is about 1 order of magnitude larger.

Introduction

Recently, research interest in isothiocyanates has become more intense because of their wide variety of medicinal, pharmacological, or industrial applications. The cumulated $-N{=}C{=}S$ π-system contained in cruciferae plants and vegetables gives the plants a particular flavor and, most importantly, seems to possess a number of interesting medicinal properties.[1] In particular, isothiocyanates inhibit the proliferation of tumor cells both in vitro and in vivo[2,3] and are used as chemopreventive agents.[4] The initiating event for these effects seems to be acute cellular stress caused by this class of compounds,[3] although elucidation of the mechanisms is still at an early stage.

From the more general point of view of reactivity, isothiocyanates are important and versatile tools in the synthesis of heterocyclic compounds.[5,6] A simple regioselective synthesis of uracils and their thio analogues has been achieved by cyclocondensation of diazadienium iodide and isothiocyanates.[7] Cyclization reactions of acylium and thioacylium ions with isothiocyanates have recently been observed also in the gas phase.[8] In the synthesis of carbocyclic and heterocyclic fused quinolines by cascade radical annulations of unsaturated N-aryl thiocarbamates, the thiocarbamate precursors are prepared by treatment of aryl isothiocyanates with homopropargyl alcohols.[9] Many of these behavioral phenomena are undoubtedly related to their electronic structures and, in particular, to their ability to accept electrons.[10]

In gas-phase collisions, an isolated molecule can temporarily attach an electron of proper energy and angular momentum into a vacant molecular orbital (MO), the process being referred to as a shape resonance.[11] Electron transmission spectroscopy (ETS)[12] is one of the most suitable means for detecting the formation of these unstable anion states. Because electron attachment is rapid with respect to nuclear motion, temporary anions are formed in the equilibrium geometry of the neutral molecule. The (positive) 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.

Additional information can be supplied by dissociative electron attachment spectroscopy (DEAS),[11] which measures the yield of negative fragments, as a function of the impact electron energy. When suitable energetic conditions occur, the decay of unstable molecular anions formed by resonance can follow a dissociative channel which generates negative fragments and neutral radicals, in kinetic competition with simple re-emission of the extra electron

$$e^-_{(E)} + AX \rightarrow AX^{-*} \rightarrow A^\bullet + X^-$$

The lifetime of the negative fragments produced is usually sufficiently long to allow their detection by means of a mass filter. Measurements of the negative ion abundance as a function of the incident electron energy thus give insight into the nature and efficiency of the dissociative channels of resonance processes.

Within the Koopmans' theorem[13] (KT) approximation, VAEs are equal to the empty MO energies, just as the complementary

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ionization energies supplied by photoelectron spectroscopy are equal to the negative of the energies of the filled MOs. ETS has thus proven to be a powerful means for elucidating the empty level electronic structure, as important as the filled counterpart from both the theoretical and reactivity points of view.

A theoretical approach adequate for describing the energetics of unstable anion states, however, involves difficulties not encountered for neutral or cation states. The most correct approach is, in principle, the calculation of the total scattering cross section with the use of continuum functions, although complications arise when attempting to obtain an accurate description of the electron−molecule interactions.[14]

The first VAE can be obtained as the energy difference between the lowest-lying anion and the neutral state (both with the optimized geometry of the neutral species), but the description of resonance anion states (unstable with respect to electron loss) with standard bound-state methods poses a serious problem. A proper description of the spatially diffuse electron distributions of anions requires a basis set with diffuse functions.[15,16] On the other hand, as the basis set is expanded, the wavefunction ultimately describes a neutral molecule and an unbound electron inasmuch of the continuum as the basis set can emulate,[17−20] since this is the state of minimum energy, thus not accounting for the fact that during a resonance process the extra electron is confined to the molecule by a potential barrier. The choice of a basis set which gives a satisfactory description of the energy and nature of resonance processes is therefore a delicate task.[21]

The Koopmans' theorem (KT) approximation neglects correlation and relaxation effects. However, Chen and Gallup[22] and Staley and Strnad[20] demonstrated the occurrence of good linear correlations between the $\pi^*_{C=C}$ VAEs measured in a large number of alkenes and benzenoid hydrocarbons and the corresponding virtual orbital energies (VOEs) of the neutral molecules obtained with simple KT Hartree−Fock (HF) calculations, using basis sets which do not include diffuse functions. We have recently shown[17] that the neutral-state π^* VOEs obtained with B3LYP/6-31G* calculations also supply a good linear correlation with the corresponding VAEs measured over a variety of different families of unsaturated compounds.

Here, we analyze the ethyl, benzyl, and phenyl isothiocyanates ($CH_3CH_2N{=}C{=}S$, $C_6H_5CH_2N{=}C{=}S$, and $C_6H_5N{=}C{=}S$) by means of ETS and DEAS for the first time. MP2/6-31G* and B3LYP/6-31G* calculations on the neutral-state molecules are employed to characterize the localization properties of the lowest-lying empty MOs and verify whether scaling of the π^* VOEs with appropriate empirical equations reported in the literature[17,20] can supply a good quantitative prediction of the corresponding measured VAEs in these cumulated π-systems. In previous work,[23] in fact, we found that the oxygen analogues ($RN{=}C{=}O$) constitute an exception, this approach leading to a large underestimation of both the π^*_{CO} and π^*_{CN} VAEs.

In addition, the first VAE is also calculated as the total energy difference between the neutral and anion states at the B3LYP/6-31+G* level, i.e., with a basis set which includes the minimum addition of diffuse functions.

Experimental Section

Our electron transmission apparatus is in the format devised by Sanche and Schulz[12] and has been previously described.[24] 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[25] and are, therefore, related to the nearly total scattering cross section. The electron beam resolution was about 50 meV (fwhm). The energy scale was calibrated with reference to the ($1s^12s^2$) ^2S anion state of He. The estimated accuracy is ±0.05 or ±0.1 eV, depending on the number of decimal digits reported.

TABLE 1: Calculated Bond Distances (Å) and Angles

	B3LYP/ 6-31G*	B3LYP/ 6-31+G*	MP2/ 6-31G*	exptl
		$HN{=}C(t\text{-}Bu)_2$		
$d_{N=C}$	1.2786	1.2804	1.2909	
		$(t\text{-}Bu)_2C{=}S$		
$d_{C=S}$	1.6542	1.6485	1.6396	
		$CH_3CH_2N{=}C{=}S^a$		
d_{C-N}	1.4348	1.4357	1.4400	1.438
$d_{N=C}$	1.1910	1.1922	1.2071	1.187
$d_{C=S}$	1.5951	1.5945	1.5845	1.580
d_{C-C}	1.5284	1.5291	1.5209	1.520
∠CNC	152.91°	152.93°	148.08°	147.4°
∠NCS	175.88°	175.92°	174.30°	184.5°
∠CCN	111.72°	111.82°	110.73°	111.0°
		$PhCH_2NCS$		
d_{C-N}	1.4326	1.4353	1.4386	
$d_{N=C}$	1.1934	1.1949	1.2091	
$d_{C=S}$	1.5921	1.5907	1.5826	
∠CNC	149.30°	148.71°	146.39	
∠NCS	175.68°	175.56°	174.16	
dih. CCCN	3.61°	1.04°	37.02°	
		$PhN{=}C{=}S^b$		
d_{C-N}	1.3839	1.3845	1.3905	1.370(5)
$d_{N=C}$	1.1956	1.1964	1.2119	
$d_{C=S}$	1.5892	1.5882	1.5784	
∠CNC	153.29°	153.30°	147.58°	148.0(5)°
∠NCS	175.82°	175.79°	174.35°	

[a] ref 28. [b] ref 29.

The collision chamber of the ETS apparatus has been modified[26] in order to allow for ion extraction at 90° with respect to the electron beam direction. Ions are then accelerated and focused toward the entrance of a quadrupole mass filter. Alternatively, the total anion current can be collected and measured with a picoammeter at the walls of the collision chamber (about 0.8 cm from the electron beam). Measurements of the total anion current were obtained with an electron beam current about twice as large as that used for the ET experiment. The energy spread of the electron beam increased to about 120 meV, as evaluated from the width of the SF_6^- signal at zero energy used for calibration of the energy scales.

The calculations were performed with the *Gaussian 98* suite of programs.[27] Geometry optimizations on the neutral molecules were obtained at the MP2/6-31G*, B3LYP/6-31G*, and B3LYP/6-31+G* levels. The first two methods are employed for evaluation of the virtual orbital energies of the neutral molecules, and the latter for computing the first VAE as the total energy difference between anion and neutral states.

Results and Discussion

Molecular Geometries. The geometries of the neutral molecules were optimized with MP2/6-31G*, B3LYP/6-31G*, and B3LYP/6-31+G* calculations. Table 1 reports selected geometrical parameters for ethyl, phenyl, and benzyl isothiocyanate, and the reference molecules $HN{=}C(t\text{-}Bu)_2$ and (*t*-

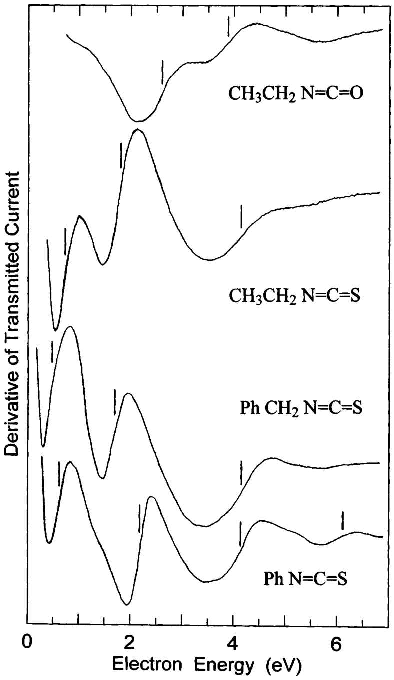

Figure 1. Derivative of transmitted current, as a function of the incident electron energy, in ethyl isocyanate and ethyl, benzyl, and phenyl isothiocyanate. Vertical lines locate the VAEs.

Bu)$_2$C═S containing the noncumulated imine and thiocarbonyl double bonds. The available electron diffraction[28] and microwave[29] gas-phase experimental data (see last column of Table 1) are satisfactorily reproduced by the calculations.

The geometrical factor which most directly affects the energy of the empty $\pi^*_{\mathrm{N=C}}$ and $\pi^*_{\mathrm{C=S}}$ MOs is the double bond length. According to the calculations, the lengths of both the imine and thiocarbonyl double bonds (mainly the former) in the cumulated N═C═S π-system are sizeably smaller than those of the reference molecules HN═C(*t*-Bu)$_2$ and (*t*-Bu)$_2$C═S, in line with the analogous results found for isocyanates.[23] Due to the antibonding character of the $\pi^*_{\mathrm{N=C}}$ and $\pi^*_{\mathrm{C=S}}$ MOs, this geometrical factor is expected to increase their VAEs on going from the reference molecules to the isothiocyanates.

The C—N (single) bond is calculated to be significantly shorter in phenyl isothiocyanate than in the ethyl and benzyl analogues, thus indicating the occurrence of mixing between the benzene and N═C═S π-systems. Because of this interaction, the N═C═S group lies in the plane of the benzene ring.

Finally, in benzyl isothiocyanate, two conformational minima are calculated, with the C(H$_2$)—N single bond nearly coplanar with the ring plane or nearly perpendicular to it. The coplanar conformer is calculated to be more stable, but the energy difference is very small (about 0.4 kcal/mol) so that also the perpendicular conformer should be significantly populated at 40 °C. However, according to the calculations, the empty π^* MO energies change only slightly between the two conformers.

ET Spectra and Empty Level Structure. Figure 1 reports the ET spectra of ethyl, benzyl, and phenyl isothiocyanate (labeled CH$_3$CH$_2$N═C═S, PhCH$_2$N═C═S, and PhN═C═S), and of ethyl isocyanate. CH$_3$CH$_2$N═C═S possesses two perpendicular empty MOs, π^*_{CS}, and π^*_{NC}, mixed by symmetry with the filled nitrogen lone pair (n$_\mathrm{N}$) and sulfur lone pair (n$_\mathrm{S}$) MO, respectively. The ET spectrum displays two resonances located at 0.75 and 1.95 eV and a broader feature centered at 4.2 eV. The previously reported[30] ET spectrum of the reference molecules (*t*-Bu)$_2$C═S does not show any evidence for distinct resonances up to 5 eV, indicating that the π^*_{CS} anion state is stable (thus not observable in ETS) or lies close to zero energy (<0.2 eV), where it can be masked by the high-energy wing of the intense electron beam signal. The π^*_{NC} VAE of HN═C(*t*-Bu)$_2$ is 1.29 eV.[30]

The occurrence of good linear correlations between the π^* VAEs measured in a large number of alkenes and benzenoid hydrocarbons and the corresponding virtual orbital energies (VOEs) of the neutral molecules obtained with basis sets which do not include diffuse functions has been demonstrated.[17,20,22] The VOEs of the present isothiocyanates supplied by B3LYP and MP2 calculations using the 6-31G* basis set are given in Table 2, together with the values (in parentheses) scaled with the appropriate empirical equations reported in the literature (MP2/6-31G*:[20] VAE = 0.64795 × VOE − 1.4298. B3LYP/6-31G*:[17] VAE = 0.805434 × VOE + 1.21099). The scaled VOEs reproduce satisfactorily the π^*_{NC} VAE of HN═C(*t*-Bu)$_2$ and confirm the stability of the π^*_{CS} anion state of (*t*-Bu)$_2$C═S, a slightly negative VAE (i.e., positive vertical electron affinity) being predicted with both theoretical methods. The same approach leads to about 0.9 eV for the π^*_{CS} VAE of CH$_3$CH$_2$N═C═S, in nice agreement with experiment, whereas the π^*_{NC} VAE (1.95 eV) is somewhat underestimated. The same discrepancy (about 0.5 eV) between the scaled VOE and the VAE of the cumulated π^*_{NC} MO is also observed in the benzyl derivative (see Table 2), in line with previous findings in the oxygen analogues.[23]

The relatively broad and weak signal centered at 4.2 eV can thus be due to electron capture into a σ^* MO with mainly C—S character (predicted to lie at about 2.5 eV higher energy than the π^*_{NC} MO by both the B3LYP and MP2 calculations). Systematic analyses[31] have in fact shown that the ET spectra of hydrocarbons containing third-row (or heavier) elements display distinct σ^* resonances at low energy, not present in the unsubstituted compounds.

The π^*_{CS} and π^*_{NC} VAEs (0.75 and 1.95 eV, respectively) of the N═C═S π-system are about 0.8 eV larger than those of the corresponding reference molecules (see Table 2 and Figure 2). This finding can be traced back to the two factors mentioned above. Both π^* MOs are destabilized by interaction with a filled lone pair MO. In addition, as shown in Table 1, the double bond lengths are significantly reduced in the cumulated double bonds, this geometrical variation resulting in a destabilization of the antibonding π^* MOs. Analogous destabilizations (relative to noncumulated reference molecules) were observed for the π^*_{CO} and π^*_{NC} MOs of benzyl and phenyl isocyanate.[23]

However, it is interesting that the π^*_{NC} VAE (1.95 eV) of ethyl isothiocyanate is sizeably smaller than the corresponding VAE (3.4 eV) measured[23] in benzyl isocyanate. For the sake of direct comparison, we have also run the ET spectrum of CH$_3$CH$_2$N═C═O (see Figure 1), where the π^*_{CO} VAE is 2.63 eV and the π^*_{NC} VAE (3.90 eV) is even higher than that of benzyl isocyanate. Therefore, not only is the electron affinity of ethyl isothiocyanate 1.7 eV larger than that of ethyl isocyanate (due to the different nature of the first anion state), but even electron attachment to the π^*_{NC} MO occurs at about 2 eV lower energy in the thio derivative. On the one hand, this could be partly due to a larger overlap (and destabilization) of the π^*_{NC} MO with the n$_\mathrm{O}$ oxygen lone pair (compared to n$_\mathrm{S}$). On the other, this finding confirms the well-known[31] stabilizing effect exerted by third-row elements on adjacent π^* anion states, consistent with participation of low-energy empty atomic 3d orbitals.

PhCH$_2$N═C═S and PhN═C═S possess three more empty π^* MOs, which derive from the benzene degenerate e$_{2u}$ (π^*)

TABLE 2: π* Virtual Orbital Energies (VOEs), VOEs Scaled with Empirical Equations (in parentheses), B3LYP/6-31+G* First VAEs Calculated as the Anion/Neutral Energy Difference, Experimental VAEs, and Peak Energies in the DEA Spectra[a]

orbital	B3LYP/6-31G* VOE (VAE)	MP2/6-31G* VOE (VAE)	B3LYP/6-31+G* VAE	exptl VAE	DEAS peak energy (int. relative to C_6H_5Cl)
$HN{=}C(t\text{-}Bu)_2$					
π^*_{NC}	0.291 (1.45)	4.696 (1.61)	1.071[b]	1.29[c]	
$(t\text{-}Bu)_2C{=}S$					
π^*_{CS}	−1.828 (−0.26)	2.123 (−0.05)	−0.06	<0.2[c]	
$CH_3CH_2N{=}C{=}S$					
				4.2	
$\pi^*_{NC}-n_S$	0.266 (1.43)	4.200 (1.29)		1.95	1.8 (≤0.07)
$\pi^*_{CS}-n_N$	−0.297 (0.97)	3.421 (0.79)	0.667	0.75	0.6 (0.44)
$PhCH_2N{=}C{=}S$					
π^*o	4.372 (4.73)[d]	9.840 (4.94)		≤4.2	4.7
$\pi^*_{NC}-n_S$	0.272 (1.43)	4.168 (1.27)		1.78	
π^*_A	−0.194 (1.05)	3.671 (0.95)			
π^*_S	−0.421 (0.87)	3.487 (0.83)			
$\pi^*_{CS}-n_N$	−0.513 (0.80)	3.230 (0.66)	0.500	0.49	0.6 sh. (18.1) 0.00 (144.9)
$PhN{=}C{=}S$					
				6.1 (c.e.)	
π^*o	4.238 (4.62)	9.761 (4.89)		≤4.2	4.7
$\pi^*_{NC}-\pi^*_S-n_S$	1.211 (2.19)	5.492 (2.13)		2.23	
π^*_A	−0.484 (0.82)	3.394 (0.77)			
$\pi^*_{CS}-n_N$	−0.473 (0.83)	3.211 (0.65)		0.62	0.6 sh. (4.6)
$\pi^*_S+\pi^*_{NC}-n_S$	−0.235 (0.22)	2.347 (0.11)	0.107	<0.2	0.06 (12.2)

[a] All values in eV. [b] The SOMO of the vertical anion is a σ^* diffuse function. [c] From ref 30. [d] Average energy of two MOs localized at the benzene ring and the CH_2 group.

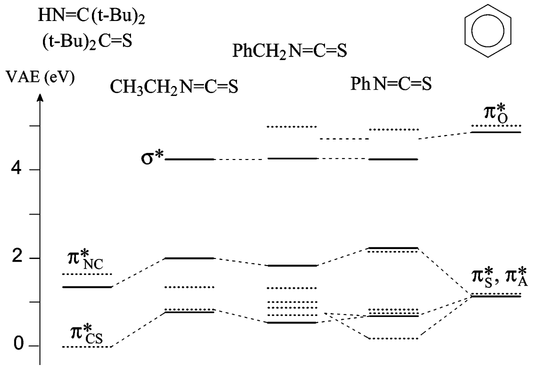

Figure 2. Correlation of the experimental VAEs (continuous lines) with the scaled π* VOEs supplied by MP2/6-31G* calculations (dashed lines) in isothiocyanates and reference molecules.

LUMO and the totally antibonding b_{2g} (π*) MO (VAE = 1.12 and 4.82 eV, respectively, in benzene[24]). In Table 2 and the correlation diagram of Figure 2, the symmetric and antisymmetric components of the benzene LUMO are labeled π^*_S and π^*_A, respectively, and the higher-lying ring π* MO is labeled π^*_O.

In benzyl isothiocyanate ($PhCH_2N{=}C{=}S$), the intermediate CH_2 group prevents mixing between the two π-systems. On the basis of the VAEs measured in ethyl isothiocyanate and benzene,[24] electron attachment to the first three empty MOs (π^*_{CS}, π^*_S, and π^*_A) is expected to occur below 1.2 eV. In this energy region, the ET spectrum displays only a single unresolved resonance centered at 0.49 eV. Consistently, the B3LYP and MP2 scaled VOEs predict the first anion state (π^*_{CS}) and the next two anion states (with mainly e_{2u} ring character) to lie close to each other (within 0.3 eV). In contrast with the ethyl derivatives, the first anion state of benzyl isothiocyanate is only 0.2 eV more stable than that of benzyl isocyanate (VAE = 0.66 eV[23]), but the localization properties are quite different: in the former the first anion state mainly possesses π^*_{CS} character, whereas in the latter, it is essentially localized on the benzene ring.

The next resonance (VAE = 1.78 eV) in the ET spectrum of $PhCH_2N{=}C{=}S$ is associated with the mainly π^*_{NC} MO, by analogy with the corresponding feature in the spectrum of the ethyl derivative. The calculations predict the VAE of the π^*_O MO of $PhCH_2N{=}C{=}S$ to be very close to that (4.82 eV[24]) measured for the corresponding b_{2g} (π*) MO of benzene. Moreover, the width (fwhm) of this resonance in benzene and substituted benzenes is about 0.6 eV.[31] In contrast, the feature displayed by the ET spectrum in this energy range (as well as that observed in the ethyl derivative) is centered at only 4.2 eV, and its width (1.1 eV) is very large. We thus assign this signal to two unresolved contributions, one likely from a mainly σ^*_{SC} MO and the other (on the high-energy side) from the π^*_O MO.

In the 0−5 eV energy range, the ET spectrum of $PhN{=}C{=}S$ looks similar to that of $PhCH_2N{=}C{=}S$, displaying three resonances at 0.62, 2.23, and 4.2 eV. However, the calculations indicate remarkable differences. Here, the benzene and $N{=}C{=}S$ π-systems can mix. The first anion state is predicted to lie close to zero energy, thus escaping detection in the ET spectrum. At variance with the ethyl and benzyl derivatives, the LUMO does not possess mainly π^*_{CS} character, but derives from (bonding) mixing between the symmetric component (π^*_S) of the e_{2u} benzene MO and the mainly π^*_{NC} MO. The quite different localization properties of the LUMO in benzyl and phenyl isothiocyanate are represented in Figure 3. The first resonance (VAE = 0.62 eV) observed in the ET spectrum of $PhN{=}C{=}S$ is associated with the unresolved contributions from the mainly π^*_{CS} MO and the (noninteracting) antisymmetric component (π^*_A) of the benzene e_{2u} MO. According to the calculations, the VAEs of these two MOs are equal within experimental error (see Table 2). The next resonance (2.23 eV) is due to the mainly π^*_{NC} MO, destabilized by interaction with the ring π^*_S MO. Consistently, its VAE is 0.4−0.5 eV higher than that of the π^*_{NC} MO of the benzyl derivative, where this

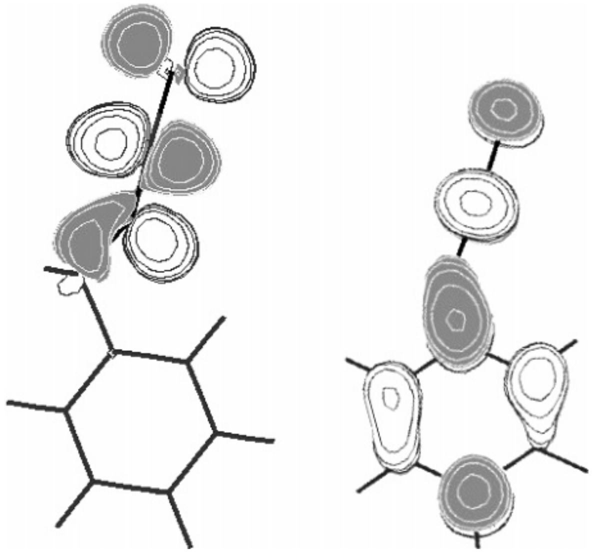

Figure 3. Representation of the LUMO of benzyl (left) and phenyl (right) isothiocyanate, as supplied by B3LYP/6-31G* calculations.

interaction does not occur. It can also be noticed that in this case the scaled VOE (with both methods) matches quite well the experimental VAE, at variance with the nonconjugated ethyl and benzyl derivatives. Again, a higher-lying broad resonance located at 4.2 eV is present, similar to that observed in the benzyl derivative. At higher energy, a distinct signal centered at 6.2 eV is ascribed to a core-excited resonance, i.e., electron capture accompanied by a simultaneous valence excitation.

As mentioned above, the choice of a basis set which gives a satisfactory description of both the energy and nature of unstable anion states is a delicate task, the dependence of the calculated energies and localization properties on the addition of diffuse functions to the basis set changing with the energy and nature of the anion state.[17,21] The first VAE of the present compounds was calculated as the total energy difference between the ground anion and neutral states at the B3LYP/6-31+G* level, i.e., with a basis set which includes a minimum addition of diffuse functions. The results, given in Table 2, reproduce very accurately the VAEs measured in ethyl and benzyl isothiocyanate together with those obtained from the scaled VOEs for $(t\text{-Bu})_2C{=}S$ and phenyl isothiocyanate (where the first anion state cannot be observed in ETS). In addition, the singly occupied MO (SOMO) of the anion is correctly predicted to be a valence π^* MO. Even the VAE calculated for $HN{=}C(t\text{-Bu})_2$ is close to the measured value, in spite of the fact that this anion is significantly more unstable. However, inspection of the localization properties reveals that in this case the SOMO is wrongly identified as a diffuse orbital of σ^* symmetry (instead of a π^*_{NC} MO) so that comparison of the calculated VAE with experiment is irrelevant. Using the 6-31G* basis set, the SOMO is correctly described as a valence π^* MO, but the calculated VAE (2.39 eV) is far too large.

DEA Spectra. Figure 4 displays the total anion current measured at the walls of the collision chamber, as a function of the incident electron energy, in the 0−5 eV energy range. The current of anions extracted from the collision chamber and mass-selected with a quadrupole filter reveals that the total anion current is essentially completely accounted for by the NCS^- fragment. The energy of the peaks, calibrated with the mass filter against the SF_6^- peak at zero energy, are reported in the last column of Table 2 together with the intensities (in parentheses) relative to the Cl^- current at 0.75 eV in chlorobenzene. The relative intensities are evaluated from the peak heights in the total anion current, normalized to the same pressure for all compounds.

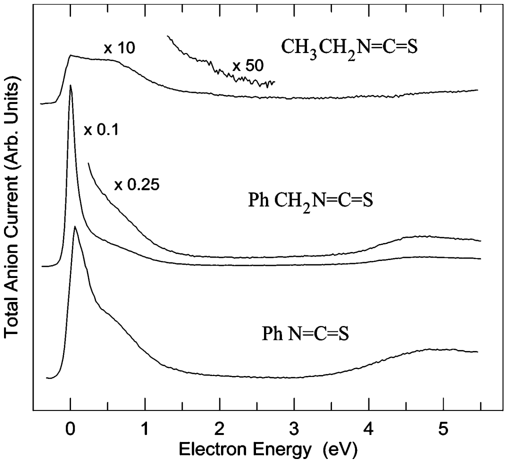

Figure 4. Total anion current, as a function of the incident electron energy, in ethyl, benzyl, and phenyl isothiocyanate.

The DEA spectrum of ethyl isothiocyanate shows a relatively weak peak at 0.6 eV, clearly associated with the π^*_{CS} resonance observed at 0.75 eV in the ET spectrum. The fact that the DEA peak energy is smaller than the corresponding VAE is well-understood[32] in terms of the kinetic competition between dissociation and electron autodetachment, the molecular anions formed on the high-energy side of the Franck−Condon envelope having a shorter survival time. The rise of the negative current at zero energy is attributed to the low-energy wing of the resonance, owing to the inverse energy dependence of the electron attachment cross section in the $l = 0$ partial wave, which causes the yield to climb at zero energy.[33] A very weak signal seems to be present at about 1.8 eV, i.e., in correspondence with the π^*_{NC} resonance.

In benzyl isothiocyanate, the π^*_{CS} VAE is smaller than in ethyl isothiocyanate (and the anion lifetime consequently longer, other factors being the same). In addition, the benzyl derivative possesses two more anion states (with mainly ring character) at about the same energy. Nevertheless, a striking feature of the DEA spectrum of benzyl isothiocyanate is the intensity of the zero energy peak, almost 2 orders of magnitude larger than that of the ethyl derivative. Moreover, the effective height, convoluted with our electron beam energy distribution, tends to be underestimated for such a sharp signal. The shoulder at about 0.6 eV is associated with (all or some of) the first three (close in energy) anion states. A maximum in the negative current is also observed at about 4.7 eV, i.e., near to the energy predicted for the ring π^*_O MO.

The DEA spectrum of phenyl isothiocyanate is similar to that of the benzyl derivative, but the zero energy peak is 1 order of magnitude less intense. In this case, calibration of the mass selected NCS^- current against SF_6^- locates the maximum at 0.06 eV, in very good agreement with the presence of the first anion state at about 0.1 eV (as discussed above). The shoulder at 0.6 eV is clearly associated with dissociation of the second and third anion states (π^*_{CS} and π^*_A).

The sizeably smaller DEA cross section at zero energy in phenyl isothiocyanate relative to the benzyl derivative, in spite of the energy proximity to its first anion state, might seem surprising. However, it is to be noted that in the phenyl compound the π^* LUMO (see Figure 3), for symmetry reasons, cannot mix with the σ^*_{CN} MO in the rigid structure of the neutral molecule. π^*/σ^* coupling relies on vibronic coupling and, for dissociation of the C−N bond to occur, distortion of the nitrogen

TABLE 3: B3LYP/6-31+G* Energy Differences (eV) Relative to the Neutral-State Molecules

	R = Ph	R = $PhCH_2$	R = CH_3CH_2
R—N=C=S	0.00	0.00	0.00
R—N=C=S^- (vert.)	0.107 (VAE)	0.500 (VAE)	0.667 (VAE)
$R^\bullet$ + N=C=$S^\bullet$	3.921 (C—N BDE)	2.630 (C—N BDE)	3.283 (C—N BDE)
$R^\bullet$ + N=C=S^-	0.449	−0.842	−0.189

atom of the NCS group out of the ring plane is needed (as described by Clarke and Coulson[34] for chlorobenzene). In contrast, in benzyl isothiocyanate, the π^*_{CS} LUMO (although of local π^* symmetry) is perpendicular to the π^*_{CN} MO and is strongly coupled with the σ^* MOs localized on the C—N bond. In addition, in order to gain insight into the energetics of the dissociation processes, we calculated the energies (relative to the neutral molecules R—N=C=S) of the (geometry-optimized) neutral fragments $R^\bullet$ and N=C=$S^\bullet$ and of the negative fragment N=C=S^- at the B3LYP/6-31+G* level (which accurately reproduces the first VAEs, thus being suitable for a correct description of the molecular ground anion states). The results are presented in Table 3.

The values in the second row of Table 3 represent the VAEs and have already been discussed above. The energy of the $R^\bullet$ and N=C=$S^\bullet$ neutral radicals (third row) relative to the neutral molecule is the C—N bond dissociation energy (BDE). The C—N BDE in benzyl isothiocyanate is predicted to be smaller and sizeably smaller, respectively, than in the ethyl and phenyl derivatives. Owing to the different BDEs, the $R^\bullet$ and N=C=S^- fragments are calculated to be more stable than the neutral molecule in ethyl (0.2 eV) and benzyl (0.8 eV) isothiocyanate, whereas in phenyl isothiocyanate, they are predicted to lie at 0.4 eV higher energy. Although the peak in the NCS^- current observed in the latter at 0.06 eV indicates that the thermodynamic threshold for dissociation is somewhat overestimated by the calculations, this factor could play a crucial role in the different DEA cross sections observed at thermal energies.

Finally, it can be noted that the difference between the (corresponding) values in the third and fourth rows of Table 3 represents the adiabatic electron affinity (energy difference between neutral and anion states each in its optimized geometry) of the N=C=$S^\bullet$ radical, which turns out to be 3.53 eV, close to that (3.62 eV) of the chlorine atom.[35]

Conclusion

The electron-acceptor properties of alkyl isothiocyanates are found to be sizeably larger than those of the corresponding isocyanates, the first π^*_{CS} anion state (π^*_{CS}) of C_2H_5N=C=S being 1.7 eV more stable than that (π^*_{CO}) of C_2H_5N=C=O. More unexpectedly, the second anion state (which possesses mainly π^*_{NC} character in both classes of compounds) is also much more stable in the thio derivatives. Another important difference (from the point of view of reactivity) is that in the arylalkyl derivatives (such as, for instance, the benzyl derivatives) the first anion state of the isothiocyanates is still mainly localized on the C=S double bond, while in the isocyanates, it possesses mainly benzene π^* character.

Only in PhN=C=S, owing to π^* ring/π^*_{NC} interaction, does the SOMO of the first anion state have a large localization on the benzene ring, as in the oxygen analogue. However, the electron affinity (close to zero) of the former is larger, being between those of benzaldehyde and styrene.

While previous work[23] has demonstrated that scaling of the neutral state VOEs with known empirical equations largely (about 0.7 eV) underestimates the π^*_{CO} VAE of cumulated π-systems (isocyanates), the same approach closely reproduces the π^*_{CS} VAE of the isothiocyanates considered here. In addition, the first VAE is also nicely reproduced as the total energy difference between anion and neutral states with B3LYP/6-31+G* calculations (i.e., using a basis set which contains a minimum addition of diffuse functions), which also correctly describe the neutral state LUMO and anion SOMO as valence π^* MOs.

The DEA spectra show production of NCS^- negative fragments at electron impact energies close to zero and 0.6 eV in all the isothiocyanates analyzed, but the dissociative cross section for capture of thermal electrons is particularly large in the benzyl derivative. This finding is consistent with factors of both thermodynamic and kinetic natures. The calculations indicate a sizeably smaller C—N bond dissociation energy in benzyl isothiocyanate than in the phenyl derivative, and a consequently larger stability of the neutral and negative fragments relative to the neutral molecule. In addition, the symmetry and localization properties of the LUMO in the benzyl and phenyl derivatives are quite different. In the former, the added electron possesses significant σ^*_{CN} character, whereas in the latter, π^*/σ^* mixing (required for dissociation of the C—N bond) relies on the occurrence of vibronic coupling on the time scale of the π^* resonance.

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