Aromatic Stabilization and Hybridization Trends in Photoelectron Imaging of Heterocyclic Radicals and Anions

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ABSTRACT: We examine the photoelectron spectra and laboratory-frame angular distributions in the photodetachment of furanide $(C_4H_3O^-)$, thiophenide $(C_4H_3S^-)$, and thiazolide $(C_3H_2NS^-)$ and compare the results to the previously reported studies of pyridinide $(C_5H_4N^-)$ and oxazolide $(C_3H_2NO^-)$. Using the mixed s-p model for the angular distributions, the results are interpreted in terms of the effective fractional p character of the highest-occupied molecular orbitals of these heterocyclic anions, revealing trends related to the aromaticity. We conclude that aromatic stabilization across a series of



systems may be tracked using the photoelectron angular distributions. In addition, we report an improved (higher-precision) electron affinity (EA) for the thiophenyl radical, $EA({}^{\bullet}C_4H_3S) = 2.089(8)$ eV. The EA of thiazolyl falls within the 2.5(1) eV range, but it is not clear if this determination corresponds to the 2- or 5-cyclic species or the 2-ring-open isomer. These results are analyzed in conjunction with the properties of other heterocyclic radicals (pyridinyl, furanyl, and oxazolyl) and interpreted in terms of the C–H bond dissociation energies (BDEs) of the corresponding closed-shell molecules. The BDEs of all five-membered-ring heterocyclics studied fall within the 116–120 kcal/mol range, contrasting the lower BDE = 110.4(2.0) kcal/mol of the more aromatic six-membered-ring pyridine. The observed aromaticity trends are consistent with the findings derived from the anion photoelectron angular distributions.

1. INTRODUCTION

Over the decades, if not centuries, great efforts have been made to quantify the stabilization of organic molecules due their aromaticity, and yet to this day aromaticity is not an unambiguously defined characteristic that can be explicitly measured. Aromatic stabilization energies (ASE) have been assigned to various molecules, considering energetic and magnetic properties of their π orbital systems, as well as geometric criteria.^{1–3} While the observed trends are generally reproduced across the studies, there does not exist a uniform standard by which to calculate the ASE. As a result, the values may vary by several kcal/mol across methods.^{4–6}

Properties of the π electron system are affected by the σ system beyond the purely geometric considerations. It is generally accepted that the σ system of aromatic molecules (such as benzene) consists of sp² hybridized orbitals on each carbon center.⁷ However, changes in the electronic structure, such as heteroatom substitutions, perturb this nominal hybridization state. One of the goals of the present work is to demonstrate the relationship of hybridization in the σ orbital system to aromaticity and stability in the π system.

Removal of a hydrogen atom from one of the carbon centers of an aromatic molecule generates a σ radical.⁸ Removal of a proton, however, creates an anion with a closed-shell electron configuration. The highest-occupied molecular orbital (HOMO) of such an anion is a σ MO that tends to be localized predominantly on the deprotonated center. It has been demonstrated that the photoelectron angular distributions (PAD) in the photodetachment of the anion reflect the s–p hybrid nature of the HOMO. 9

In this work, we use photoelectron imaging to probe the nominally sp²-hybridized σ electron systems of furanide (C₄H₃O⁻), thiophenide (C₄H₃S⁻), and thiazolide (C₃H₂NS⁻) and compare the results to the previous reports for pyridinide (C₅H₄N⁻)⁹ and oxazolide (C₃H₂NO⁻).¹⁰ For convenient reference, the structures are summarized in Figure 1. While



Figure 1. Anions discussed in this work. The squiggle lines across the C2–S bond in 2-thiazolide indicate that the anion undergoes a ringopening reaction upon the deprotonation of the thiazole precursor molecule.

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The Journal of Physical Chemistry A

furanide and thiophenide have been previously studied via photoelectron imaging,^{8,11} here we present a new quantitative investigation of the previously unreported PADs. We report an order-of-magnitude more precise determination of adiabatic electron affinity (EA) of thiophenyl (${}^{\bullet}C_{4}H_{3}S$) and the first attempt at a spectroscopic measurement of the EA of thiazolyl (${}^{\bullet}C_{3}H_{2}NS$). The observed trends are used to define the approximate C–H bond dissociation energies (BDEs) for the corresponding closed-shell molecules.

2. EXPERIMENTAL METHODS

The experiments were performed using the negative-ion photoelectron imaging spectrometer described in detail elsewhere.^{12,13} The anions were generated by introducing a neutral precursor gas mixture into the high-vacuum ion source chamber through a pulsed supersonic nozzle (General Valve, Series 9) operated at a repetition rate of 20 to 70 Hz and a 1.5 atm backing pressure. The precursor gas mixture consisted of roomtemperature furan, thiophene, or thiazole vapor seeded in argon carrier gas, with minor O2 and water contaminants from ambient air trapped in the gas delivery lines. Anions were formed via slow secondary electron attachment following bombardment of the precursors with high-energy (1 keV) electrons.¹⁴ Atomic oxygen anions generated from O₂ impurities assisted with the deprotonation¹⁵ of furan, thiophene, and thiazole. The anions were separated and characterized in the time-of-flight mass-spectrometer.¹⁶

Anion photodetachment was studied at 306, 355, 390, 406, 532, 563, and 612 nm for furanide, at 306, 355, 390, 406, 416, and 532 nm for thiophenide, and at 355 and 393 nm for thiazolide. The 390-393 nm light was obtained by frequency doubling the fundamental output of an amplified Ti:sapphire laser (Spectra Physics; < 1 mJ/pulse, 100 fs pulse width). The 532 and 355 nm laser beams were the second and third harmonics, respectively, of a Nd:YAG laser (Spectra Physics; 25 and 5 mJ/pulse, respectively, ~6 ns pulse duration). The 563 and 612 nm radiations were the fundamental output of a Continuum, Inc. Surelight II-20 Nd:YAG pumped (532 nm) ND6000 dye laser, operating on the Rhodamine 590 or Rhodamine 640 dye, respectively, and delivering 20 mJ, ~10 ns duration pulses. The 306 nm light was obtained by frequency doubling the 612 nm dye laser output. The 406 and 416 nm beams were obtained by frequency doubling the fundamental output of the same laser operating on the LDS 821 dye, delivering 15 mJ, ~10 ns duration pulses. The laser beams were collimated using a 2 m focal length lens positioned ~1.2 m before the laser-ion interaction region.

Details of the photoelectron¹⁷ imaging^{18,19} assembly are described elsewhere.^{12,13} All images in this work were recorded with the repeller, middle, and acceleration electrodes of the velocity-map²⁰ imaging lens at -330, 0, and 912 V, respectively. The reported images each correspond to multiple experimental runs combined to span $\sim 1 \times 10^6$ experimental cycles. The results were analyzed by means of the inverse Abel transformation¹⁹ using the BASEX software package.²¹

3. RESULTS

3.1. Photoelectron Images and Spectra. The new experimental results for the furanide, thiophenide, and thiazolide anions are presented in Figures 2, 3, and 4, respectively. The photoelectron images obtained at the wavelengths indicated are displayed on the right, with the



Figure 2. Photoelectron imaging results for furanide obtained at 306, 406, 532, 563, and 612 nm. (right) Composite photoelectron images, with the left and right halves representing the raw and Abel-inverted data, respectively. (left) Corresponding photoelectron spectra. The laser polarization axis is vertical in the plane of the images, as indicated by the double arrow on the bottom right corner.

resultant photoelectron spectra on the left. The left and right halves of the composite images represent the raw and Abelinverted ^{19,21} data, respectively. Additional furanide and thiophenide data obtained at 266, 355, and 390 nm were reported previously.⁸ The relevant past results are included in the following analysis, but the corresponding raw data are not reproduced here to avoid repetition. The thiazolide images in Figure 4 are shown on a color scale to highlight the salient transition details. The laser polarization axis is vertical in all images shown, as indicated by the double-sided arrow in the bottom right of each figure. For direct comparison of data collected at different wavelengths, all spectra in Figures 2–4 are plotted versus electron binding energy, eBE = $h\nu - \varepsilon$, where $h\nu$ is the photon energy and ε is electron kinetic energy (eKE).

The lowest-eBE bands in Figures 2–4 originate from the removal of an electron from the σ HOMOs of the respective anions, to form the ground electronic states of the neutral radicals. The 406 and 306 nm images and spectra in Figures 2 and 3 reveal additional bands that correspond to excited electronic states. These states of furanyl and thiophenyl were discussed previously⁸ and will not be the focus of this work.

Vibrational resolution in the 612, 563, and 532 nm furanide spectra (Figure 2) allows for determination of the onset of the ground-state transition. From the band origin, we are able to assign the adiabatic electron affinity of furanyl, $EA({}^{\bullet}C_{4}H_{3}O) = 1.855(5)$ eV. This value agrees with the previous determination of EA = 1.853(4) eV by the Lineberger group¹¹ and dramatically improves the precision of our own past result EA = 1.84(7) eV.⁸

The Journal of Physical Chemistry A



Electron Binding Energy / eV

Figure 3. Photoelectron imaging results for thiophenide obtained at 306, 406, 416, and 532 nm. (right) Composite photoelectron images, with the left and right halves representing the raw and Abel-inverted data, respectively. (left) Corresponding photoelectron spectra. The laser polarization axis is vertical in the plane of the images, as indicated by the double arrow on the bottom right corner.



Figure 4. Photoelectron imaging results for thiazolide obtained at 355 and 393 nm. (right) Composite photoelectron images, with the left and right halves representing the raw and Abel-inverted data, respectively, shown on a color scale to highlight the salient features. (left) Corresponding photoelectron spectra. The laser polarization axis is vertical in the plane of the images, as indicated by the double arrow on the bottom right corner.

The hint of a vibrational progression in the 532 nm thiophenide spectrum (Figure 3) also allows for an accurate determination of the band origin. We assign the EA of thiophenyl as $EA({}^{\bullet}C_{4}H_{3}S) = 2.089(8)$ eV. This result is consistent with the previously reported value of 2.05(8) eV,⁸ yet—again—improves the precision by an order of magnitude. The spacing between the partially resolved vibrational peaks in the 532 nm thiophenide spectrum is 720 ± 50 cm⁻¹. This progression likely corresponds to the in-plane (*a'*) ν_3 bending

mode of the thiophenyl radical.⁸ The B3LYP/aug-cc-pVDZ calculations²² predict this mode's frequency to be 750 cm⁻¹.

Determination of band origins and, therefore, EA in the 393 and 355 nm photoelectron spectra of thiazolide (Figure 4) presents a challenge. We tentatively assign the EA to the broad interval indicated in Figure 4, EA(\cdot C₃H₂NS) = 2.5(1) eV. The two measurements of the band's maximum (355 and 393 nm) yield the vertical detachment energy of C₃H₂NS⁻, VDE = 2.85(2) eV. The progression of peaks seen in the spectra in Figure 4 could, in principle, correspond to high-frequency (~2000 cm⁻¹) vibrations in the ground electronic state of thiazolyl. However, since no such high-frequency progressions were observed in the analogous spectra of the other anions studied in this work, it is more likely that the peaks in Figure 4 represent the photodetachment bands of different isomers of C₃H₃NS⁻ (see Section 4.1).

3.2. Photoelectron Angular Distributions. The PADs for all anions studied were analyzed in a consistent manner over varying energy intervals, depending on the spectral resolution. For the higher-resolution images (typically corresponding to small average eKE), the PADs were analyzed over a progression of consecutive intervals 0.08 eV wide. For low-resolution images (large average eKE), such as the 266 nm data for furanide and thiophenide,⁸ the PADs were integrated over the full width at half-maximum of the transitions. The resulting anisotropy parameters are plotted versus eKE in Figure 5 for (a) furanide and (b) thiophenide and in Figure 6b for thiazolide. The data points are color-coded to the corresponding wavelengths.

For completeness of the five-membered-ring data set, the corresponding previously reported results for oxazolide¹⁰ are included in Figure 6a. For overall comparison, the PAD data for pyridinide (six-membered ring) are presented in Figure 7.⁹ As seen in the anisotropy plots, the PADs for each anion tend to be nearly isotropic at near-zero eKE, become predominantly perpendicular with respect to the laser polarization direction (β < 0) at small eKEs, then gradually turn parallel (β > 0) at increasing eKEs. Pyridinide (Figure 7) exhibits the most pronounced negative dip in the anisotropy, reaching β values as low as -0.59, while oxazolide displays the shallowest minimum in $\beta(\varepsilon)$, only reaching negative β values of ca. -0.18. In the next Section, we discuss the relationship of these trends to the amount of p character in the parent detachment orbital.

4. DISCUSSION

4.1. Structure and Energetics of the Thiazolide Anion. The properties of furanide,^{8,11} thiophenide,⁸ oxazolide,¹⁰ and pyridinide⁹ in the context of photoelectron imaging spectroscopy have been discussed elsewhere. Here, we focus on the corresponding features of thiazolide.

The 2-, 4-, and 5- isomers of the thiazolide anion generated by deprotonation of thiazole are analogous to those of oxazolide,¹⁰ with the oxygen replaced by a sulfur atom. Similarly, intuition suggests that C4 is the least acidic center in the thiazole molecule. Accordingly, calculations show that the 4-thiazolide isomer is thermodynamically not favorable by over half an electronvolt, compared to the 2- and 5-thiazolide anions.²³ We therefore exclude 4-thiazolide from further consideration. The 2- and 5-thiazolide cyclic structures are shown in Figure 6b.

The previous studies have shown that under our experimental conditions oxazole is deprotonated selectively at the C2 position.¹⁰ This conclusion is supported by other



Figure 5. Photoelectron anisotropy parameter values for the photodetachment of (a) furanide and (b) thiophenide as functions of eKE. The 266, 355, and 390 nm data are from the previous work;⁸ the rest are from the new results presented in Figures 1 [for (a)] and 2 [for (b)]. Solid curves: the mixed s–p model eq 1 fits to the data, as described in the text, emphasizing the depth of the $\beta(\varepsilon)$ minima. The fits assumed $A = 0.75 \text{ eV}^{-1}$, B/A = 8/3, $\cos \delta_{2,0} = 0.95$, and relied on $\gamma_{\rm p}$ as a free adjustable parameter. The curves shown correspond to (a) $\gamma_{\rm p} = 0.70$ for furanide and (b) $\gamma_{\rm p} = 0.74$ for thiophenide.

studies indicating that the C2 position is the most acidic in the oxazole molecule.²³ By analogy, one may expect the corresponding 2-isomer to be the dominant thiazolide structure contributing to the results in Figures 4 and 6b. However, thiazole has been shown to undergo deprotonation at both C2 and C5.²⁴ It reacts with HO⁻ to form the 2- and 5- anions in similar yield,²⁵ although reactions with phenyl lithium yield exclusively the 2-lithio derivative.²⁶ Attempting to resolve the ambiguity as to which isomer(s) of thiazolide is (are) generated in our experiment, we performed selective deuteration of thiazole, in a manner similar to the previously reported D-oxazole synthesis.¹⁰ The resulting anion mass spectra indicated that thiazole deprotonation takes place at both the C2 and C5 positions, generating a mix of the 2-thiazolide and the 5-thiazolide anions.²⁷

To complicate the analysis further, the 2-thiazolide anion may undergo ring-opening along the C2–S bond, as indicated by the squiggle lines in the 2-structure in Figures 1 and 4. A mechanism for this process has been proposed previously.^{24,28} The 5-thiazolide anion, however, does not undergo ring opening. We must, therefore, consider possible contributions to the thiazolide data in Figure 4 from both the ring-closed and ring-open 2-thiazolide structures, in addition to ring-closed 5thiazolide.

4.2. Modeling the Photoelectron Angular Distributions. The PADs for cyclic deprotonated anions can be described with good accuracy and conceptual insight using the mixed s-p model,^{9,29,30} which is a partial case of the general mixing theory presented recently.³¹ The mixed s-p model



Figure 6. Photoelectron anisotropy parameter values for the photodetachment of (a) oxazolide and (b) thiazolide as functions of eKE. Solid curves: the mixed s-p model eq 1 fits to the data, as described in the text, emphasizing the depth of the $\beta(\varepsilon)$ minima. The fits assumed $A = 0.75 \text{ eV}^{-1}$, B/A = 8/3, $\cos \delta_{2,0} = 0.95$, and treated γ_p as an adjustable parameter. The curves shown correspond to (a) $\gamma_p = 0.67$ for oxazolide and (b) $\gamma_p = 0.71$ for thiazolide.



Figure 7. Photoelectron anisotropy parameter values as a function of eKE for the photodetachment of pyridinide (data from ref 9). Solid curve: the mixed s-p model eq 1 fit to the data, as described in the text, emphasizing the depth of the $\beta(\varepsilon)$ minima. The fit assumed $A = 0.75 \text{ eV}^{-1}$, B/A = 8/3, cos $\delta_{2,0} = 0.95$, and treated γ_p as an adjustable parameter. The curve shown corresponds to $\gamma_p = 0.858$.

approximates the MO of the parent anion, from which the observed photoelectrons are (nominally) emitted, with a model function ψ_{sp} , defined as a superposition of one s and one p-type functions, with the $(1 - \gamma_p)^{1/2}$ and $(\gamma_p)^{1/2}$ amplitudes, respectively. The following dependence of the anisotropy parameter β on $\varepsilon \equiv$ eKE is predicted in the photodetachment with linearly polarized light:

$$\beta(\varepsilon) = \frac{2[(B_1/A_1)(1-\gamma_p)/\gamma_p]A_1\varepsilon + 2(A_1\varepsilon)^2 - 4A_1\varepsilon\cos\delta_{2,0}}{[(B_1/A_1)(1-\gamma_p)/\gamma_p]A_1\varepsilon + 1 + 2(A_1\varepsilon)^2}$$
(1)

9773

This s-p mixing equation can be viewed as a generalization of Hanstorp et al.'s formulation³² of the Cooper-Zare formula^{33,34} for the case of a mixed s-p initial state. In eq 1, A_1 is the Hanstorp coefficient describing the relative scaling of the p \rightarrow d and p \rightarrow s photodetachment channels (subscript 1 is for l = 1, corresponding to the p component of the initial orbital), while $\delta_{2,0}$ is the phase shift between the outgoing d and s electron waves, induced by their interaction with the neutral core.³¹ As these interactions are typically weak in the case of anion photodetachment, the phase shift is expected to be small. Past studies fitting the Cooper-Zare central-potential formula to experimental $\tilde{\beta}(\varepsilon)$ trends for anions have indicated cos $\delta_{2,0}$ values of ~0.90–0.95.^{32,35} Our own past work has shown that the choice of $\cos \delta_{2,0} = 0.95$ instead of 1 results in only minor changes in the mixed s-p model predictions.⁹ In view of these findings and acknowledging that the phase shift exists but is small, we will set $\cos \delta_{2,0} = 0.95$ throughout the analysis. This choice is somewhat arbitrary but does not affect the overall trends discussed.

At the heart of the mixed s-p model is the composite mixing parameter $(B_1/A_1)(1 - \gamma_p)/\gamma_p$ appearing in both the numerator and the denominator of eq 1.³⁰ In it, γ_p is the fractional p character of the parent MO, while B_1 describes the relative scaling of the s \rightarrow p and p \rightarrow s photodetachment channels,²⁹ in a manner similar to A_1 for p \rightarrow d and p \rightarrow s. Hence, $(B_1/A_1)(1 - \gamma_p)/\gamma_p$ describes the relative intensities of the s \rightarrow p and p \rightarrow s, d channels (via B_1/A_1), weighted by the contributions of the s and p components to the initial state, $(1 - \gamma_p)/\gamma_p$.

To facilitate the discussion, thumbnail-size plots of all anion HOMOs discussed in this work determined from the B3LYP/ aug-cc-pVDZ calculations²² are given in Table 1. The plots reveal the dominant character of each HOMO as a hybrid sp^x orbital localized predominantly on the deprotonated carbon atom. Therefore, as in our previous work,^{9,10,30} we will adopt the A_1 value corresponding to photodetachment from atomic carbon anion, $A_1 = 0.75 \text{ eV}^{-1}$.^{30,36} Furthermore, under certain assumptions, the B_1/A_1 ratio for a 2s–2p mixed-character orbital (such as all the hybrid MOs in this work), simplifies to $B_1/A_1 = 8/3$.³⁰ The only remaining free parameter in eq 1 is γ_{p} , describing the effective p character of the anion HOMO.

In our previous work,^{9,30,37} we developed a procedure for constructing the s-p model function ψ_{sp} . In brief, ψ_{sp} is defined as a superposition of hydrogenic 2s and 2p functions located on the deprotonated carbon center. The 2s and 2p amplitudes ((1 $(-\gamma_p)^{1/2}$ and $(\gamma_p)^{1/2}$ define the (nominal) sp^x hybridization state of the orbital via $x = \gamma_p/(1 - \gamma_p)$, while the spatial extent of $\psi_{\rm sp}$ is controlled by the effective nuclear charge parameter ζ^{30} Å global fit of ψ_{sp} , depending parametrically on γ_p and ζ , to the computed ab initio HOMO or the corresponding Dyson orbital^{38,39} then yields the optimal γ_p and ζ model values. This procedure has been illustrated on the benchmark case of pyridinide.⁹ It does, however, have disadvantages. First, it relies on the a priori knowledge of the parent anion or Dyson orbital. Second, it depends sensitively on the details of ab initio calculations and the three-dimensional fitting procedure, which essentially projects the complex MO on a basis set of only two functions.

However, a reverse procedure may often be desired for deducing the information about the anions studied from the photoelectron imaging data, rather than vice versa. Here, we take this inverted approach and instead of relying on ab initio calculations to model the experimental results,⁹ use the mixed s-p model to determine the effective hybridization state of the

Table 1. Correlation between the Heterocyclic-AnionHOMO Properties and the Energetics of the CorrespondingNeutral Radicals

Anion	HOMO ^a	Anisotropy Figure number	p character $(\gamma_p)^b$	Radical EA (eV)	C–H BDE (kcal/mol) ^j
Pyridinide C5H4N ⁻		7	0.858(12) ^{c,d}	1.480(6) ^f	110.4(2.0) ^f
Thiophenide C ₄ H ₃ S ⁻		5b	0.74(2) ^c	2.089(8) ^c	116(3) ^{<i>c,k</i>}
2- and 5- Thiazolide $C_3H_2NS^-$		6 b	0.71(3) ^c	2.5(1) ^c	117(4) ^{<i>c</i>,<i>l</i>}
Furanide C ₄ H ₃ O ⁻		5a	0.70(3) ^c	1.855(5) ^{<i>c,h</i>} 1.853(4) ^{<i>g,h</i>}	119.8(2) ^g
2-Oxazolide C ₃ H ₂ NO ⁻		6a	0.67(2) ^{c,e}	2.21(2) ^{<i>i</i>}	116.7(1.7) ^{<i>c,m</i>}

^aThe thumbnails of orbitals shown are from B3LYP/aug-cc-pVDZ calculations. ^bThe γ_p values listed in the Table were determined by fitting eq 1 to the experimental data in the corresponding figures, as discussed in the text. ^{*c*}This work. ^{*d*}For comparison, in ref 9, $\gamma_{\rm p} = 0.88$ and 0.86 were determined by fitting the mixed s-p model function to the CCSD/6-31+G* HOMO of the anion and the EOM-IP-CCSD/6-31+G* Dyson orbital, respectively, rather than by fitting eq 1 to the experimental data, as in this work. ^eFor comparison, $\gamma_p = 0.64$ was previously determined¹⁰ by fitting the mixed s-p model function to the B3LYP/aug-cc-pVDZ HOMO of the anion. See also footnote d above. ^{*f*}From ref 41. ^{*g*}From ref 11. ^{*h*}The EA = 1.853(4) eV for furanyl reported in ref 11 is in agreement with the EA = 1.855(5) eV determined in the present work. Owing to the smaller error bars, the 1.853(4) eV value is recommended. ^{*i*}From ref 10. ^{*j*}The C-H BDEs of the parent closed-shell molecules: pyridine, thiophene, thiazole, furan, and oxazole. These values are calculated from the electron affinities of the corresponding radicals, using the electron affinity/acidity thermodynamic cycle discussed in ref 40 and the references indicated in this column. ^{*k*}In ref 8, the BDE = 115(3) kcal/mol was determined for thiophene using a less precise determination of the thiophenyl radical EA. The new value in the table, BDE = 116(3) kcal/mol, is based on the improved EA determination. It is in agreement with the previous result. The BDE error bars are unaffected, because they reflect the uncertainty of the best available thiophene acidity determination, $\Delta_{acid}H_{298}(C_4H_4S) = 381 \pm 3 \text{ kcal/mol.}^{42}$ ^{*l*}An estimate corresponding to the C5 position. See the text for details. "A combined experimental/theoretical estimate. See the text for details.

parent orbitals from the experimental data. This approach does not rely on the modeling of the spatial (radial) extent of the orbitals via ζ .

It is realized by keeping A_1 , B_1/A_1 , and $\cos \delta_{2,0}$ fixed at the values discussed above ($A_1 = 0.75 \text{ eV}^{-1}$, $B_1/A_1 = 8/3$, $\cos \delta_{2,0} = 0.95$) and using the remaining parameter γ_p to fit the $\beta(\varepsilon)$ function in eq 1 to the experimental data in Figures 5–7. These fits were performed with a caveat. As discussed previously,^{9,10,30} the model is most reliable at low-to-moderate eKEs, where the Wigner-like scaling of the partial cross-section ratios holds up well. Hence, we emphasized the low-to-moderate eKE data (effectively limiting the fit range to eKE < 1.5 eV) and specifically aimed to reproduce the depths of the minima of the

observed $\beta(\varepsilon)$ curves. The weighted procedure yielded the effective γ_p values for the different anions studied, summarized in Table 1. The resulting $\beta(\varepsilon)$ curves are superimposed with the experimental data in Figures 5–7.

4.3. Aromaticity Trends. While aromatic stabilization energies vary across methods, all previous studies agree on the general aromaticity trend of pyridine > thiophene > thiazole > furan > oxazole,^{2,3,6} where pyridine has the most aromatic stability and oxazole the least. When considering this series in the context of the present work, note that while pyridinide is deprotonated opposite the heteroatom, all the other anions are deprotonated at positions adjacent to a heteroatom. Nonetheless, as seen from Table 1, as the aromatic stability of the parent molecule increases, the fractional p character of the corresponding deprotonated anion HOMO increases too. The observed increases relative to $\gamma_p = 0.67$ expected for a nominal sp² orbital are attributed to the contributions of the neighboring atoms to the overall MOs (i.e., delocalization and aromaticity).

Effects of heteroatom substitution can be evaluated by comparing thiophenide to thiazolide and furanide to oxazolide. In these pairs, the C3 carbon of the first anion is replaced by a nitrogen atom in the second, resulting in the deprotonated carbon center being adjacent to two, instead of one, electron-withdrawing groups. The substitution of an additional electron-withdrawing group is known to decrease the aromatic stabilization of the parent molecule,³ consistent with the p character trends in Table 1.

4.4. C–H Bond Dissociation Energies. Table 1 also lists the adiabatic EAs of the radicals (R) and the C–H bond dissociation energies (BDEs) of the closed-shell molecules that yield these radicals. The BDEs given are $DH_{298}(R-H)$, calculated from the EAs and the gas phase acidities of the parent molecules (at the position indicated), using the standard⁴⁰ acidity/EA thermodynamic cycle.^{8,11,41} The significant uncertainly ranges of the BDEs are in most cases the consequence of the uncertainties of the corresponding acidity determinations.

Two of the BDE values in Table 1, for thiazole and oxazole, warrant elaboration. The BDE of oxazole, corresponding to the C2 position, was estimated as follows. The acidity of oxazole at the C5 position was recently determined using the experimental "bracketing" technique as $\Delta_{acid}H^{\circ} = 380.8(1.6)$ kcal/mol (this result is obtained by bracketing the raw data for ethanol and toluene presented in ref 23, as recommended by the authors). This value must be corrected to yield the desired acidity of the C2 (rather than C5) center. Using the theoretical prediction made by the same authors that C2 should be more acidic than C5 by 1.5 kcal/mol,²³ we arrive at $\Delta_{acid}H^{\circ}$ = 379.3(1.6) kcal/mol as a combined experimental/theoretical estimate for the C2 acidity of the oxazole molecule. Substituting this value, together with our EA = 2.21(2) eV for 2-oxazoly1¹⁰ into the acidity/EA cycle,⁴⁰ we obtain $BDE(H-C_3H_2NO) =$ 116.7(1.7) kcal/mol (at the C2 position). This result, similar to all other results in Table 1, neglects the typically small (~0.3 kcal/mol) thermal correction in the acidity/EA cycle.⁴⁰

Determination of the C–H BDE of thiazole is even more complicated, because the thiazolyl EA data in the present work likely reflect contributions of two or more anion isomers (see Section 4.1). We will assume that the EA of the stable ringclosed 5-thiazolide falls within the broad experimental range indicated in Figure 4, EA = 2.5(1) eV. The 0.1 eV or 2.3 kcal/ mol wide EA uncertainty range (very poor for photoelectron spectroscopy) is still not worse than the uncertainty of the corresponding acidity value for thiazole at the C5 position, $\Delta_{\rm acid}H^{\circ} = 373(3)$ kcal/mol.²³ Substituting these results into the acidity/EA cycle,⁴⁰ we estimate BDE(H–C₃H₂NS) = 117(4) kcal/mol (at the C5 position).

The BDE is inversely related to the resulting radical stability: larger BDEs indicate less stable radicals.⁴⁰ The BDEs in Table 1 fall into two groups: the relatively small BDE of the sixmembered-ring pyridine (110.4 kcal/mol) and the larger BDEs of the five-membered-ring thiophene, thiazole, furan, and oxazole, all of which fall in the 116-120 kcal/mol range. These two groups loosely correlate with the fractional p character values determined in this work and ultimately with the depths of the $\beta(\varepsilon)$ anisotropy curves for the anions. The most aromatic molecule on the list, pyridine, has the smallest C-H BDE, the largest effective p character, and the deepest minimum in the anion anisotropy trend (Figure 7). The less aromatic fivemembered-ring systems have larger BDEs (less stable radicals), smaller p characters, and more shallow minima of the anisotropy curves, as seen clearly by comparing Figures 5 and 6 to Figure 7.

5. CONCLUSIONS

We have reported an investigation of heterocyclic radicals and their anions using negative-ion photoelectron imaging spectroscopy. The investigation included a systematic analysis of the electron affinities of the furanyl, thiophenyl, oxazolyl, thiazolyl, and pyridinyl radicals, photoelectron angular distributions in the photodetachment of their respective anions (furanide, thiophenide, oxazolide, thiazolide, and pyridinide) and the C– H BDEs of the closed-shell parent molecules (furan, thiophene, oxazole, thiazole, and pyridine).

The electron affinities of furanyl and thiophenyl are determined to be $EA({}^{\bullet}C_4H_3O) = 1.855(5)$ eV and $EA({}^{\bullet}C_4H_3S) = 2.089(8)$ eV. The former result confirms the recent determination of $EA({}^{\bullet}C_4H_3O) = 1.853(4)$ eV by the Lineberger group,¹¹ while the latter improves by an order of magnitude the uncertainty range of our own previously published value.⁸ The EA of thiazolyl is within the 2.5(1) eV range, but this determination corresponds to an uncertain combination of the two- and five-cyclic species and the two-ring-open isomer.

We conclude that the aromatic stabilization across a series of systems is reflected in the corresponding anion PADs. The character of the deprotonated HOMOs loosely correlates with the aromatic stabilization of the parent molecule. More aromatic molecules tend to have smaller C–H BDEs, as well as deeper minima for the corresponding anion photoelectron anisotropy curves. These curves, in turn, reflect the mixed s–p composition of the detachment orbitals. As the aromatic stabilization decreases, the hybridization of the HOMO, localized predominantly on the deprotonated carbon, approaches the nominal sp² limit.

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Notes

The authors declare no competing financial interest.

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