the interaction between the filled $\sigma_{C-H}$ orbital and the carbanion (n) is essential to the formation of the HOMO orbital $\psi_1$ (Figure 3). A comparison between the HOMO ($\psi_1$) arising from this hypothetical argument and that determined (4-31G) for the transition state (Figure 4) is gratifying. The ground-state sp$^2$ anionic center has a significant contribution from the carbon 2s orbital. As one proceeds along the reaction coordinate for elimination, the carbon 2s coefficient decreases from 0.43 to 0.07 at the transition state. The electron density is essentially equally distributed on both sides of the carbon in consonance with the idea of inversion of configuration attending the elimination step (Figure 4).

The HOMO level of the syn ground state anion 1 is 1.2 kcal/mol higher in energy than that of the corresponding anti anion 2, reflecting their relative stabilities. At the transition state the HOMO of the syn anion 1a is 7.2 kcal/mol higher in energy than the anti anion 2a. In going from the ground state anion 1 to the transition state 1a, a carbon-carbon bond contraction (0.1 Å) is evident, as well as an elongation of the C$_r$-X bond length as a result of the H-C$_r$-C$_o$ bond angle expanding.

Finally, we wish to address the question of competitive elimination of HX from a 1,2-dihaloalkene. Examination of the relative energies of the isomeric anions derived from 1-chloro-2-fluoroethylene shows that the $\alpha$-chloro anion 7 is about 10 kcal/mol (4-31G) more stable than $\alpha$-fluoro anion 8 (eq 3).

\[ \text{H} \quad \text{Cl} \quad \text{C} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \text{F} \quad \text{H} \quad \text{F} \]

\[ \begin{align*}
-634.45369 \text{ au} & \quad -634.41765 \text{ au}
\end{align*} \] (3)

In going from the ground state anion to the transition state for a syn elimination from either anion is E1cb-like, and the relative rates reflect the stability of the incipient anion, then one would predict a preferential elimination of HF favoring coordination between the base counteranion and the leaving group along with conformational arguments concerning the carbanion was invoked in explanation of these interesting results. We suggest that the relative stabilities of the two potential incipient anions are an equally plausible explanation.

In conclusion, vinyl anions bearing a $\beta$-halo substituent will exhibit a lower inversion barrier while $\alpha$-halo substituents have the opposite effect and will add to the inversion barrier. The activation energies for $\beta$-elimination from vinyl substrates are markedly higher than those of halo-substituted aliphatic substrates. The activation barriers for elimination of vinyl substrates may be largely, if not entirely, attributable to the electronic effects associated with inversion of the carbanionic center. Finally, these data suggest that 1,2-dihaloalkenes should exhibit E1cb-like behavior. As a consequence of the inversion barriers, the potential for observing hydrogen-deuterium exchange under elimination reaction conditions should be quite high if nucleophilic substitution at vinyl carbon can be excluded. Many of the mechanistic suggestions that we have presented on the basis of this theoretical study were made many years ago by Miller in his insightful series of papers on vinyl anions.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. We are also grateful to the Wayne State University Computing Center for their generous amounts of computational time, Professor H. B. Schlegel for his assistance with the computations, and Professor H. F. Koch for his helpful discussions.


Determination of the Singlet–Triplet Splitting and Electron Affinity of $\alpha$-Benzyne by Negative Ion Photoelectron Spectroscopy

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Abstract: The photoelectron spectrum of the $\alpha$-benzyne negative ion displays transitions to both the $\tilde{X}^1A_1$ and $\tilde{A}^3B_2$ states of the neutral molecule. Results yield adiabatic electron affinities of 0.560 (10) and 0.551 (10) eV for C$_6$H$_4$ and C$_6$D$_4$, respectively. These values are consistent with extrapolations from studies of larger strained cycloalkynes and imply that the lowest unoccupied MO of $\alpha$-benzyne is primarily an antibonding acetylenic orbital. The $\alpha$-benzyne singlet–triplet splitting is determined to be 37.7 (6) kcal/mol. Several new vibrational frequencies for the neutral and anionic species are also reported.

I. Introduction

The determination of the electronic and molecular structure of $\alpha$-benzyne (1,2-dehydrobenzene, C$_6$H$_4$) has attracted considerable interest since the first demonstration of its existence by Roberts et al. over 30 years ago. This species is among the simplest of highly strained conjugated hydrocarbons. Thus, it provides a benchmark system for theoretical models of the structural and energetic consequences of ring strain. Much attention has focused on the effects of its unique geometry on the well-studied solution chemistry of this reactive intermediate.

Figure 1. Qualitative illustration of the electronic structure of neutral and anionic \( \text{o}-\)benzene. Molecular orbitals labeled \( n_1 + n_2 \) and \( n_1 - n_2 \) represent the bonding and antibonding combinations, respectively, of the lone-pair-like orbitals relatively localized on the dehydrocarbons. In the singlet ground state of the neutral molecule, the \( n_1 + n_2 \) highest occupied orbital is filled, producing a "triple" bond between these carbon atoms. In the present experiment, both the singlet ground state and the lowest triplet excited state of neutral \( \text{o}-\)benzene are accessed by photodetachment of an electron from the doublet ground state of the negative ion.

As a consequence of its high reactivity, \( \text{o}-\)benzene has proved difficult to study spectroscopically, and much of our present understanding has been obtained from numerous ab initio3-8 and semiempirical9-18 studies. These results indicate a \( \Delta \)1 ground state in which double occupancy of the in-plane bonding molecular orbital centered on the two dehydrocarbons produces a so-called "acyclic" carbon-carbon bond (see Figure 1). Although calculated \( \pi \)-bond overlap populations display marked alternation around the ring,24 much of the aromaticity of benzene is predicted to be retained. There have been several calculations5,7,14,15,18 of the energy gap between the \( \pi \)/\( \Delta \)1 state and the lowest energy \( (\text{B}_2) \) triplet state, in which an electron is promoted from the bonding to the antibonding dehydrocarbon orbital. A splitting of 28 kcal/mol has been reported from ab initio studies which include configuration interaction and limited geometry optimization.4 The only direct spectroscopic result concerning the geometry and bonding of \( \text{o}-\)benzene have been obtained in matrix IR studies by Chapman and co-workers19 and Dunkin and MacDonald20 which have yielded ten \( \text{C}_6 \text{H}_4 \) and eleven \( \text{C}_6 \text{D}_4 \) vibrational frequencies. Most significantly, the observation of \( \text{C}_6 \text{H}_4^{+} \) stretching modes near 2090 cm\(^{-1}\) for both species provides strong support for the proposed closed-shell singlet aryne structure. Two normal coordinate analyses based on these results have been reported.21,22

The connection between the electrophilicity of \( \text{o}-\)benzene and its strained acetylic bond has been investigated by Houk, Jordan, Krebs, and co-workers,23-25 using a combination of theoretical and spectroscopic methods. Ab initio24,26 and extended Hückel27 calculations of acetylene indicate a dramatic stabilization of the lowest unoccupied molecular orbital (LUMO) on cis bonding of the molecule. Consistent with this prediction, electron transfer spectroscopy of cycloalkynes23 indicates an increase in electron affinity with decreasing ring size. From an extrapolation based upon these results, the \( \text{o}-\)benzene anion has been predicted23 to be stable with respect to the neutral, with a vertical electron affinity of 0.1-0.6 eV. The implied stability of its LUMO has been related by frontier orbital concepts to a preferential stabilization of the molecule. Consistent with this prediction, electron transmission spectroscopy, results provide firm spectroscopic evidence that the signal carrier is indeed the \( \text{o}-\)benzene anion. As indicated by the orbital descriptions in Figure 1, photodetachment transitions from the negative ion access both the singlet ground state and the previously unobserved lowest triplet state of the neutral molecule, providing measurements of its electron affinity and singlet-triplet splitting. In addition, vibronic structure resolved in the two band systems yields several new vibrational frequencies for neutral and anionic \( \text{o}-\)benzene.

II. Experimental Method

The flowing afterglow negative ion photoelectron spectrometer employed in these studies has recently been described in detail.28-30 Briefly, sample ions are prepared in a field-free flowing afterglow ion-molecule reactor, where they are rotationally and vibrationally relaxed by collisions with a room-temperature helium buffer gas and molecular species seeded in the helium flow. The ions sampled from the afterglow are accelerated in the collisionless regions of the spectrometer and mass analyzed. The mass-selected ion beam is crossed in a field-free interaction region by the focused intracavity beam of a cw Ar II laser operated at 4880 or 4579 Å. The laser polarization is set at the \( \lambda \)-magic angle of 54°.45° with respect to the direction of an electron afterflow to ensure that observed photoelectron transition intensities reflect average photodetachment cross sections.31 Electrons ejected into the acceptance angle of a hemispherical electrostatic monochromator are energy analyzed and detected by a position-sensitive detector. Spectra reported here were obtained at an instrumental resolution of 10-20 meV. Briefly, \( \text{C}_6 \text{H}_4^{+} \) (and \( \text{C}_6 \text{D}_4^{+} \)) were prepared by the following \( \text{H}_2 \) transfer reaction, previously observed by Jennings and coworkers27 using chemical ionization mass spectrometry (CIMS):
\[
\text{O}^+ + \text{CH}_3 \rightarrow \text{C}_6 \text{H}_4^{+} + \text{H}_2 \text{O}
\]
\( \text{O}^+ \) was produced by dissociative electron attachment to \( \text{N}_2 \text{O} \) injected at


displaced from that of the anion. The origin band of this system, modelling of the spectrum. This assignment is supported by the electron kinetic energy (eKE) signify a transition to a state of the o-benzyne. Spectra were obtained with the 488 and 458 nm Ar detector sensitivity was applied to obtain the intensities of peaks below compression currents, the reported spectra required approximately 15-h integrations. In view of our limited mass resolution. Thus, the peak widths of (-1 30 about 60 cm from the electron gun, and the ions were sampled about cm further downstream through a 1 mm diameter aperture. The helium flow was regulated at 150 STP cm³ s⁻¹, establishing a pressure of about 0.6 T in the flow tube and a flow velocity of ~10 cm s⁻¹. These conditions yielded mass-selected sample ion currents of about 1 pA. At these currents, the reported spectra required approximately 15-h integrations. In our view of limited mass resolution (m/Δm ~40), photoelectron spectra were obtained at various points on the appropriate mass peaks. Results confirmed that all spectra reported here are due to C₆H₄⁺ or C₆D₄⁺ ions.

Absolute energy scale calibrations were obtained with use of O⁺, S⁺, and Cs⁺ reference ions, whose electron binding energies have been determined previously. Corrections for an observed linear energy scale compression (=1.0%) were made by using measured fine structure splittings in the W⁺ photoelectron spectrum. These procedures enable the determination of absolute electron energies to ±5 meV over the range covered by the o-benzyne spectrum. A correction for a decrease in detector sensitivity was applied to obtain the intensities of peaks below 0.5 eV electron kinetic energy (eKE).

Consideration of the calculated o-benzyne geometry indicates small (±0.2 cm⁻¹) rotational constants whose changes on electron attachment are unlikely to substantially broaden spectral peaks at our present instrumental resolution. Thus, the peak widths of 17 meV (fwhm) observed in the high eKE region of the o-benzyne spectrum, obtained at an instrumental resolution of 11 meV, are most likely to be broadened by unresolved vibrational sequence structure. Consistent with this broadening mechanism, calculated frequencies for neutral o-benzyne suggest that only ~60% of the ions are in the zero-point vibrational level at 300 K. In the absence of sufficient information to correct for these effects, electron affinities and singlet-triplet splittings reported here reflect origin band maxima, and quoted uncertainties include contributions from the observed half-widths of these bands.

III. Results

Figure 2 shows the C₆H₄⁺ photoelectron spectrum; arguments presented in the next section demonstrate that the carrier of this spectrum is the o-benzyne anion. Two band systems are observed, and their constant relative intensities under varied ion source conditions confirm that both arise from the ground electronic state of the same isomer. The extended progressions of peaks at high electron kinetic energy (eKE) signify a transition to a state of the neutral molecule whose equilibrium geometry is significantly displaced from that of the anion. The origin band of this system, indicated in the figure, is readily identified by a Franck–Condon modelling of the spectrum. This assignment is supported by the observed variation with differing ion source conditions in the relative intensity of the weaker peak at ~2.05 eV (eKE), consistent with its assignment to a vibrationally excited state of the anion. Subtraction of the observed origin band eKE of 1.980 (10) eV from the 2.540 eV photon energy yields an electron affinity of 0.560 (10) eV for C₆H₄⁻. The main vibrational progression is associated with a 605 (30) cm⁻¹ mode in the neutral molecule, and the observed hot band indicates a corresponding anion frequency of 600 (30) cm⁻¹. Two additional upper state intervals, of 1040 (20) and 1860 (15) cm⁻¹, are observed in combination with the 605-cm⁻¹ progression, as shown by the Franck–Condon analysis presented below. Corresponding results for C₆D₄⁻ yield an electron affinity of 0.551 (10) eV and deuteration shifts of less than 8% for the vibrations active in the photoelectron spectrum.

The second band system observed by the C₆H₄⁺ spectrum corresponds to a transition to an excited electronic state of the neutral molecule. The separation between its 0.343 (15) eV (eKE) origin band and that of the first band system establishes a splitting of 1.637 (25) eV between the two electronic states. The prominence of the origin band in the second band system suggests a closer resemblance between the equilibrium structures of the ion and the excited electronic state of the neutral molecule. The weak peak at ~0.27 eV (eKE) can be assigned to an upper state vibrational level at 570 (30) cm⁻¹. The stronger feature at ~0.16 eV shows a red shift of ~150 cm⁻¹ on perdeuteration, which exceeds the shifts observed for the origin bands of the high and low eKE band systems by factors of 2 and 5, respectively. On the other hand, the observed shift of the ~0.16-eV peak is consistent with a vibrational frequency reduction of about 10% on deuteration, a reasonable value for a ring vibration. These considerations suggest the assignment of this feature to a vibronic transition in the second band system, rather than to a third electronic state. This assignment implies an upper state vibrational frequency of 1440 (30) cm⁻¹. Results for the corresponding C₆D₄⁻ system yield a 0.347 (15) eV (eKE) origin band and upper state frequencies of 550 (30) and 1330 (30) cm⁻¹.

In addition to these two prominent band systems, a number of considerably weaker features, shown in Figure 3, were observed.

in the 0.5-0.8 eV region. The intensities of these peaks, relative to those discussed above, depended sensitively on ion source in the 0.5-0.8 eV region. The intensities of these peaks, relative to a minor isomer, which is proposed in the following section to be the ground state. However, no such transition is observed.

equally spaced peaks with decreasing intensities toward lower kinetic energy allows the straightforward assignments of the origin bands of the weak C6H4- and C6D4- systems to peaks at 0.779 (15) and 0.781 (15) eV (eKE), respectively. In view of the possibility that additional transitions to lower electronic states of the corresponding neutral molecules may be obscured by the relatively high eKE band systems of o-benzyne, these values provide only upper limits for the electron affinities. Vibrationless progressions observed in the weak band systems indicate upper state frequencies of 980 (30) and 960 (40) cm⁻¹, respectively, for the protonated and perdeuterated species.

IV. Discussion

A. Identification of the Signal Carrier. It is first necessary to establish that the C6H4⁺ ion associated with the photoelectron spectrum shown in Figure 2 is indeed the o-benzyne isomer. A ring structure is initially suggested by the synthetic route employed, which involves the abstraction of H₂⁺ from benzene. The CIMS studies by Jennings and coworkers of O⁻ reactions with 1,3,5-trideuterobenzene showed primarily HD⁻ loss, providing evidence for ortho over para abstraction. The electron binding energy of 0.59 (10) eV measured here further argues against both p- and m-benzyne anions as the signal carrier, since considerably higher binding energies are expected for these species in view of the 1.1 eV value for phenyl anion. Additional arguments against assignment to these isomers are provided by ab initio calculations of the singlet-triplet energy separations in the corresponding neutral molecules. The splitting of only 0.06 eV predicted for p-benzyne is not consistent with the high eKE photoelectron band system, which is well modelled by a single electronic transition (see section IVB). Similarly, the 0.53 eV energy gap calculated for m-benzyne is smaller by a factor of three than the separation between the two major band systems observed here. However, both the electron affinity and the singlet-triplet splitting measured in the present study are consistent with predictions for o-benzyne.

In addition to the position of the signal carrier, there is an open chain structure. Anions of most (but not all) closed-shell unstrained hydrocarbons are unstable with respect to autodetachment in the gas phase, clearly inconsistent with the observed 0.560 (10) eV binding energy. On the other hand, ions of open-chain radicals, resulting from carbon-carbon bond cleavage of an initially prepared cyclic structure, will contain C=C, C≡C, or C≡C groups likely to yield C6H4⁻ species with binding energies substantially higher than the observed value. For example, the three linear acetylide hydrocarbon radicals studied to date, C≡CCH₃, C≡CCH₂, and C≡C≡C≡CH, have electron affinities in excess of 2.4 eV. Similarly, the allene-like molecules C₃H, C₂H, and C₂H₂ have electron affinities of 1.8 eV or greater, and the allenyl ion, HCCCH₂⁺, is bound by 0.893 (25) eV. The electron affinities of unsaturated hydrocarbon radicals are generally observed to increase with increasing molecular size as well as with extended conjugation.⁴¹ C₆H₄⁺ species containing such radical groups are expected to exhibit even higher electron affinities than their shorter chain counterparts. Similarly, conjugated derivatives of the vinylidene radical, CH₂⁺, are likely to have electron affinities which substantially exceed the 0.47 (2) eV value for unsubstituted vinylidene. Thus, the measured binding energy of the observed C₆H₄⁺ ion appears to be too high for an anion of a closed-shell unstrained hydrocarbons and too low for an anion of the highly electron deficient radical species that might be produced by a ring opening. In addition, the apparent simplicity of the vibronic structure in the high eKE band system, despite the occurrence of a significant geometry displacement on detachment, suggests a highly symmetric anion.

Thus, we have carefully considered open-chain C₆H₄⁺ isomers and m- and p-benzyne anions as the signal carriers of the spectrum in Figure 2. All evidence supports the conclusion that this spectrum is associated with the o-benzyne anion.

In view of this assignment for the major C₆H₄⁺ isomer, a plausible assignment for the signal carrier of the much weaker band system shown in Figure 3 is to either p- or m-benzyne. This suggestion is consistent with the measured electron binding energy of 2.176 eV, in view of the 1.1 eV value for C₆H₄⁺, as well as with the observed frequency and deuteration shift of the active vibrational mode, which resembles that of the symmetric ring breathing vibrations in benzyne and m-benzyne systems.⁴³ However, there are clearly a number of possible alternative assignments, and additional experiments using specific m- and p-benzyne precursors are needed before the source of this spectrum can be considered to be positively identified.

B. Electron Affinity and Singlet-Triplet Splitting of o-Benzene. The unusual stability of the o-benzyne anion can be understood from the electron transmission experiments of Jordan and coworkers on a series of cyclic alkenes. The stabilities of these (metastable) anions were observed to increase with increasing deviation of the R-C≡C-R groups in the neutral molecules from their preferred linear geometry. This trend extrapolates to a vertical electron affinity of 0.1-0.6 eV for a cycloalkyne constrained at a calculated o-benzyne angle, in excellent agreement with the photoelectron spectrum reported here. Thus, the electron affinity of o-benzyne suggests a triple-bonded structure, whose LUMO is primarily acetylenic. Consistent with this view, the 2084 cm⁻¹ carbon-carbon stretching mode observed for o-benzyne in matrix IR studies indicates that the dehydrocarbon bond is nearly triple bond in character.

Combining with the previously reported value of 118 (5) kcal/mol for the heat of formation of o-benzyne, the electron affinity measured here implies a vertical electron affinity of 1.76 eV or greater, for o-benzyne anion. Using the known heats of formation of C₆H₄⁻ and H⁺, this result implies a gas-phase acidity for the ortho proton of the phenyl radical (C₆H₅⁻ → o-C₆H₄⁻ + H⁺) of ΔHₖₒₐ₅ = 391 (7) kcal/mol.

The band system observed in the low eKE region in figure 2 can be assigned to a transition to the 3º B1 state of o-benzyne, in view of the substantially higher energies expected for transitions to excited singlet states. The implied singlet–triplet splitting of 1.637 (25) eV [37.7 (6) kcal/mol] is 30% higher than the value predicted by previously reported ab initio calculations for partially

(37) Jordan, K. D.; Burrow, P. D.; Acc. Chem. Res. 1978, 11, 341. For example, it has been concluded that the hexatriene anion is bound from the lack of an observed transition to the anion ground state in electron transmission studies (Burrow, P. D.; Jordan, K. D. J. Am. Chem. Soc. 1982, 104, 5247).
Electron Affinity of o-Benzene

**Figure 4.** Solid lines show the observed $X'A_1 + \epsilon$ → $X'B_2$ band systems of o-benzyne-$h_4$ (top) and $d_4$ (bottom). Dashed lines show simulated spectra based on a multimode harmonic Franck–Condon fitting to the experimental spectra, for the frequencies and normal mode displacements listed in Table I. Upper-state vibrational assignments for the labeled transitions, all from the zero-point level of the $v_n$, are indicated (v*, v'*, v'); $v_1$ in order of decreasing intensity. $\epsilon = 0.00 \{v_*' = 605 \text{ cm}^{-1} - h_4, 585 \text{ cm}^{-1} - d_4\}; \xi = 0.01 \{v_*' = 980 \text{ cm}^{-1} - h_4, 980 \text{ cm}^{-1} - d_4\}; \Delta = 0.01 \{v_*' = 1860 \text{ cm}^{-1} - h_4, 1860 \text{ cm}^{-1} - d_4\}$. Additional 00n progression in combination with a fourth mode ($v_4' = 1400 \text{ cm}^{-1}$) is included in the C$_6$D$_4$ simulation (labeled "+"), but this assignment is highly tentative; see text. Insert shows the $v_4' = 1$ hot band (600 cm$^{-1}$ C$_6$H$_4^-$, 580 cm$^{-1}$ C$_6$D$_4^-$), whose intensity indicates an anion vibrational temperature of 300 K.

![Figure 4](image_url)

**Table I.** o-Benzyne: Summary of Results

<table>
<thead>
<tr>
<th></th>
<th>C$_6$H$_4$</th>
<th>C$_6$D$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>electron affinity</td>
<td>0.560 (10) eV</td>
<td>0.551 (10) eV</td>
</tr>
<tr>
<td>$\Delta E(1B_2^+ - A_1^-)$</td>
<td>1.637 (25) eV</td>
<td>1.642 (25) eV</td>
</tr>
<tr>
<td>$37.7 (6) \text{kcal/mol}$</td>
<td>37.9 (6) \text{kcal/mol}</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>active vibrations</th>
<th>freq (cm$^{-1}$)</th>
<th>(displacements (dimensionless))</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X'A_1 + \epsilon$ → $X'B_2$</td>
<td>1860 (15) [1.38]</td>
<td></td>
</tr>
<tr>
<td>$v_1'$</td>
<td>1040 (20) [0.84]</td>
<td>980 (20) [0.78]</td>
</tr>
<tr>
<td>$v_2'$</td>
<td>605 (15) [2.19]</td>
<td>585 (15) [2.16]</td>
</tr>
<tr>
<td>$v_3'$</td>
<td>600 (30)</td>
<td>580 (30)</td>
</tr>
<tr>
<td>$2B_2 + \epsilon$ → $X'B_2$</td>
<td>1440 (30)</td>
<td>1330 (30)</td>
</tr>
<tr>
<td>570 (30)</td>
<td>550 (30)</td>
<td></td>
</tr>
</tbody>
</table>

In the $X'A_1 + \epsilon$ → $X'B_2$ system, the three most prominent vibrational modes are arbitrarily numbered in order of decreasing frequency and in Figure 4. Frequencies listed for the $a^2B_2 + \epsilon$ → $X'B_2$ system refer to upper state fundamentals. Harmonic normal mode displacements used to generate the simulated spectra shown in Figure 4 are given in brackets.

Figure 4 compares the observed photoelectron spectra with our best fits (shown by the dashed lines), generated by the convolution of calculated multimode harmonic Franck–Condon factors with a 1.7-eVMHz Lorentzian line shape. In these simulations, vibrational frequencies for the active modes in the ions were assumed equal to the observed neutral molecule frequencies. Frequencies and dimensionless normal mode displacements obtained from these fits are listed in Table I. The latter values, in combination with a normal coordinate analysis of the neutral molecule, provide useful constraints on the anion equilibrium geometry. The active vibrations have been arbitrarily numbered in order of decreasing frequency; i.e., $v_1' = 1860 \text{ cm}^{-1}$, $v_2' = 1040 \text{ cm}^{-1}$, and $v_3' = 605 \text{ cm}^{-1}$ for C$_6$H$_4^-$. Vibrational levels in C$_6$H$_4$ and C$_6$D$_4$ associated with the strongest observed transitions are indicated in the figure by their ($v_1', v_2', v_3'$) quantum numbers.

In addition to these three modes, the C$_6$D$_4^-$ simulation includes a relatively weak 1400-cm$^{-1}$ upper-state progression whose main effect is to fill in valleys between peaks; the activity of this mode is summarized in a single tentative vibration. Vibrations occurring at $v_4' = 1$ levels of the anions to the vibrationless levels of the neutral molecules are shown in expanded inserts. The intensities of these features imply anion vibrational temperatures of 300 K.

These results show that the most intense peaks are comprised of progressions in upper-state 00n (i.e., $v_n' = n$) levels alone (indicated as "*") and in combination with 100 (unlabeled "A") and 200 (unlabeled "B") excitations. Shoulders to the right of the main peaks are associated with combination bands involving 01n (labeled "X") and 1n upper-state levels. The excellent agreement between the simulated and observed spectra for overall intensity profiles, and for peak positions below 1.7 eV (eKE) in the C$_6$D$_4^-$ spectrum, provides a strong argument in favor of the proposed 1860-cm$^{-1}$ interval. Attempts to model either spectrum with use of a frequency differing from this value by one or more ~600-cm$^{-1}$ intervals produced substantially degraded fits.

The relative simplicity of the photoelectron spectra suggests that the neutral and ionic species are of the same symmetry, and thus that the active vibrations correspond to totally symmetric modes. Thus, the most likely assignment for the 605 and 585-cm$^{-1}$ vibrations is to the in-plane ring deformation corresponding to $v_6a$ in benzene (Wilson numbering). The activity

of this mode is reasonable, since occupation of the antibonding dehydrocarbon orbital is expected to reduce the triple-bond character in the anion, producing less strain-induced deviation from 120° ring angles than in the neutral singlet. This frequency has not been observed in matrix IR studies of o-benzyne, but the present assignment is supported by the similar frequencies of 630 and 608 cm$^{-1}$ reported for the protonated and perdeuterated forms of the isoelectronic pyridazine molecule. The weak IR intensity calculated for this mode in o-benzyne, and observed in pyridazine, also supports its identification with the interval observed here, rather than with one of the low-frequency modes observed in the matrix studies. The present assignment conflicts with the normal coordinate analysis of C$_6$H$_4$ reported by Laing and Berry, in which the observed 469-cm$^{-1}$ IR frequency was assigned to this vibration, as well as with the more recent analysis observed in the matrix studies. The present assignment conflicts with the normal coordinate analysis of C$_6$H$_4$ reported by Nam and Leroi, which predicts an even lower frequency of 395 cm$^{-1}$. The present assignment indicates that the in-plane skeletal bends of the strained ring system in singlet o-benzyne are less planar than has been suggested by these analyses.

The 1040 (20)- and 980 (20)-cm$^{-1}$ frequencies observed here for C$_6$H$_4$ and C$_6$D$_4$, respectively, probably correspond to the totally symmetric ring stretch identified by Nam and Leroi with the 1056-cm$^{-1}$ fundamental observed in the IR spectrum of C$_6$H$_4$. The deuterium shift for this mode is calculated to be 4%, consistent with the shift observed here. This vibration is described as involving stretching motions of the CC bonds adjacent and opposite to the dehydrocarbon bond. Its activity in the photoelectron spectrum is again reasonable in view of the predicted lengthening of the latter bond in the neutral singlet and the more benzenoid bond length expected in the less aryne-like anion.

Finally, the 1860-cm$^{-1}$ interval inferred from both the C$_6$H$_4$ and C$_6$D$_4$ photoelectron spectra is most straightforwardly assigned to a stretching vibration involving the acetylenic CC bond, a motion clearly likely to be excited on detachment. No frequency in this region was attributed to o-benzyne in the matrix studies (although an 1838-cm$^{-1}$ mode assigned to a carbonyl-containing byproduct of the o-benzyne synthesis has been noted). The present assignment conflicts with the results of Nam and Leroi, in which no ring-stretching frequencies are found between the observed 2084-cm$^{-1}$ triple-bond stretch and a calculated fundamental at 1657 cm$^{-1}$. The earlier normal mode analysis did predict an 1856-cm$^{-1}$ fundamental with a relatively small deuterium shift, but this was assigned to a B$_2$ mode not likely to be excited in the photoelectron spectrum. Applying Laing and Berry’s argument for the nonobservance of a proposed higher frequency (2450 cm$^{-1}$) stretching mode in matrix studies to the present case, we can suggest that an 1860-cm$^{-1}$ stretching mode may have thus far escaped detection due to a relatively small change in the z-component of the molecular dipole moment during this oscillation, producing a weak IR intensity. In view of these discrepant results, and the somewhat inferential nature of the 1860-cm$^{-1}$ frequency determination in the present experiment, it appears prudent to postpone a discussion of the stiffness of CC stretches in the strained ring system until more complete IR data are available.

V. Summary

The negative ions of o-benzyne-h$_4$ and -d$_4$ have been prepared in a flowing afterglow ion source and investigated by photoelectron techniques. Spectroscopic results confirm the structure of the anions. Adiabatic electron affinities are determined to be 0.560 (10) eV for C$_6$H$_4$ and 0.551 (10) eV for C$_6$D$_4$. Combined with known heats of formation, the former value provides a measurement of the heat of formation of o-benzyne anion ($\Delta H^\circ_{f,an} = 104 (5)$ kcal/mol) and the gas-phase acidity of the ortho proton (0.55 eV for C$_6$D$_4$). The positive electron affinity of o-benzyne is not common for a closed-shell hydrocarbon but is consistent with extrapolations from electron transmission studies of larger strained cycloalkynes. Thus, the observed electron affinity suggests a triple-bonded structure whose LUMO is primarily an antibonding acetylenic (rather than benzenoid) orbital. From observed photodetachment transitions to both the X'$A_1$ and $\beta$B$_2$ states, singlet-triplet splittings are determined to be 37.7 (6) kcal/mol for C$_6$H$_4$ and 37.9 (6) kcal/mol for C$_6$D$_4$.

An extended vibrational progression in the 1820-cm$^{-1}$ band system, with upper-state intervals of 605 (15) cm$^{-1}$ for C$_6$H$_4$ and 585 (15) cm$^{-1}$ for C$_6$D$_4$, is assigned to a totally symmetric ring deformation not previously observed in matrix IR studies. This assignment suggests that in-plane skeletal bends of the strained ring are less planar than indicated by previous normal coordinate analyses. Additional intervals are observed at 1040 (20) and 1860 (15) cm$^{-1}$ in C$_6$H$_4$ and 980 (20) and 1860 (15) cm$^{-1}$ in C$_6$D$_4$. The 1860-cm$^{-1}$ intervals probably involve the stretching vibration of the acetylenic C–C bond. No a$_1$ fundamentals in this region have previously been observed or predicted. Dimensionless normal mode displacements obtained from multimode harmonic Franck-Condon analyses of the spectra are also reported; given an accurate normal mode picture for the neutral singlet, these values provide useful constraints on the anion equilibrium geometry. The vibronic profile of the B$_2$ ← B$_2$ system is more vertical, implying a greater resemblance between the equilibrium geometries of the anion and the neutral triplet.

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