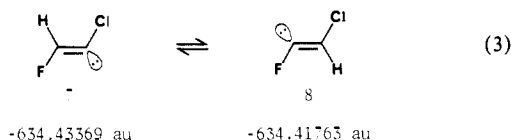


that the interaction between the filled  $\sigma_{C-X}$  orbital and the carbanion ( $n$ ) is essential to the formation of the HOMO orbital  $\psi_2$  (Figure 3). A comparison between the HOMO ( $\psi_2$ ) arising from this hypothetical argument and that determined (4-31G) for the transition state (Figure 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  $C_\alpha-X$  bond length as a result of the  $H-C_\beta-C_\alpha$  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). If



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 provided that the inversion barrier of the two anions were comparable. Thus, the leaving group abilities of  $F^-$  and  $Cl^-$  would be compromised and the course of the reaction would be controlled

by carbanion stability. In a recent study of the elimination of HX from erythro-1-chloro-2-fluoro-1,2-diphenylethane, Baciocchi<sup>20</sup> made the striking observation of a  $k_{Cl}/k_F$  value for syn elimination that was substantially less than unity. In that process it was concluded that fluorine is eliminated in preference to chlorine. A favorable 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<sup>15</sup> 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.<sup>15</sup>

**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.

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## Determination of the Singlet-Triplet Splitting and Electron Affinity of *o*-Benzyne by Negative Ion Photoelectron Spectroscopy

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**Abstract:** The photoelectron spectrum of the *o*-benzyne negative ion displays transitions to both the  $\bar{X}^1A_1$  and  $\bar{a}^3B_2$  states of the neutral molecule. Results yield adiabatic electron affinities of 0.560 (10) and 0.551 (10) eV for  $C_6H_4$  and  $C_6D_4$ , respectively. These values are consistent with extrapolations from studies of larger strained cycloalkynes and imply that the lowest unoccupied MO of *o*-benzyne is primarily an antibonding acetylenic orbital. The *o*-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

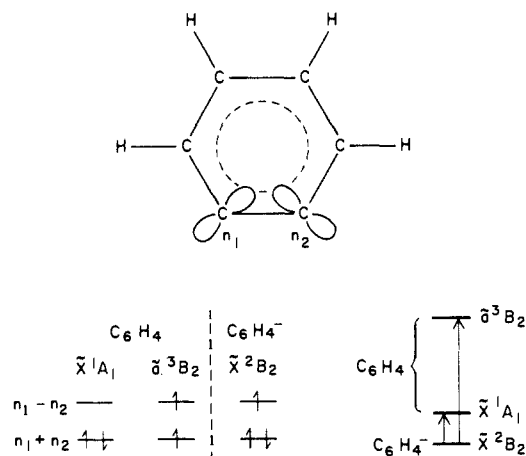
The determination of the electronic and molecular structure of *o*-benzyne (1,2-dehydrobenzene,  $C_6H_4$ ) has attracted considerable interest since the first demonstration of its existence by Roberts et al.<sup>1</sup> over 30 years ago. This species is among the simplest of highly strained conjugated hydrocarbons. Thus, it

provides a benchmark system for theoretical models<sup>2</sup> of the structural and energetic consequences of ring strain. Much attention has focussed on the effects of its unique geometry on the well-studied solution chemistry<sup>3</sup> of this reactive intermediate.

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**Figure 1.** Qualitative illustration of the electronic structure of neutral and anionic *o*-benzyne. Molecular orbitals labelled  $n_1 + n_2$  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 *o*-benzyne are accessed by photodetachment of an electron from the doublet ground state of the negative ion.

As a consequence of its high reactivity, *o*-benzyne has proved difficult to study spectroscopically, and much of our present understanding has been obtained from numerous *ab initio*<sup>4-8</sup> and semiempirical<sup>9-18</sup> studies. These results indicate a  $^1A_1$  ground state in which double occupancy of the in-plane bonding molecular orbital centered on the two dehydrocarbons produces a shortened "acetylenic" carbon-carbon bond (see Figure 1). Although calculated  $\pi$ -bond overlap populations display marked alternation around the ring,<sup>6-8</sup> much of the aromaticity of benzene is predicted to be retained. There have been several calculations<sup>5,7,14,15,18</sup> of the energy gap between the  $\tilde{X}^1A_1$  state and the lowest energy ( $^3B_2$ ) 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.<sup>7</sup>

The only direct spectroscopic results concerning the geometry and bonding of *o*-benzyne have been obtained in matrix IR studies by Chapman and co-workers<sup>19</sup> and Dunkin and MacDonald,<sup>20</sup> which have yielded ten  $C_6H_4$  and eleven  $C_6D_4$  vibrational frequencies. Most significantly, the observation of C $\equiv$ C 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.<sup>21,22</sup>

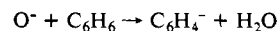
The connection between the electrophilicity of *o*-benzyne and its strained acetylenic bond has been investigated by Houk, Jordan, Krebs, and co-workers,<sup>23-25</sup> using a combination of theoretical and spectroscopic methods. *Ab initio*<sup>24,26</sup> and extended Hückel<sup>27</sup> calculations of acetylene indicate a dramatic stabilization of the lowest unoccupied molecular orbital (LUMO) on cis bending of the molecule. Consistent with this prediction, electron transmission spectroscopy of cycloalkynes<sup>23</sup> indicates an increase in electron affinity with decreasing ring size. From an extrapolation based upon these results, the *o*-benzyne anion has been predicted<sup>23</sup> 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 transition states involving electron donation to *o*-benzyne.<sup>24</sup>

We have prepared  $C_6H_4^-$  and  $C_6D_4^-$  in a flowing afterglow negative ion source and have studied these ions by photoelectron spectroscopy. Results provide firm spectroscopic evidence that the signal carrier is indeed the *o*-benzyne 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 *o*-benzyne.

## II. Experimental Method

The flowing afterglow negative ion photoelectron spectrometer employed in these studies has recently been described in detail.<sup>28,29</sup> Briefly, sample ions are prepared in a field-free flowing afterglow ion-molecule reactor,<sup>30</sup> 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 focussed intracavity beam of a cw Ar II laser operated at 4880 or 4579 Å. The laser polarization is set at the "magic" angle of 54° 45' with respect to the direction of electron collection to ensure that observed photoelectron transition intensities reflect average photodetachment cross sections.<sup>31</sup> 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.

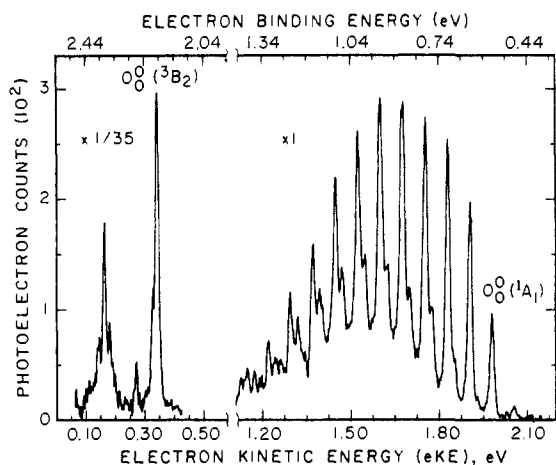
$C_6H_4^-$  (and  $C_6D_4^-$ ) were prepared by the following  $H_2^+$  transfer reaction, previously observed by Jennings and coworkers<sup>32</sup> using chemical ionization mass spectrometry (CIMS):



$O^-$  was produced by dissociative electron attachment to  $N_2O$  injected at

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**Figure 2.** Photoelectron spectrum of the  $\bar{X}^1A_1 + e^- \leftarrow \bar{X}^2B_2$  and  $\bar{a}^3B_2 + e^- \leftarrow \bar{X}^2B_2$  transitions of the *o*-benzynes anion. Origin bands (labeled  $0_0^0$ ) observed at electron kinetic energies of 1.980 (10) and 0.343 (15) eV determine the electron affinity and singlet-triplet splitting of neutral *o*-benzynes. Spectra were obtained with the 488 and 458 nm Ar II laser lines for the singlet and triplet band systems, respectively; for clarity, both portions of the spectrum are drawn as for 488-nm (2.540 eV) excitation.

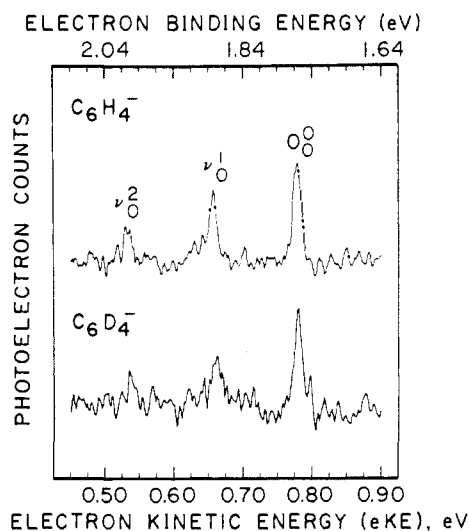
a flow rate of 0.03 STP  $\text{cm}^3 \text{s}^{-1}$  downstream of an electron impact ionizer. The ionizer was composed of a thoriated iridium filament biased at -130 V with respect to a grounded acceleration grid and operated at an emission current of 10 mA. Benzene vapor was injected at 0.1 STP  $\text{cm}^3 \text{s}^{-1}$  about 60 cm from the electron gun, and the ions were sampled  $\sim 40$  cm further downstream through a 1 mm diameter aperture. The helium flow was regulated at 150 STP  $\text{cm}^3 \text{s}^{-1}$ , establishing a pressure of about 0.6 T in the flow tube and a flow velocity of  $\sim 10^4 \text{ cm s}^{-1}$ . These conditions yielded mass-selected sample ion currents of about 1 pA. At these currents, the reported spectra required approximately 15-h integrations. In view of our limited mass resolution ( $m/\Delta m \sim 40$ ), photoelectron spectra were obtained at various points on the appropriate mass peaks. Results confirmed that all spectra reported here are due to  $\text{C}_6\text{H}_4^-$  or  $\text{C}_6\text{D}_4^-$  ions.

Absolute energy scale calibrations were obtained with use of  $\text{O}^-$ ,  $\text{S}^-$ , and  $\text{Cs}^-$  reference ions, whose electron binding energies<sup>33</sup> have been determined precisely. Corrections for an observed linear energy scale compression ( $\sim 1.0\%$ ) were made by using measured fine structure splittings in the  $W^-$  photoelectron<sup>33</sup> spectrum. These procedures enable the determination of absolute electron energies to  $\pm 5$  meV over the range covered by the *o*-benzynes 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*-benzynes geometry<sup>6,8,13-15,21</sup> indicates small ( $\leq 0.2 \text{ cm}^{-1}$ ) 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*-benzynes 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*-benzynes suggest that only  $\sim 60\%$  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  $\text{C}_6\text{H}_4^-$  photoelectron spectrum; arguments presented in the next section demonstrate that the carrier of this spectrum is the *o*-benzynes 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



**Figure 3.** Band systems due to minor  $\text{C}_6\text{H}_4^-$  and  $\text{C}_6\text{D}_4^-$  isomers, tentatively assigned as *m*- or *p*-benzynes anions. These bands were typically about 2% as intense as the triplet *o*-benzynes system. The observed origin band ( $0_0^0$ ) positions correspond to electron binding energies of 1.761 (15) eV for  $\text{C}_6\text{H}_4^-$  and 1.759 (15) eV for  $\text{C}_6\text{D}_4^-$ . Since transitions to lower energy states may be hidden beneath the stronger *o*-benzynes bands, these values provide upper limits for the electron affinities. The active vibrational progression has upper state intervals of 980 (30)  $\text{cm}^{-1}$  for  $\text{C}_6\text{H}_4^-$  and 960 (40)  $\text{cm}^{-1}$  for  $\text{C}_6\text{D}_4^-$ .

observed variation with differing ion source conditions in the relative intensity of the weaker peak at  $\sim 2.05$  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  $\text{C}_6\text{H}_4^-$ . The main vibrational progression is associated with a 605 (15)- $\text{cm}^{-1}$  mode in the neutral molecule, and the observed hot band indicates a corresponding anion frequency of 600 (30)  $\text{cm}^{-1}$ . Two additional upper state intervals, of 1040 (20) and 1860 (15)  $\text{cm}^{-1}$ , are observed in combination with the 605- $\text{cm}^{-1}$  progression, as shown by the Franck-Condon analysis presented below. Corresponding results for  $\text{C}_6\text{D}_4^-$  yield an electron affinity of 0.551 (10) eV and deuterium shifts of less than 8% for the vibrations active in the photoelectron spectrum.

The second band system observed in the  $\text{C}_6\text{H}_4^-$  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  $\sim 0.27$  eV (eKE) can be assigned to an upper state vibrational level at 570 (30)  $\text{cm}^{-1}$ . The stronger feature at  $\sim 0.16$  eV shows a red shift of  $\sim 150 \text{ cm}^{-1}$  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  $\sim 0.16$ -eV peak is consistent with a vibrational frequency reduction of about 10% on deuteration, a reasonable value<sup>34,35</sup> 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)  $\text{cm}^{-1}$ . Results for the corresponding  $\text{C}_6\text{D}_4^-$  system yield a 0.347 (15) eV (eKE) origin band and upper state frequencies of 550 (30) and 1330 (30)  $\text{cm}^{-1}$ .

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

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in the 0.5–0.8-eV region. The intensities of these peaks, relative to those discussed above, depended sensitively on ion source conditions. This dependence suggests that they are due either to a different  $C_6H_4^-$  (or  $C_6D_4^-$ ) isomer or to a transition from an excited electronic state of the same isomer to the triplet state of the neutral molecule. In the latter case, the observed separation between the highest eKE bands of both systems, corresponding to an anion excited state at  $\sim 0.44$  eV, would suggest the occurrence at about 2.4 eV (eKE) of a corresponding transition to the ground state. However, no such transition is observed. Therefore, the most likely assignment for the weak system is to a minor isomer, which is proposed in the following section to be *m*- or *p*-benzyne anion. The observation of three approximately equally spaced peaks with decreasing intensities toward lower kinetic energy allows the straightforward assignments of the origin bands of the weak  $C_6H_4^-$  and  $C_6D_4^-$  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 intense high eKE band systems of *o*-benzyne, these values provide only upper limits for the electron affinities. Vibronic 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  $C_6H_4^-$  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  $H_2^+$  from benzene. The CIMS studies by Jennings and co-workers<sup>32</sup> of  $O^-$  reactions with 1,3,5-trideuteriobenzene showed primarily  $HD^+$  loss, providing evidence for ortho or para abstraction. The electron binding energy of 0.560 (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<sup>36</sup> for phenyl anion. Additional arguments against assignment to these isomers are provided by ab initio calculations<sup>7</sup> 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 IVC). 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<sup>7,23</sup> for *o*-benzyne.

In addition, we can consider the possibility that the signal carrier has an open chain structure. Anions of most (but not all)<sup>37</sup> 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  $\cdot C\equiv$ ,  $:C=$ , or  $-C\dot{=}$  groups likely to yield  $C_6H_4^-$  species with binding energies substantially higher than the observed value. For example, the three linear acetylide hydrocarbon radicals studied to date,  $\cdot C\equiv CH$ ,<sup>38</sup>  $\cdot C\equiv CCH_3$ ,<sup>39</sup> and  $\cdot C\equiv CC\equiv CH$ ,<sup>40</sup> have electron affinities in excess of 2.4 eV. Similarly, the allene-like molecules  $C_3$ ,  $C_3H$ , and  $C_3H_2$  have electron affinities of 1.8 eV or greater,<sup>40</sup> and the allenyl ion,  $HCCCH_2^-$ , is bound by 0.893 (25) eV.<sup>39</sup> The electron affinities of unsaturated hydrocarbon radicals are gen-

erally observed to increase with increasing molecular size as well as with extended conjugation,<sup>41</sup> so  $C_6H_4$  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,  $\cdot CCH_2$ , are likely to have electron affinities which substantially exceed the 0.47 (2)-eV value<sup>42</sup> for unsubstituted vinylidene. Thus, the measured binding energy of the observed  $C_6H_4^-$  isomer appears to be too high for an anion of a closed-shell unstrained hydrocarbon 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.<sup>43</sup>

Thus, we have carefully considered open-chain  $C_6H_4^-$  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  $C_6H_4^-$  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  $\leq 1.76$  eV, in view of the 1.1-eV value for  $C_6H_5^-$ ,<sup>36</sup> as well as with the observed frequency and deuterium shift of the active vibrational mode, which resemble those for symmetric ring breathing vibrations in benzenoid systems.<sup>34,35</sup> 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*-Benzyne.** The unusual stability of the *o*-benzyne anion can be understood from the electron transmission experiments of Jordan and co-workers<sup>23</sup> on a series of cyclic alkynes. The stabilities of these (metastable) anions were observed to increase with increasing deviation of the  $R-C\equiv C-R$  groups in the neutral molecules from their preferred linear geometry. This trend extrapolates<sup>23</sup> to a vertical electron affinity of 0.1–0.6 eV for a cycloalkyne constrained at a calculated<sup>21</sup> *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<sup>19,20</sup> indicates that the dehydrocarbon bond is very nearly triple bond in character.<sup>22</sup>

Combined with the previously reported value of 118 (5) kcal/mol for the heat of formation of *o*-benzyne,<sup>44</sup> the electron affinity measured here implies a  $\Delta H_f^\circ$  value of 104 (5) kcal/mol for *o*-benzyne anion. Using the known heats of formation of  $C_6H_5$ <sup>45</sup> and  $H^+$ ,<sup>46</sup> this result implies a gas-phase acidity for the ortho proton of the phenyl radical ( $C_6H_5 \rightarrow o-C_6H_4^- + H^+$ ) of  $\Delta H_{acid}^\circ = 391$  (7) kcal/mol.

The band system observed in the low eKE region in figure 2 can be assigned to a transition to the  $\tilde{a}^3B_2$  state of *o*-benzyne, in view of the substantially higher energies expected for transitions to excited singlet states.<sup>5</sup> 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<sup>7</sup> for partially

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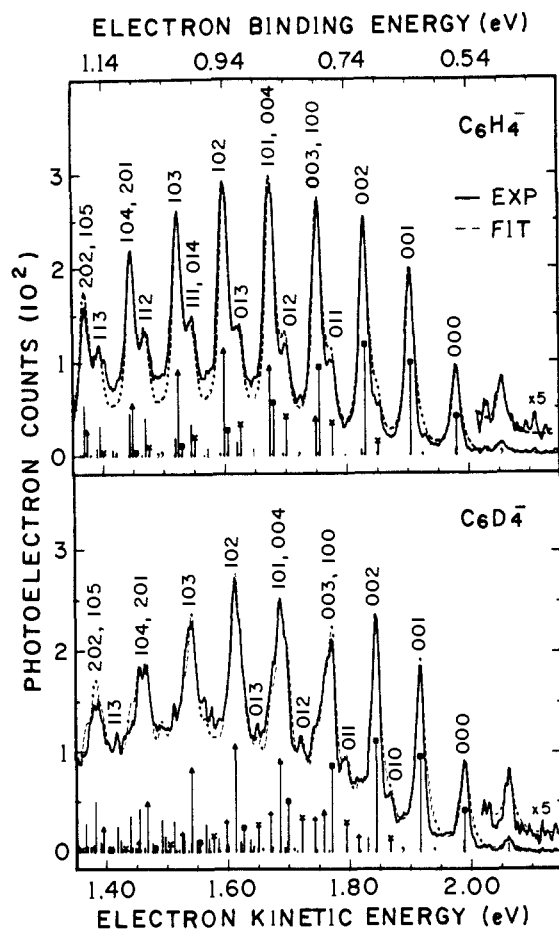
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**Figure 4.** Solid lines show the observed  $\tilde{X}^1A_1 + e^- \leftarrow \tilde{X}^2B_2$  band systems of *o*-benzyne- $h_4$  (top) and  $-d_4$  (bottom). Dashed lines show simulated spectra based on a multimode harmonic Franck–Condon fitting 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 ion, are indicated ( $\nu_1'$ ,  $\nu_2'$ ,  $\nu_3'$ ) in order of decreasing intensity. ■ =  $00n$  ( $\nu_3' = 605 \text{ cm}^{-1}$   $-h_4$ ,  $585 \text{ cm}^{-1}$   $-d_4$ ); × =  $01n$  ( $\nu_2' = 1040 \text{ cm}^{-1}$   $-h_4$ ,  $980 \text{ cm}^{-1}$   $-d_4$ ); ▲ =  $10n$  ( $\nu_1' = 1860 \text{ cm}^{-1}$   $-h_4$ ,  $-d_4$ ). An additional  $00n$  progression in combination with a fourth mode ( $\nu' = 1400 \text{ cm}^{-1}$ ) is included in the  $C_6D_4^-$  simulation (labeled “+”), but this assignment is highly tentative; see text. Insert shows the  $\nu_3'' = 1$  hot band ( $600 \text{ cm}^{-1}$   $C_6H_4^-$ ,  $580 \text{ cm}^{-1}$   $C_6D_4^-$ ), whose intensity indicates an anion vibrational temperature of 300 K.

optimized equilibrium geometries. One possible contribution to this discrepancy is the exaggeration, pointed out by these authors,<sup>7</sup> of strain energies calculated with 4-31G basis sets, an effect which preferentially destabilizes the more strained singlet state.

**C. Vibrational Analysis of the  $\tilde{X}^1A_1 \leftarrow \tilde{X}^2B_2$  System of *o*-Benzyne.** The  $\tilde{X}^1A_1 \leftarrow \tilde{X}^2B_2$  photodetachment systems of  $C_6H_4^-$  and  $C_6D_4^-$  are expanded in Figure 4. On casual inspection, the main bands appear to comprise a single upper-state progression in  $\sim 600\text{-cm}^{-1}$  intervals. However, a more detailed analysis indicates the activity of at least two additional vibrational modes in each spectrum. One of these, with upper-state intervals of  $1040$  ( $20$ )  $\text{cm}^{-1}$  in  $C_6H_4^-$  and  $980$  ( $20$ )  $\text{cm}^{-1}$  in  $C_6D_4^-$ , is evidenced by partially resolved features on the high eKE shoulders of the main bands. The activity of a third mode is suggested by the intensities and positions of peaks below  $1.7 \text{ eV}$  (eKE) in both spectra, which cannot be adequately modelled by a single progression. For example, although peak positions down to  $1.77 \text{ eV}$  (eKE) in the  $C_6D_4^-$  spectrum are consistent with a single progression in harmonic  $585$  ( $15$ )  $\text{cm}^{-1}$  intervals, lower eKE peaks appear shifted from this pattern by about  $100 \text{ cm}^{-1}$ . Since this shift is observed for several consecutive peaks, it is clearly not due simply to a Fermi resonance. In both the  $C_6H_4^-$  and  $C_6D_4^-$  spectra, an harmonic Franck–Condon simulation based on a single progression with intensities fit to observed transitions to  $v = 0, 1,$  and  $2$  upper-state levels significantly underestimates the strengths of major peaks

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

	$C_6H_4^-$	$C_6D_4^-$
electron affinity	0.560 (10) eV	0.551 (10) eV
$\Delta E(^3B_2 - ^1A_1)$	1.637 (25) eV	1.642 (25) eV
	37.7 (6) kcal/mol	37.9 (6) kcal/mol
active vibrations: <sup>a</sup>		
freq ( $\text{cm}^{-1}$ ) and		
[displacements		
(dimensionless)]		
$\tilde{X}^1A_1 \leftarrow \tilde{X}^2B_2$		
$\nu_1'$	1860 (15) [1.38]	1860 (15) [1.38]
$\nu_2'$	1040 (20) [0.84]	980 (20) [0.78]
$\nu_3'$	605 (15) [2.19]	585 (15) [2.16]
$\nu_3''$	600 (30)	580 (30)
$\tilde{a}^3B_2 \leftarrow \tilde{X}^2B_2$		
	1440 (30)	1330 (30)
	570 (30)	550 (30)

<sup>a</sup> In the  $\tilde{X}^1A_1 \leftarrow \tilde{X}^2B_2$  system, the three most prominent vibrational modes are arbitrarily numbered in order of decreasing frequency here and in Figure 4. Frequencies listed for the  $\tilde{a}^3B_2 \leftarrow \tilde{X}^2B_2$  system refer to upper state fundamentals. Harmonic normal mode displacements used to generate the simulated spectra shown in Figure 4 are given in brackets.

to lower eKE; e.g., the strength of the  $\sim 1.60\text{-eV}$  (eKE) band is underestimated by more than a factor of 4. These observations point to the activity of a third vibrational mode with a fundamental frequency approximately equal to an overtone of the  $605\text{-cm}^{-1}$  progression in  $C_6H_4^-$  and about  $100 \text{ cm}^{-1}$  higher than a  $585\text{-cm}^{-1}$  overtone in  $C_6D_4^-$ . Optimum fits to the observed spectra were obtained for a frequency of  $1860$  ( $15$ )  $\text{cm}^{-1}$  for both species.

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<sup>47</sup> with a  $17\text{-meV}$  fwhm 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.,  $\nu_1' = 1860 \text{ cm}^{-1}$ ,  $\nu_2' = 1040 \text{ cm}^{-1}$ , and  $\nu_3' = 605 \text{ cm}^{-1}$  for  $C_6H_4^-$ . Vibrational levels in  $C_6H_4^-$  and  $C_6D_4^-$  associated with the strongest observed transitions are indicated in the figure by their ( $\nu_1'$ ,  $\nu_2'$ ,  $\nu_3'$ ) quantum numbers. In addition to these three modes, the  $C_6D_4^-$  simulation includes a relatively weak  $1400\text{-cm}^{-1}$  upper-state progression whose main effect is to fill in valleys between peaks; the activity of this mode is at best tentative. Vibrational hot bands from the  $\sim 600 \text{ cm}^{-1}$   $\nu_3'' = 1$  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.,  $\nu_3' = n$ ) levels alone (indicated as “■”) and in combination with  $100$  (▲) and  $200$  (unmarked) excitations. Shoulders to the right of the main peaks are associated with combination bands involving  $01n$  (labelled “×”) and  $11n$  upper-state levels. The excellent agreement between the simulated and observed spectra for overall intensity profiles, and for peak positions below  $1.7 \text{ eV}$  (eKE) in the  $C_6D_4^-$  spectrum, provides a strong argument in favor of the proposed  $1860\text{-cm}^{-1}$  interval. Attempts to model either spectrum with use of a frequency differing from this value by one or more  $\sim 600\text{-cm}^{-1}$  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.<sup>43</sup> Thus, the most likely assignment for the  $605$  and  $585\text{-cm}^{-1}$  vibrations is to the in-plane ring deformation corresponding to  $\nu_{6a}$  in benzene (Wilson numbering<sup>48</sup>). The activity

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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,<sup>19,20</sup> but the present assignment is supported by the similar frequencies of 630 and 608 cm<sup>-1</sup> reported<sup>35</sup> for the protonated and perdeuterated forms of the isoelectronic pyridazine molecule. The weak IR intensity calculated for this mode in *o*-benzyne,<sup>16</sup> and observed in pyridazine,<sup>35</sup> 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<sub>6</sub>H<sub>4</sub> reported by Laing and Berry,<sup>21</sup> in which the observed 469-cm<sup>-1</sup> IR frequency was assigned to this vibration, as well as with the more recent analysis by Nam and Leroi,<sup>22</sup> which predicts an even lower frequency of 395 cm<sup>-1</sup>. The present assignment indicates that the in-plane skeletal bends of the strained ring system in singlet *o*-benzyne are less pliant than has been suggested by these analyses.

The 1040 (20)- and 980 (20)-cm<sup>-1</sup> frequencies observed here for C<sub>6</sub>H<sub>4</sub> and C<sub>6</sub>D<sub>4</sub>, respectively, probably correspond to the totally symmetric ring stretch identified by Nam and Leroi with the 1056-cm<sup>-1</sup> fundamental observed in the IR spectrum of C<sub>6</sub>H<sub>4</sub>. The deuterium shift for this mode is calculated to be 4%, consistent with the shift observed here. This vibration is described<sup>22</sup> 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<sup>7</sup> and the more benzenoid bond length expected in the less aryne-like anion.

Finally, the 1860-cm<sup>-1</sup> interval inferred from both the C<sub>6</sub>H<sub>4</sub><sup>-</sup> and C<sub>6</sub>D<sub>4</sub><sup>-</sup> 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<sup>-1</sup> mode assigned to a carbonyl-containing byproduct of the *o*-benzyne synthesis has been noted<sup>19</sup>). The present assignment conflicts with the results of Nam and Leroi, in which no ring-stretching frequencies are found between the observed 2084-cm<sup>-1</sup> triple-bond stretch and a calculated<sup>22</sup> fundamental at 1657 cm<sup>-1</sup>. The earlier normal mode analysis<sup>21</sup> did predict an 1856-cm<sup>-1</sup> fundamental with a relatively small deuterium shift, but this was assigned to a B<sub>2</sub> mode not likely to be excited in the photoelectron system. Applying Laing and Berry's argument for the nonobservance of a proposed higher frequency (2450 cm<sup>-1</sup>) C≡C stretching mode in matrix studies to the present case, we can suggest that an 1860-cm<sup>-1</sup> 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<sup>-1</sup>

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*<sub>4</sub> and -*d*<sub>4</sub> 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<sub>6</sub>H<sub>4</sub> and 0.551 (10) eV for C<sub>6</sub>D<sub>4</sub>. Combined with known heats of formation, the former value provides a measurement of the heat of formation of *o*-benzyne anion ( $\Delta H_f^\circ = 104$  (5) kcal/mol) and the gas-phase acidity of the ortho proton of the phenyl radical ( $\Delta H_{\text{acid}}^\circ = 391$  (7) kcal/mol). 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  $\tilde{X}^1A_1$  and  $\tilde{a}^3B_2$  states, singlet-triplet splittings are determined to be 37.7 (6) kcal/mol for C<sub>6</sub>H<sub>4</sub> and 37.9 (6) kcal/mol for C<sub>6</sub>D<sub>4</sub>.

An extended vibrational progression in the  $^1A_1 \leftarrow ^2B_2$  band system, with upper-state intervals of 605 (15) cm<sup>-1</sup> for C<sub>6</sub>H<sub>4</sub> and 585 (15) cm<sup>-1</sup> for C<sub>6</sub>D<sub>4</sub>, 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 pliant than indicated by previous normal coordinate analyses. Additional intervals are observed at 1040 (20) and 1860 (15) cm<sup>-1</sup> in C<sub>6</sub>H<sub>4</sub> and 980 (20) and 1860 (15) cm<sup>-1</sup> in C<sub>6</sub>D<sub>4</sub>. The 1860-cm<sup>-1</sup> intervals probably involve the stretching vibration of the acetylenic C-C bond. No a<sub>1</sub> 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  $^3B_2 \leftarrow ^2B_2$  system is more vertical, implying a greater resemblance between the equilibrium geometries of the anion and the neutral triplet.

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