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Is the 1,3,5-Tridehydrobenzene Triradical a Cyclopropenyl Radical Analogue?

Harvey A. Lardin, John J. Nash, and Paul G. Wenthold*

Contribution from the The Department of Chemistry, Purdue University, West Lafayette, Indiana 47907-1393

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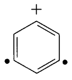
Abstract: The gas-phase heat of formation ($\Delta H_{f,298}$) of the 1,3,5-tridehydrobenzene triradical has been determined by using a negative ion thermochemical cycle. The first three measurements carried out were of the gas-phase acidity of 3,5-dichlorobenzoic acid, the enthalpy for decarboxylation of 3,5-dichlorobenzoate, and the enthalpy for chloride loss from 3,5,-dichlorophenide and constitute the measurement of the heat of formation for 5-chloro-*m*-benzyne. The last two measurements, the electron affinity of 5-chloro-*m*-benzyne, and the threshold for chloride loss from 5-chloro-*m*-benzyne, when combined with $\Delta H_{f,298}$ of 5-chloro-*m*-benzyne, give the heat of formation of the triradical. The 5-chloro-*m*-benzyne heat of formation is 116.2 ± 3.7 kcal/mol. The heat of formation of the 1,3,5-tridehydrobenzene triradical measured in this work is 179.1 ± 4.6 kcal/mol. This heat of formation was used to derive the bond dissociation energy (BDE) at the 5-position of *m*-benzyne, a third BDE in benzene. The BDE, at 109.2 ± 5.6 kcal/mol, is ca. 4 kcal/mol lower than the first BDE in benzene (112.9 kcal/mol) and significantly higher than the BDE of phenyl radical at the meta position. The agreement between the first and third BDEs implies that the triradical is best described as a phenyl radical that interacts little with a *m*-benzyne moiety. The experimentally measured BDE is in good agreement with multireference configuration interaction calculations, which predict a $^2A_1$ ground state for the Jahn−Teller distorted triradical. The trends in the first, second, and third BDEs of benzene are similar to those found for cyclopropane, suggesting a cyclopropenyl-like electronic structure within the six-membered ring of the 1,3,5-benzene triradical.

Introduction

In 1979, Schleyer and co-workers proposed that the 3,5-didehydrophenyl cation (**1**) should be "doubly aromatic."[1,2] In addition to the stability resulting from the $4n + 2$ electrons through the conjugated π system, the interaction of two nonbonding σ electrons gives rise to a cyclopropenyl cation-like three-center, two-electron configuration (Figure 1) or "in-plane aromaticity".[1,2] Consistent with the theoretical prediction, reactivity studies by Nelson and Kenttämaa[3] indicate that **1** is the global minimum along the cation's potential energy surface, presumably as a result of the double aromaticity. Similarly, Hu and Squires[4] have prepared the 3,5-didehydrophenyl anion (**2**) and characterized its reactivity. Ion **2** can be considered to be the "antiaromatic" analogue of **1** because of the three-center, four-electron σ system, reminiscent of the electronic structure of cyclopropenyl anion.[5,6] In this system, two electrons populate a higher energy, antibonding molecular orbital (MO; Figure 1). The observed reactivity[4] of **2** is consistent with that for a ground-state singlet anion with a Jahn−Teller distorted, C_{2v} structure.[7] While the properties of the tridehydrobenzene ions have been examined previously, those for the neutral triradical, **3**, have not been considered. Simple electronic structure considerations suggest that the three-center, three-electron system (Figure 1) should adopt a Jahn−Teller distorted (C_{2v}) doublet ground state[8] consisting of a phenyl radical that can interact with a *m*-benzyne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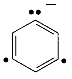
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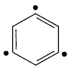
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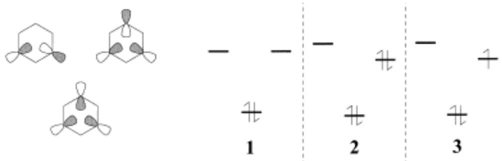

Figure 1. Molecular orbital diagram showing the three σ nonbonding basis orbitals (left) for tridehydrobenzene species **1**−**3** and their relative energy levels (right). The energy levels for the cation, **1**, correspond to those for the D_{3h} molecule, whereas the energy levels for **2** and **3** are those for Jahn−Teller distorted systems with C_{2v} symmetry.

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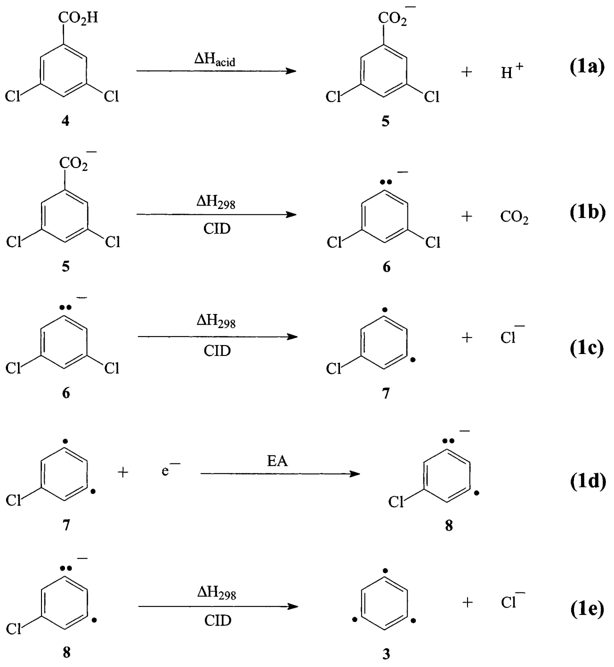
moiety. However, the extent of the three-center, three-electron interaction in the triradical is not known. Thermochemical studies offer unique insight into the structure and stability of this benzene triradical.

Here we report an experimentally determined heat of formation ($\Delta H_{f,298}$) of 1,3,5-tridehydrobenzene, **3**. The approach used to determine the heat of formation of 1,3,5-tridehydrobenzene is outlined in eqs 1a−e. The first three steps (eqs 1a−c) constitute a measurement of the heat of formation of 5-chloro-*m*-benzyne (**7**). From biradical **7**, two measurements are used to determine the heat of formation of triradical **3**. The electron affinity (EA) of **7** (eq 1d) leads to the heat of formation of 5-chloro-*m*-benzyne anion (**8**), and the threshold energy for chloride loss from **8** (eq 1e) can be used to obtain the heat of formation of **3**. Altogether, the heat of formation of **3** is calculated according to eq 2.



$$\Delta H_f(\mathbf{3}) = \Delta H_f(\mathbf{4}) + \Delta H_{acid}(\mathbf{4}) + \Delta H_{298}(\text{eq1b}) + \Delta H_{298}(\text{eq1c}) - \text{EA}(\mathbf{7}) + \Delta H_{298}(\text{eq1e}) - \Delta H_f(\text{H}^+) - \Delta H_f(\text{CO}_2) - 2\Delta H_f(\text{Cl}^-) \quad (2)$$

$$= \Delta H_f(\mathbf{7}) - \text{EA}(\mathbf{7}) + \Delta H_{298}(\text{eq1e}) - \Delta H_f(\text{Cl}^-)$$

The approach shown in eq 1 is similar to that used recently for the determination of the heat of formation of the 1,3,5-tris(methylene)benzene triradical.[9] As shown in that study, the uncertainty in the triradical heat of formation measured using this approach is reasonably expected to be about ±4 kcal/mol. In this work, we use the measured heat of formation of **3** to calculate the C−H BDE at the 5-position of *m*-benzyne, the third C−H BDE in benzene, and find that the strength of the third C−H bond in benzene is comparable to the first, indicating little interaction between the radical formed and the *m*-benzyne moiety. Last, we show that the trend in the three BDEs in benzene reflects that for the BDEs in cyclopropane, highlighting the similarity between the benzene triradical and cyclopropenyl radical.

Experimental Section

The experiments were carried out in a flowing afterglow triple-quadrupole apparatus that has been described in detail previously.[10,11] Under typical operating conditions, $P(\text{He}) = 400$ mTorr, corresponding to a flow rate of 190 cm^3(STP) s^{-1}. Fluoride ion (F^-) was generated in the ion source via 70 eV electron ionization (EI) of fluorine gas (F_2, 5% mixture in He from Spectra Gases). Ions **5** and **6** were prepared in high yield by fluoride-induced desilylation[12] of trimethylsilyl-3,5-dichlorobenzoate (prepared in situ by the reaction of *N*,*O*-bis(trimethylsilyl)acetamide and 3,5-dichlorobenzoic acid)[13] and (3,5-dichlorophenyl)-trimethylsilane, respectively, in the downstream portion of the flow tube. The distonic 5-chloro-*m*-benzyne negative ion (**8**) was prepared from the reaction of 1,3-bis(trimethylsilyl)-5-chlorobenzene with fluoride to make 3-chloro-5-trimethylsilylphenyl anion, which subsequently reacts with F_2 in the flowing afterglow by desilylation.[14−16]

The gas-phase acidity of dichlorobenzoic acid (**4**) and the electron affinity of biradical **7** were measured by using the Cooks kinetic method with full entropy analysis, as has been described previously.[17−21] Proton-bound dimers of carboxylate **5** were generated by ternary addition of reference acids to the carboxylate or by addition of **4** to the conjugate base ions created from reference acids, including pentafluorobenzoic acid,[22] 3,5-bis(trifluoromethyl)benzoic acid,[23] 4-nitrophenol,[24] and 4-formylbenzoic acid.[25] The order of addition did not have a measurable effect on the final results. The experimental CID branching ratios, *r*, for the proton-bound dimers are related to $\Delta H_{acid}(\mathbf{4})$ and ΔH_{acid} of the reference acids, B_i, according to eq 3,[26]

$$\ln(r)_E = \frac{\Delta H_{acid}(\mathbf{4}) - \Delta H_{acid,av} + T_{eff}\Delta S}{RT_{eff}} - \frac{\Delta H_{acid}(B_i)}{RT_{eff}} \quad (3)$$

where the ΔS term is the average difference between the activation entropies for the two channels upon the dissociation of the proton-bound dimer,[27] R is the gas constant, T_{eff} is the "effective temperature"[28] of the dissociation at collision energy, E, and $\Delta H_{acid,av}$ is the average gas-phase acidity of the references.[26] According to eq 3, a plot of ln(*r*) vs $\Delta H_{acid}(B_i)$ will have a slope of $m_E = -1/RT_{eff}$ and an intercept of y_E

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$= [\Delta H_{\mathrm{acid}}(\mathbf{4}) - \Delta H_{\mathrm{acid,av}} + T_{\mathrm{eff}}\Delta S]/RT_{\mathrm{eff}}$. A second plot of y_E vs m_E has a slope $\Delta H_{\mathrm{acid}}(\mathbf{4}) - \Delta H_{\mathrm{acid,av}}$ and an intercept of $-\Delta S/R$.[26] Collision-induced dissociation branching ratios were measured at different pressures and extrapolated to $p = 0$, the single-collision limit.

The electron affinity (EA) of **7** was measured by using a single-reference version of the Cooks kinetic method based upon eq 3,[15,29−31] where r was replaced by ($r_{\mathrm{BSO2}}/r_{\mathrm{7SO2}}$), the quotient of branching ratios of CID of SO_2 adducts of the references and the analyte, **7**.[31] CID branching ratios as a function of collision energy were measured for SO_2 adduct ions of **7** and reference ions, including phenyl radical,[32] *p*-benzyne,[33] and α-naphthyl radical.[34] The sulfoxide ions required for measurement of the electron affinity of **7** were prepared by the addition reaction of SO_2 with **8** or with the negative ions of references B_i. In this single-reference version of the kinetic method, the entropy term becomes $\delta\Delta S$, the average difference between activation entropies for the dissociation of the SO_2 adducts of the references and the analyte ($\delta\Delta S = \Delta S_{\mathrm{BSO2}} - \Delta S_{\mathrm{7SO2}}$).

Energy-resolved CID was used to determine the enthalpies of the reactions in eq 1b,[35] 1c,[36] and 1e. Energy-resolved CID cross section data were fit according to the model shown in eq 4,[37−39]

$$\sigma(E) = \sigma_0 \sum_i g_i (E + E_i - E_0)^n / E \qquad (4)$$

where E is the total energy of the ion, E_0 is the 0 K dissociation energy, n is an adjustable parameter that reflects the energy deposition function upon collision,[40] and σ_0 is a scaling factor. Convoluted into the fit are the internal and kinetic energy distributions of the ions, Doppler broadening due to thermal motion of the target, and the dissociation probability calculated by using the RRKM dissociation rate. Analysis is carried out with the CRUNCH program developed by Armentrout and co-workers.[37−39] Cross-sections for dissociation are calculated using $I_P/I = \sigma N l$, where I_P and I are the measured intensities of the product and reactant ions, respectively, N is the number density of the target gas, and l is the effective path length of the collision cell. As with the kinetic method branching ratios above, the cross-sections measured in this work have been extrapolated to zero pressure to account for the effects of multiple collisions.

It has been found previously that high-energy ion isomers prepared in the flowing afterglow can rearrange in the presence of acid catalyst.[36] Because neither ion **6** nor ion **8** is likely to be the lowest energy isomer, it is important to be able to account for any rearrangements that occur. Therefore, the CID experiments were carried out with the deuterated ions to ensure isomeric purity. Deuterium labeling of the 3,5-dichlorophenyl anion was used to obtain the CID cross-sections for chloride ion formation (eq 1c) from a single ion isomer, with molecular formula $C_6D_3Cl_2$ (*m*/*z* 148). To account for impurities due to $C_5{}^{13}CHD_2Cl_2^-$, which has the same *m*/*z* as $C_6D_3Cl_2^-$ and has an intensity that is ca. 6% of that for *m*/*z* 147, the (single collision) cross-sections were measured as a function of the *m*/*z* 147/*m*/*z* 148 ratio, adjusted by adding water, and extrapolated to where the ratio = 0, as has been described in detail previously.[36]

For CID of 5-chloro-*m*-benzyne anion, isomerization of the *m*-benzyne anion is not the only potential source for contamination because the chlorophenyl anion, $C_6HD_3Cl^-$ (*m*/*z* 114), is also formed in these experiments, presumably by reaction of the deuterated 3-chloro-5-trimethylsilylphenyl anion with HF impurity in the fluorine.[41] A single H/D exchange in the chlorophenyl anion upon reaction with adventitious acid results in the formation of the $C_6H_2D_2Cl^-$ ion, which has the same *m*/*z* as $C_6D_3Cl^-$. Therefore, we have modeled the isotope distributions over the range from ${}^{12}C_6H_3{}^{35}Cl^-$ (*m*/*z* 110) to ${}^{13}C^{12}C_5HD_3{}^{37}Cl^-$ (*m*/*z* 117) to determine the extent of $C_6D_3{}^{35}Cl^-$ in the *m*/*z* 113 signal. By adding water, the extent of $C_6D_3{}^{35}Cl^-$ is varied, and the ${}^{35}Cl^-$ cross sections are measured as a function of the *m*-benzyne fraction and extrapolated to where the fraction is 1, corresponding to isomerically pure $C_6D_3Cl^-$. The ion $C_6D_3{}^{35}Cl^-$ constitutes about 60% of the *m*/*z* 113 signal under conditions with no water added, with most of the remaining signal due to $C_6HD_3{}^{35}Cl^-$ that has undergone a single H/D exchange. The extent of H/D exchange in the chlorophenyl anion estimated from the modeling procedure is comparable to that observed in control experiments with the fully deuterated chlorophenyl anion ($C_6D_4Cl^-$) prepared under similar conditions.

Materials. All reagents except for the mono- and bis(trimethylsilyl)-chlorobenzenes were obtained from commercial suppliers. The (trimethylsilyl)chlorobenzenes were prepared by quenching the Grignard reagent of chlorotrimethylsilane with the appropriate chlorobenzene precursor.[42]

Computational Details. MCSCF calculated geometries for benzene, phenyl radical, and *m*-benzene were taken from a previous study.[43] In this work, geometries of three electronic states of the triradical were calculated at the MCSCF(9,9)/3-21G level of theory, where the active space included the six π orbitals and the three nonbonding σ orbitals. Energy calculations were carried out at the CASPT2 level, using the MCSCF geometries. Zero-point and thermal energy corrections were calculated from frequencies obtained at the BLYP/cc-pVDZ level of theory. The CASPT2 calculations were carried out using the MOLCAS suite of programs, while density functional calculations were performed using GAUSSIAN 98W.[44]

Results

In this section we report the measured energetics for each of the reactions shown in eq 1, starting with the gas-phase acidity of **4,** and use the data to calculate the heat of formation of triradical **3**. All of the measured thermochemical properties and supplemental thermochemical data are shown in Table 1.

Gas-Phase Acidity and Heat of Formation of 3,5-Dichlorobenzoic Acid. First regression plots of $\ln(r)$ vs $\Delta H_{\mathrm{acid}}(B_i) - \Delta H_{\mathrm{acid,av}}$ at selected collision energies and second regression plots of y_E vs $-m_E$, the intercepts and slopes from first regression plots (eq 3) for each of 64 different collision energies ranging from 1.4 to 4.0 eV (c.m.) are provided as Supporting Informa-

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Table 1. Heats of Formation and Various Thermochemical Quantities Measured or Cited in This Work[a]

species	quantity	ref
298 K Heats of Formation		
1,3,5-tridehydrobenzene (**3**)	179.1 ± 4.6	this work
3,5-dichlorobenzoic acid	83.2 ± 1.4	48
CO_2	94.054	50
Cl	54.36	51,52
H^+	365.7	53
Gas-Phase Acidity		
3,5-dichlorobenzoic acid	330.1 ± 1.6	this work
pentafluorobenzoic acid	323.6 ± 2.1	22
3,5-bis(trifluoromethyl)benzoic acid	324.4 ± 2.1	23
4-nitrophenol	327.8 ± 2.1	24
4-formylbenzoic acid	332.8 ± 2.1	25
Ion Dissociation Energies		
$\Delta H_{298}(R^- {-} CO_2)$		
3,5,-dichlorobenzoate (**5**)	49.7 ± 1.6	this work
$\Delta H_{298}(R{-}Cl^-)$		
3,5-dichlorophenide (**6**)	36.9 ± 2.5	this work
5-chloro-*m*-benzyne anion (**8**)	35.5 ± 2.5	this work
Electron Affinities		
5-chloro-*m*-benzyne	27.0 ± 1.4	this work
phenyl radical	25.3 ± 0.1	32
p-benzyne	29.2 ± 0.2	33
α-naphthyl radical	32.4 ± 0.3	34
CH Bond Dissociation Energies		
m-benzyne (5-position)	109.2 ± 5.6	this work
benzene	112.9 ± 0.5	63
phenyl radical (3-position)	93.5 ± 3.1	36
cyclopropane	106.3 ± 0.3	74,79
cyclopropyl	54.7 ± 0.7	73
cyclopropene[b]	99.099.9	76,77

[a] Values shown in kilocalories per mole. [b] Computed value.

tion. Reference acids and their gas-phase acidities are shown in Table 1. From the slope of the second plot, the gas-phase acidity of **4** is found to be 330.1 ± 1.6 kcal/mol, where the uncertainty reflects ±40% error in the effective temperature of dissociation,[28] uncertainty in the second regression slope, and the uncertainties of the reference acids. The acidity of **4** is close to that of *o*-nitrobenzoic acid ($\Delta H_{acid} = 331.8 \pm 2.2$ kcal/mol),[45] such that chloro substitution at the 5-position of 3-chlorobenzoic acid ($\Delta H_{acid} = 335.2 \pm 2.1$ kcal/mol)[46] lowers its acidity by ca. 4 kcal/mol. This effect is comparable to that of chloro substitution at the 3-position of benzoic acid, which lowers the acidity by ca. 5 kcal/mol.[47] The intercept of the second regression plot gives the ΔS term, the average difference in the activation entropies of dissociation for proton-bound dimers,[27] to be −1.5 cal/(K·mol). The low value for ΔS suggests that there are small entropic differences in the transition states for dissociation of the activated proton-bound dimer to form ion **5** or to form reference carboxylate or phenoxide ions.

The heat of formation of **4** is not known experimentally, but a reliable empirical estimate can be obtained by using a bond additivity approach,[48] whereby it is assumed that effect of substituting a carboxylic acid group for a hydrogen in the 5-position of 1,3-dichlorobenzene lowers the heat of formation to the same extent as substituting a carboxylic acid group at the *m*-position in chlorobenzene. Density functional calculations (B3LYP/cc-pVDZ) confirm that the differences between the heats of formation of chlorobenzene and 3-chlorobenzoic acid and those for 1,3-dichlorobenzene and **4** agree to within 0.7 kcal/mol. The uncertainty assigned to the heat of formation is conservatively estimated to be 2 times this value.

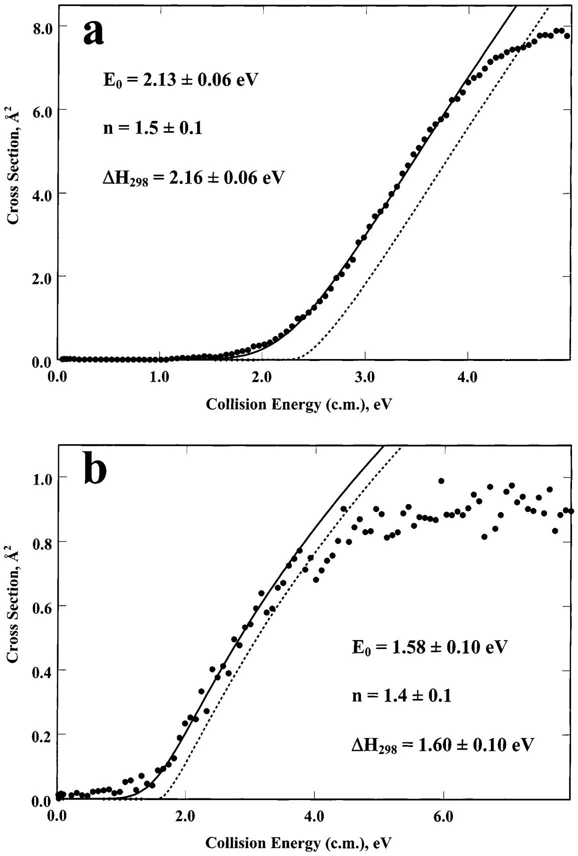

Figure 2. (a) Cross-sections for decarboxylation of 3,5-dichlorobenzoate (formation of 3,5-dichlorophenide) upon collision-induced dissociation with Ar target gas. (b) Cross-sections for chloride loss (formation of 5-chloro-*m*-benzyne) from 3,5-dichlorophenide upon collision-induced dissociation with Ar target gas. Solid circles represent the experimental cross-section, the solid line is the best fit to the data, and the dashed line is the unconvoluted fit of the data.

CID Cross-Sections for Formation of 3,5-Dichlorophenide and 5-Chloro-*m*-benzyne. Single collision cross-sections for decarboxylation of **5** and chloride loss from **6** are shown in Figure 2a,b, respectively. The cross-sections in Figure 2b have been extrapolated to account for isomeration, as described in the Experimental Section. Average fitting parameters for the decarboxylation of **5** are $E_0 = 2.13 \pm 0.06$ eV and $n = 1.5 \pm 0.1$ (±1 standard deviation). The measured 0 K bond dissociation energy is converted to the 298 K enthalpy by using the differences in integrated heat capacities for the reactants and products to give $\Delta H_{298} = 2.16 \pm 0.06$ eV (49.7 ± 1.6 kcal/mol).[49] The average fitting parameters for chloride loss from **6** are $E_0 = 1.58 \pm 0.10$ eV and $n = 1.4 \pm 0.1$, with a corresponding ΔH_{298} of 1.60 ± 0.10 eV (36.9 ± 2.5 kcal/mol).[49]

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(45) Yamdagni, R.; McMahon, T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1974**, *96*, 4035−4037.

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(48) Benson, S. W. *Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters*, 2nd. ed.; Wiley: New York, 1976.

(49) The assigned uncertainties include the standard deviation in the measured threshold values, a 0.15 eV (laboratory) contribution due to uncertainty in the absolute energy scale and a contribution due to uncertainty in the transition state chosen for the RRKM calculation. For decarboxylation of **5**, the transition-state contribution is 0.01 eV, while a value of 0.03 eV is included in the halide elimination reaction. These correspond to ±2 eu uncertainties in the activation entropies.

From the measured energies and reference thermochemistry in Table 1,[48,50−53] the heat of formation of 5-chloro-*m*-benzyne, **7**, is calculated to be 116.2 ± 3.7 kcal/mol, ca. 6 kcal/mol lower than the heat of formation of *m*-benzyne.[33] The difference in the heats of formation of *m*-benzyne and 5-chloro-*m*-benzyne is about 1 kcal/mol smaller than the difference in the heats of formation of benzene[54,55] and chlorobenzene,[54,56] indicating that the chloro substituent interacts little with the *m*-benzyne moiety. The small deviation from bond additivity in 5-chloro-*m*-benzyne is consistent with Johnson and Cramer's prediction that substitution at the 5-position of *m*-benzyne should have only a weak effect on the electronic structure of the biradical.[57,58]

Electron Affinity of 5-Chloro-*m*-benzyne. The electron affinity of 5-chloro-*m*-benzyne was determined using the single reference kinetic method with full entropy analysis.[29−31,36] Although more accurate electron affinities can generally be obtained from a photodetachment technique like negative ion photoelectron spectroscopy (NIPES), the NIPES approach is not well-suited for measuring the electron affinity of *m*-benzyne because there is an excessively large difference between the geometries of the ion and neutral.[33] Similar problems would be expected for the spectroscopy of the chlorine-substituted *m*-benzyne ion. However, the kinetic method does not rely on photodetachment and can be used to measure electron affinities even in cases where the ion and neutral geometries differ significantly.[59]

Figure 3 shows a plot of $(\mathrm{EA}(\mathbf{7}) - \mathrm{EA}_{\mathrm{av}} + T_{\mathrm{eff}}\delta\Delta S)/RT_{\mathrm{eff}}$ vs $-1/RT_{\mathrm{eff}}$ over an energy range from 4.5 to 8.0 eV, where $\mathrm{EA}_{\mathrm{av}}$ is the average EA of the references, 1.05 eV. The data shown in the plot correspond to y_{E} vs $-m_{\mathrm{E}}$ from the plots of $\ln(r_{\mathrm{BSO2}}/r_{\mathrm{7SO2}})$ vs $\mathrm{EA}_{\mathrm{Bi}} - \mathrm{EA}_{\mathrm{av}}$ at each collision energy measured over the given range. The slope and intercept of the plot shown in Figure 3 are −0.12 eV and −0.50, respectively, and $r^2 = 0.48$, which is comparable to values obtained previously for this type of measurement.[31] Adding $\mathrm{EA}_{\mathrm{av}}$ to the second regression slope yields EA(**7**) = 1.17 ± 0.06 eV, where the uncertainty includes the average error of the references, the error in the slope of the second regression plot, and a 40% error in the effective temperature.[31] Despite the low correlation coefficient, the statistical error in the slope of this plot is small because of the large number of data points employed. The EA of **7** measured in this work indicates that a chlorine substituent in the 5-position of *m*-benzyne increases the EA by about 0.32 eV. The second regression intercept, upon multiplication by *R*, yields $\delta\Delta S = -1.1$ cal/K-mol, indicating small differences between the transition state for dissociation of the SO_2 adduct of **7** and those of the SO_2 adducts of the references.

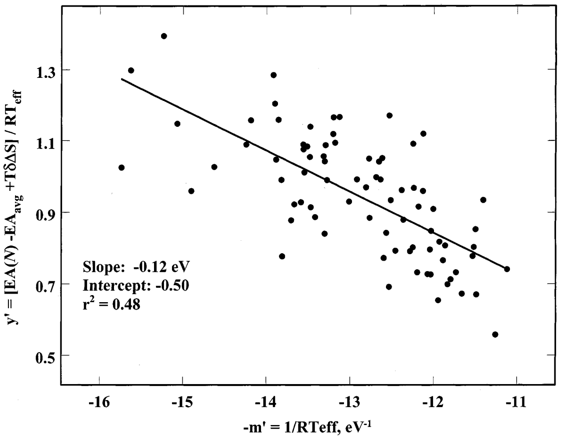

Figure 3. Second regression plot of $[\mathrm{EA}(\mathbf{7}) - \mathrm{EA}_{\mathrm{av}} + T_{\mathrm{eff}}\delta\Delta S]/RT_{\mathrm{eff}}$ vs $-1/RT_{\mathrm{eff}}$ for the electron affinity measurement of 5-chloro-*m*-benzyne.

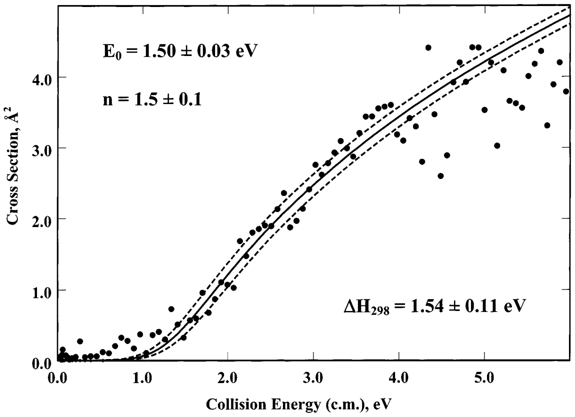

Figure 4. Cross-sections for chloride loss (1,3,5-tridehydrobenzene formation) from 5-chloro-*m*-benzyne ion, **8**, upon collision-induced dissociation with Ar target gas. The cross-sections have been extrapolated to zero contamination and $p = 0$, as described in the Experimental Section. Solid circles represent the experimental cross-section, the solid line is the best fit to the data, and the dashed lines are the fits that would be obtained for dissociation energies that are 0.08 higher and lower than the optimal values.

CID Cross-Section for Formation of 1,3,5-Tridehydrobenzene. Collision-induced dissociation of the 5-chloro-*m*-benzyne anion, **8**, with Ar target leads to the formation of chloride as the only ionic product. The single-collision cross-sections for Cl^- formation upon CID of isotopically and isomerically pure 5-chloro-*m*-benzyne anion are shown in Figure 4. Because the reactant ion signal is weak, the data are more scattered than is generally observed in these experiments. The fully optimized fit to the data is shown as the solid line in Figure 4. Average fitting parameters for four independent data sets are $E_0 = 1.50 \pm 0.03$ eV and $n = 1.5 \pm 0.1$. The dashed lines shown in Figure 4 are the curves that would be obtained by using dissociation energies that are 0.08 eV higher or lower than the optimized value. Because most of the data points over the fitting range (~1 to ~4 eV) fall between these two dashed lines, they can be considered reasonable limits to the error in the threshold due to scatter of the data. The measured 0 K bond dissociation energy is converted to the 298 K enthalpy by using the differences in integrated heat capacities for the reactants and products to give $\Delta H_{298} = 1.54 \pm 0.11$ eV (35.5 ± 2.5 kcal/

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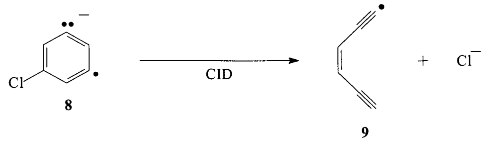
mol).[60] Combining the measured enthalpy values for the processes shown in eq 1d and eq 1e with the heat of formation of 5-chloro-*m*-benzyne discussed above gives a value of 179.1 ± 4.6 kcal/mol for the heat of formation of the 1,3,5-tridehydrobenzene triradical.

Discussion

In this section, we discuss the measured thermochemical properties and compare them to those for cyclopropenyl radical and to results of molecular orbital calculations. However, we first discuss the structure of the neutral product formed in the experiment.

Product Structures. The neutral products of the CID reactions are not detected in these experiments but can be deduced on the basis of energetics and kinetics. For example, rearrangements of negative ions and radicals typically have energy barriers higher than the dissociation energies measured in these experiments and have tight transition states that would lead to slow dissociation. Therefore, direct bond cleavage to form the bi- or triradical is expected to be the favored process. The excellent agreement between the *p*-benzyne heat of formation measured by using energy-resolved CID[36] and that obtained from an independent kinetic procedure[61] supports the assumption that rearrangement to lower energy biradical isomers does not occur during dissociation. Rearrangement in the formation of the triradical is even less likely because less energy is required for halide elimination and it is less energetically favorable, as the energy differences between the three triradical isomers is predicted much smaller than the energy differences between the benzynes.[8]

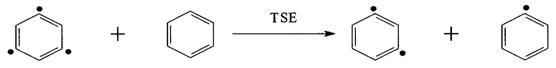
Formation of ring-opened products can also be ruled out on the basis of reaction energetics. For example, ring opening to the 3-hexen-1,5-diynyl radical, **9**, (eq 5) can be ruled out because the heat of formation of **9** is ca. 30 kcal/mol higher in energy than the C_6H_3 heat of formation measured in this work.[62] Other ring-opened isomers can be ruled out in similar fashion, as they are all at least 10 kcal/mol higher in energy than the product formed in this work. On this basis, and the results of the previous studies of the benzynes, we conclude that the neutral CID products in reactions 1c and 1e are the *m*-benzyne and 1,3,5-tridehydrobenzene triradicals, respectively.



(5)

Thermochemical Properties. The C−H BDE in the 5-position of *m*-benzyne, i.e., the third BDE in benzene, is calculated to be 109.2 ± 5.6 kcal/mol from the heat of formation of **3** measured in this work and the previously reported heat of formation of *m*-benzyne (122.0 ± 3.1 kcal/mol).[36] The measured value for the third BDE of benzene is approximately 4 kcal/mol lower than the C−H BDE of benzene (112.9 kcal/mol)[63] and almost 17 kcal/mol higher than the second BDE of benzene to form *m*-benzyne.[36] The small difference[64] between the first and third BDEs in benzene is interpreted to indicate slight interaction between the third unpaired electron and the *m*-benzyne moiety. Therefore, the 1,3,5-benzene triradical is best described as a *m*-benzyne moiety with a noninteracting phenyl radical, consistent with what is expected for a Jahn−Teller distorted ground state, as shown in Figure 1.

Preliminary molecular orbital calculations have been performed on 1,3,5-tridehydrobenzene.[65] At the CASPT2/cc-pVDZ//MCSCF(9,9)/3-21G level of theory, the $^2A_1$ electronic state was found to be less than 1 kcal/mol lower in energy than the $^2B_2$ state. In addition, a quartet state ($^4B_2$) lies 24.8 kcal/mol above the $^2A_1$ state. In both the doublet states and the quartet state, the distance between two of the dehydrocarbons is shortened, as compared to the 1,3,5-tridehydrobenzene cation, while the distance to the third dehydrocarbon lengthened. Essentially, the geometry is similar to that calculated for singlet *m*-benzyne[43,66−69] and substituted singlet *m*-benzynes.[57,58,70,71] Similar conclusions were obtained by Bettinger et al., who calculated the geometry of **3** at the CCSD/DZP level of theory.[8] The third C−H bond dissociation energy of benzene can be calculated from the theoretical results by using the triradical stabilization energy (TSE). The TSE is defined by the isodesmic equation in eq 6 and is the energy for hydrogen atom transfer between benzene and the 1,3,5-tridehydrobenzene triradical to form *m*-benzyne and phenyl radical.[72]



(6)

$$\mathrm{TSE} = \Delta H_{\mathrm{rxn}} = \Delta H_f(m\text{-benzyne}) + \Delta H_f(\text{phenyl radical}) - \Delta H_f(\text{triradical}) - \Delta H_f(\text{benzene})$$

$$= \mathrm{BDE}(\text{benzene}) - \mathrm{BDE}(m\text{-benzyne})$$

The TSE can be considered to be a direct calculation of the interaction of the third unpaired electron in the triradical with the biradical centers. The TSEs calculated using the energies for the $^2A_1$ and $^2B_2$ states of 1,3,5-tridehydrobenzene are 3.25 and 2.54 kcal/mol, respectively. The positive value indicates that there is a slight stabilizing interaction between the triradical's third unpaired electron and the *m*-benzyne moiety. The calculated third BDEs of benzene, as derived from the $^2A_1$ and a $^2B_2$ TSEs, are 109.7 and 110.4 kcal/mol, respectively. These values are indistinguishable from each other and agree with the

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(60) The assigned uncertainty includes the standard deviation in the measured threshold values (0.03 eV), a 0.15 eV (laboratory frame) contribution due to uncertainty in the absolute energy scale, and a 0.01 eV contribution due to uncertainty in the transition state chosen for the RRKM calculation. To account for weak parent ion signal yields and errors in deconvolution of multiple H−D exchange products, two additional terms (0.08 eV for scatter and 0.05 eV for extrapolation error) were combined with the overall uncertainty.

(61) Roth, W. R.; Hopf, H.; Horn, C. *Chem. Ber.* **1994**, *127*, 1765−1779.

(62) The heat of formation of **9** is estimated by using the heat of formation of the 3-hexen-1,5-diyne (128.6 kcal/mol [61]) and the C−H BDE in acetylene (133.3 kcal/mol [63]).

(63) Ervin, K. M.; DeTuri, V. F. *J. Phys. Chem. A*, in press.

(64) The uncertainties in the experimental BDEs give a range of −1.9−9.3 kcal/mol for the difference between the first and third BDEs in benzene. Even at the extreme, the difference between these BDEs is much smaller than that between the BDEs of benzene and the meta-position of the phenyl radical.

(65) Computational results are included in the Supporting Information.

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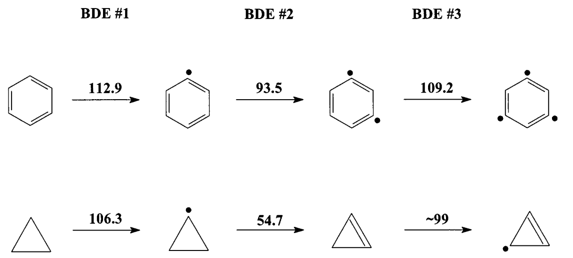
experimental BDE reported in this work. Therefore, the geometry and energy calculations are consistent with the conclusion that 1,3,5-tridehydrobenzene is a ground-state doublet that closely resembles a phenyl radical with *m*-benzyne on the opposite side of the ring. By energies alone, it is impossible to determine which doublet electronic state is being generated in the CID experiments. However, vibrational analysis at the BLYP/aug-cc-pVDZ level of theory[58,66] shows that the $^2B_2$ state has a single imaginary mode. (See Supporting Information.) This suggests that it is a transition state rather than a true minimum. The TSE calculated for the $^4B_2$ state is -23.1 kcal/mol, showing that the resulting quartet triradical is significantly destabilized with respect to singlet *m*-benzyne isolated from a lone phenyl radical. However, the TSE calculated using the energies of the $^4B_2$ state and *triplet m*-benzyne is -5.6 kcal/mol, indicating a small destabilizing interaction between the three unpaired electrons in the quartet triradical.[9]

As discussed above, the electronic structure of the 1,3,5-tridehydrobenzene triradical is in principle similar to that for cyclopropenyl radical. If this is true, then the energetics for formation of cyclopropenyl from cyclopropane should mirror those for the formation of the triradical from benzene. The experimental C−H BDEs for the formation of the 1,3,5-triradical and cyclopropenyl[73−79] radical are summarized in eq 7. The general trend is that the second C−H BDEs are significantly lower than the first, reflecting the strong electronic interactions both in *m*-benzyne and in cyclopropene. Most importantly, the third C−H BDE in cyclopropane is only slightly lower than the first, similar to what is found for benzene, such that the similarities in electronic structure are confirmed by the thermochemical properties.[80]



(7a)

(7b)

Conclusion

The heats of formation of the biradical 5-chloro-*m*-benzyne and the triradical 1,3,5-tridehydrobenzene have been measured. At 116.2 ± 3.7 kcal/mol, the heat of formation of 5-chloro-*m*-benzyne is ca. 6 kcal/mol lower than that of unsubstituted *m*-benzyne, indicating that chlorine substitution has little effect on the stability of the *m*-benzyne moiety. The heat of formation of 1,3,5-tridehydrobenzene is 179.1 ± 4.6 kcal/mol. A third BDE of benzene, the BDE at the 5-position of *m*-benzyne, was derived from the heat of formation of the triradical. The measured value for the third BDE, 109.2 ± 5.6 kcal/mol, is ca. 4 kcal/mol lower than the first BDE in benzene and ca. 16 kcal/mol greater than the second.

Preliminary calculations show that there are two low-lying doublet electronic states of the triradical. The $^2A_1$ state appears to be the ground state, and a $^2B_2$ state (about 1 kcal/mol higher in energy) has one imaginary vibrational mode, implying that it is a transition state. The third BDE of benzene, as derived from the calculated $^2A_1$ energy, is 109.7 kcal/mol and is in agreement with the value measured in this work.

The first, second, and third BDEs of benzene and those for cyclopropane show similar trends. The first and third BDEs are similar, while the second BDEs are much lower. The lower second BDEs reflect a stabilizing interaction between the two electrons in *m*-benzyne and cyclopropene, while the higher first and third BDEs indicate the formation of phenyl and cyclopropyl radicals. The similarity in the BDE trends for formation of the 1,3,5-triradical and cyclopropenyl radical indicates similar electronic structures between the two Jahn−Teller distorted systems.

Acknowledgment. This work was funded by the National Science Foundation (Grant CHE-9732696). We thank the donors of the Petroleum Research Foundation, administered by the American Chemical Society, for partial support of this work. Thanks also to Prof. Anna Krylov, University of Southern California, for sharing preliminary computational results and for insightful discussion on the electronic structures of triradicals.

Supporting Information Available: First regression calibration curve slopes and intercepts for the kinetic method determination of ΔH_{acid} of 3,5-dichlorobenzoic acid, first and second regression plots for the kinetic method determination of the acidity of 3,5-dichlorobenzoic acid, first regression calibration curve slopes and intercepts for the kinetic method determination of the EA of 5-chloro-*m*-benzyne, MCSCF(9,9)/3-21G and BLYP/cc-pVDZ optimized C−C bond lengths and C−C−C bond angles calculated for the $^2A_1$, $^2B_2$, and $^4B_2$ electronic states of 1,3,5-tridehydrobenzene, vibrational frequencies calculated for the $^2A_1$, $^2B_2$, and $^4B_2$ electronic states of 1,3,5-tridehydrobenzene at the BLYP/aug-cc-pVDZ level of theorym, CASPT2/cc-pVDZ electronic energies, zero-point vibrational energies, and enthalpic thermal corrections for the $^2A_1$, $^2B_2$, and $^4B_2$ electronic states of 1,3,5-tridehydrobenzene and other species used to calculate triradical stabilization energies (TSEs) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(80) The fact that the third C−H BDEs in both systems are 4−7 kcal/mol less than the first C−H BDE is likely fortuitous. The energy of the cyclopropenyl radical is lowered by pyramidalization at one of the carbon atoms (see refs 75 and 76) such that the three-center, three-electron interaction predicted by simple MO theory is not enforced, as it is in the planar triradical. Therefore, the C−H BDE for the formation of planar cyclopropenyl radical would be expected to be slightly higher than 99 kcal/mol, and the difference between the first and third BDEs is smaller for the formation of planar cyclopropenyl than for the triradical. The difference may be due to additional geometric stabilization in the triradical or uncertainty in the experimental measurement.