Molecular Structure of *o*-Benzyne from Microwave Measurements

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Received: December 31, 2003

The *o*-benzyne molecule has been known for many years to be an important, but short-lived, reaction intermediate in substitution reactions and more recently in cyclization reactions of enediynes. Although there has been widespread interest in this transient molecule, previous experimental structural data were very limited. In the present work, rotational transitions for *o*-benzyne were measured with a pulsed-beam, Fourier transform microwave spectrometer for all unique, singly substituted ^{13}C and single-D isotopomers. The *o*-benzyne was efficiently produced by flowing a dilute mixture of isotopically enriched benzene in neon through a pulsed-DC discharge beam source. The new data, combined with previous data for the normal isotopomer, provide a complete set of structural parameters for this molecule. The r_s substitution coordinates and the coordinates from a least-squares fit are reported and are in good agreement. When using the least-squares fit to obtain structural parameters, correction terms arising from harmonic terms in the vibrational averaging were subtracted from the measured rotational constants to obtain a better representation of the planar equilibrium structure. Further improvements in the fits were obtained by applying small, mass-dependent adjustments to the atom coordinates. Structural parameters obtained from the fit to these modified rotational constants are an acetylenic $C_1{\equiv}C_2$ bond length of 1.264(3) Å, and the other bond lengths $C_2{-}C_3 = 1.390(3)$ Å, $C_3{-}C_4 = 1.403(3)$ Å, $C_4{-}C_5 = 1.404(3)$ Å, $C_3{-}H_1 = 1.095(9)$ Å, and $C_4{-}H_2 = 1.099(4)$ Å. The $C_1{\equiv}C_2$ bond is only 0.057 Å longer than the free acetylene bond. The other C−C bond lengths are within 0.01 Å of those of benzene C−C bonds. New spectral data for the single-D isotopomers were used to obtain better values for the deuterium quadrupole coupling. Bond-axis deuterium quadrupole coupling constants are $eQq_{zz}(D_1) = 188(2)$ kHz, and $eQq_{zz}(D_2) = 185(10)$ kHz, which agree well with the value for benzene-D_1. The new structural parameters are compared here with theoretical parameters and with an NMR measurement of the $C_1{-}C_2$ bond length.

I. Introduction

The structures of reactive intermediates in chemical reactions are topics of interest in many areas of chemistry. Accurate, quantitative descriptions of chemical bonding require accurate and reliable measurements of the three-dimensional structures of molecules. For short-lived transient molecules, such as *o*-benzyne, microwave spectroscopy, gas-phase electron diffraction, or low-temperature NMR are the methods most likely to succeed. Only the first two methods are free from distortions caused by crystal packing forces or nearby atoms in a matrix. The first microwave data for the normal isotopomer of *o*-benzyne were reported by Brown et al.[1] This molecule was produced using a pyrolysis system, and more recent, similar data are described by Robertson et al.[2] In other work, the $C_1{-}C_2$ bond length for *o*-benzyne was obtained from an NMR measurement of the ^{13}C dipolar coupling for 1,2-$^{13}C_2$ *o*-benzyne produced in an argon matrix.[3]

The *o*-benzyne isomer (1,2 didehydrobenzene) is the earliest and the most extensively studied of a large variety of arynes. Over the past 60 years, *o*-benzyne has progressed from a postulated reaction intermediate to a well-established, but transient, free-molecule. The early work by Wittig[4,5] and Roberts[6] identified *o*-benzyne as a reaction intermediate in elimination reactions of halobenzenes. Gas-phase spectroscopic data for free *o*-benzyne were reported by Leopold et al.,[7] who obtained the singlet−triplet splitting, electron affinity, and $C_1{-}C_2$ stretching vibrational frequency $\nu_1 = 1860$ cm^{-1}. This vibrational frequency was confirmed by measurements of the infrared spectrum of *o*-benzyne in various inert-gas matrixes by Radziszewski et al.[8] An extensive review of reactions and properties of a much wider variety of arynes was presented recently by Wenk et al.[9]

There has been considerable interest, over an extended period, in the details of the $C_1{-}C_2$ bonding in this transient intermediate. Although experimental structural information was not available until very recently, there have been numerous calculations on the structure and energies of *o*-benzyne and related molecules. These calculations favor aryne structures with $C_1{-}C_2$ distances near the acetylene C≡C bond length. Kraka and Cremer[10] reported CCSD(T) calculations of structures and relative energies of *o*-benzyne, *m*-benzyne, and *p*-benzyne, which are shown in Figure 1.

Their results show ΔH_f°(*o*-benzyne) < ΔH_f°(*m*-benzyne) < ΔH_f°(*p*-benzyne), suggesting that *p*-benzyne or *m*-benzyne produced in a discharge could be readily converted to the lowest energy isomer, *o*-benzyne. Their CCSD(T) value for the $C_1{-}$

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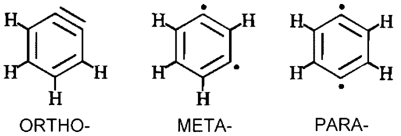

Figure 1. Structural isomers of didehydrobenzene: *ortho*-benzyne, *meta*-benzyne, and *para*-benzyne.

C_2 bond length of *o*-benzyne is 1.27 Å. Cramer et al.[11] used CASSCF and CASPT2 methods to obtain a C_1-C_2 bond length of 1.25 Å, even closer to the acetylene bond length. Recent DFT calculations[12,13] also yield a C_1-C_2 bond length of 1.25 Å. Other recent DFT calculations[14] indicate that formation of *o*-benzyne from the phenyl radical is less endothermic than ring-opening reactions. This may mean that *o*-benzyne plays a significant role in the combustion of lead-free gasoline, which contains a significant fraction of small aromatics such as benzene, toluene, and xylenes. Wenthold et al.[15] reported electron affinities and singlet−triplet splittings for *o*-benzyne and *p*-benzyne. Vibrational frequencies were obtained for all three isomers from the UV photoelectron spectroscopy.

The phenyl radical is also readily produced in a benzene discharge similar to the system described below, and its microwave spectrum was recently reported by McMahon et al.[16]

II. Experimental Section

A pulsed-valve, electric discharge supersonic beam source, coupled with a Fabry−Perot cavity Fourier transform microwave spectrometer, is an extremely rich source of spectra for new carbon chains,[17,18] ring-chains,[19] and other transient molecules.[20,21] The spectrometer used here is described in earlier work by McCarthy et al.[22] In the present experiments, a dilute-(0.5%) mixture of benzene in neon, at a total pressure of 2.6 atm, was pulsed through the small discharge region(0.5 cm dia. x 1.0 cm long), into the Fabry−Perot microwave cavity. The discharge voltage (800−1400 V) was gated off between the beam pulses. The beam pulse repetition rate was 6 Hz. Quite efficient production of *o*-benzyne can be achieved with this system. A S/N ratio of 10 000 can be obtained on stronger transitions, with liquid-nitrogen cooling of the mirrors and microwave preamplifier, and a 10 min integration time.

The spectrum of the $0_{00} \rightarrow 1_{11}$ transition for the normal isotopomer is shown in Figure 2. One advantage of a discharge nozzle for producing benzyne and other short-lived, transient molecules is that fairly simple precursors can be used, relative to those required for the pyrolysis method.[2] A disadvantage of the discharge nozzle source is that a wide variety of other polar molecules are produced which possess transitions throughout the microwave region. This can make it quite difficult to find and identify the correct transitions for singly substituted ^{13}C transitions in a natural abundance sample (i.e., a sample with all of the isotopic masses in the “natural abundance” distribution). In our earlier work,[13] only one of the three possible unique, singly substituted ^{13}C isotopomers was identified and rotational constants obtained. This was for ^{13}C substituted at the C_3 position (see Figure 3), which is very close to the a inertial axis.

For the present measurements, a singly substituted ^{13}C-enriched sample of benzene was purchased from ICON ISOTOPES (Summit, NJ). Measuring and assigning the spectra for all three of the unique, singly substituted ^{13}C isotopomers was greatly facilitated with this enriched sample. The composition was independently verified by mass spectroscopy to be greater than 95% singly substituted ^{13}C benzene. Even with this enriched sample, a 20 MHz portion of the spectrum near the expected singly substituted ^{13}C *o*-benzyne transitions would typically contain four to eight transitions of comparable intensity from other molecules.

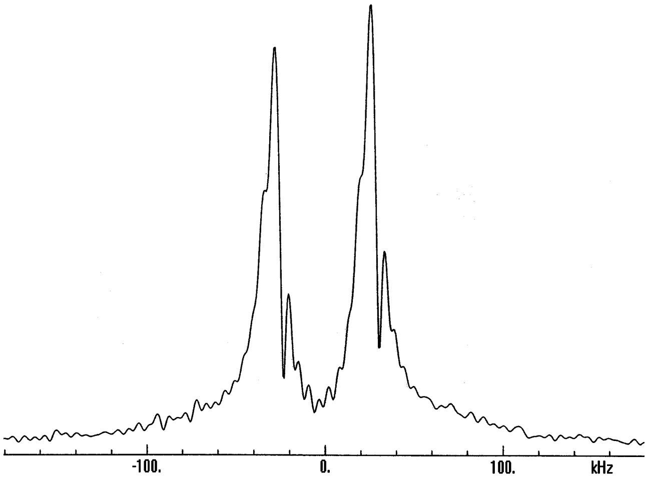

Figure 2. Example spectrum of the $0_{00} \rightarrow 1_{11}$ transition for the normal isotopomer of *o*-benzyne. This spectrum is an average of 200 beam pulses over a 33 s period. The large splitting of 54 kHz is due to doppler effects in the coaxial-beam system and the smaller splitting of 8 kHz is likely due to spin−spin or spin-rotation interactions involving the H-atoms. The frequencies are relative to 10130.1 MHz.

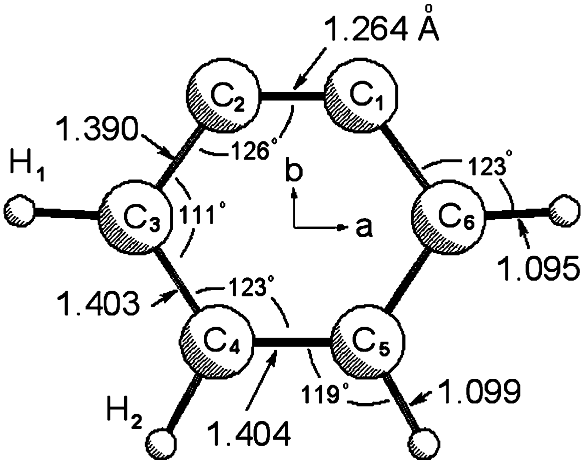

Figure 3. Structure of *o*-benzyne, showing the atom-numbering scheme and many of the measured structural parameters.

The new measured and calculated (using the least-squares fit) transition frequencies for the $^{13}C_1$, $^{13}C_3$, and $^{13}C_5$ singly substituted ^{13}C isotopomers are listed in Table 1. Preliminary values for transition frequencies for these three unique ^{13}C isotopomers were calculated using our best previous *o*-benzyne structure.[13] Measured lines close to these predictions were used in trial least-squares fits to obtain rotational constants. If fits could be obtained, with deviations less than 2 kHz for the newly included lines, these lines were retained in the final fit. Data for the D_1, and D_2 singly substituted deuterium isotopomers, including some previously measured transitions, are given in Table 2. None of the listed $^{13}C_1$ or $^{13}C_5$ lines were reported earlier, but six of the $^{13}C_3$ lines and many of the D_1 and D_2 lines were reported earlier.[13] A sufficient number of newly measured D_2 lines have been obtained to substantially improve the determination of the quadrupole coupling constants for D_2. The new data for singly substituted D isotopomers were obtained using a singly substituted D-benzene sample from ISOTEC-(Aldrich).

TABLE 1: Measured and Measured−Calculated (M−C) Rotational Transition Frequencies for the $^{13}C_1$, $^{13}C_3$, and $^{13}C_5$, Singly Substituted ^{13}C Isotopomers of *o*-Benzyne[a]

transition		$^{13}C_1$		$^{13}C_3$		$^{13}C_5$	
$J'_{K'aK'c}$	J_{KaKc}	measured	M−C	measured	M−C	measured	M−C
2_{11}	2_{02}	8043.3985	−0.0012	7879.2170	−0.0004		
1_{11}	0_{00}	9965.6748	−0.0001	10089.1582	−0.0005	9985.5127	0.0002
2_{21}	2_{12}	11262.5552	0.0010	11669.0165	−0.0009	11311.3692	0.0022
2_{02}	1_{11}	14674.6260	−0.0003	14417.7378	0.0014	14660.8448	0.0010
2_{12}	1_{01}	16177.1441	0.0005	16288.6216	−0.0024	16200.5474	−0.0007
3_{03}	2_{12}	21560.9717	−0.0003	21432.1475	−0.0009	21565.4346	0.0002
2_{21}	1_{10}	23685.5049	0.0014				
3_{13}	2_{02}			21985.4737	0.0003	21961.1875	−0.0005
2_{21}	1_{10}			24067.9619	0.0023	23741.4502	0.0002
3_{12}	2_{21}	24876.9981	0.009			24808.9023	0.0008
2_{20}	1_{11}	27974.7165	−0.0005	28057.5030	−0.0001	28002.5850	−0.0026
3_{22}	2_{11}	29896.9316	−0.0014			29956.4473	0.0008
σ_{FIT}		0.0011		0.0016		0.0015	

[a] The molecular parameters obtained from the least-squares fits are reported Table 3. All values are in MHz.

TABLE 2: Measured Frequencies and Residuals (M−C) for D_1 (Nearest the C≡C) and D_2 (opposite the C≡C) Single D Substitution *o*-Benzyne Transitions Frequencies[a]

transition							
$J'_{K'aK'c}$	F′	$J''_{K''aK''c}$	F″	measured (D_1)	M−C (D_1)	measured (D_2)	M−C (D_2)
1_{11}	1	0_{00}	1	10008.7349	−0.0026	9677.9517	−0.0010
1_{11}	2	0_{00}	1	10008.7618	−0.0025	9677.9305	0.0002
1_{11}	0	0_{00}	1	10008.8037	−0.0007	9677. 8941	−0.0018
2_{21}	2	2_{12}	2	11904.9117	0.0000	10834.7647	0.0014
2_{21}	3	2_{12}	3	11905.0020	−0.0012	10834.8034	0.0016
2_{21}	1	2_{12}	1	11905.0542	0.0001	10834.8235	0.0003
2_{02}	1	1_{11}	0	13750.9653	−0.0021		
2_{02}	1	1_{11}	1			14416.4361	−0.0006
2_{02}	3	1_{11}	2	13751.0352	−0.0001	14416.4751	−0.0002
2_{02}	1	1_{11}	0			14416.4898	−0.0053
2_{02}	2	1_{11}	1	13751.1089	−0.0032		
2_{02}	2	1_{11}	2			14416.5005	−0.0023
2_{12}	2	1_{01}	1	16049.1488	0.0000	15744.2708	0.0018
2_{12}	3	1_{01}	2	16049.1718	−0.0016	15744.2456	0.0021
2_{12}	1	1_{01}	0	16049.2378	−0.0023	15744.2343	−0.0009
2_{12}	2	1_{01}	2			15744.2784	0.0031
3_{03}	4	2_{12}	3	20751.0420	0.0000	21086.0225	0.0039
3_{03}	3	2_{12}	2	20751.0635	0.0035		
3_{13}	2	2_{02}	2			21397.5741	0.0046
3_{13}	3	2_{02}	2	21546.5224	−0.0019	21397.6289	0.0054
3_{13}	4	2_{02}	3	21546.5284	−0.0002	21397.6142	0.0032
3_{13}	3	2_{02}	3	21546.5762	0.0018	21397.6523	0.0013
2_{21}	2	1_{10}	2	23985.7656	0.0004		
2_{21}	2	1_{10}	1	23985.7920	−0.0025		
2_{21}	3	1_{10}	2	23985.8223	−0.0029	22967.4365	0.0045
3_{12}	4	2_{21}	3			24611.1778	−0.0022
2_{21}	1	1_{10}	1	23985.8867	−0.0013		
2_{20}	2	1_{11}	2	27556.4727	−0.0001		
2_{20}	2	1_{11}	1	27556.5000	0.0003	27278.0552	0.0023
2_{20}	3	1_{11}	2	27556.5215	−0.0013	27278.1064	0.0027
2_{20}	1	1_{11}	1	27556.5811	0.0036		
2_{20}	1	1_{11}	0			27278.1563	0.0023
3_{22}	3	2_{11}	2	30026.1709	0.0044		
3_{22}	4	2_{11}	3	30026.1982	0.0031		

[a] Frequencies and M−C values are in MHz. The standard deviations are $\sigma = 2.1$ kHz for D_1 and $\sigma = 2.8$ kHz for D_2 fits. The molecular parameters are listed in Table 3.

III. Data Analysis and Results

The measured transitions listed in Tables 1 and 2 were fit using the Pickett program SPFIT,[23] to determine the rotational constants for all of the unique, singly substituted isotopomers of *o*-benzyne, and these results were verified using two otherspectral fitting programs.[24] The rotational constants so obtained are listed in Table 3. Since the numbers of observed transitions were limited and the values for the centrifugal distortion constants are not expected to change significantly with isotopic substitution, the centrifugal distortion constants for the ^{13}C and D data analyses were fixed at values obtained earlier by fitting 27 transitions of the normal isotopomer.[13] The rotational constants for the normal and all-^{13}C isotopomer, used in the present least-squares fit structural analysis, are also listed in Table 3. Once 3−4 transitions had been successfully fit for the single-^{13}C data, additional transitions could be predicted and found, giving reasonably high confidence to the assignments of quantum numbers, for each of the singly substituted ^{13}C isotopomers, to the measured frequencies. Very good fits to the experimental data were obtained, with standard deviations for

TABLE 3: Rotational Constants and Deuterium Quadrupole Coupling Constants in the Inertial Axis System Obtained by Fitting the *o*-Benzyne Singly Substituted ^{13}C and D Isotopomer Transitions Listed in Tables 1 and 2[a]

parameter	$^{13}C_1$	$^{13}C_3$	$^{13}C_5$	*o*-benzyne D_1	*o*-benzyne D_2
A	6859.9380(2)	6989.4240(3)	6877.9924(2)	6988.5521(2)	6644.7742(4)
B	5679.5173(2)	5574.2492(5)	5673.1204(3)	5322.5306(5)	5584.6945(5)
C	3105.7385(1)	3099.7367(2)	3107.5219(2)	3020.2096(2)	3033.1617(2)
eQq_{aa}				0.1870(21)	0.0209(34)
$eQq_{bb} - eQq_{cc}$				0.0084(44)	0.1767(36)

parameter	normal	^{13}C-6 (all ^{13}C)
Δ_J(kHz)	0.70(1)	
Δ_{JK}(kHz)	0.36(4)	
Δ_K(kHz)	1.46(3)	
δ_J(kHz)	0.278(6)	
δ_K(kHz)	1.01(2)	
A(MHz)	6989.7292(4)	6511.63520(1)
B(MHz)	5706.8062(4)	5342.26122(1)
C(MHz)	3140.3709(3)	2933.37422(1)

[a] The centrifugal distortion constants were fixed at values obtained for the normal isotopomer[13]and are listed as positive(standard convention) not as negative values from spfit. Rotational constants are in MHz. Listed error limits are σ.

TABLE 4: Atomic Coordinates (Å), in the Center of Mass (abc) System from (A) Kraitchman Analysis, (B) Least Squares, Best-Fit Structure, Using Rotational Constants with Vibrational Corrections Subtracted (See Table 5) (σ(fit) = 0.08 MHz)[a]

	A. Kraitchman		B. A_C, B_C, C_C fit	
atom	a_s	b_s	a_f	b_f
C_1	0.628(4)	1.191(7)	0. 6320(15)	1.1933(18)
C_3	−1.458(21)	0.0626(1)	−1. 4580(7)	0. 0754 (18)
C_5	0.702(7)	−1.107(11)	0.7019(14)	−1. 1062(18)
H_1	−2.536(6)	0.1221(3)	−2. 5510(28)	0.135(1)
H_2	−1.224(7)	−2.056(11)	−1. 2316(24)	−2. 0693(24)

[a] The indicated error limits are 2σ.

the ^{13}C data ranging from 1.1 to 1.6 kHz and 2.1 to 2.8 kHz for the D data. The ^{13}C standard deviations are within experimental uncertainties, but the single-D standard deviations are slightly larger, due to incomplete resolution of all of the hyperfine components, particularly for the D_2 data. The hyperfine splittings for the D_2 spectrum are smaller, due to the smaller value of eQq_{aa}.

IV. Structural Parameters

(a) Substitution Structure. A Kraitchman analysis[25] was carried out for the five, singly substituted isotopomers to determine the substitution coordinates for all atoms in *o*-benzyne, giving the r_s structure. This analysis provides the absolute values of coordinates for the substituted atoms, in the center of mass system for the parent (normal) isotopomer, using differences in moments of inertia for the parent and singly substituted molecules. The accuracy of these coordinates is significantly reduced when the substituted atom lies close to a principal axis or the center of mass. The new rotational constants for the singly substituted isotopomers, along with the previous data for the normal isotopomer (see Table 3), were used to determine the a_s and b_s substitution coordinates listed in Table 4, column A. Since only the magnitudes of these coordinates were obtained from the Kraitchman analysis, results from the least-squares fits (also listed in Table 4) and the theoretical calculations were used to determine the signs of coordinates. There are possible ambiguities in the signs of Kraitchman-derived coordinates for *b* coordinates for C_3 and H_1, since these atoms lie close to the *a* axis.

(b) Least-Squares Structure Fit. The inertial defect for the normal isotopomer of *o*-benzyne is $\Delta = 0.06935(1)$ amu Å^2. Although entirely consistent with a planar structure, this value is sufficiently large that, when trying to fit the measured *A*, *B*, and *C* rotational constants with a planar structure, some of the deviations will be as large as 1 MHz. Most of the same vibrational averaging effects which contribute to the differences between the r_0 and r_e coordinates will also contribute to this inertial defect. If a calculation of the multidimensional potential surface and complete vibrational analysis were carried out, the calculated differences between the B_e and B_0 rotational constants could be used to correct the measured B_0 constants. This would substantially reduce the errors in the fitting caused by the inertial defect and provide structural parameters much closer to the equilibrium values. A complete vibrational analysis is beyond the scope of the present work, but partial corrections can be readily made using the procedure described by Watson,[26] relating the vibrational averaging corrections to the measured centrifugal distortion constants. This procedure was carried out using *o*-benzyne centrifugal distortion data for the normal isotopomer (Table 3), to obtain harmonic contributions to the vibrational modifications of the moments of inertia: $I_0^{aa} - I_e^{aa} = -0.04747$ amu Å^2, $I_0^{bb} - I_e^{bb} = -0.04770$ amu Å^2, and $I_0^{cc} - I_e^{cc} = -0.02378$ amu Å^2. The larger differences for the in-plane moments result in the positive inertial defect. These differences were then subtracted from the experimental moments, and the resulting corrected rotational constants were fit to obtain the coordinates. When fitting the normal and the five singly substituted isotopomers, larger deviations were obtained for the D-isotopomers. In addition, when the structural parameters obtained from this fit were used to predict rotational constants for the all-^{13}C isotopomer, the predicted rotational constants were too small by 0.3−1.0 MHz. These discrepancies are due to the well-known shrinkage of vibrationally averaged coordinates with increasing isotopic mass. This effect was discussed for C−D vs C−H bonds by Laurie and Hershbach.[27] The use of mass-dependent coordinates (r_m) to address this problem was disscussed by Watson.[28] We included small, mass-dependent adjustments to the atomic coordinates to improve the fits and to include the all-^{13}C isotopomer data, without introducing large deviations. The Cartesian coordinates for ^{13}C-substituted atoms were multiplied by the factor C(^{13}C) = 0.9999092, and coordinates of D-substituted atoms were multiplied by the factor *C*(D) = 0.9971(3). The *C*(D) factor was optimized by fitting. The empirical value determined for the shortening of the C−D bonds is 0.0029 Å, and this value is consistent with the values obtained by Laurie and Hershbach.[27] The variable parameters

TABLE 5: Measured Rotational Constants for *o*-Benzyne (Column 1), Values Corrected for Harmonic Vibrational Averaging Terms (Column 2), and the Best Fit Rotational Constants (Column 3) Obtained from the Least Squares Fit to the Corrected Rotational Constants[a]

	measured A, B, C	corrected A, B, C	best fit values	deviation (M−C)
normal A	6989.7292	6985.336	6985.391	−0.055
B	5706.8062	5703.733	5703.711	0.022
C	3140.3709	3139.907	3139.911	−0.004
$^{13}C_1$ A	6859.9380	6855.707	6855.796	−0.090
B	5679.5173	5676.474	5676.453	0.021
C	3105.7385	3105.285	3105.317	−0.032
$^{13}C_3$ A	6989.4240	6985.031	6984.910	0.122
B	5574.2492	5571.317	5571.298	0.019
C	3099.7367	3099.284	3099.265	0.020
$^{13}C_5$ A	6877.9924	6873.738	6873.858	−0.120
B	5673.1204	5670.085	5670.065	0.020
C	3107.5219	3107.068	3107.100	−0.032
D_1 A	6988.5521	6984.161	6984.143	0.018
B	5322.5306	5319.858	5319.883	−0.025
C	3020.2096	3019.781	3019.729	0.052
D_2 A	6644.7742	6640.804	6640.799	0.005
B	5584.6945	5581.752	5581.763	−0.011
C	3033.1617	3032.729	3032.700	0.029
All-^{13}C A	6511.6353	6507.8228	6507.691	0.132
B	5342.2612	5339.5684	5339.609	−0.041
C	2933.3743	2932.9692	2933.033	−0.064

[a] Rotational constants are in MHz. Standard deviation for the fit is 0.07 MHz.

in the least-squares fit are the a_f and b_f carbon atom coordinates and the hydrogen atom coordinates, relative to the adjacent carbon atom. The a_f and b_f coordinates obtained from this fit are listed in Table 4. The experimental, corrected and best-fit rotational constants are listed in Table 5.

We note that most of the a_s and b_s substitution coordinates are in very good agreement with the a_f and b_f coordinates. The Kraitchman analysis was done using measured rotational constants, without applying any of the vibrational corrections discussed above. The error limits for the a_f and b_f coordinates are smaller that those for the substitution coordinates. The error limits for the a_s coordinate for C_3 are larger, as would be expected, since this atom is close to the *a* axis. The C_1-C_2 bond length from the fit is slightly longer than the substitution value, and the fit value is preferred, since a larger data set was used, and the error limits are smaller. The H_1 (and H_4) atoms lie quite close to the *a* axis, and converged fits can be obtained with either positive, or negative *b* coordinates for H_1, depending on initial conditions for the fit. The standard deviation for the fits with positive *b* values for H_1 were lower however, so these results are believed to be the best values and are listed in Table 4. Structural parameters and the atom-numbering scheme are shown in Figure 3.

The bond lengths and interbond angles for *o*-benzyne are given in Table 6. The present experimental C_1-C_2 bond length is 1.264 Å, which is consistent with most of the calculated values. It is slightly longer than the NMR value of 1.24 Å, and our previous preliminary value[13] of 1.24 Å, but is within the experimental uncertainties of both. We note that for the substitution parameters (Table 6, column 2), the C_2-C_3 bond is slightly longer than the C_3-C_4 bond, but the converse is true for the least-squares fit results (column 3). For all of the listed calculations, the C_3-C_4 bond is longer than the C_2-C_3 bond. We also note that the C−H bonds are longer for the least-squares fit data, and these represent r_0 bond lengths, since 0.003 Å was subtracted from these values in fitting the D_1 and D_2 data. If we assume that the mass dependence of the bond lengths varies as $m^{-1/2}$, then the equilibrium C−H bond lengths would be near 1.078 Å. The fact that the $C_2-C_3-H_1$ angle is smaller than the $C_1-C_2-C_3$ angle indicates that the C_3-H_1 bond is rotated by 3° relative to the *a* axis for the experimental structure. For the CCSD(T), and other theoretical structures, this C_3-H_1 bond axis is nearly parallel to the *a* axis.

V. Deuterium Quadrupole Coupling

The deuterium quadrupole coupling constants provide data on the electronic charge distribution associated with the C−D bonds. It is important to have more accurate and precise hyperfine structure data, and analysis for these singly substituted D isotopomers for two reasons: (1) to obtain improved eQq values and, more importantly, (2) to obtain better rotational constants for use in the structure determination. Quadrupole coupling constants were reported in earlier work,[13] but due to the limited data available and difficulty in resolving hyperfine structure, particularly for the D_2 position, the precision was quite low. The new measurements reported here, which include additional transitions, allow a factor of 5 or more reduction in the experimental uncertainties for some of the quadrupole coupling constants. The data listed in Table 2 contain 8 new transitions for D_1 and 10 new ones for D_2. Better measurements were obtained for some of the previously reported transitions.

The new quadrupole coupling constants obtained by fitting all of the available single-D isotopomer data are listed in Table 5. The C−D bond axis for the D_1 isotopomer is nearly parallel (+12.3° angle) to the *a* inertial axis, so for this isotopomer, eQq_{aa} is very nearly equal to the bond axis quadrupole coupling eQq_{zz}. In this case, we can readily determine accurate values for the quadrupole coupling constants in the bond-axis system. We assume that one principal axis for the deuterium quadrupole coupling tensors is aligned with the C−D bond direction and this is designated as the *z* axis. We assume that the *x* axis is in the plane of the molecule and *y* is perpendicular to the molecular plane and is parallel to the *c* inertial axis.

The C−D bond axis for the D_2 isotopomer is at an angle of 51° relative to the *o*-benzyne *a* axis, so the projection factor ($3\cos^2\theta - 1$) is only 0.183, resulting in a rather small eQq_{aa} for D_2. The small hyperfine splittings make the hyperfine analysis more difficult for this isotopomer.

The procedure for calculating the C−D bond-axis quadrupole tensor components from the inertial-axis components is discussed in earlier work.[13] The results of carrying out this analysis for the present data, using improved structural parameters are shown in Table 7, along with a value obtained previously for benzene, by Bauder et al.[29] The eQq_{zz} values are components along the C−D bond directions, and eQq_{xx} components lie in the plane of the molecule. The new asymmetry parameters for *o*-benzyne, $\eta = 0.04$ and 0.07, are apparently opposite in sign to those for benzene. Both of the bond-axis eQq_{zz} values of *o*-benzyne are quite close to the value for benzene. It is somewhat surprising that the electronic structure associated with the adjacent C−H bonds is not more highly perturbed on removal of two H atoms from benzene.

VI. Discussion: Theory and Experiment

Experimental data on the structure of *o*-benzyne (or *m*-benzyne) were not previously available, but there were numerous publications of theoretical structural results, not all in agreement. Theoretical methods have been very useful as a guide to understanding the electronic properties, equilibrium geometry, and reactivity of *o*-benzyne and *m*-benzyne. However, it is always very desirable to have accurate experimental structural

TABLE 6: Structural Parameters for *o*-Benzyne[a]

parameter	Kraitchman (substitution)	A, B, C fit	B3LYP/(6-31G(d,p))	BPW91/cc-pVDZ	CCSD(T)/(6-31G(d,p))
C_1-C_2	1.255(8)	1.264(3)	1.251	1.266	1.269
C_2-C_3	1.40(2)	1.390(3)	1.385	1.391	1.394
C_3-C_4	1.39(2)	1.403(3)	1.412	1.423	1.411
C_4-C_5	1.404(14)	1.404(3)	1.407	1.412	1.413
C_3-H_1	1.08(2)	1.095(9)	1.085	1.098	1.081
C_4-H_2	1.084(9)	1.099(4)	1.087	1.100	1.084
$\angle C_1-C_2-C_3$	126(1)°	126(1)°	127.1°	127.2°	126.4°
$\angle C_2-C_3-C_4$	111(1)°	111(1)°	110.4°	110.2°	111.2°
$\angle C_3-C_4-C_5$	123(1)°	123(1)°	122.5°	122.7°	122.4°
$\angle C_2-C_3-H_1$	123(1)°	123(2)°	127.0°	127.3°	126.4°
$\angle C_4-C_5-H_3$	119(1)°	119(2)°	118.9°	118.9°	118.8°
see ref. no.			13	11	10

[a] The bond lengths are given in Å, and interbond angles are given in degrees. The A, B, and C fit values are for the least-squares fit to rotational constants corrected for harmonic vibrational terms (Table 5).

TABLE 7: Deuterium Quadrupole Coupling Tensor Diagonal Elements for D_1 (Nearest the $C{\equiv}C$) and D_2 (Opposite the $C{\equiv}C$)[a]

molecule	eQq_{aa}	eQq_{bb}	eQq_{zz}	eQq_{xx}	η	θ(°)
o-benzyne (D_1)	187(2)	−89(2)	188(2)	−90(3)	0.04	12.3[b]
o-benzyne (D_2)	21(3)	78(3)	185(10)	−86(4)	0.07	51.1[c]
benzene (D_1)[d]			186.1(18)	−97.2(23)	−0.045(12)	0

[a] Values are reported in kHz, in the *a*-, *b*-, and *c*-axis system and the C−D bond axis system. Listed error limits are σ. The C−D bond axis is *z*, and the molecule lies in the *x*−*z* plane. Asymmetry parameter $\eta = (eQq_{xx} - eQq_{yy})/eQq_{zz}$. Angle for tensor transformation is θ (°). [b] Rotate 12.3° from *a* axis to *z* axis. [c] Rotate 51.1° from *a* axis to *z* axis. [d] See ref 29.

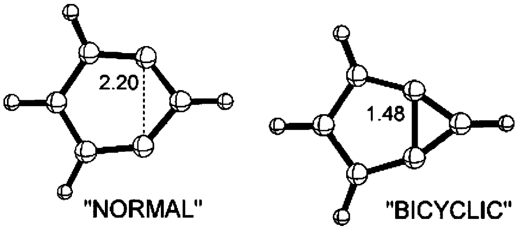

Figure 4. Calculated structures[30] for *m*-benzyne range from a "NORMAL" structure, which is similar to benzene, to a "BICYCLIC" structure with abnormally short C_1-C_3 distance.

parameters for comparison and selection of the best theoretical results and methods. The theoretical methods, which have been proven to be accurate, using these comparisons can then be extended to molecules which are more complex or more difficult to measure. The density functional theory (DFT) method, which is readily available as an option in the Gaussian 98 software (and later versions), allows economical calculations which appear to give reasonably accurate structures. The high-level coupled cluster (CCSD, CCSD(T)), Moller−Plesset(MP2), and multireference perturbation theory (CASPT2), with large basis sets, are often considered to give more reliable results, but sometimes do not achieve the best agreement with experimental results[3]. The calculation of structural parameters for *m*-benzyne is much more challenging than for *o*-benzyne. Structures calculated using different methods and basis sets show much larger variations than results for *o*-benzyne. Winkler and Sander[30] recently calculated the structure for *m*-benzyne using a wide variety of methods and basis sets and found structures ranging from a "bicyclic" structure with $r(C_1-C_3) = 1.48$ Å to a more "normal" (benzene-like) structure with $r(C_1-C_3) = 2.20$ Å. These structures are shown in Figure 4. Their preferred structure, from high-level calculations, had an intermediate value of $r(C_1-C_3) = 2.02$ Å.

There is much better agreement for *o*-benzyne structures, which have been calculated using different methods, and many of these results are quite close to the present experimental results. Structural parameters from three calculations are given in Table 6, along with the present experimental results. Results of DFT calculations from our earlier work[13] and from the work of Cramer et al.[11] are given in columns 4 and 5. Results from high-level CCSD(T) calculations of Kraka and Cremer[10] are given in column 6. There appears to be quite good agreement between theory and experiment for the C−C bond lengths. All C−H bond lengths are in reasonably good agreement, with slightly longer (near r_0 values) values for the BPW91 calculation (column 5). The largest discrepancy between experimental and theoretical parameters is for the $C_2-C_3-H_1$ angle. The calculated values for this angle are nearly equal to the $C_1-C_2-C_3$ angle (near 127°), which would make the C_3-H_1 bond nearly parallel to the *a* axis of the molecule. The experimental values are 3° smaller and this would move the H_1 atom up (in the $+b$ direction, toward the C_1-C_2 bond) by 0.08 Å. This discrepancy could be partially the result of vibrational effects, combined with the fact that the H_1 atom is very close to the *a* axis.

The characterization of the C_1-C_2 bond as "acetylinic" is, at best, approximate. The experimental C_1-C_2 bond length of 1.264 Å falls between the acetylene C−C of 1.207 Å and the ethylene bond of 1.339 Å, although slightly closer to that of acetylene. Benzene C−C bond lengths[31] are 1.396 Å and C−H bond lengths 1.083 Å, and these are very close to the C_2-C_3, C_3-C_4, and C_4-C_5 bond lengths and all C−H bond lengths for *o*-benzyne. With the exception of the C_1-C_2 bond length and the C−C−C interbond angles, the basic structure of benzene evidently is little perturbed by removal of two H atoms. This is consistent with the small observed difference between the deuterium quadrupole coupling constants of benzene and *o*-benzyne. The key to significant reduction in the experimental uncertainties in structural parameters obtained by fitting the measured rotational constants was the subtraction of the vibrational correction terms following Watson's procedure,[26] and including mass-dependent coordinate corrections for the different isotopomers. Even if these vibrational corrections are only accurate to ±10%, the uncertainties in structural parameters can be reduced by nearly a factor of 10, and the uncertainties in the fit due to the nonzero inertial defect are reduced even further.

Acknowledgment. We are grateful to the National Science Foundation for support of this research. James K. G. Watson provided extremely valuable help and advice on making vibrational corrections to moments of inertia. Carl Gottlieb provided helpful discussions on this work and a program for analysis of rotational data. Chakree Tanjaroon provided calculations and helped with the data analysis. We thank E. S. Palmer and John Dudek for help in operation of the Harvard FT spectrometer. James Cheesemen of Gaussian, Inc provided results of calculations on *o*-benzyne.

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