^{13}C Dipolar NMR Spectrum of Matrix-Isolated *o*-Benzyne-*1,2*-$^{13}C_2$

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Abstract: The ^{13}C dipolar NMR spectrum of *o*-benzyne-*1,2*-$^{13}C_2$ in an argon matrix at a temperature of about 20 K is reported. The *o*-benzyne was generated from matrix-isolated phthalic anhydride-*1,2*-$^{13}C_2$ by UV irradiation. The average conversion to *o*-benzyne over the entire sample was about 53%; however, spectral simulations of the pure phthalic anhydride and of the *o*-benzyne−phthalic anhydride mixture were adequate to extract the NMR spectral parameters of both compounds. The simulation of the spectrum of *o*-benzyne gives a bond length of 1.24 ± 0.02 Å for the "triple" bond, in good agreement with the results of *ab initio* geometry optimizations. The experimental principal values of the chemical shift tensor of the labeled carbon in *o*-benzyne are 266, 240, and 73 ppm relative to TMS. The δ_{33} component is not perpendicular to the molecular plane as is common in aromatic systems. Instead, the principal axis system is very similar to that of the alkyne carbon in natural abundance cycloctyne, with δ_{33} in the molecular plane and about 7° from the "triple" bond. *Ab initio* calculations of the chemical shift tensor of *o*-benzyne were completed at the SCF, MP2, and DFT levels using the GIAO method. The DFT calculations agree best with the experimental results.

Introduction

o-Benzyne has been the focus of many studies,[1−15] both experimental and theoretical, since it was first postulated as a reaction intermediate, and there has been some confusion concerning the identification of its IR vibrations. As the detailed history of these studies has been presented elsewhere[14] only a brief treatment is given here.

The first IR spectrum of *o*-benzyne providing an assignment of the vibrational band due to the "triple" bond stretch was reported by Chapman *et al*. in 1975.[2] Work by other groups, both experimental[4,9,10] and theoretical normal mode analyses,[3,6] supported Chapman's assignment of 2085 cm^{-1} as the "triple" bond stretching frequency. This frequency is typical for a normal triple bond.

In 1986, Leopold *et al*.[8] reported the assignment of this "triple" bond stretch as 1860 cm^{-1}, based on a gas-phase electron photodetachment experiment of the *o*-benzyne radical anion. Subsequently, the IR band at 2085 cm^{-1} was shown to be due to the cumulene bond of cyclopentadienylideneketene.[12] More extensive calculations also lend support to the new assignment[13,14] of 1860 cm^{-1}, which lies between the frequencies expected for typical double and triple bond stretching. Most recently, Radziszewski *et al*.[14] have reported IR spectra of *o*-benzyne (C_6H_4) and two of its isotopomers (C_6D_4 and C_6H_4-*1,2*-$^{13}C_2$) and assigned a band at 1846 cm^{-1} to the "triple" bond stretching frequency, in good agreement with the gas-phase photodetachment value. This vibrational band was not observed in the earlier IR spectra, most likely due to its very low intensity. In addition, this recent work[14] uses a second irradiation of the matrix to convert the side product, cyclopentadienylideneketene, to *o*-benzyne before recording the IR spectrum of *o*-benzyne, eliminating the band at 2085 cm^{-1} as the "triple" bond stretch. Finally, recent calculations[15] demonstrate that a high level of theory (MCSCF CAS) and anharmonic corrections are necessary to reproduce the IR frequencies of *o*-benzyne. Therefore, on the basis of IR frequency, there now seems to be a consensus in the literature that the "triple" bond is actually somewhere between a double and a triple bond, in a manner similar to a typical aromatic bond being between a single and double bond.

While the IR stretching frequency is a good indication that the bond between the two dehydrogenated carbons is intermediate between a double and triple bond, a direct measurement of the bond length is important to corroborate this finding. Theoretical treatments place this bond between 1.223 and 1.275

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Å, depending on the basis set used and the level of the calculation.[11,15] As the compound is only stable in a matrix at low temperatures, recording a dipolar NMR spectrum provides a technique for experimentally determining this bond length. There have been a number of molecules in which dipolar NMR spectra have been used to measure the separation between two labeled carbons,[16,17] and bond lengths obtained in this manner compare favorably with those from standard single-crystal X-ray diffraction. Moreover, the chemical shift tensor obtained from the NMR studies can provide further information on the bonding environment about the "triply bonded" carbon. The chemical shift tensors of both normal sp hybridized carbons[18] and typical aromatic carbons[19,20] have been previously studied and are well understood. However, this work is the first to explore the effect forcing the two sp hybridized bonds of an alkyne carbon to be nonlinear has on the chemical shift tensor. In this work this structural feature is also studied by comparing the *o*-benzyne spectrum with a static spectrum of cyclooctyne, the smallest stable cycloalkyne.

In this paper the dipolar spectrum of *o*-benzyne-*1,2*-$^{13}C_2$ is reported. Doubly labeled *o*-benzyne was produced via irradiation of the doubly labeled phthalic anhydride in an argon matrix, using the photochemical scheme presented in the work of Radziszewski *et al*.[14] to ensure the production of only *o*-benzyne. The resulting ^{13}C spectrum obtained was analyzed to obtain the ^{13}C chemical shift tensor of the two labeled carbons and to determine the length of the "triple" bond. In addition to the experimental results, quantum mechanical calculations of the chemical shift tensor using several different theoretical approaches are reported. These calculations were also performed for cyclooctyne, acetylene, and methylacetylene, in order to aid in the interpretation of the chemical shift tensor of *o*-benzyne.

Experimental Section

Synthesis. Maleic anhydride-*1,2*-$^{13}C_2$ (^{13}C, 99.9%) was obtained from ICON Laboratories and converted to phthalic anhydride-*1,2*-$^{13}C_2$ by the addition of butadiene, followed by dehydrogenation.[21] Before use the phthalic anhydride was purified by sublimation. Cycloctyne was synthesized following the literature procedure.[22]

Deposition and Photochemistry. The rate of deposition of phthalic anhydride was controlled by the temperature of the sample and the flow rate of argon (Cryogenic Rare Gas, 99.9995%). The phthalic anhydride was held at 40 ± 2 °C with the use of a heat gun. The argon flow rate corresponded to a pressure drop of 1.5 Torr/min from a volume of approximately 0.5 L. The deposition and photochemistry was done in layers at the bottom temperature of the cryogenic apparatus (Air Products Displex unit, Model DE-202). This temperature is estimated to be approximately 20 K based on the temperature at which pure argon sublimes. A deposition period of 7−8 min was followed by 5−6 h of irradiation using a focused Hg−Xe arc lamp (PTI model LPS200) operating at 200 W. The light from the arc lamp was passed through a solution filter of $NiCl_2$ and $CoCl_2$ to narrow the spectral output to between 250 and 350 nm. An aluminum cylindrical mirror was placed behind the shroud to reflect the light that passed through the cell and to focus it back on the sample. The 5−6 h irradiation was divided into three time periods. First, irradiation was done straight onto the sample (about 2 h), followed by irradiation from the top and bottom (for about 1.5 h each). This was done in order to increase the conversion of phthalic anhydride to *o*-benzyne. The irradiation at 250−350 nm was followed by 30−45 min of irradiation at 254 nm with a coiled low-pressure Hg lamp. The irradiation by 254 nm for the conversion of the side product, cyclopentadienylideneketene, to *o*-benzyne has been described in the literature.[14] The phosphorescence of the sample was monitored to determine when to terminate the 350 nm irradiation. This procedure was repeated for a total of five layers, after which the shroud was sealed off and the cryostat was placed in the magnet. After acquisition of the dipolar spectrum the material on the cold tip was trapped and a solution ^{13}C NMR was recorded to obtain information on the degree of photochemical conversion from phthalic anhydride to *o*-benzyne. The solution spectrum indicated only the presence of unreacted phthalic anhydride along with biphenylene and triphenylene (the dimer and trimer of *o*-benzyne, respectively).

NMR Spectroscopy. A complete description of the cryogenic apparatus and probe used will be published elsewhere.[23] The cryostat was mounted horizontally on a track with a screw drive mechanism, such that the sample on the cold finger could be inserted into a probe in the bore of a horizontal bore magnet. The probe is a doubly tuned (^{13}C and ^{1}H) design and utilizes a 12 mm saddle coil to accommodate the cryogenic cold finger. It is capable of achieving a Hartmann−Hahn match with a proton 90° pulse of 5.3 μs and decoupling fields of 65 KHz. A spectrum of cyclooctyne was obtained using the same equipment, except that a three-stage closed cycle refrigeration unit (RMC Cryosystems, model LTS-1C-4.5) with a bottom temperature of about 8 K was used.

Static solid state spectra were recorded on a Varian XL-200 spectrometer system using the standard cross-polarization pulse sequence along with a high-power proton decoupling. A contact time of 3 ms and a recycle time of 5 s were used. The proton 90° pulse length was 5.3 μs, and the power level was not increased during decoupling. The spectra were transferred to a VAX computer for processing and fitting. The POWDER approach,[24] capable of fitting two overlapping dipolar patterns and utilizing a standard SIMPLEX fitting routine, was used to fit the spectra. Errors in spectral parameters (i.e., dipolar coupling constants, chemical shift tensor principal values, line broadening and angles) are reported as the change in the parameter which corresponds to a 10% change from the best fit sum of squares between the experimental spectrum and the pattern produced by the fitting routine. These uncertainties are only a function of the nonlinear fitting procedure and do not reflect possible systematic errors due to the neglect of the indirect coupling tensor, *J*. The inclusion of the *J* coupling in the spectral fitting procedure was attempted with the results discussed below. Further, possible errors in the principal values due to referencing are not considered. The interatomic distance was calculated directly from the dipolar coupling constant without any correction for thermal motions and/or anisotropic contributions from the *J* coupling tensor.[16a]

Calculations. Geometry optimizations and calculations of the nuclear shielding tensors at the SCF and MP2 levels were performed using the TURBOMOLE[25,26] and the ACESII[27] computer programs. DFT (density functional theory)[28] calculations employed the BYLP (Becke, Yang, Lee, Parr) exchange correlation functional[29] as imple-

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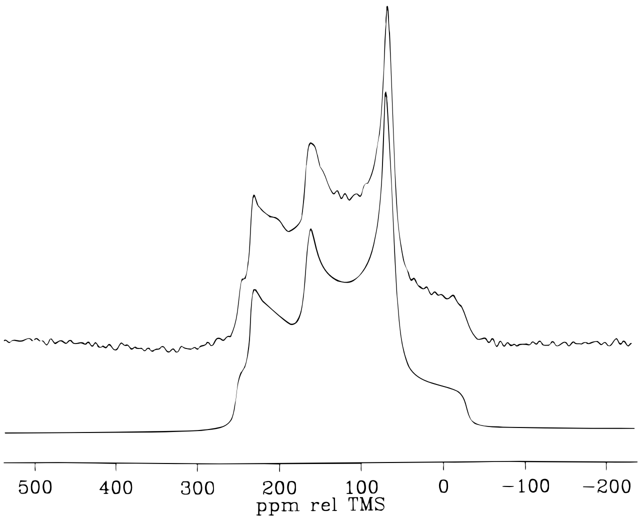

Figure 1. Dipolar ^{13}C NMR spectrum of phthalic anhydride-*1,2*-$^{13}C_2$ along with its best fit.

mented in the Gaussian 94 computer program.[30] The DFT calculation used a coupled perturbation scheme without including the magnetic field effect in the exchange correlation functional.[31] The same program was used to calculate the harmonic vibrational constants. All the shielding calculation employed the GIAO approach.[32] Dunning basis sets, as specified in the tables, were used in all calculations.[33]

Transformation of the calculated nuclear shieldings to chemical shifts on the TMS scale was achieved by estimating the shielding of the carbon in TMS as the chemical shielding calculated for methane, with the corresponding basis set and method, minus 7 ppm, which corresponds to the relative shifts between gas-phase methane and liquid TMS.[34] The methane carbon chemical shielding values, in ppm, calculated by the various methods and basis sets used are as follows: SCF/DZ, 203; SCF/DZP, 199; MP2/DZ, 206; MP2/DZP, 204; DFT/DZ, 194; DFT/DZP, 192.

Results

1. Spectral Analysis. Phthalic Anhydride-*1,2*-$^{13}C_2$. The dipolar spectrum of the pure phthalic anhydride-*1,2*-$^{13}C_2$ along with its best fit is presented in Figure 1. The parameters obtained from this spectrum are in Table 1, and the orientation, determined from the fitting procedure, is shown in Figure 2. The molecular plane of symmetry forces one component of the chemical shift tensor to be perpendicular to this plane, and therefore, only a single angle (α) is necessary to relate the chemical shift tensor principal axis systems of the two carbons to the orientation of the dipolar vector. Therefore, parameters of the spectral fitting routine include the angle α, the three principal chemical shift values, the dipolar coupling constant, and a Lorentzian line broadening function. Inclusion of an additional Gaussian line broadening function failed to improve the fit. Note that the sign of α is not known due to the axial symmetry of the dipolar interaction and therefore two possible orientations of the tensor are consistent with the experimental measurement. However, α is believed to be in the direction shown in Figure 2, which establishes the δ_{11} direction to be nearly along the aromatic ring substituent C−C bond. This finding is consistent with the orientation of the chemical shift tensor determined for the substituted aromatic carbon in acetophenone,[35] where the δ_{11} direction is 4° from the substituent C−C bond. Furthermore, the result is consistent with the general finding that δ_{11} tends to lie along the substituent bond for substituted aromatic carbons.[19] Theoretical calculations of the chemical shift tensor are also in good agreement with the experimental values. Results of DFT calculations at the DZP basis set level are principal values of 219, 139, and 33 ppm and an angle α of 19°. The internuclear separation obtained from the dipolar coupling constant is 1.39 ± 0.01 Å, in good agreement with the bond length of 1.40 Å measured by X-ray diffraction.[36] Inclusion of the *J* tensor and its orientation into the fitting procedure did not significantly change the fit, indicating that the spectrum is not sensitive to this parameter. This is not surprising, since the *J* value for an aromatic carbon carbon bond is typically about 50−60 Hz[37] and therefore represents a small fraction of the dipolar coupling and hence a small correction (approximately 0.01 Å) to the C−C bond distance.

Table 1. Spectral Parameters of Labeled Carbons in Phthalic Anhydride-*1,2*-$^{13}C_2$ and *o*-Benzyne-*1,2*-$^{13}C_2$ and the Triply Bonded Carbon of Cyclooctyne from Best Fit Simulations[a]

parameter	phthalic anhydride	*o*-benzyne	cyclooctyne[b]
δ_{11}/ppm	227 ± 2	266 ± 10	181 ± 2
δ_{22}/ppm	140 ± 1	240 ± 4	172 ± 2
δ_{33}/ppm	28 ± 1	73 ± 10	−68 ± 2
α/deg[c]	24 ± 1		
β/deg[c]		6.7 ± 2.4	
D/Hz	2790 ± 34	4000 ± 260	
r/Å	1.39 ± 0.01	1.24 ± 0.02	

[a] Principal values are given relative to TMS. [b] For cyclooctyne, only the principal values of the chemical shift tensor could be determined from the spectrum. [c] The sign of α and β relative to the internuclear vector is not known as explained in the text; however, the sign consistent with other experimental data or theoretical results is reported in Figures 2 and 4.

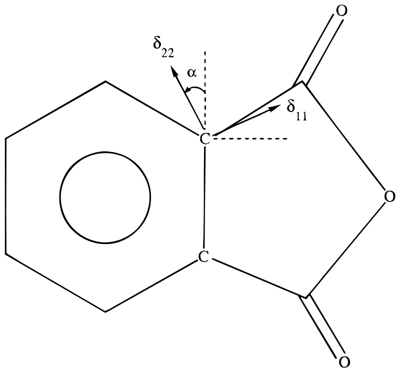

Figure 2. Orientation of the principal axis system in phthalic anhydride-*1,2*-$^{13}C_2$.

***o*-Benzyne-*1,2*-$^{13}C_2$ and Phthalic Anhydride-*1,2*-$^{13}C_2$ Mixture.** The dipolar spectrum of the mixture of *o*-benzyne-*1,2*-$^{13}C_2$ and phthalic anhydride-*1,2*-$^{13}C_2$ is given in Figure 3a, along with the best fit. The dipolar spectrum of the mixture was simulated using a routine for two independent overlapping dipolar patterns, with the parameters for the phthalic anhydride

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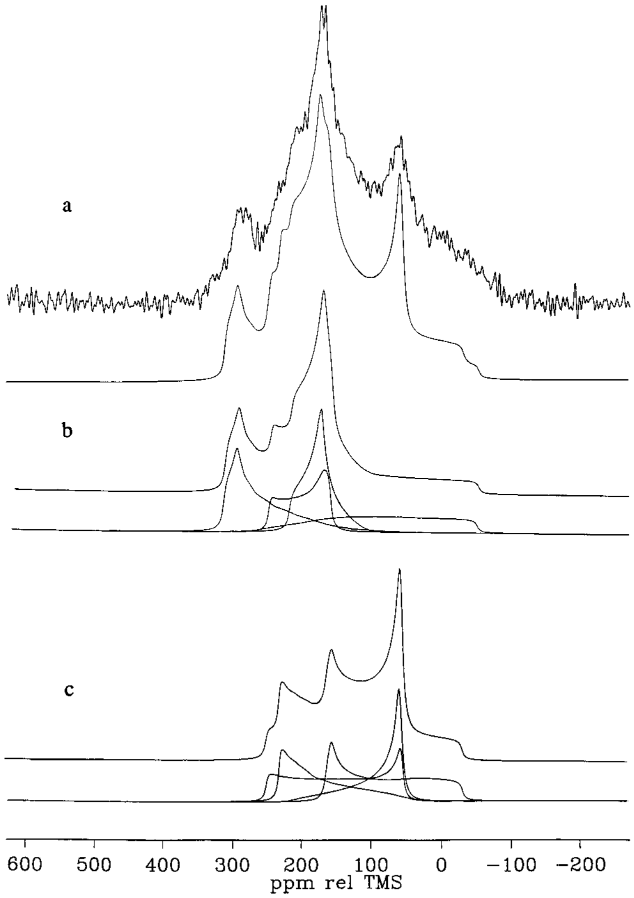

Figure 3. (a) Dipolar ^{13}C NMR spectrum of a mixture of *o*-benzyne-*1,2*-$^{13}C_2$ and phthalic anhydride-*1,2*-$^{13}C_2$. Below the experimental spectrum is the best fit. (b) Simulation of the dipolar ^{13}C NMR pattern of pure *o*-benzyne-*1,2*-$^{13}C_2$ based on the best fit parameters from the fit of the mixture spectrum. Bottom traces show the four individual spectral components to the Pake pattern. (c) Simulation of the dipolar ^{13}C NMR pattern of pure phthalic anhydride-*1,2*-$^{13}C_2$ based on the best fit parameters from the fit of the mixture spectrum. Bottom traces show the four individual spectral components to the Pake pattern.

locked at the values obtained from the best fit of the pure phthalic anhydride spectrum. The intensity ratio between the phthalic anhydride and *o*-benzyne spectra was allowed to vary as an independent parameter in the fitting procedure, along with the *o*-benzyne spectral parameters, i.e. the dipolar coupling, the three components of the chemical shift tensor, the Lorentzian line broadening, and the one angle (β) needed to relate the principal axis system (PAS) of the chemical shift tensor of the two carbons to each other and to the internuclear $^{13}C-^{13}C$ vector. Addition of a Gaussian line broadening function did not significantly improve the fit. In addition, spectral fitting was also done including the *J* tensor among the fitting parameters. However, this expansion in the number of fitting parameters did not significantly change the fitting results, indicating that the spectrum is insensitive to the *J* tensor. Apparently, the components of the *J* tensor in *o*-benzyne are much smaller than the dipolar coupling, and probably are below 200 Hz. Figure 3bc shows the decomposition of the simulation into its four-component transitions for the individual patterns for *o*-benzyne-*1,2*-$^{13}C_2$ (Figure 3b) and for phthalic anhydride-*1,2*-$^{13}C_2$ (Figure 3c) based on the parameters obtained in the fit on the mixture. This decomposition of the overall Pake powder pattern is useful in order to identify the prominent spectral features required to extract the spectral parameters. The phthalic anhydride simulation is the same as that given in Figure 1; however, it is included here to show the spectral components on the same spectral width scale as the *o*-benzyne simulation.

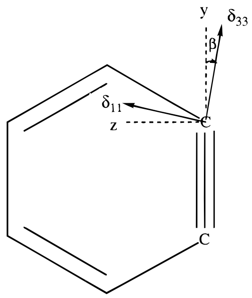

Figure 4. Orientation of the principal axis system in *o*-benzyne-*1,2*-$^{13}C_2$. The axis system labeled *x, y, z* is that used in the theoretical calculations of *o*-benzyne and related molecules.

The spectral parameters obtained for *o*-benzyne are given in Table 1, and the relative orientation of the chemical shift tensor is shown in Figure 4. Again, the experimental sign of the angle β is unknown. However, theoretical results (see below) suggest that the orientation is as shown in Figure 4. In the next section a comparison of these parameters with the theoretical calculations will be discussed. The bond length calculated from the dipolar coupling is 1.24 ± 0.02 Å, in good agreement with the bond lengths from the geometry optimizations reported in the literature (see Introduction). Consideration of the *J* coupling in the determination of the bond length may increase or decrease the reported value by as much as 0.02 Å, depending on the sign of the anisotropy of the coupling constant. The results of the fitting routine estimate that 53 ± 2% of the starting material was converted to *o*-benzyne. It should be noted that the entire sample was within the NMR sample coil and therefore measurable, whereas it was impossible to efficiently irradiate the tip of the matrix due to both the geometry of the glass shroud and the thickness of the matrix at this point. The photolysis efficiency was considerably reduced as this tip accounts for a large percentage of the total sample volume. In other regions of the sample the actual conversion to *o*-benzyne was much higher.

Cyclooctyne. In addition to the dipolar spectra discussed above, the spectrum of natural abundance cyclooctyne was also obtained. This spectrum was recorded to compare the effects that the nonlinear C—C≡C—C moiety in *o*-benzyne would have on the principal values of the chemical shift tensor of the "triple" bond carbons. The spectrum obtained, along with its best fit, is shown in Figure 5, and the principal values of the chemical shift tensor measured for the alkyne carbon are reported in Table 1. The average of the tensor components is 95 ppm, in good agreement with the isotropic solution value of 94.7 ppm. No attempt was made to extract the principal values of the three magnetically distinct methylene groups present in the molecule due to the extensive overlap of these bands.

In linear alkynes, such as acetylene, the C_∞ symmetry axis requires the chemical shift tensor to be axially symmetric with the unique component directed along the triple bond. This unique component is normally found to be around −90 ppm.[18] This component is entirely due to the diamagnetic component of the nuclear shielding, as the symmetry quenches any paramagnetic contributions along the δ_{33} axis. The other components, perpendicular to this symmetry axis, are in the range of 150 ppm. In the case of cyclooctyne the C—C≡C moiety deviates from linearity by 28.5°, thereby breaking the axial symmetry and lifting the degeneracy of the perpendicular components. The splitting of the two perpendicular components is 9 ppm, and there is a significant, almost component-independent, increase of about 20 ppm in each of the three

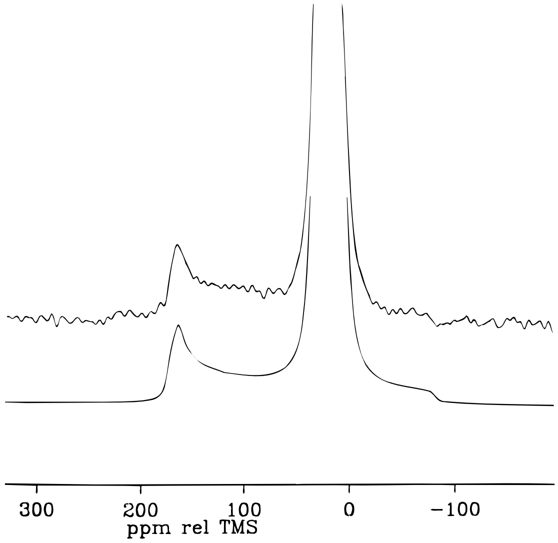

Figure 5. ^{13}C NMR powder pattern for natural abundance cyclooctyne along with the best fit. Note that the narrow signal for the six methylene carbons is off scale and generally featureless. Thus, no attempt was made to fit this peak with three distinct powder patterns.

Table 2. Comparison between Calculated and Experimental Chemical Shift Tensor Principal Values and Orientational Angle for Triply Bonded Carbons of *o*-Benzyne and Cyclooctyne[a]

	$\delta_\perp$/ppm	δ_n/ppm	$\delta_{\|\|}$/ppm	β/deg
		o-Benzyne[b]		
exptl	266	240	73	±6.7
DFT[c]	254	244	65	16.4
DFT[d]	249	240	60	16.0
SCF[d]	366	263	7	21.5
MP2[d]	163	202	4	−34.4
		Cyclooctyne[e]		
exptl[f]	181	172	−68	
DFT	169	162	−72	9.3
SCF	177	205	−86	16.4
MP2	144	122	−63	−8.3

[a] All shift values are referenced to TMS as explained in the text. [b] Calculations of the chemical shielding were done using Dunning's DZP basis.[33] [c] Values calculated using the geometry optimized by the DFT method with a DZP basis set. [d] Values calculated using the fully optimized MP2/TZ2P geometry. [e] Calculations were done using a DZ basis and the experimental geometry.[38] [f] Only the principal values were determined experimentally. Experimental values have been assigned using the rank order of the DFT calculated values.

principal shift values between acetylene and cyclooctyne. These differences are not merely due to the presence of substituents on the alkyne carbons, since large differences, especially in δ_{11} and δ_{22}, still exist in a comparison with dimethylacetylene.

2. Calculations. GIAO calculations of the chemical shielding tensor in *o*-benzyne were completed using the SCF, MP2, and DFT approaches. The calculated principal values of the chemical shift tensor for the "triple" carbon of *o*-benzyne are compared with the experimental results in Table 2. Due to the presence of a plane of symmetry, one of the principal values must lie along the x axis; this component is designated as δ_n. The other two components must be in the plane of the molecule. The orientation of the two in-plane components relative to the y and z axes is given by the angle β. The direction of rotation indicated in Figure 4 is consistent with a calculated positive value of β, as reported in Table 2. The component nearest the y axis is referred to as $\delta_{||}$, while the component nearest to the z axis is designated $\delta_\perp$. The geometry used for each of these calculations is specified in the table. Also in the table is the angle β between the $\delta_{||}$ direction and the C≡C triple bond. The discrepancies between the experimental principal values and calculated values for both the SCF and MP2 methods are so large that one can question the validity of these approximations to calculate the electronic structure of *o*-benzyne. This is perhaps not surprising when a single-determinant-based method is applied to an inherently biradicaloid molecule. It is interesting to note that MP2 calculations reproduce reasonably well the C≡C interatomic distance and the vibrational spectrum of *o*-benzyne, indicating that the chemical shift tensor would seem to be a much more sensitive probe of the molecular electronic structure. The agreement of the DFT-calculated values with the experimental values is quite remarkable, with the calculated values lying almost within the uncertainties in the measured values. This extraordinary agreement in a molecule for which the importance of the electronic correlation effects has been widely recognized suggests that the BYLP exchange correlation potential provides a good approximation to the exact exchange correlation potential. Moreover, the excellent agreement obtained for the calculated IR frequencies (see below) indicates that this method can also represent the electronic force constants of *o*-benzyne adequately.

In Table 2, a similar comparison is also made for the alkyne carbon of cyclooctyne. In cyclooctyne, the lack of a symmetry plane slightly distorts the exact orientation of δ_n. However, the direction of this principal value remains close to being perpendicular to the plane defined by the C—C≡C—C moiety. The exact orientation of δ_n can be obtained by the diagonalization of the full chemical shift tensor given in Table 3. The experimental tensor values resemble more closely the axially symmetric tensor of acetylene. Again, of the three theoretical approaches, DFT does the best job of reproducing the experimental principal values of the shift tensor. The DFT calculations are the only ones that reproduce the small difference between the two downfield components perpendicualr to the triple bond. For cyclooctyne the SCF calculations produce results in qualitative agreement with the experimental values, but the δ_n component is calculated to be about 20 ppm too far downfield and the difference between the two components perpendicular to the triple bond is greatly overestimated. The MP2 corrections move in the right direction but overestimate the electronic correlation effects, shifting the calculated components too far upfield, i.e., to smaller chemical shift values. The good agreement of the DFT calculations suggests that this method correctly estimates the contribution of electronic correlation effects to chemical shielding.

The dominant features of the chemical shift tensor of *o*-benzyne are not associated with the unusual C≡C bond length. Calculations in a molecule of acetylene with an elongated (1.257 Å) C≡C bond and in ethylene with a compressed (1.257 Å) C═C bond show characteristic chemical shift tensors with principal values similar to those calculated at their normal C—C bond distances. This is an indication that the chemical shift tensor of *o*-benzyne reflects an electronic structure that is perhaps unique and that its description as *intermediate* between a double and a triple bond may be misleading. The *o*-benzyne chemical shift tensor portrays a much more complex electronic structure than the intermediate bond lengths and carbon stretching frequencies indicate. This ability of chemical shift studies to highlight the importance of variations in the three-dimensional electronic structure stresses the synergism between theoretical and experimental shift tensors.

Correlation Effects on the Chemical Shielding Tensors. The effect of electron correlation on the calculation of ^{13}C

Table 3. Calculated Chemical Shift Tensors of Triply Bonded Carbons of Acetylene, Cyclooctyne, and *o*-Benzyne[a]

method		acetylene			cyclooctyne			*o*-benzyne		
		x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
SCF	*x*	137.9	0.0	0.0	177.0	−12.0	4.3	260.1	0.0	0.0
	y	0.0	−81.9	0.0	−2.7	−62.6	6.8	0.0	80.0	42.6
	z	0.0	0.0	137.9	8.3	−162.9	181.4	0.0	−294.7	327.1
MP2	*x*	122.0	0.0	0.0	144.0	−10.3	4.3	180.7	0.0	0.0
	y	0.0	−79.6	0.0	0.9	−59.2	4.2	0.0	71.7	30.2
	z	0.0	0.0	122.0	−2.1	48.1	118.1	0.0	163.2	82.7
DFT	*x*	132.0	0.0	0.0	165.7	7.6	4.9	240.0	0.0	0.0
	y	0.0	−92.9	0.0	−3.1	−65.7	5.8	0.0	84.3	28.5
	z	0.0	0.0	132.0	0.9	−80.8	158.5	0.0	−135.2	241.1

[a] All calculations performed with a DZ basis set. Values reported are in ppm relative to TMS, are in the (x,y,z) axis system depicted in Figure 4, and are for the carbon on which the axes are shown.

Table 4. Antisymmetric Contributions Calculated for Triply Bonded Carbons of Deformed Methylacetylene[a]

	$(\delta_{yz} - \delta_{zy})/2$	
$\mathrm{C{\equiv}C{-}CH_3}$ angle	**C**(CH$_3$)	**C**(H)
0	0.0	0.0
10	0.7	−1.5
20	−0.2	−1.5
30	−4.7	1.8
40	−14.6	10.3
50	−30.1	24.3
60	−46.2	38.6

[a] All values in ppm calculated using a DZ basis set and MP2 level of approximation. The axis system depicted in Figure 4 and discussed in the text was used. Angles are given in degrees.

chemical shift tensors has attracted attention in recent years.[39] Most of the work has been done on small molecules and has concentrated on the prediction of the isotropic chemical shift value only. However, it is important to analyze electron correlation effects on individual shift components since they can vary greatly, as is the case for *o*-benzyne.

The complete calculated chemical shift tensors using the SCF, MP2, and DFT methods for acetylene, cyclooctyne, and *o*-benzyne are given in Table 3. The calculations were done at the DZ basis set level as MP2 calculations for cyclooctyne with a larger basis set were not feasible with the current computational resources. The (x,y,z) axis system shown for the case of *o*-benzyne in Figure 4 is used. The x axis is perpendicular to the plane containing the $\mathrm{C{-}C{\equiv}C{-}C}$ group, the y axis is parallel to the “triple” bond, and the z axis is in the molecular plane and perpendicular to the “triple” bond. Note, for cyclooctyne, none of the axes correspond to principal axes of the chemical shift tensor due to the nonplanar structure of the molecule.

The component nearly along the $\mathrm{C{\equiv}C}$ bond, δ_{yy}, which is very insensitive to the dynamic electron correlation taken into account by the MP2 approximation, exhibits a small change upon going to DFT. In the case of acetylene this results in a modest improvement, i.e., better agreement with the experimental values, in going from the SCF method to the DFT approach.

The component approximately perpendicular to the plane of the molecule, δ_{xx}, shows significant dynamic correlation effects in both acetylene and cyclooctyne. In both cases the SCF method gives principal values that are too large. The MP2 correction to the SCF approximation results in an overcorrection and gives principal values that are too small. For these molecules the DFT values are between the SCF and MP2 values, indicating that the dynamic electron correlation in the MP2 treatment is overestimating the contribution to the chemical shielding, as expected. However, for *o*-benzyne, the DFT value is shifted to an even higher chemical shift than calculated by the MP2 method. In light of the excellent agreement with the experimental values, one is forced to conclude that DFT, by also including the static correlation, takes into account the total contribution of electron correlation. Note that for acetylene and cyclooctyne there should not be any contributions from static correlation as the electronic structure of these molecules can be described to a good degree of approximation by a single determinant.

The correlation effects are particularly large for the δ_{zz}, δ_{yz}, and δ_{zy} terms. In all cases the δ_{zz} value for the DFT calculations is intermediate between the SCF and the MP2 values. For acetylene the (x,y,z) axis system is the principal axis system; therefore, the δ_{yz} and δ_{zy} terms must be zero. For cyclooctyne and *o*-benzyne, the values of the δ_{yz} and δ_{zy} components are critical for reproducing both the values and the orientation of the in-plane components of the chemical shift tensors. In the case of *o*-benzyne this amounts to an improvement of nearly 60 ppm in $\delta_{\|}$ and about 90 ppm in $\delta_{\perp}$ and may be an indication that it is necessary to include the biradical nature of *o*-benzyne to reproduce the chemical shielding along its $\mathrm{C{\equiv}C}$ “triple” bond.

Antisymmetric Components of the Shielding Tensor. Comparison of the tensors calculated for *o*-benzyne and cyclooctyne suggests that the signature of these tensors is characteristic of a strained triple bond. The main feature observed in both tensors is the large antisymmetric component between δ_{yz} and δ_{zy}. Large antisymmetric components in the chemical shielding tensor have been predicted for three-membered rings[40,41] and measured by relaxation studies in substituted cyclopropenes.[42] The calculations reported in this paper also predict large antisymmetric components in cyclic compounds containing a strained triple bond.

To prove that the antisymmetric terms originate from strain at this triply bonded carbon caused by the departure from normal sp hybridization, a series of calculations have been performed in distorted methyl acetylene, with the $\mathrm{C{\equiv}C{-}CH_3}$ angle varying from 0° to 60°. The values of the antisymmetric components for the shielding tensors of both triply bonded carbons, as a function of the $\mathrm{C{\equiv}C{-}CH_3}$ angle, are given in Table 4. It is apparent from the table that the antisymmetric components increase with the angle between the single bond and the triple bond. As was predicted by Hansen and Bouman,[41] an angularly distorted multiple bond introduces large antisymmetric terms in the shielding tensor. These antisymmetric terms originate in strongly interacting $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ excitations involving σ bonds that are distorted.

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Table 5. Comparison of the DFT/BYLP and CASSCF Optimized C−C Distances in Benzynes[a]

	DFT/BYLP/D95**	CASSCF(8,8)/DZP
	o-benzyne	
$C_1-C_{1'}$	1.270	1.262
C_1-C_2	1.401	1.406
C_2−C3	1.431	1.397
$C_3-C_{3'}$	1.421	1.426
	m-benzyne	
C_1-C_2	1.382	1.384
C_1-C_3	1.389	1.387
C_3-C_4	1.422	1.403
	p-benzyne	
C_1-C_2	1.366	1.387
$C_1-C_{1'}$	1.493	1.415

[a] All values in angstroms. Numbering scheme used and values for CASSCF(8,8)/DZP are taken from ref 43.

DFT Geometries, Energies, and IR Frequencies of Benzynes. The extraordinary agreement between the experimental chemical shift tensor principal values and the calculated values using the DFT method in *o*-benzyne led us to explore the question of how universal this success may be. A full study of this matter is outside of the scope of this paper, but the DFT reliability in reproducing other properties of benzynes will be discussed briefly.

The C≡C bond distance is not a sensitive indicator because almost all the calculated values presented here and elsewhere[11,15,43] are in reasonable agreement with our experimental estimate. Note that the lack of information on the *J* coupling constants in *o*-benzyne prevents a refinement of our estimate of the C≡C bond distance to a point which would allow discrimination among the different calculated values. Nevertheless, as shown in Table 5, our calculated bond distances for *o*- and *m*-benzyne using the DFT/BYLP/D95** are in good agreement with those recently reported by Lindh *et al.* using the CASSCCF(8,8)/DZP method.[43] The agreement in the case of *p*-benzyne, however, is not as good, especially for the $C_1-C_{1'}$ bond.

Extensive theoretical studies have been completed on the IR spectrum of *o*-benzyne. The DFT method was used to calculate the harmonic frequencies of *o*-benzyne. The DFT result for the "triple" C−C symmetric stretch is 1919 cm^{-1}, in good agreement with the best theoretical estimate (full CAS MCSCF) of 1930 cm^{-1}. Moreover, assuming that the anharmonic correction for the DFT method is similar to the one for the MCSCF, a DFT frequency of 1884 cm^{-1} is obtained. This is in better agreement with the experimental value of 1846 cm^{-1} than any other calculated value, except for Pulay's UNO CAS value of 1816 cm^{-1}.[44] This later result has been scaled by the empirical factors chosen such that the theoretical results reproduce the experimental vibrational spectrum of benzene.

The other piece of relevant experimental information available on the benzynes is the energy differences between the three isomers: *o*-benzyne, *m*-benzyne, and *p*-benzyne. A recent CASSCF study has shown that this method is able to reproduce well the experimental values.[45] Therefore, DFT geometry optimizations were completed on all three isomers in order to determine these energy differences. Shown in Table 6 is a comparison of the CASSCF results, the values estimated using the DFT/BYLP method and the experimental values. The DFT results agree with the experimental values as well as the highly correlated methods discussed by Lindh *et al.*[43]

Table 6. Comparison of the Energy Differences between Isomers of Benzyne[a]

	ortho−meta	meta−para	ortho−para
exptl[b]	15.3	15.4	30.7
DFT/BYLP	10.3	18.1	28.4
CASSCF(8,8)[b]	16.62	10.88	27.50
CASPT2[g1][b]	12.19	14.66	26.85

[a] All values in kcal/mol. [b] From ref 43.

These results are a clear indication that the agreement between the calculated and experimental chemical shift values is not fortuitous but reflects the ability of DFT to reproduce the highly correlated electronic structure of the benzynes. Even in the cases of *p*- and *m*-benzyne, which have more biradical character than *o*-benzyne, it appears that DFT/BYLP compares favorably with recent CASSCF results.[43]

Conclusions

In summary, the bond length and the chemical shift tensor are reported for *o*-benzyne-*1,2*-$^{13}C_2$ isolated in an argon matrix at a temperature of approximately 20 K. The bond length of 1.24 Å is in good agreement with that predicted by theory, especially by techniques which include correlation effects. The orientation of the chemical shift tensor is similar to that for a triple bond, with the lowest chemical shift (73 ppm) being nearly along the "triple" bond axis and the two largest chemical shifts (266 and 240 ppm) being perpendicular (or nearly perpendicular) to this bond. There are significant differences, however, between the principal values in *o*-benzyne and a normal linear triple bond. Theoretical calculations show that these differences are not a function of the bond length but are related to the strain in the bonds of the carbon due to the deviation from linearity.

GIAO calculations of the chemical shift tensor were completed at different levels of theory: SCF, MP2, and DFT. The results using DFT are in much better agreement with the experimental values than those for SCF or MP2 calculations, as expected due to the biradical nature of *o*-benzyne. It is also shown that the DFT method is also able to reproduce the structure and the IR vibrational frequencies of *o*-benzyne along with the energy differences among *o*-, *m*-, and *p*-benzyne as well as the CASSCF method. These successes on a broad front suggest that the DFT approach properly describes the electronic structure of the three benzynes.

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