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Infrared Spectrum of *o*-Benzyne: Experiment and Theory

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Abstract: The complete set of vibrational frequencies and absolute infrared intensities has been determined for *o*-benzyne and two of its isotopomers: C_6D_4 and 1,2-$^{13}C_2C_4H_4$. In addition, for the majority of the transitions symmetries were assigned from infrared linear dichroism of the matrix-isolated samples, photooriented with polarized light during several photochemical transformations. Thermal relaxation of the high static pressure created by the initial photofragmentation causes dramatic changes of the fine site structure of each band of *o*-benzyne and results in a single-site infrared absorption spectra. A high-resolution, single-site vibrational spectrum was also obtained independently from laser hole-burning experiments. Band-shape analysis in different inert gas matrices (Ne, Ar, Xe, N_2, and CO) greatly facilitates the correlation of isotopomer bands with those of unlabeled *o*-benzyne. The triple bond stretching vibration appears at 1846 cm^{-1} in a Ne matrix, with an experimental absolute intensity of 2.0 ± 0.4 km/mol in the unlabeled *o*-benzyne and is polarized along the symmetry axis. It is red-shifted by 2 cm^{-1} in the perdeutero-*o*-benzyne and by 53 cm^{-1} in the doubly ^{13}C-labeled compound, in very good agreement with our theoretical prediction (MP2/6-31G**) and previous gas-phase data for *o*-benzyne.

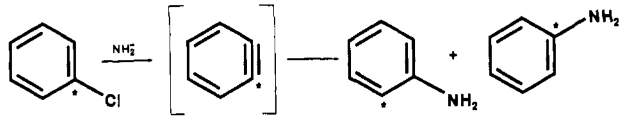
Introduction

In 1902 Stoemer and Kahlert reported treatment of 3-bromobenzofuran with strong base in the presence of alcohol yields 2-ethoxybenzofuran.[1a] They suggested the intermediate in the reaction might be didehydrobenzofuran which appears to be the first mention of the intermediacy of an aryne in the chemical literature and makes arynes one of the oldest reactive intermediates proposed in organic chemistry. Benzyne itself was first suggested as an intermediate in 1930.[1b] In 1953 Roberts' experiments on the conversion of ^{14}C-labeled chlorobenzene to aniline gave strong support to the intermediacy of *o*-benzyne (**1a**) in this and related reactions.[2] He found that treatment of [1-^{14}C]chlorobenzene with potassium amide gives a 1:1 mixture of [1-^{14}C]- and [2-^{14}C]aniline. Numerous other experiments have implicated the intermediacy of benzyne in a wide range of reactions.[3,4] It has also been studied extensively theoretically.[5]

Although additional direct evidence for the existence of benzyne was provided by the observation of its UV and mass spectra,[6,7] it was not until 1973 that direct spectroscopic proof was obtained for its existence as an observable reaction intermediate. Using a photochemical reaction, Chapman was able to prepare *o*-benzyne in a matrix at 77 K and to observe its infrared spectrum.[4b] In a subsequent paper Chapman assigned a band at 2085 cm^{-1} to the triple bond stretch in *o*-benzyne,[4c] and his assignment was later supported by others.[4f,h] In particular Wentrup[4h] assigned a band observed at 2080 cm^{-1} to the triple bond in *o*-benzyne in a matrix of phthalic anhydride at 77 K. By careful warming of the matrix he was able to separate this band from that of another species which absorbed at 2080 cm^{-1}, which he suggested might be due to cyclopentadienylideneketene. Normal coordinate analyses gave support to the assignment of the band observed at 2080 cm^{-1} to the triple bond in 1a.[8] Of the 20 IR allowed transitions, 12 bands have been previously reported for **1a**, including two matrix-isolated water peaks, and 11 for C_6D_4 (**1b**).[4f]

In contrast to matrix experiments Leopold, Miller, and Lineberger,[9] in a recent study of the gas-phase electron photodetachment spectrum of **1a**, have assigned its triple bond stretch to a feature at 1860 cm^{-1}. Prompted by disagreement between the experimentalists, Schaefer[5k] carried out extensive calculations on the vibrational spectrum of *o*-benzyne. After a careful analysis of results at several levels of theory, he concluded that the triple bond stretch of *o*-benzyne should lie in the range of 1965–2010 cm^{-1} and questioned the earlier assignments of it in the vicinity of 2085 cm^{-1}. Very recently Schweig was able to show the band at 2087 cm^{-1} was indeed not due to *o*-benzyne but rather to cyclopentadienylideneketene.[4a]

Scheme I



Experimental Section

Samples isolated in Ne, Ar, Xe, N_2, and CO were used (the matrix ratio was higher than 1300:1). All IR spectra were recorded on a Nicolet 60-SXR FTIR with 0.25-cm^{-1} resolution.

Matrix samples were prepared on CsI or CaF_2 spectroscopic windows mounted on a cold tip of the closed-cycle helium refrigerator systems: either a two-stage 10 K Displex (Air Products) or a three-stage 4 K Heliplex (APD Cryogenics). The following lasers were used as photo-

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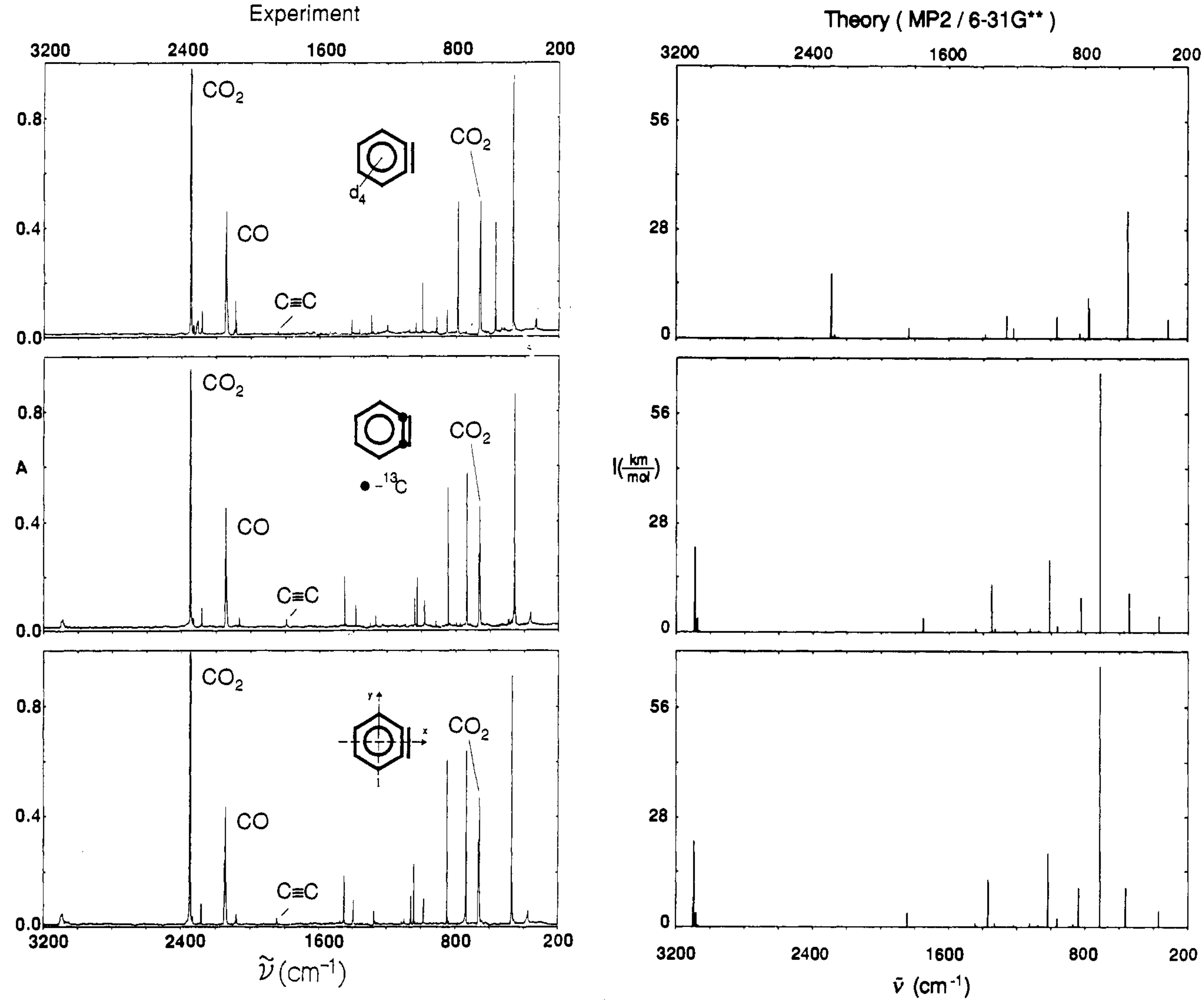

Figure 1. Infrared absorption spectrum of *o*-benzyne (bottom, left), 1,2-$^{13}C_2C_4H_4$ (center, left), and C_6D_4 (top, left) isolated in a Ne matrix. Peaks on the right side of ν_1 of CO_2 originate from naturally abundant $^{13}CO_2$ and $C^{16}O^{18}O$. The peak in the region 2090–2060 cm^{-1} is due to a trace of **3**. Residual amount of **2** was removed from the spectrum by computer subtraction: computed (MP2/6-31G**) spectra of **1a** (right, bottom), **1b** (right, center), and **1c** (right, top). All calculated frequencies were scaled by an arbitrary factor of 0.94 in these plots.

chemical light sources: Lambda Physik, pulsed excimer (KrF, 248 nm; XeCl, 308 nm; and XeF, 351 nm); output from the Coherent 699-21 cw ring dye laser, doubled R6G (282 nm) and doubled DMC (348 nm). For unpolarized irradiations a scrambler was inserted into the cw laser beam, and for polarized irradiations a Glan-Thompson polarizer was used with excimer light. Typically we used between 0.5 and 1.2 W of average power for irradiation of the sample. A high degree of conversion was achieved with very long (10–20 h) irradiation times.

In the IR polarization measurements performed on partially oriented samples we have used IGP-225 (KRS-5), IGP-227 (CaF_2), or IGP-223 (PE) wire grid polarizers (Cambridge Physical Sciences). For frequencies below 400 cm^{-1} we have used as a detector a helium-cooled Si bolometer and CsI beamsplitter. A high sensitivity, narrow-range MCT detector and a CaF_2 beamsplitter were employed in order to record very weak bands in the 3300–1800-cm^{-1} region.

UV-visible spectra were recorded using a Varian Cary 2300 spectrophotometer.

Precursors for **1b** and **1c** were obtained by dehydration of phthalic acid-α,α'-^{13}C and of phthalic-*3,4,5,6-d*$_4$ acid (both MSD, 99% isotopic purity) with acetic anhydride.

Results and Discussion

Given the great interest in *o*-benzyne, we decided to undertake an extensive matrix isolation study of *o*-benzyne, as well as to interpret its spectrum with the assistance of ab initio calculations. While Schaefer's earlier calculations[5k] were extremely useful in this latter regard, we realized that the isotopomers he calculated would not really aid in the definitive assignment of the triple bond stretch of *o*-benzyne. Consequently, we repeated the vibrational calculations for *o*-benzyne and a number of isotopomers at the MP2/6-31G** level.[10] We found that the calculated spectrum of the 1,2-di-^{13}C (**1b**) isotopomer of *o*-benzyne predicts a large shift for its triple bond stretch relative to that of the parent system (see below). Our calculations for the parent system as well as for the **1c** isotopomer compare very favorably with Schaefer's MP2/DZ+P results.

Figure 1 presents the IR spectra of **1a**, **1b**, and **1c** isolated in the Ne matrices. The samples of each of the isotopomers, along with CO and CO_2, were obtained in two photochemical steps (see reaction scheme). In the first, phthalic anhydride (**2**) was completely (>99%) decomposed to a mixture of *o*-benzyne and cyclopentadienylideneketene[11] (**3**) by irradiation at 308 nm. Subsequent irradiation at 282 nm led to complete (>99%) conversion of **3** back to **1** without decomposition of **1**. Prolonged irradiation

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(10) All vibrational calculations were carried out with the program CADPAC: Amos, R. D., Rice, J. E., issue 4.0, Cambridge, 1987.

(11) We have recorded spectra of **3a**, **3b**, and **3c**. Cumulative double bond stretch (=C=C=) in **3a** was found in Ne matrix at 2085 cm^{-1}, in **3b** at 2068 (Δ = 17) cm^{-1}, and in **3c** at 2091 (Δ = −6) cm^{-1}. Theory, in the harmonic approximation (SCF/6-31G*), predicts this vibration at 2439, 2415 (Δ = 24), and 2438 (Δ = 1) cm^{-1}. Due to the site splitting, in the spectra of all of the isotopomers this absorption appears as a complicated multiplet, which changes substantially its line shape upon the change of the guest material. A full report of our investigation of **3** will be given: Radziszewski, J. G.; Hess, B. A., Jr., submitted for publication.

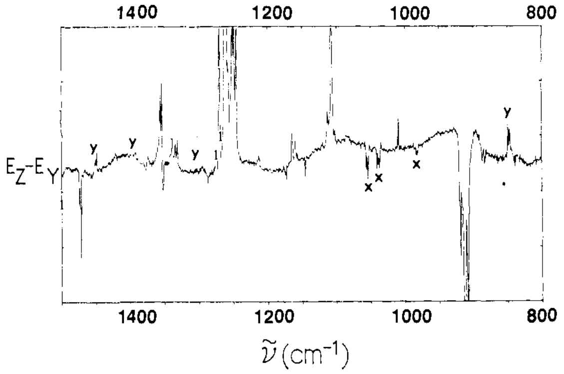
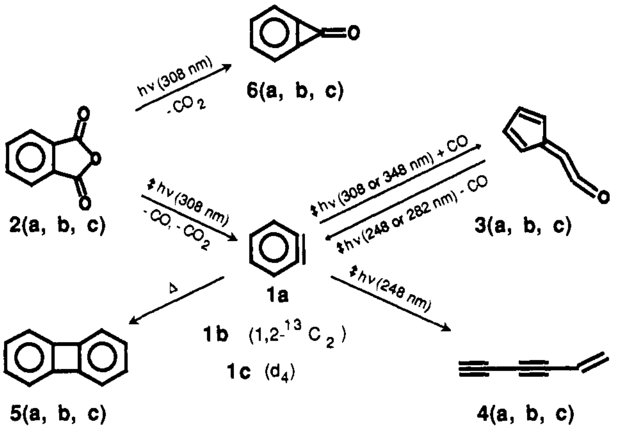


Figure 2. Segment of a difference ($E_Z - E_Y$) between polarized infrared absorptions obtained after polarized irradiation at 248 nm of Ne matrix containing **1a** and **2a**. Bands originating in **1a** are marked with appropriate polarizations. Remaining bands belong to **2a** or **3a**.

Scheme II



‡ indicates plane polarized light

of **1** at 248 nm transforms it to hex-1-ene-3,5-diyne[12] (**4**), whereas the irradiation of **1** at 348 nm produces **3**[13] (CO is present in the matrix). All three spectra presented in Figure 1 were obtained under nearly the same photochemical conditions. By careful and repetitive monitoring the kinetics of formation and decay of various spectral features simultaneously in both the IR and UV[14] regions, we were able to separate the transitions belonging to **1** from those due to other species[15] in a unique fashion.

The symmetries of all but the four weakest transitions were obtained from dichroic IR spectra measured on photooriented[16] samples. Irradiation of **2** with polarized light at 308 nm induces a small positive linear dichroism for the $C\equiv C$ stretch[17] (x,a_1) as well as for all the remaining IR transitions of **1** directed along the symmetry axis. All other transitions of **1** (z, b_1; y, b_2) show negative dichroism. Irradiation of **2** with polarized light at 248 nm results in a change of sign of the dichroism for all but the out-of-plane transitions of **1**, giving a basis for the unique assignment. An example of the polarized IR spectra is given in Figure 2 in the form of a difference between the absorptions ($E_Z - E_Y$) obtained along the direction of the electric vector of light (248 nm) used in this phototransformation and in the direction perpendicular to it. We need to stress that the degree of photoinduced infrared dichroism of **1** was always small. The dichroic ratios d, $d = E_Z/E_Y$ were typically equal to 0.94 and 1.05. Our confidence of symmetry assignments is based on numerous repetitions of the experiment.

For each band of **1**, the absolute intensity has been determined using bands of concurrently generated CO (2144 cm^{-1}) and CO_2 (2348 and 661 cm^{-1}) as internal standards. The absolute intensities for CO and CO_2 were determined, in separate experiments, using a quartz microbalance and laser interference techniques.[18] In the Ne matrix, we have obtained values of 485 ± 15 km/mol for the band at 2348 cm^{-1} and 62 ± 2 km/mol for the band at 661 cm^{-1} of CO_2 and 64 ± 2 km/mol for the band at 2144 cm^{-1} of CO. The latter can be compared with the value of 66.5 ± 2.4 km/mol obtained from the Ar matrix.[19] The ratio of integrated intensities of CO vs CO_2 bands (including the bands due to naturally abundant isotopes) is not significantly affected by the presence of **1**.

Integrated intensities were determined using three half-widths at half-height as integration limits on each side of the center of a peak. In a few cases of overlapping bands a simple deconvolution procedure was applied in order to obtain precise integrated intensities of each component.

After initial irradiation of **2** or its isotopomers under higher resolution (0.25 cm^{-1}), each IR absorption of **1a**, **1b**, and **1c** appears as a multiplet, with the largest splittings in Ar matrices (0.3 to 3 cm^{-1}). An example of such a spectrum is shown at the bottom of Figure 3. Matrix warmup to ~13 K results in a dramatic intensity exchange between components in each multiplet originating in **1**, CO or CO_2, but not for other species present (Figure 3, top). These changes could be attributed to the release of high hydrostatic pressure exerted on **1** by CO and CO_2 molecules or perhaps could be explained in terms of a dissociation process of pressure-induced van der Waals complex of **1** with CO or CO_2. Use of this phenomenon dramatically increases the spectral resolution and was utilized to separate transitions in congested regions (e.g., C–H stretches).

As was described above, laser irradiation of **1a**, **b**, or **c** in Ar, N_2, and Xe matrices at 248 or 348 nm transforms it to other species. The rate of conversion is different for molecules of **1** trapped in different sites. For instance, monochromatic light at 348 nm causes faster conversion of **1c** in site B than in site A (Figure 4). Similar site dependence is observed in all other photochemical steps described in this paper. Effectively, the hole burning in electronic absorptions of **1**, **2**, and **3** results in semi-single-site infrared spectra, in which the line width is limited by instrumental resolution.

The results obtained in the Ne, Ar, Xe, N_2, and CO matrices for all three isotopomers allow for a clear-cut separation of the matrix site splittings from overlapping vibrations. In addition, Ne matrices, besides being of superior optical quality, offer a few cm^{-1} blue shift for most of the vibrations in the 1500–3500-cm^{-1} region. In this case, site- and Fermi-resonance patterns, and the

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[12] **4** was identified by comparison of its UV (Ar matrix, 10 K: 275, 260, 246, 234, and 223 nm) and IR (3324, 2250, 1615, 1243, 972, 630, and 615 cm^{-1}) absorption with the literature data: Böhm-Gössl, T.; Hunsmann, W.; Rohrschneider, L.; Ziegenbein, W. *Chem. Ber.* **1963**, *96*, 2504.

[13] From a kinetic study of the photodecomposition of **2** we have determined that **3** is formed by photocarbonylation of **1** and is not an intermediate in the conversion of **2** to **1**. We have observed at least one other carbonyl-containing compound and its two corresponding isotopomers. The carbonyl absorption of the unlabeled compound was found at 1852 cm^{-1}. It was red shifted (8 cm^{-1}) to 1844 cm^{-1} in 1,2-di-^{13}C labeled compound and blue shifted (-2 cm^{-1}) in the perdeuterated species. The position of this band and the isotopic shifts of the isotopomers as well as the remainder of the spectra compare favorably with the calculated (SCF/6-31G*) spectra of benzocyclopropenone (**6a**, 2089 cm^{-1}) and its isotopomers (**6b**, 2082 cm^{-1} and **6c**, 2088 cm^{-1}). We should emphasize that under all examined experimental conditions **6** was generated only in very small quantities and only in the early stages of irradiation. In order to eliminate the possibility that this compound was produced from an impurity of **2**, anhydrides **2**(**a**, **b**, and **c**) were sublimed, under high vacuum, four times immediately before sample preparation. Presumably **6** is formed in a "cage-induced" reaction which occurs only for those molecules of **2** trapped in specific sites where "crowding" does not allow for **1** and CO to exist separately.

[14] The lowest energy electronic absorption of **1a** and **1c** isolated in the Ne matrix (3.8 K) occurs at 348.0 nm (I = 170 km/mol) and at 347.3 nm in **1b**.

[15] After warming the matrix to 38 K we have observed directly the formation of biphenylene (**5**), which obeyed second-order kinetics.

[16] Thulstrup, E. W.; Michl, J. *Elementary Polarization Spectroscopy*; VCH Publishers: New York, 1989.

[17] Note the $C\equiv C$ stretch is polarized along the x axis as expected for a *cis*-bent acetylene.

[18] C. Lu In *Methods and Phenomena, Their Applications in Science and Technology*; Volsky, S. P., Czanderna, A. W., Eds.; Elsevier: Amsterdam, 1984; Vol. 7, p 19.

[19] Jiang, G. J.; Person, W. B.; Brown, K. G. *J. Chem. Phys.* **1975**, *62*, 1201.

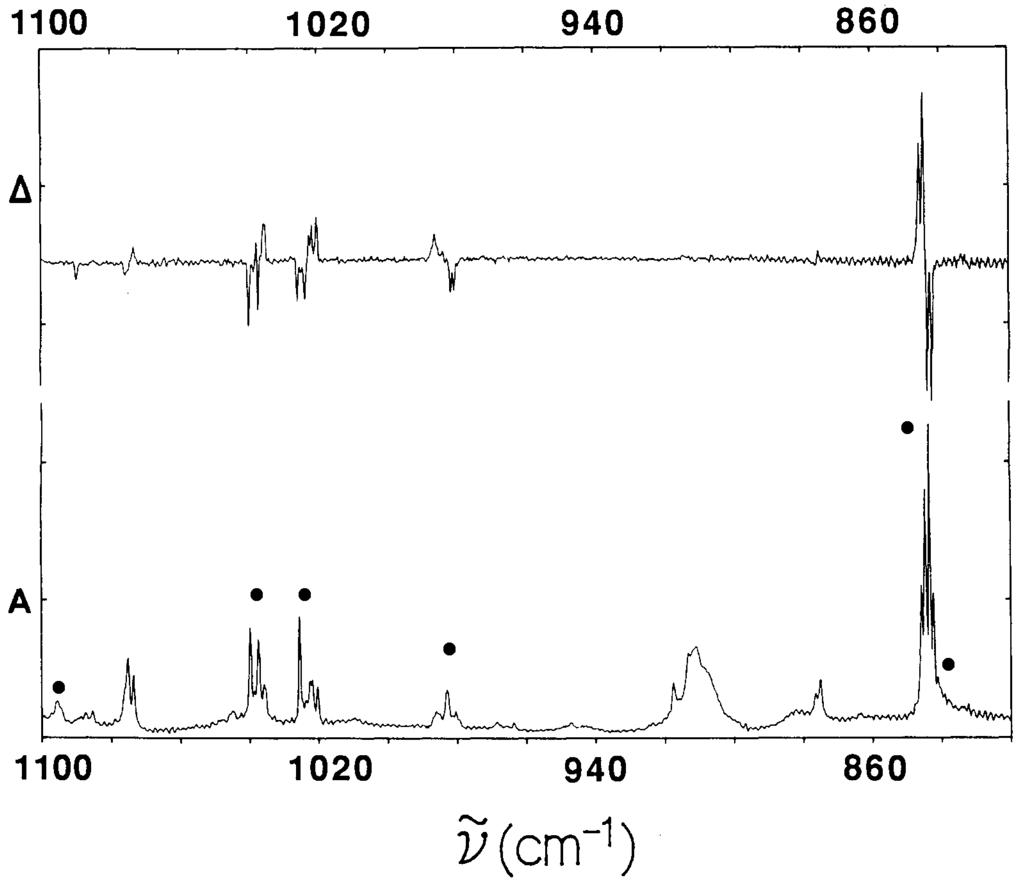

Figure 3. Segment of a difference spectrum between absorptions measured after initial irradiation of a Ar matrix containing **1b** (marked by dots), **2b**, and **3b** at 308 nm, at 10 K, and after a matrix warmup to 13 K (top). Initial spectrum is presented in the bottom of the figure.

Table I. IR-Active Vibrations of *o*-Benzyne[a]

	C_6H_4				$1,2\text{-}^{13}C_2C_4H_4$						C_6D_4						
	exptl		calcd		exptl			calcd			exptl			calcd			
sym	$\tilde{\nu}$	I	$\tilde{\nu}$	I	$\tilde{\nu}$	(Δ)	I	$\tilde{\nu}$	(Δ)	I	$\tilde{\nu}$	(Δ)	I	$\tilde{\nu}$	(Δ)	I	assignment
a_1	3094	5.7	3291	5.4	3093	(1)	5.1	3291	(0)	5.4	2311	(783)	4.7	2440	(851)	5.4	CH str
	3071	0.9	3268	3.5	3070	(1)	0.8	3268	(0)	3.5	2295	(776)	0.3	2415	(853)	0.5	CH str
	1846	2.0	1961	3.3	1793	(53)	1.8	1889	(72)	3.4	1844	(2)	0.4	1955	(6)	2.5	CC str
	1415	0.1	1528	0.4	1414	(1)	0.1	1525	(3)	0.3	1364	(51)	1.0	1475	(53)	1.1	ring str and CH def
	1271	1.3	1410	0.8	1266	(5)	1.9	1410	(0)	0.9	1198	(73)	2.6	1295	(115)	2.6	ring str and CH def
	1055	7.4	1196	0.7	1040	(15)	7.0	1196	(0)	0.9	853	(202)	3.9	862	(334)	0.2	CH def
	1039	10.4	1086	18.7	1024	(15)	9.5	1070	(16)	18.5	995	(44)	5.9	1025	(61)	5.6	ring str
	982	5.2	1023	2.2	981	(1)	5.5	1022	(1)	1.6	792	(190)	4.3	824	(199)	7.7	ring str
	589	0.1	615	0.1	586	(3)	0.1	608	(7)	0.1	579	(10)	0.1	595	(20)	0.1	ring def
b_1	838	0.3	895	0.5	835	(3)	0.3	895	(0)	0.6	679	(159)	0.1	718	(177)	0.1	CH wagging
	737	47.4	753	66.3	736	(1)	43.7	752	(1)	66.5	571	(166)	23.5	584	(169)	32.7	CH wagging
	388	4.2	387	4.0	383	(5)	4.0	385	(2)	3.8	336	(52)	4.2	337	(50)	4.8	ring torsion
b_2	3086	9.1	3287	21.7	3085	(1)	8.6	3287	(0)	21.7	2314	(772)	5.8	2435	(852)	17.0	CH str
	3049	0.6	3254	0.3	3049	(0)	0.5	3254	(0)	0.3	2285	(764)	0.1	2398	(856)	0.1	CH str
	1451	9.1	1530	0.6	1450	(1)	11.2	1527	(3)	0.9	1411	(40)	3.0	1492	(38)	0.3	ring str
	1394	5.5	1448	12.4	1385	(9)	4.9	1438	(10)	12.2	1293	(101)	2.5	1342	(106)	5.9	ring str and CH def
	1307	0.2	1297	0.1	1298	(9)	1.0	1284	(13)	0.4	1112	(195)	0.2	1011	(286)	0.3	ring str and CH def
	1094	1.3	1140	0.5	1092	(2)	1.1	1138	(2)	0.4	875	(219)	0.1	882	(258)	1.3	ring str and CH def
	849	24.8	882	10.0	846	(3)	23.8	876	(6)	8.9	790	(59)	26.4	826	(53)	10.6	ring def
	472	81.0	592	10.2	457	(15)	77.2	575	(17)	9.9	469	(3)	79.1	584	(8)	8.9	ring def

[a] $\tilde{\nu}$ in cm^{-1}; I, absolute intensity in km/mol; all observed and calculated (unscaled) isotopic shifts (Δ, in cm^{-1}) are to the red.

position of strong carbonyl absorptions in **2**, are substantially changed and shifted in Ne by about 10 cm^{-1}; thus allowing for the easy detection of the weak triple bond stretch in **1**. In an Ar matrix, this small but important range was blocked from observation and became accessible only after a very high degree of conversion of **2**.

Table I presents a comparison between experimental and theoretical data for **1a**, **1b**, and **1c**, and complete symmetry assignments of all of the IR-active transitions of **1**. The assignment is based on the comparison of our experimental and computational (MP2/6-31G**)[10] results for the energies, polarizations, frequency shifts, and absolute intensities of transitions of **1** and its two isotopomers, **1b** and **1c**. The fact that we were able to obtain experimental polarizations of most of the observed transitions allowed us to compare the experimental and calculated frequencies separately for each type of symmetry (a_1, b_1, and b_2). Such a comparison is depicted in Figure 5 for *o*-benzyne and perdeuterated *o*-benzyne. This method greatly simplifies the correlation between calculated and experimental results. Such a technique should prove to be generally very useful in the interpretation of the

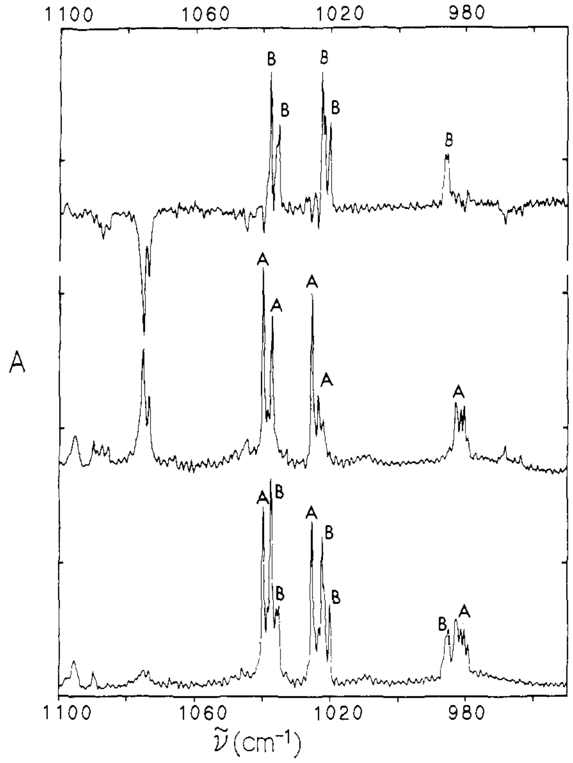

Figure 4. Hole-burning in electronic absorption of **1c** at 348 nm results in its semi-single-site infrared spectra. The absorption of **1c** in site A is presented in the center and in site B at the top of the figure. The top trace was obtained as a difference between the initial spectrum (bottom) and the one measured after irradiation (center).

vibrational spectra of larger molecules.

The triple bond stretch is assigned to a band at 1846 cm^{-1}, with an intensity of 2.0 ± 0.4 km/mol in **1**. This band is shifted to the red by 2 cm^{-1} in **1b** (to 1844 cm^{-1}) and by 53 cm^{-1} in **1c** (to 1793 cm^{-1}), in very good agreement with our calculations and earlier gas-phase data.[4] This assignment is in disagreement with a prediction[5k] that the harmonic triple bond stretch should lie in the range of 1965–2010 cm^{-1}. However, this prediction was based on comparison of the experimental and calculated frequencies for the triple bond stretch in acetylene. Given the unusual geometry of the triple bond in *o*-benzyne, we suggest that the triple bond stretch in acetylene is not an appropriate model for *o*-benzyne. The observed transition frequency for the "triple bond" stretch in *o*-benzyne lies almost halfway in between a pure double (ethylene: 1655 cm^{-1}) and triple (acetylene: 1974 cm^{-1}) bond. We note that MP2-6-31G** calculations overestimate the double bond stretch in ethylene by 61 cm^{-1}.[20]

Additional clear-cut assignments are given in Table I. The highly mixed nature of the remaining normal modes prevents their description in a straightforward and unique way. However, a detailed description of these in terms of dominant contributions to diagonal potential energy distribution can be found in Tables II and III of ref 5k.

In the a_1 symmetry block all nine fundamentals have now been observed. Six of them were not reported previously in matrix isolation studies. Both CH and CD stretches were resolved. The triple bond vibration was discussed above. We did not observe any of the bands close to 1600 cm^{-1} which were previously reported. We suspect that they originated from matrix-isolated water. Presumably, the confusion came from the fact that the infrared spectrum of matrix-isolated water changes dramatically upon ultraviolet irradiation. The agreement between observed and computed positions and isotopic shifts for both a very weak ring stretch mixed with CH deformation, at 1415 cm^{-1}, and ring deformation at 589 cm^{-1} leaves no doubt about these assignments. The same holds for the ring stretches at 1039 and 982 cm^{-1}. However, the proposed fundamentals at 1271 (ring stretch and CH deformation) and 1055 cm^{-1} (CH deformation) are more problematic. The proximity of the latter one to the ring stretch at 1039 cm^{-1} and the large discrepancy between its experimental and calculated frequency and isotopic shifts leads us to consider the two following possibilities; either the theory, in this approximation, is unable to account for the unusual nature of this strained ring, or there is a more trivial reason, such as Fermi resonance. After all, the combination of the ring torsion at 388 cm^{-1} with a wagging at 737 cm^{-1} in **1a** would give an a_1 band at approximately the right frequency to fall into Fermi resonance with a fundamental calculated at 1196 cm^{-1}. But such reasoning is immediately inconsistent with the observed shift in **1b**. In addition, inspection of the line shapes in Figure 6 leads us to choose the first alternative

In the b_1 symmetry block, both frequencies and isotopic shifts of the ring torsion at 388 cm^{-1} and a CH wagging at 838 cm^{-1}, which were not observed before, as well as the CH wagging at 737 cm^{-1} are well reproduced by theory.

Of all eight fundamentals of b_2 symmetry now observed, four are reported for the first time. Again, CH and CD stretches were resolved. The assignments of the three ring stretches coupled with ring deformations at 1394, 1307, 1094 cm^{-1} and of the ring deformation at 848 cm^{-1} are straightforward. The position of the b_2 ring deformation at 472 cm^{-1}, substantially shifted in **1** in comparison to benzene (604 cm^{-1}) and to all available theoretical predictions, could be a manifestation of ring "flexing" by the triple bond or is due to the lack of anharmonic corrections in our treatment. The symmetries of vibrations at 1394, 1011, and at 882 cm^{-1} were previously incorrectly assigned to a_1 symmetry.[5k]

Of the 11 bands reported[4f] for **1c**, five could not be confirmed in this study. They originate from **3c**.[11]

Introduction of the ^{13}C labels in **1b** turned out to be particularly beneficial. It represents a highly localized vibrational perturbation. It affects strongly only one vibration, the C≡C stretch, thus allowing for its definitive assignment. It has a small, but measurable influence on the reminder of the spectrum. Since the nature of the normal modes in **1b** is basically unchanged, the correlation with corresponding modes of unlabeled *o*-benzyne and also between experiment and theory becomes trivial and unique.

In addition to the bands listed in Table I, we have observed a number of very weak transitions definitely originating from **1**. A broad band at 1587 cm^{-1} in **1a** (shifted in **1b** to 1584 cm^{-1}, and **1c** to 1538 cm^{-1}) could be a combination between 849 and 736 cm^{-1}, but then the origin of its partner in **1c** is difficult to explain. It is much too high for that calculated at 1528 cm^{-1}, an a_1 ring stretch mixed with a CH deformation, although the magnitude of isotopic shifts would be correct. The additional argument for rejecting it as candidate for a fundamental comes from the agreement between calculated and observed frequencies, intensities and isotopic shifts for the 1415-cm^{-1} vibration. In particular, the increase of observed intensity upon deuteration is well predicted by the theory.

A few more weak bands of **1** were observed at the following frequencies: 1172, 1031 (also 1031 cm^{-1} in **1b**), 1016 (also 1016 cm^{-1} in **1b**), and 783 shifted to 775 cm^{-1} in **1b**, and presumably to 760 cm^{-1} in **1c**. In **1c**, the band at 1283 cm^{-1} could not be easily proposed as an alternative to any fundamental vibration.

Finally, we note that on irradiation of phthalic anhydride in a nitrogen matrix a diazo compound is formed. This might arise from the formation of cyclopentadienylidenecarbene and its subsequent addition to molecular nitrogen. Some support is provided for this in that in other matrices a few bands are observed which might be due to cyclopentadienylidenecarbene.[21]

Conclusions

Clearly, only the combined use of high-resolution, single-site infrared spectra, with isotopic shifts, calculated frequencies, and

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(20) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.

(21) See Burton, N. A.; Quelch, G. E.; Gallo, M. M.; Schaefer, H. F. *J. Am. Chem. Soc.* **1991**, *113*, 764, for a recent theoretical study of cyclopentadienylidenecarbene.

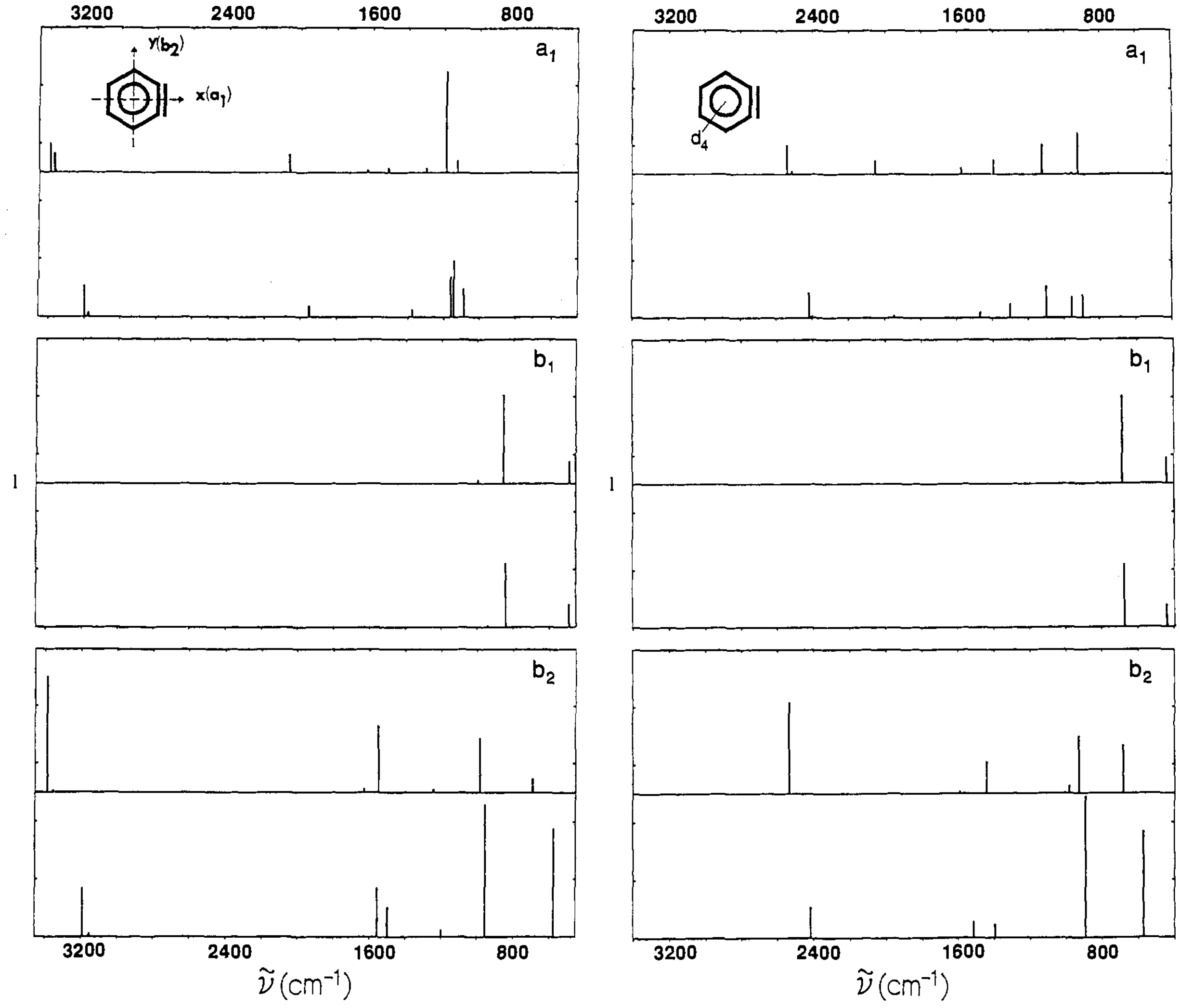

Figure 5. Comparison of experimental (bottom part for each symmetry species) and theoretical spectra (top) of *o*-benzyne (left) and perdeutero-*o*-benzyne (right) classified by symmetry. No frequency scaling was applied.

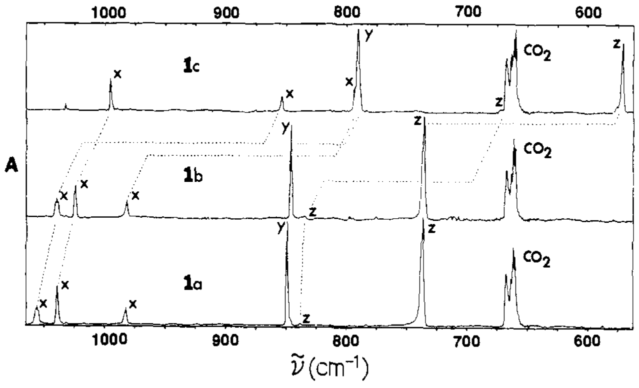

Figure 6. Segment of finger-print region of the IR spectra of *o*-benzyne (bottom), 1,2-$^{13}C_2C_4H_4$ (center), and perdeutero-*o*-benzyne (top). The dashed lines indicate proposed correlation between absorption of isotopomers.

experimental symmetries as well as line shapes and in part intensities has allowed definitive assignments for the infrared spectrum of *o*-benzyne. For molecules of the size considered here, the quality of theoretical predictions of IR intensities even at our highest level (MP2/6-31G**) is not sufficiently good for use in definitive assignments. However, with an average ~25% deviation from the experimental values they can be used as supporting evidence in the assignments.

Before the definitive force field determination for **1** can be attempted Raman spectra have to be measured. This will provide the missing a_2 vibrations and hopefully confirm our assignments of the weakest bands in the infrared spectrum. Work in this area is in progress in our laboratory.

The fact that no "cyclohexatriene"-type bands are observed in *o*-benzyne suggests that the benzene π-electron delocalization in *o*-benzyne is preserved to a large extent. This is further supported by the computed structure and the coherence of the calculated and observed spectrum of **1**. Furthermore, the frequency of the now observed triple bond stretch (1846 cm^{-1}) indicates substantial loss of alkyne character in *o*-benzyne.

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Registry No. 1a, 462-80-6; **1b**, 121000-98-4; **1c**, 67356-66-5.