Communications to the Editor

Microwave Spectrum of Benzyne

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Although the concept of o-benzyne (1) as a reaction intermediate dates back at least 40 years[1,2] and it has been accepted for many years that o-C_6H_4 is a physically stable, if highly reactive, molecule, the characterization of benzyne in the gas phase by the methods of structural chemistry has remained elusive. Apart from the report of a featureless UV absorption[3] there is only the low-temperature matrix-isolated infrared spectrum[4] from which to infer a molecular structure.[5]


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We now wish to report the observation of the microwave spectrum of benzyne. As a culmination of numerous unsuccessful attempts over many years, weak lines were observed when benzocyclobutene-1,2-dione was pyrolyzed in a short quartz oven and the pyrolysate pumped through a short waveguide Stark cell. The rotational spectrum was simulated by using a published ab initio geometry.[6] The observed lines, their assignment, and the derived spectroscopic constants are listed in Table I. The transition frequencies are believed to be accurate to 50–60 kHz. Finally we have been able to detect the same weak lines where two other benzyne precursors—phthalic anhydride and triketohydrindene monohydrate (ninhydrin)—were used instead of the dione.

The spectral assignment is for a compound in a singlet electronic state. The small value of the inertial effect ($\Delta = +0.067$ uÅ^2) strongly indicates that the molecule is planar. The 6_{16}–5_{05} and 6_{06}–5_{15} transitions have relative intensities in the ratio 0.58 ± 0.05, consistent with the spin weighting for a molecule possesing two pairs of equivalent hydrogen nuclei. The presence of spin weighting in these *b*-type transitions indicates that the molecule has C_2 symmetry about the *b* principal axis. This is further supported by the fact that only *b*-type rotational transitions could be observed. The symmetry group of the molecule is therefore C_{2v}.

The conclusion that o-benzyne is the only compound compatible with the method of preparation employed, the deduced symmetry and planarity, and the observed rotational constants were reinforced from consideration of possible alternatives, viz., a number of potential pyrolysis products **2**–**7** of our precursors. Their rotational constants, based on chemically plausible geometries and the direction of the electric dipole moment, are given in Table II. Only those molecules possessing all three of the following properties have been considered: (i) planarity; (ii) C_{2v} symmetry; (iii) two pairs of equivalent hydrogen nuclei. Four of the alternatives have the dipole moment along the *a* axis and therefore would show a completely different type of spectrum. All of the other six molecules are expected to have rotational constants that differ significantly from the observed values. Smaller pyrolysis fragments than those considered here can be rejected, since their rotational constants would be even larger than those listed for cyclopentadiene carbene (**7**).

Table I. Observed Microwave Transitions and Derived Rotational Constants for o-Benzyne

transition $J_{K_{-1},K_{+1}} \leftarrow J'_{K'_{-1},K'_{+1}}$	obsd, MHz	obsd – calcd, MHz
$15_{9,6} \leftarrow 15_{8,7}$	27 590.48	0.0211
$12_{9,3} \leftarrow 12_{8,4}$	27 717.04	−0.0255
$4_{0,4} \leftarrow 3_{1,3}$	28 230.17	−0.0371
$14_{10,4} \leftarrow 14_{9,5}$	28 440.70	−0.0565
$16_{11,5} \leftarrow 16_{10,6}$	29 066.15	−0.0684
$19_{12,7} \leftarrow 19_{11,8}$	29 292.50	0.0493
$18_{12,6} \leftarrow 18_{11,7}$	29 868.00	0.0242
$18_{11,7} \leftarrow 18_{10,8}$	30 109.86	−0.0318
$10_{5,5} \leftarrow 10_{4,6}$	30 462.93	−0.0083
$14_{8,6} \leftarrow 14_{7,7}$	30 576.71	−0.0901
$20_{13,7} \leftarrow 20_{12,8}$	31 110.02	0.0172
$11_{8,4} \leftarrow 11_{7,5}$	31 801.34	0.1577
$6_{0,6} \leftarrow 5_{1,5}$	40 828.18	0.0143
$6_{1,6} \leftarrow 5_{0,5}$	40 830.00	0.0101

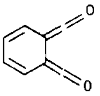
A, MHz	6989.665 (8)	D_{JK},[a] kHz	1.55 (1)
B, MHz	5706.759 (7)	d_2,[a] kHz	−0.241 (3)
C, MHz	3140.384 (4)	Δ,[b] uÅ^2	+0.0673

[a] Defined according to Watson[8] in the *S* reduced I^r representation. [b] Inertial defect: $\Delta = I_c - I_a - I_b$; conversion factor of 505 379.05 uÅ^2 MHz used.

Table II. Estimated Properties of Possible Pyrolysis Products

	rotational constants, MHz			dipole moment
molecule[a]	*A*	*B*	*C*	direction
1[b]	7049	5684	3147	*b* axis
2	1900	1200	740	*a* axis
3	5900	1700	1300	*a* axis
4	10000	1100	1000	*a* axis
5	9900	4700	3200	*a* axis
6	6300	3000	2100	*b* axis
7	10100	9100	4800	*b* axis

[a] Possible products alternative to o-benzyne:



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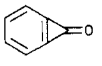

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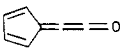

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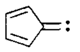
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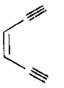
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[b] Properties derived from an ab initio geometry: Table Il in ref 6 (6-31G* basis set).

The predicted constants from the o-benzyne ab initio calculation agree to better than 1% with the observed values. We therefore conclude that the spectrum observed is that of o-benzyne in its singlet state and the lack of other unassigned lines is suggestive that the ground state of benzyne is singlet. There has been some mention in the literature, not supported by recent ab initio calculations, of a possible triplet ground state.[7] The chance that the chemically transient singlet species we have observed is in a metastable excited electronic state seems remote.

The species has a gas-phase lifetime at low pressures (~0.2 Pa) of considerably less than the cell residence time of about 1

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s. Even a small increase in the pressure in the cell leads to decreased line intensities, indicating rapid gas-phase dimerization. To the limit of our sensitivity no other lines were observed (apart from weak lines of the small amount of unpyrolyzed precursor).

Work is continuing to improve the sensitivity of the spectrometer to enable other isotopic species to be studied and the full geometry to be determined. The present observations are, however, consistent with the ab initio MO predictions of a short acetylenic C≡C bond rather than the cumulene structure sometimes suggested for benzyne.

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Registry No. Benzyne, 462-80-6.

A New Method for Studying Chain Conformation. Proof of Nonradial Binding to Micelles; Chain-Bending at an Enzyme Surface

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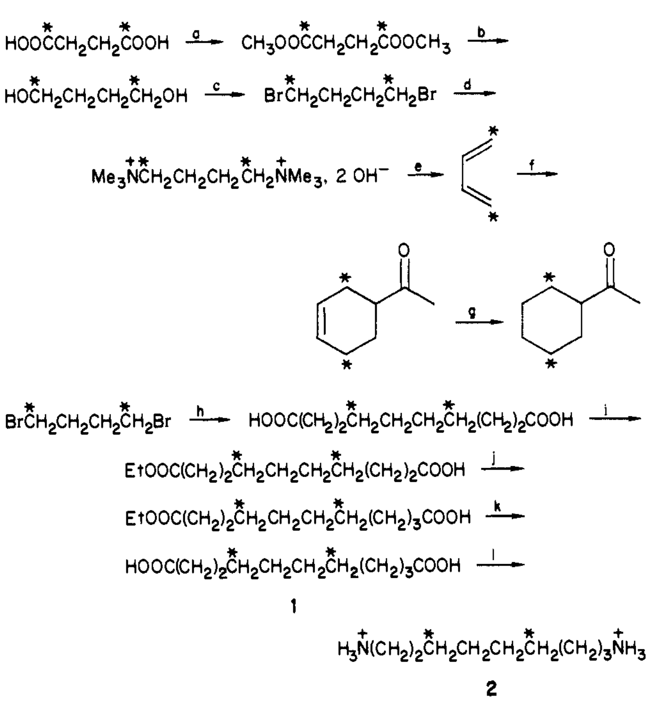
The ability of hydrocarbon chains to fold influences the structure of micelles,[1] the permeability of membranes,[2] and the binding to enzymes.[3] Given the obvious importance of chain folding, it is surprising how little is known about the subject. Raman scattering reveals the approximate number of gauche linkages per chain,[4] but the exact location of the "kinks" usually cannot be determined. Deuterium NMR provides an "order parameter" which varies from 0 to 1 according to the alignments of a C–D vector in the chain.[5] Since, however, order parameters encompass an extremely complex set of motions, they are primarily useful for qualitative comparisons (e.g., determining whether addition of cholesterol to a membrane increases or decreases the order of the chains). "Mobility parameters" such as T_1 are also difficult to interpret mechanistically.[6] Indeed, even the relationship between "chain order" and "chain mobility" is not well understood. In the present paper, we discuss a new experimental approach for studying chain conformation. The conceptually simple method (a) furnishes the trans–gauche populations at specific sites along a chain, (b) involves no potentially disruptive probe, and (c) works equally well for ordered and disordered systems. As will be shown, the method can be used to examine, for the first time, the conformation of a chain bound to an enzyme in solution.

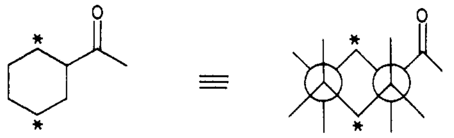
Our experiments are based upon the long-range coupling, ^3J, between two ^{13}C atoms spaced four carbons apart (C^*_1–C_2–C_3–C^*_4). Past theoretical and experimental work[7,8] indicates that the coupling between C_1 and C_4 depends on the dihedral angle about the C_2–C_3 bond in a typical Karplus-type function. Thus, $^3J_{\text{trans}}$ = 3.5–4.0 Hz, whereas $^3J_{\text{gauche}}$ = 1.5 Hz. By synthesizing chains bearing two ^{13}C atoms at known locations, we can deduce the time-averaged conformation at a particular linkage.

Scheme I^a



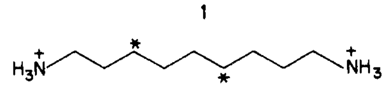
^{a}(a) CH_2N_2; (b) DIBAL-H; (c) HBr; (d) Me_3N, Ag_2O; (e) heat; (f) $CH_2{=}CHCOCH_3$; (g) H_2 + Pd/C; (h) $LiC{\equiv}CCO_2Li$, H_2 + Pd/C; (i) EtOH + H_2SO_4; (j) $SOCl_2$, CH_2N_2, $C_6H_5CO_2Ag$; (k) KOH; (l) NaN_3 + H_2SO_4.

Before embarking on the synthesis of di-^{13}C-labeled chains, we had to assure ourselves that the literature coupling constants, especially $^3J_{\text{gauche}}$, are indeed correct. Toward this end, we prepared a di-^{13}C-labeled acetylcyclohexane (Scheme I) in which a



gauche relationship is enforced upon the two ^{13}C atoms. This compound manifests a $^3J_{\text{gauche}}$ of 1.8 Hz in three solvent systems ($CDCl_3$, Me_2SO-d_6, and 20% H_2O in Me_2SO-d_6) in agreement with literature data. Coupling constants (±0.1 Hz) were secured from INADEQUATE spectra by using 0.13 M compound (8% dilabeled), a 1602-Hz sweep width, 352 scans, 16.5 s/scan, and a spectrometer programmed for the 32-phase sequence of Bax, Freeman, and Kempsell.[9]

Di-^{13}C-labeled chain experiments focused on the two "bolaform" electrolytes[10] drawn below. Their syntheses are presented in



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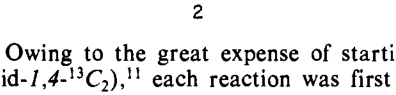

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Scheme I. Owing to the great expense of starting material (succinic acid-*1,4*-$^{13}C_2$),[11] each reaction was first carried out repeatedly with unlabeled materials in order to optimize the yields. The coupling constants vary neither with the medium nor with the concentration. Thus, ^3J = 3.8, 3.7, 3.6, 3.6, and 3.4 Hz for 50 mM diacid **1** in tetrahydrofuran, ethanol, dioxane, dimethyl sulfoxide, basic deuterium oxide (pD 13), and basic deuterium

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