paratus. Triethylammonium chloride (Eastman) was recrystallized three times from absolute ethanol.

pH Measurements. A Beckman research pH meter was used. The pH of the reaction mixtures was measured in a small glass reservoir fused directly to the top of the nmr sample tube. A glass-Ag|AgCl combination electrode (Beckman Model 39030) was used in all measurements.

Proton Exchange in H$_2$O. The rate of NH-OH proton exchange between triethylammonium ion and water was determined from nmr measurements of exchange broadening of the dominant water line. The exchange broadening was taken as $T_2^{-1} - T_1^{-1}$. T_2 and T_1 were measured by spin-echo techniques and rates were calculated as described previously.[23] The chemical shift between NH and OH protons was found to be 4.32 ppm in moderately dilute aqueous solution at 30°. The rate calculations also required knowledge of J_{NH}, the ^{14}N-H spin-spin coupling constant, and of T^I, the relaxation time of the ^{14}N nucleus in triethylammonium ion. However, the result is not sensitive to these variables and semiquantitative estimates are sufficient. We used the values, $J_{NH} = 55$ Hz and $T^I = 2.5 \times 10^{-3}$ sec, that were obtained for trimethylammonium ion. (Actual measurements were made in methanol; the T^I value obtained in methanol was then corrected for the change in solvent viscosity to yield the value listed above.)

Proton-Deuteron Exchange in D$_2$O-DCl. Production of HOD in D$_2$O-DCl after introduction of triethylammonium chloride was measured by repeated scanning of the HOD proton nmr line in quasi-slow passage. A known weight of BHCl salt was introduced quickly into an nmr sample tube containing a known amount of D$_2$O-DCl at room temperature (25°). The mixture was stirred at once to dissolve the BHCl, and placed in the sample probe of the nmr magnet. Scanning of the HOD line was begun immediately. Since the D$_2$O initially contained *ca.* 0.5 *M* HOD, the plot of HOD signal height *vs.* time consisted of two distinct regions: (1) an initial, rapid, increase (with time constant T_1) as the HOD protons in the sample attain equilibrium with the magnetic field; (2) a subsequent, slower, increase as the HOD concentration increases due to exchange with BH$^+$. This second portion was used to evaluate k_e. T_1 for the HOD protons in representative reaction mixtures was found to be 5-7 sec.

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Nuclear Magnetic Resonance Spectroscopy. Benzene-^{13}C[1a]

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Received January 23, 1967

Abstract: The high-resolution ^{13}C spectrum of benzene has been analyzed. The long-range carbon-proton coupling constants, $J_{CCH} = +1.0$ Hz, $J_{CCCH} = +7.4$ Hz, and $J_{CCCCH} = -1.1$ Hz, have been related to proton-proton coupling constants in selected model compounds.

The practical use of ^{13}C nuclear magnetic resonance has been hindered by low natural abundance of this nucleus (1.1%), low inherent sensitivity to nmr detection (1.6% relative to protons at constant field), and long relaxation times. Various methods have been used to overcome these difficulties including the use of enriched materials,[2] observation of the spectrum under rapid-passage conditions in either the dispersion or absorption mode[3] (which sacrifices resolution for better signal-to-noise ratios), complete proton decoupling[4] which enhances the signal-to-noise ratios at the expence of coupling information, internuclear double resonance,[5] and flow techniques.[6] The development of field-frequency stabilization techniques[7] has made time-averaging[8] techniques both possible and practical.

Previously reported ^{13}C spectra of benzene were obtained either under rapid-passage conditions[3] and showed only a broad doublet due to the one-bond C-H coupling, or with proton decoupling[4] and gave only a single line. Bernstein[9] has recently studied the proton spectrum of 2,3,4,5-tetradeuterio-1,2-^{13}C$_2$-benzene and has determined the four coupling constants in this AA'XX' system. The especially interesting result is the two-bond coupling J_{CCH} which was found to be +1.0 Hz. The one-bond coupling J_{CH} has been determined by several workers and is ~159 Hz.[3,10]

Experimental Section

The benzene sample used in this study contained 10% carbon disulfide and 10% tetramethylsilane (v/v). The sample was degassed and sealed under nitrogen in a 10-mm, precision-bore sample tube.[11]

The deuteriobenzenes were obtained from Merck Sharpe and Dohme of Canada.

The spectrometer used in this work was a special instrument developed for us by F. Nelson and V. Burger of Varian Associates and features a digital frequency sweep for ^{13}C at 15 MHz provided by a Hewlett-Packard 5110-5100A frequency synthesizer controlled by a Varian Associates V-4355 digital programmer. The probe was double tuned to 15 and 60 MHz with the 60 MHz for field-frequency stabilization being derived from the stable driver frequency of the synthesizer. The field was locked by conventional techniques to the proton resonances in the sample, in the present case to tetramethylsilane. Spectra were accumulated on a Varian C-1024 computer of average transients. A block diagram of the spectrometer system is shown in Figure 1.

Comparison spectra for the seven-spin system of ^{13}C and six protons were calculated using the Swalen-Reilly NMRIT[12] program

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[3] P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838 (1961).

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[7] R. V. Pound and R. Freeman, *Rev. Sci. Instr.*, **31**, 103 (1960).

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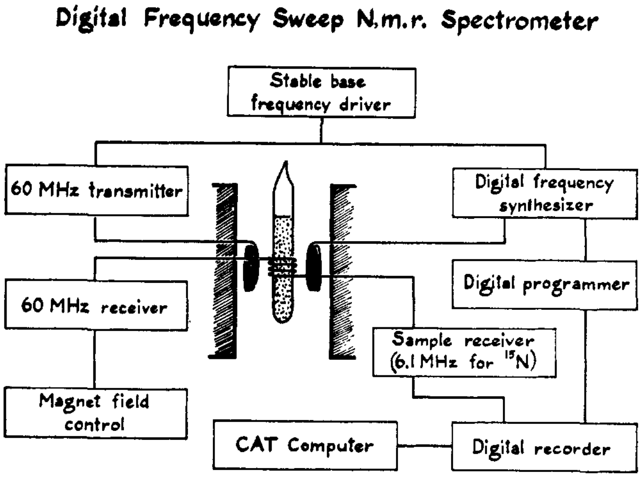

Figure 1. Digital frequency sweep nmr spectrometer.

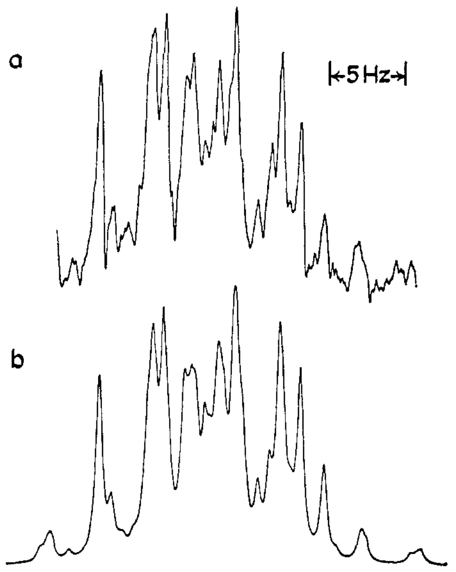

Figure 2. (a) Natural abundance ^{13}C spectrum of benzene showing the high-frequency half, taken with a sweep rate of 0.25 Hz/sec for 67 scans using TMS as internal reference at 60,006,000 Hz. The left edge of this spectrum is at 15,084,550 Hz and the right edge is at 15,084,525 Hz. (b) Calculated spectrum obtained with the parameters in Table I.

with an IBM 7094 computer and the resulting spectra were plotted on a CalComp plotter.

Results and Discussion

The chemical shift of benzene-^{13}C relative to internal carbon disulfide in the sample used in this work was found to be 968.0 ± 0.3 Hz, or 64.1 ppm at 15.1 MHz. One-half of the experimental spectrum of benzene is shown in Figure 2a. Because of the complexity of this spectrum, it was found helpful to study some deuterated benzenes to aid in the interpretation. The ^{13}C spectrum of 1,2,3,5-tetradeuteriobenzene, which was particularly useful in this respect, is shown in Figure 3. The carbons attached to deuterium appear as a broad triplet, in contrast to the previous observation[13] that such carbons cannot be observed at all because of extremely short relaxation times. The carbons directly attached to a proton show the effect of long-range coupling to the other proton in the molecule. Since all proton–proton, proton–deuterium, and carbon–deuterium couplings in this particular case are small compared to the carbon–proton couplings, the three-bond coupling constant J_{CCCH} was determined to be ±7.4 Hz from a first-order analysis of the spectrum. The magnitude of this coupling is confirmed by the observation of a doublet of triplets for the carbons attached to protons in 1,3,5-trideuteriobenzene, with the small coupling constant again being 7.4 Hz.

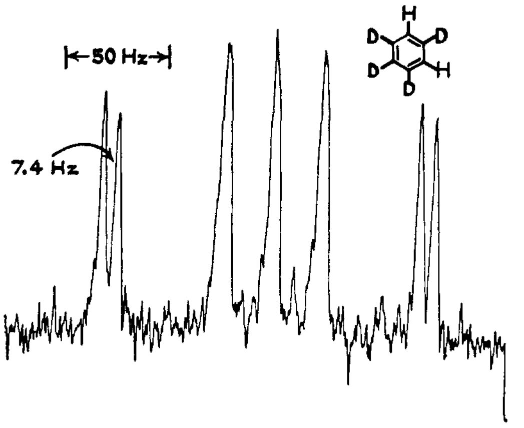

Figure 3. Natural abundance spectrum of 1,2,3,5-tetradeuteriobenzene after 217 scans. The outer four lines arise from ^{13}C–H while the middle three lines arise from ^{13}C–D.

The ^{13}C spectrum of benzene was calculated using the proton–proton coupling constants determined from observation of the ^{13}C satellites in the proton spectrum[14] or interpolation of the observed variation of proton–proton coupling constants of substituted benzenes with electronegativity,[15] two long-range coupling constants determined from deuterated benzenes, and a value for the four-bond coupling constant calculated from the difference between J_{CCCCH} and J_{CCH} and the known value of J_{CCH}. The parameters used are shown in Table I and the calculated spectrum in Figure 2b. The agreement is excellent.

Table I. Benzene Coupling Constants Calculated by the Extended Hückel Theory

J	Calcd, Hz	Obsd, Hz
CH	98.3	157.5
CCH	−5.9	+1.0
CCCH	1.4	+7.4
CCCCH	0.13	−1.1
HCCH	3.7	+7.7,[a] 7.7[b]
HCCCH	0.25	+1.37,[c] 1.4[b]
HCCCCH	0.63	+0.59,[c] 0.6[b]

[a] Reference 9. [b] Reference 15. [c] Reference 14.

Recently attempts have been made to calculate carbon–proton coupling constants[16] using the extended Hückel theory of Hoffmann.[17] Calculations of this

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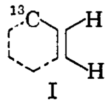
type have been performed on benzene and the results are shown in Table I.

The agreement between observed and calculated coupling constants is rather poor. The discrepancies seem general for π-electronic systems and have been accounted for[16] through neglect of $\sigma-\pi$ interaction, coupling through the π system which is not taken into account, and other factors.

Since the available data for proton–proton couplings are much more extensive than for carbon–proton coupling, it would be particularly desirable to be able to relate couplings involving ^{13}C and protons to those involving only protons. A theoretical basis for this has already been described,[18] but the treatment has only been applied to aliphatic systems, and with limited success. Assuming that the carbon in question is in the same steric and electronic environment as a certain proton and that the Fermi contact term is the dominant coupling mechanism, the two coupling constants such as J_{CCCH} and J_{HCCH} can be related by a single parameter which depends only on the hybridization of the carbon in question. Assuming a specific form for the carbon 2s orbital (a Slater orbital with exponent 3.25 was used), the constant relating the two couplings[18] was determined as 0.40 for an sp^2 carbon giving the relationship $J_{CCCH} = 0.4J_{HCCH}$. Previously this relationship has only been applied to intramolecular comparison of coupling constants,[19] but with the correct choice of model compounds, there seems to be no reason why it should not be extended to intermolecular comparisons. Several compounds (II–IV) are proposed as models for benzene (I). The predicted benzene coupling constants based on the relevant coupling constants for these compounds are given in Table II.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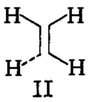
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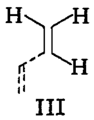
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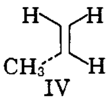
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Table II. Relationship of CH and HH Coupling Constants

	J_{CCH}	J_{CCCH}
Benzene (obsd)	+1.0	+7.4
Calcd from J_{HH} in		
Ethylene[a]	+1.0	+7.6
Butadiene[b]	+0.7	+6.8
Propene[c]	+0.8	+6.8

[a] R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc.* (London), **A269**, 385 (1962). [b] R. T. Hobgood and J. H. Goldstein, *J. Mol. Spectry.*, **12**, 76 (1964). [c] P. C. Lauterbur and R. J. Kurland, *J. Am. Chem. Soc.*, **84**, 3405 (1962).

The choice of a correct model compound for the four-bond coupling is difficult. Although the analogy is imperfect, a negative sign has been predicted for the four-bond, proton–proton coupling constant in allene[20] which is 7.1 Hz.[21] There are two equivalent paths possible for transmission of the spin information in allene, and they are expected to give an additive effect. On this basis a single path with three intervening sp^2-hybridized carbon atoms should lead to a proton–proton coupling constant of -3.5 Hz which with Karabatsos' formulation leads to prediction of -1.4 Hz for the four-bond coupling constant J_{CCCCH} in benzene.

The general agreement is excellent and it appears profitable to investigate further the relation between the magnitudes of the two- and three-bond, carbon–proton coupling constants with those in analogously constituted systems involving proton–proton coupling.

Acknowledgments. We thank Professor G. W. Robinson for loaning us samples of the deuterated benzenes used in this investigation and George Petersson for a copy of his program for extended Hückel molecular orbital calculations.

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(19) The poor agreement originally found by Karabatsos and coworkers[18] may be due to the choice of model compounds and neglect of the possibility of opposite signs for some of the coupling constants.

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