during the lifetime of B·HA. Since the direction of the residual polarization is such as to favor the formation of the dipole moment in the transition state, as shown in Fig. 3b, we expect a reduction of the free energy of activation from this effect. An analogous reduction would not be expected for the process discussed in water because here the formation of the reactive encounter is preceded by the diffusion of un-ionized reactants.

In summary, if we adopt the model of a polar transition state and of irreversible dielectric interactions resulting from $\tau_* < \tau_D$, we expect k_2 in acetic acid to be greater than k_2 in water. It should be noted that this prediction is opposite to predictions based on reversible electro*static* models.

Tris(hydroxymethyl)methylammonium Acetate.—We were interested in the rate of proton exchange of this substance because of the possibility that the cyclically hydrogen-bonded ion pair (II) is the dominant subspecies.

$$R_2C—NH_3^+\cdots OAc^-·HOAc$$

The product of proton transfer of II would also have a cyclic structure (IV), whereas the analog of solvated

ammonia would have the acyclic structure III. In the cyclic complex IV, the amine molecule is bonded to the adjacent acetic acid molecule by two hydrogen bonds, whereas in III it is held less firmly by a single hydrogen bond. Since displacement of the adjacent acetic acid molecule by acetic acid from the bulk solvent is the probable rate-determining step in proton exchange, and since the rate constant for that displacement is measured by kK_i, we would expect a marked decrease in kK_i if II were the dominant subspecies.[20]

The relevant data for TRIS·OAc are included in Table V. It is seen that the value of kK_i is not exceptional, being nearly the same as that obtained for trimethylamine. Moreover, the activation parameters ΔH^* and ΔS^* for TRIS·OAc continue the systematic trends established by ammonia and the methylamines when compared with $\Delta H°$ and $\Delta S°$ for acid dissociation in water. It therefore appears that the mechanism of proton exchange for TRIS·OAc is entirely analogous to that for the other amines. As a corollary, the cyclic ion pair II is not the dominant subspecies.

(20) For example, for the cyclically hydrogen-bonded dimer of ε-caprolactam, the rate constant for breaking only one of the two hydrogen bonds is about 10^9–10^{10} sec.$^{-1}$; that for breaking both hydrogen bonds is 10^5 sec.$^{-1}$; data reported by M. Eigen, *Chem. Eng. News*, **41**, Dec. 2, 38 (1963).

(21) R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **70**, 948 (1948).

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Carbon-13 Magnetic Resonance. I. Improved Carbon-13 Magnetic Resonance Spectra Obtained by Proton Decoupling and Rapid Sample Spinning

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Experimental methods for improving the observation of carbon-13 magnetic resonance spectra are presented. Saturation effects common to the carbon-13 nuclei resulting from its relatively long relaxation time can be partially circumvented with proton decoupling and sample spinning. In addition to improved signal heights realized from multiplet collapse, a nuclear Overhauser enhancement of the resonant peak allows carbon-13 magnetic resonance spectroscopy to be extended to considerably larger molecules and more dilute samples. Spinning of the sample also results in greater resolution and enhanced signal intensity. By accurately determining the proton decoupler and carbon-13 transmitter frequencies, the chemical shift of a given peak can be determined within an error of ±0.07 p.p.m. at 15.1 Mc.p.s. Optimum operating conditions are discussed.

I. Introduction

The combination of a low natural abundance and a relatively long nuclear relaxation time for the carbon-13 magnetic isotope has offered a formidable obstacle in the study of its magnetic resonance. Use of adiabatic rapid passage techniques on the dispersion mode[1–4] has been relatively successful in the study of compounds

of low molecular weight which are neat liquids or solids of high solubility in some solvent. The sensitivity of

(1) P. C. Lauterbur, *J. Chem. Phys.*, **26**, 217 (1957); *Ann. N. Y. Acad. Sci.*, **70**, 841 (1958); *J. Am. Chem. Soc.*, **83**, 1839, 1846 (1961); *J. Chem. Phys.*, **38**, 1406, 1415, 1432 (1963).

(2) C. H. Holm, *ibid.*, **26**, 707 (1957).

(3) H. Spiesecke and W. G. Schneider, *ibid.*, **35**, 722 (1960).

(4) H. Spiesecke and W. G. Schneider, *Tetrahedron Letters*, 468 (1961).

Fig. 1.—Spectral traces of the carbon-13 resonance of benzene are portrayed for various settings of the proton decoupler. As the decoupler frequency is adjusted to the proton resonance position corresponding to the magnetic field of the carbon-13 resonance, the doublet collapses into a singlet with an intensity which is stronger than twice the intensity of the doublet lines. This enhancement above that normally expected for doublet collapse is due to a nuclear Overhauser effect. The maximum value in the intensity vs. decoupler frequency curve is used to determine the proton resonance frequency.

the method, however, has not been adequate for larger molecules in which self-dilution becomes a problem nor for solids which can only be investigated as solutions of limited concentration. Rapid sweep rates also limit the resolution of closely positioned spectral peaks and decrease the accuracy with which the chemical shift can be determined from a previously calibrated sweep rate. Working with spinning samples on the absorption mode, Shoolery[5] has developed a technique in which the resolution is greatly improved due to better field homogeneity. However, the sensitivity of this method, which utilizes side band modulation and phase detection, appears to be no better at present than that observed for the rapid passage technique.

In a proton decoupling experiment Lauterbur and Yajko[6] first observed an enhancement in the carbon-13 resonance signal which exceeded that normally expected from the collapse of the multiplet induced by proton spin–spin coupling. This enhancement is reminiscent of the effect observed by Overhauser[7] in electron spin work and was suggested, although not

observed, by Bloom and Shoolery[8] in their early paper on heteronuclear double irradiation work. By capitalizing on this nuclear Overhauser effect along with the increased signal resulting from the multiplet collapse, it is possible to observe the carbon-13 resonance in many new compounds which could not be studied previously. Furthermore, it is possible to obtain as an additional benefit of the method more accurate chemical shift data by carefully measuring simultaneously the two irradiating frequencies at the instant when the proton decoupled carbon-13 resonance signal is maximized.[9] The method is essentially that proposed by Roydon[10] in which she measured the ratio of the carbon-13 to proton resonance frequencies in an enriched sample of CH_3I. Her experiment was the reverse of those contained herein as she observed the collapse of the proton multiplet while irradiating the carbon-13 nuclei.

This paper will analyze the effect of the various experimental quantities upon the spectral features and suggest optimum conditions for observing proton decoupled carbon-13 spectra.

II. Experimental

A. General Technique.—To determine accurately the chemical shift parameter of a carbon-13 resonance signal with a proton decoupler, the spectral peak is consecutively observed for various frequency settings of the decoupler. If the decoupler frequency, f, is in the range of the resonance frequency, $\gamma_i H/2\pi$, of the protons coupled to the carbon-13 nuclei at the instant when the signal of this nuclei is being observed, then the proton-induced multiplet is collapsed, and in its place a much stronger resonance singlet is found. By plotting the intensity of the decoupled carbon-13 singlet vs. f in the manner portrayed in Fig. 1, it is possible to determine $\gamma_i H/2\pi$, which will be referred to as f_i henceforth. Figure 1 exhibits five spectral traces obtained on the absorption mode which shows how the doublet in benzene collapses as f is adjusted to equal $f_{C_6H_6}$. In general, spectral traces for both forward and reverse field sweeps are plotted to guard against saturation effects which distort the intensity plots of the type given in Fig. 1. Only for negligible saturation in the carbon-13 signal will equal forward and reverse sweeps give intensity curves which maximize at the same decoupler frequency.

Successful data have been obtained in this laboratory by sweeping back and forth through the carbon-13 resonance signal as the decoupler frequency is varied in the range ±50 c.p.s. about the proton resonance f_i. Data are normally taken every 2–5 c.p.s. in the outer regions of this range and every 1 c.p.s. for spectral traces of maximum intensity in the center of the plot where greater accuracy in the determination of the intensity is required. To obtain data which are reproducible, both forward and reverse sweep rates must be adjusted to the same rate and the period of sweeping in both directions made equal. A period of 60 sec. for the increasing and decreasing sweeps was found to be sufficiently long to avoid saturation effects. A convenient mode of operation consists of sweeping past a signal in one direction for 30 sec., reversing the sweep for 60 sec., and then repeating the performance every 60 sec. If the sweep rates in both directions are equal, the resonance signal appears every minute midway in each sweep. After each forward and reverse sweep the frequency of the decoupler is changed slightly, and the intensity of the signal is recorded for a new frequency which is determined with a high frequency electronic counter.

B. Equipment.—A Varian high resolution spectrometer with a V-4311 transmitter operating at 15.1 Mc.p.s. was used to observe the carbon-13 resonance. This spectrometer was used with the standard 12-in. Varian electromagnet equipped with a flux stabilizer and homogeneity coils. Proton decoupling was effected with a Varian V-4320 n.m.r. spin decoupler operating at

(5) J. N. Shoolery, Third Conference on Experimental Aspects of Nuclear Magnetic Resonance Spectroscopy, Pittsburgh, Pa., March 2–3, 1962.

(6) P. C. Lauterbur and P. J. Yajko, private communication.

(7) A. W. Overhauser, Phys. Rev., **92**, 411 (1953).

(8) A. L. Bloom and J. N. Shoolery, ibid., **97**, 1261 (1955).

(9) This method of obtaining carbon-13 chemical shifts was reported simultaneously by P. C. Lauterbur and D. M. Grant at the Third Conference on Experimental Aspects of Nuclear Magnetic Resonance Spectroscopy Pittsburgh, Pa., March 2–3, 1962.

(10) V. Roydon, Phys. Rev., **96**, 543 (1954).

60 Mc.p.s. A V-4331 high resolution probe was used which had been modified by Varian for dual frequency irradiation. The probe could be fitted either with the standard 5-mm. probe insert and Varian spinner for 5-mm. sample tubes, or with a 15-mm. insert for 12- and 15-mm. sample tubes. The 12-mm. tubes could be spun with a Wilmad spinner assembly.

A Hewlett–Packard 524C electronic counter equipped with a Model 525A frequency converter was used to determine the frequency of both the spectrometer and the decoupler to ±1 c.p.s. The decoupler frequency was checked continuously while the frequency of the spectrometer was monitored at selected intervals only to ensure that it had not changed during a given series of runs.

It is imperative that the frequency of the 15.1 Mc.p.s. unit be maintained constant while taking data used in an intensity vs. decoupler frequency plot. Any instability in the 15.1 Mc.p.s. transmitter will distort these intensity plots and limit the accuracy of the carbon-13 chemical shift determination. This unit could be maintained to ±1 c.p.s. over a period of 1 hr. by maintaining the room temperature to better than ±1° once the spectrometer had reached thermal equilibrium with the room. A warm-up time of 6–8 hr. was normally required to achieve this high degree of stability.

The best field homogeneity is obtained with a 5-mm. spinning sample of neat acetic acid enriched to 24 atom % carbon-13 in the carboxyl carbon. Evidence of good resolution is indicated by maximized peak heights and a favorable amount of ringing. At the same time, drift in the magnetic field is eliminated so that sweeps in both directions are equal. The 5-mm. insert then is replaced with the 15-mm. insert and the probe positioned as nearly as possible in the same place. For the 15-mm. nonspinning samples, a minor amount of additional adjustment is made in the homogeneity controls to maximize the oscilloscopic trace of a signal obtained with proton decoupling. With the 12-mm. spinning samples, more refined adjustments are possible because of the greater field uniformity resulting from spinning.

III. Results and Discussion

A. The Carbon-13 Chemical Shift Parameter.—

The relationships existing between the chemical shift values and the experimental parameters determined in a double irradiation experiment are portrayed schematically in Fig. 2 for a reference and sample compound. The quantities f_i and ν_i are the respective resonance frequencies of the ith set of hydrogen and carbon-13 nuclei for a given magnetic field H_i. The respective proton and carbon-13 magnetogyric ratios are given by γ_H and γ_C and their chemical shift parameters in p.p.m. from a given reference compound by δ_H and δ_C. The zero subscript is used to distinguish the values of the reference compound. Using Fig. 2, it follows that

$$\frac{\nu_0}{\gamma_C} = \frac{f_0}{\gamma_H} = H_0$$

$$\frac{\nu_i}{\gamma_C(1 - \delta_C)} = \frac{f_i}{\gamma_H(1 - \delta_H)} = H_i \qquad (1)$$

from which the following expression can be obtained

$$\delta_C = (1/f_i)[f_i - (f_0/\nu_0)(1 - \delta_H)\nu_i] \qquad (2)$$

Equation 2 is a general expression relating δ_C to the determinable quantities f_i, ν_i, and δ_H, whereas the quantity f_0/ν_0 is obtained for the reference compound selected as a standard. Values of f_0/ν_0 found in this laboratory for benzene and tetramethylsilane, two common standards are, respectively, 3.9764492 ± 0.0000004 and 3.9769331 ± 0.0000004. This corresponds to a carbon-13 chemical shift between these two compounds of 129.0 ± 0.1 p.p.m. (lit. 129[1] and 129.0 p.p.m.[3]) when the difference between the two f_0/ν_0
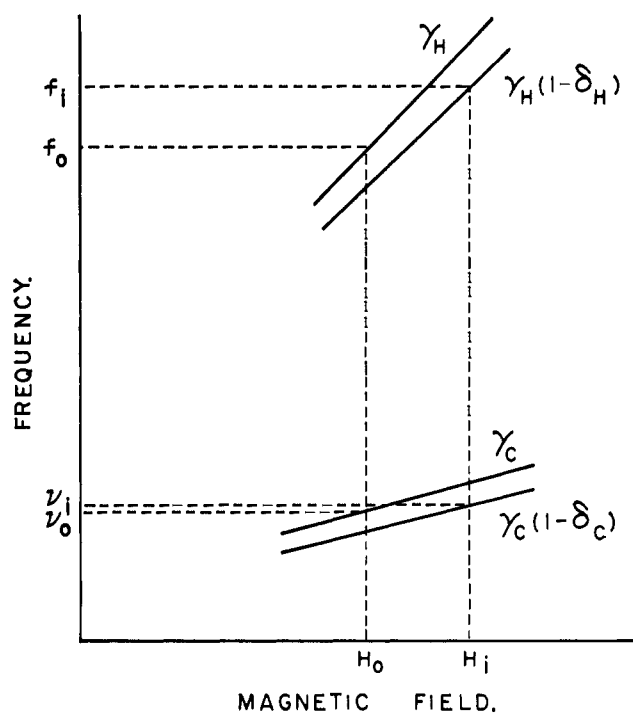

Fig. 2.—This schematic representation shows the relationships existing between the proton decoupler frequency, f_i, and the carbon-13 transmitter frequency, ν_i, for a sample compound and the corresponding values for a reference compound.

values are corrected for the difference in the hydrogen chemical shifts.

B. The Effect of H_1 and Sweep Rate.—

As H_1 is increased from zero, the carbon-13 resonance signal increases in a directly proportional manner until saturation begins to affect detrimentally the signal intensity. At this point the intensity curves vs. decoupler frequency begins to exhibit distortion between the forward and reverse sweeps. Figure 3 shows this effect as H_1 is increased above 0.09 mgauss for a constant sweep rate of 3.3 mgauss/sec. For large H_1 values the signal saturates and the maxima of the forward and reverse sweeps gradually separate. This separation can be explained in terms of the greater band width and increased intensity expected for a resonance signal in which larger H_1 power is used. When the value of H_1 exceeds that for which saturation is noted, then the spectral trace will start up the leading side of the spectral peak, saturate the transition before reaching the center of the resonance peak, and then fall off to zero intensity. The maxima in the observed signal, therefore, will be on either side of the true signal maxima depending upon whether an increasing or decreasing field sweep is used. Thus, if the intensities are plotted against the decoupler frequency, the resulting curves will show a discrepancy between the forward and reverse maxima. When combined with the broadened intensity plots resulting from higher H_1 power, this distortion decreases the accuracy with which the proton resonance frequency can be determined and also places limitations on the accuracy of the carbon-13 chemical shift obtained from this quantity. Furthermore, as no significant improvement is noted in the signal to noise level for increased H_1, once saturation becomes evident it can be concluded that H_1 should be held below the value where the two maxima begin to separate.

BENZENE
$H_1 = 0.70$ mg.
$H_2 = 106$ mg.
S.R. $= 3.3$ mg./sec.

30 cps.

$H_1 = 0.25$ mg.

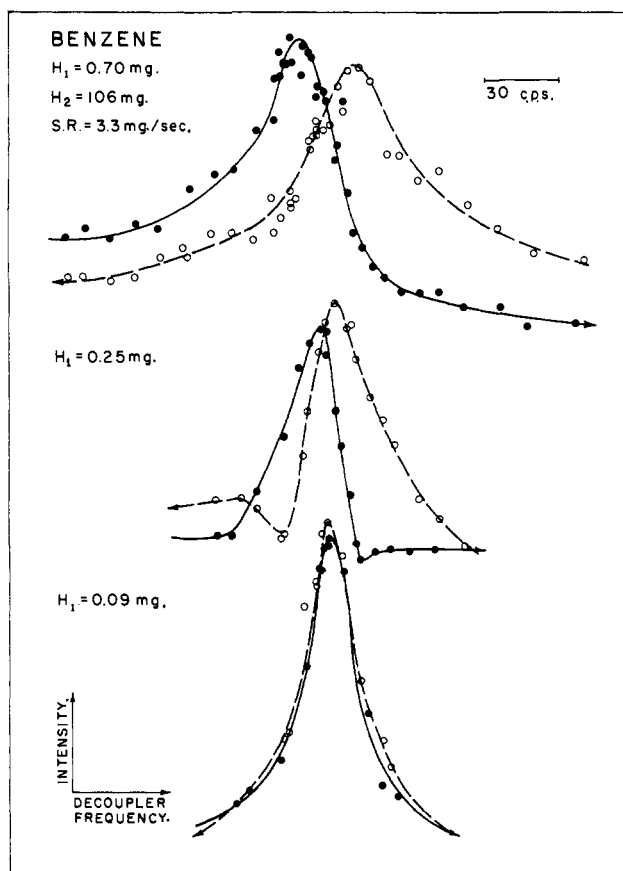$H_1 = 0.09$ mg.

INTENSITY

DECOUPLER FREQUENCY.

Fig. 3.—The effect of H_1 upon an intensity vs. decoupler frequency curve is shown in this figure. As H_1 increases for a given sweep rate, distortion due to saturation affects the position at which the intensity plots maximize for the forward and reverse sweeps. Negligible saturation is verified whenever the maxima of the forward and reverse sweeps are coincident.

The sweep rate will affect the intensity plots of the type shown in Fig. 3 only when one has avoided saturation for large H_1 values by rapidly sweeping through the signal. In these cases a slower sweep rate will lead to saturation owing to concentrating the H_1 power on the signal for a longer period, and the same distortion as described above will result. If, however, the H_1 power level is such that the number of induced transitions is small when compared with the number of transitions associated with the normal relaxation processes, then changes in sweep rate cannot lead to saturation along with the associated undesirable effects. To detect carbon-13 in natural abundance, however, requires a relatively high H_1 power level, and therefore a careful adjustment of both the H_1 intensity and the sweep rate is needed to achieve the proper balance required to avoid saturation.

Another reason for avoiding saturation follows from the difficulty in eliminating drifts in the magnetic field which will create different forward and reverse sweep rates. In this condition the forward and reverse maxima associated with a saturating resonance signal will not fall equidistance on each side of the decoupled proton resonance position. This bias therefore will contribute error in the determination of the value of f_i. As a mode of operation, the H_1 power level and sweep rate therefore should be restricted to the range in which the forward and reverse maxima are coincident. Within this limitation the best compromise

in H_1 and the sweep rate is found by a trial and error method. This is done while remembering that high H_1 and slow sweep rates lead to saturation and broaden signals, a low H_1 may give a poor signal to noise ratio, and sweep rates which are too fast result in poor resolution and poor system response times.

We also have been prevented from going to very slow sweep rates by the inherent instability in the frequency of our proton decoupler. Changes of a few c.p.s. in the decoupler frequency over the period of a very slow sweep contribute errors which more than offset the advantages obtained from using very slow sweep rates for which saturation is absent.

C. The Effect of H_2.—Bloom and Shoolery[8] have given a detailed mathematical analysis of the effect of H_2 upon a decoupled spectrum. Under conditions of moderate power and for the decoupler frequency adjusted exactly to the proton resonance (i.e., $f = f_i$), they exhibited that the following equations could be used in a field sweep experiment to describe the resonance pattern of the principal nucleus which in this case is carbon-13

$$\Delta H = 0 \tag{3}$$

$$(\Delta H)^2 = \frac{J^2(\gamma_{C-13}^2 - \gamma_H^2) + 4\gamma_{C-13}^2\gamma_H^2 H_2^2}{4\gamma_{C-13}^2(\gamma_{C-13}^2 - \gamma_H^2)} \tag{4}$$

The positions of the lines are given by ΔH in gauss from the center of the spectrum, and J is the spin–spin coupling constant in c.p.s. Use was made of eq. 4 in calibrating in gauss the effective power, H_2, of the decoupler with a carbon-13 enriched sample of formic acid. For this compound a central peak (given by eq. 3) and two lines (described by eq. 4) equidistant about the center were found in the resonance spectra. As H_2 was increased, the intensity of the central line grew and the outer lines converged to the center while at the same time decreasing in intensity. By accurately determining the position of the outer lines ($\pm \Delta H$), H_2 can be calculated directly from eq. 4 if the value for J is known.

In the limit as the two outer lines of a partially decoupled doublet collapse into a singlet, the value of H_2 in terms of J can be determined for $\Delta H = 0$ from eq. 4 as

$$H_2 = J(\gamma_H^2 - \gamma_{C-13}^2)^{1/2}/2\gamma_H\gamma_{C-13} =$$
$$(0.452 \text{ mgauss/c.p.s.})J \tag{5}$$

Thus, for benzene with $J = 158$ c.p.s. the minimum decoupler power required barely to collapse the doublet is 71.4 mgauss. Equation 5 can be used therefore to suggest a convenient operating level for the decoupler power. It should be remembered, however, that eq. 5 gives the level of power required to collapse a doublet when the decoupler is centered on the proton resonance. In order to obtain data of the type shown in Fig. 1 in which f is varied by 50 c.p.s. about the proton resonance position, it has been found convenient to increase H_2 by 30 to 40% above that suggested by eq. 5.

For $H_2 \gg 0.452 J_{CH}/\gamma_H$, only two lines will appear in a decoupled doublet independent of the value for $(f_i - f)$. Under this condition the relationship between $\Delta H, f_i - f, J$, and H_2 is given by eq. 6.[11]

(11) Equation 6 is obtained by setting $H_0 = H_0 + \Delta H$ in eq. 13 of ref. 8 and solving for ΔH under the condition of a field sweep experiment in which $(\Delta W/h) - \gamma_1 H_0 = 0$. Our nomenclature, $(f_i - f)$, is used for $(\gamma_2 H_0 - W_2)$.
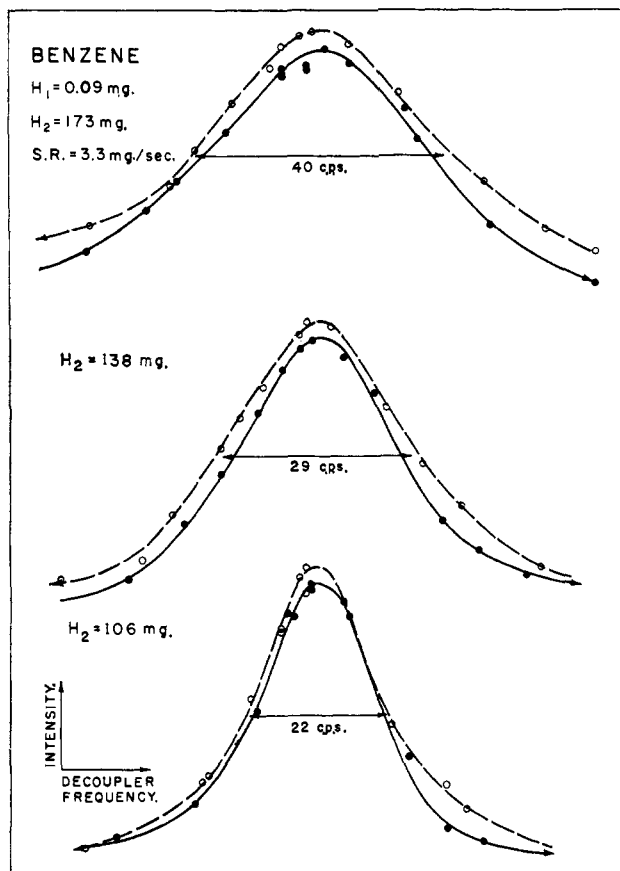
Fig. 4.—As the decoupler power, H_2, is increased the intensity plots broaden as shown. The maximum intensity of the spectra, however, is not affected when $f = f_i$. A minimum value of H_2 therefore should be used which will completely collapse the proton-coupled multiplets.

$$\Delta H = \pm J(f_i - f)/\gamma_{\text{C-13}}[(f_i - f)^2 + (\gamma_H H_2)^2]^{1/2} \quad (6)$$

Equation 6 describes the spectral features portrayed in Fig. 1, in which the benzene doublet collapses into a singlet for a relatively large but constant value of H_2 as $(f_i - f)$ approaches zero. It is interesting to note that a nuclear Overhauser enhancement of the line closest to the setting for f is observed before the doublet is collapsed. This enhancement is reflected in the intensity vs. decoupler frequency plot as a gradual increase in the resonance signal on both sides of the bell-shaped region of the curve which is due primarily to the coalescence of the two lines of the doublet.

From eq. 6 it is evident that the two spectral lines can be collapsed for a given value of $(f_i - f)$ if H_2 is sufficiently large. Conversely, the plot of intensity vs. $(f_i - f)$ will broaden as H_2 is increased. This effect is shown graphically in Fig. 4. While the intensity plots exhibit greater widths at higher H_2 power levels, no significant change is noted in the maximum intensity observed for the various H_2 values and the values for H_1 and for the sweep rate used to collect this set of data. This being the case, excessively large H_2 settings are undesirable as the accuracy is decreased in determining the center of the broader intensity curves required to calculate the carbon-13 chemical shift.

The relationship between the width of the intensity vs. $(f_i - f)$ plot and the value of H_2 at "half-height"[12]

(12) "Half-height" corresponds to the intensity which is intermediate between the value for the two separate lines just before they begin to collapse and the maximum intensity value where the two lines have completely coalesced.
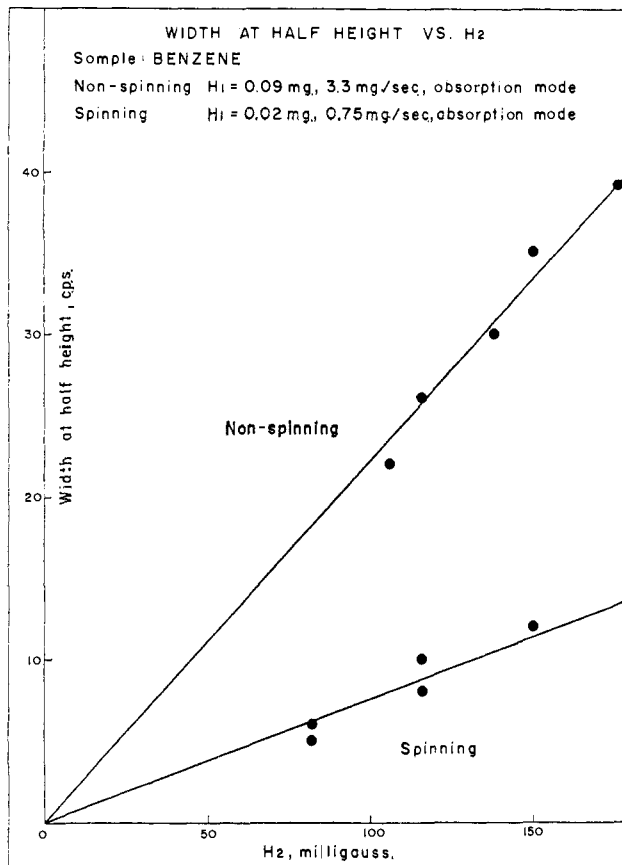
Fig. 5.—The width of intensity plots is shown to be directly proportional to the decoupler power, H_2, in this plot of "half-height" widths vs. H_2. The difference in slopes between the spinning and nonspinning cases is due to unequal field homogeneity.

can be obtained from eq. 6 if ΔH is assumed to be the same to give an equal "half-height" intensity. The expression giving the slope of a plot of $(f_i - f_{1/2})$ vs. H_2 is given in eq. 7

$$(f_i - f_{1/2})/H_2 = \gamma_H \gamma_{\text{C-13}} \Delta_{1/2}/(4J^2 - \gamma_{\text{C-13}}^2 \Delta^2)^{1/2} \quad (7)$$

The subscript $1/2$ is used to denote the value of f and Δ corresponding to the "half-height" intensity, and Δ is equal to the difference in ΔH^+ and ΔH^- where the $+$ and $-$ denote the sign used in eq. 6. Data of $(f_i - f_{1/2})$ vs. H_2 plotted in Fig. 5 confirms that a direct proportionality exists between these two quantities for a spinning 12-mm. sample and for a nonspinning 15-mm. sample. The difference in slopes corresponds to dissimilar band widths in the carbon-13 resonance signals which result from unequal field homogeneity in the two cases.

D. Improved Field Homogeneity from Spinning.—The effect of spinning upon intensity plots is dramatically shown in Fig. 6 where results are compared for the same 12-mm. sample of benzene with and without spinning. Approximately a fivefold enhancement is realized in the intensity plots for the rapidly rotating sample. This is due undoubtedly to the improved homogeneity in the effective magnetic field over the whole sample. Furthermore, narrower band widths greatly improve the resolution and increase the accuracy with which f_i can be determined. Not all of the enhancement due to greater field homogeneity can be claimed for the technique, however, as H_1 had
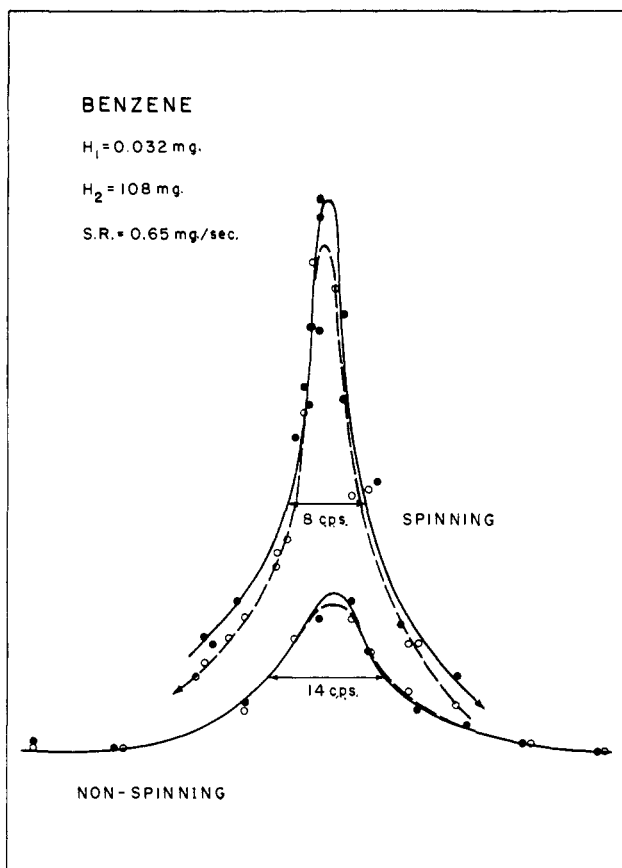
Fig. 6.—Much improved field homogeneity realized from spinning results in a greatly enhanced signal height. Better resolution also follows from the narrower band widths.

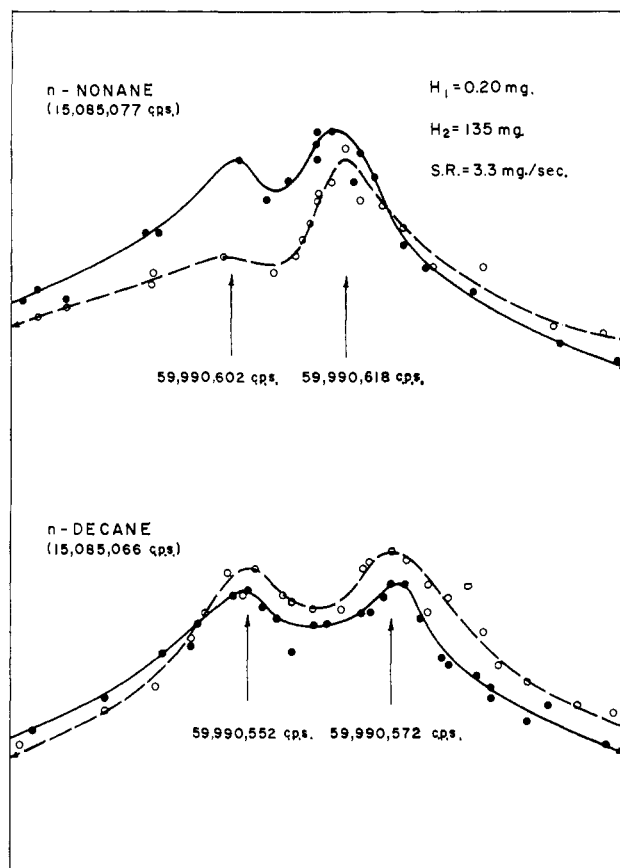

Fig. 7.—Intensity plots for nonspinning samples of n-nonane and n-decane show that the separate resonance positions for closely spaced resonance peaks can be sorted out even though the two peaks cannot be resolved in the spectral traces from which the intensity plots were constructed.

to be decreased from the 0.09 mgauss used in Fig. 5 to 0.032 mgauss to avoid electrical noise induced by spinning vibrations in the probe. Nevertheless, a significant improvement in the signal to noise ratio was observed, and future improvement in technique and instrumentation which is so critical in obtaining spectra on spinning samples can be expected to lead to still better sensitivity.

E. Resolution and Precision of the Method.—The limit of resolution of two closely spaced peaks is somewhat better for the intensity plot method than that noted for the individual spectral traces used in constructing this curve. This is evident in Fig. 7 for nonspinning samples of n-nonane and n-decane in which the resonance peaks of the fourth and fifth carbons are separated by 0.27 and 0.33 p.p.m., respectively, for the two compounds. In each of these cases only one peak was observed in the spectral trace, but when the intensity of each of these traces was plotted vs. the decoupler frequency a binodal curve was obtained. That the plot is due indeed to two separate spectral peaks can be concluded with assurance in that plots of this kind were never observed for any case in which one would not expect to find more than a single decoupled resonance peak, and, furthermore, the 2:1 relative intensities expected for the fourth and fifth carbon atoms in n-nonane is clearly observed in the unequal shape of the binodal intensity curve for this compound. It was on the basis of this intensity argument that we[13] assigned the lower field resonance to the fifth carbon and the higher field peak

(13) E. G. Paul and D. M. Grant, J. Am. Chem. Soc., **85**, 1701 (1963).

to the two fourth carbons. In the n-decane plot both nodes are roughly equivalent in accordance with the equal number of fourth and fifth carbon atoms. Based on the data shown in Fig. 7 we have concluded that our limit of resolution for nonspinning samples is of the order of 0.25 p.p.m. or about 4 c.p.s. for a 15.085 Mc.p.s. frequency unit. This compares with a natural line width of the order of 16 c.p.s. The accuracy of estimating the chemical shift position from the center of the intensity plots is approximately ±1 c.p.s or ±0.07 p.p.m. This is a four- or fivefold improvement over the calibrated sweep method used in rapid passage experiments which claims an accuracy of about ±0.3 p.p.m.

Spinning data taken on the fourth and fifth carbons in n-nonane and n-decane show the improved resolution due to better field homogeneity. With proton decoupling, Fig. 8 contains actual carbon-13 spectral traces of the resolved resonance peaks for both compounds. In the case of n-nonane the 2:1 intensity ratio confirms the previous assignment of the fourth and fifth carbons. The band widths of the spectral peaks are about 1 c.p.s., and, as can be observed, the separations of 4 and 5 c.p.s. are easily resolved in n-nonane and n-decane, respectively. The proton decoupler was reset from the value required to decouple the first peak to that of the second in order to portray both resonance peaks in the same sweep. Intensity data taken from spectra on spinning samples for the fourth and fifth carbons in n-decane are plotted in

n - NONANE
5TH & 4TH CARBONS
DEC H
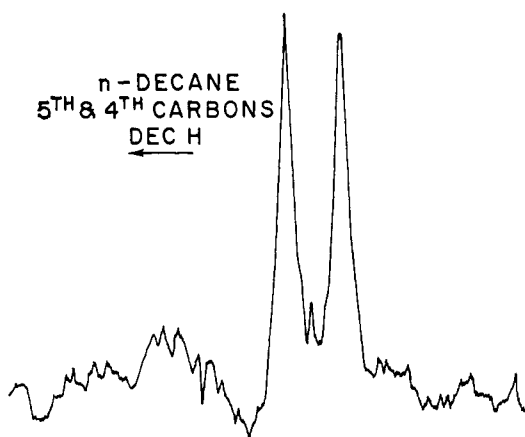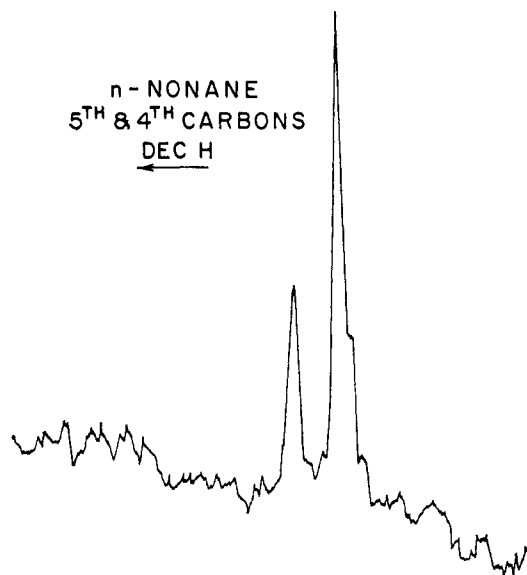←

n - DECANE
5TH & 4TH CARBONS
DEC H
←

Fig. 8.—Carbon-13 spectra for the fourth and fifth carbons of *n*-nonane and *n*-decane are given to show the resolution obtained for a 12-mm. sample with rapid spinning. Proton-induced multiplets have been eliminated with proton decoupling, and only a single resonance peak is present for each of the two nonequivalent nuclei. In order to enhance both peaks in the same sweep the proton decoupler has to be quickly readjusted from the setting required for the first peak to that of the second resonance position during the approximately 5-sec. period between recording the two peaks.

Fig. 9 in the same manner as for the nonspinning example in Fig. 7 to facilitate a direct comparison of the
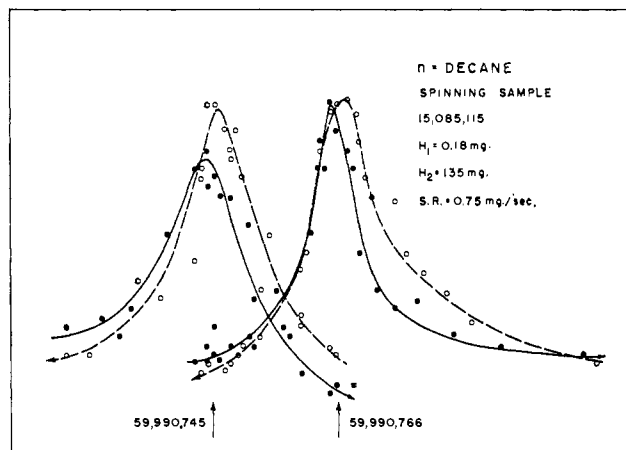

Fig. 9.—With spinning the resonance transitions corresponding to the fourth and fifth carbons in *n*-decane are resolvable. The intensities of these various spectral traces are plotted in the same manner as in Fig. 7 to facilitate a direct comparison of the two techniques.

plots obtained from the two techniques. From the intensity curves in Fig. 9 it can be observed that only one of the two resonance peaks enhance to any appreciable extent for a given decoupler frequency. This accounts for the need to readjust the decoupler during the spectral sweep in order to obtain spectra of the type given in Fig. 8 where each resonance transition is portrayed at maximum intensity. Resolution of peaks separated by about 0.1 p.p.m., or 1.5 c.p.s., at 15.085 Mc.p.s. is proposed for the spinning method on the basis of the resolution shown in Fig. 8, although this figure has not been experimentally confirmed for want of a spectra in which two peaks were this closely spaced. While it might appear that greater accuracy is possible in determining the chemical shift value from these narrower intensity plots, the limitation in determining a frequency value for the carbon-13 transmitter within ±1 c.p.s. still limits the accuracy of the chemical shift determination to the previously estimated ±0.07 p.p.m.