Monthly
Ecumenical
Letters from
Laboratories
Of
N - M - R

No. 12

PETROLEUM AND ITS PRODUCTS

GULF RESEARCH & DEVELOPMENT COMPANY

P. O. DRAWER 2038 · PITTSBURGH 30, PA.

N. D. COGGESHALL
DIRECTOR
COMPOSITION AND STRUCTURE DIVISION

August 27, 1959

Drs. A. A. Bothnerby and B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.

Gentlemen:

In many instances the quantity of sample available for an nmr analysis may be limited. One such instance is in dealing with fractions obtained from a separation by gas chromatography. The usual sample requirement when using standard 5 mm O.D. glass sample tubes is approximately 0.2 cc. A Varian Technical Information Bulletin (Vol. 2, No. 3) describes a technique whereby the sample requirements can be reduced somewhat by the use of nylon plugs, although attempts to carry this too far result in a decrease in resolution due to the distortion of the magnetic field by the plugs.

We have had good success by using a different approach to the problem. This consists in raising the sample tube so that the bottom of the tube is very near to the bottom of the receiver coil. In order to allow spinning of the sample, a nylon bushing is inserted into the probe insert above the receiver coil as shown in the accompanying figure. The bushing is made to fit tightly into the insert and the hole is made large enough to allow the sample tube to rotate freely in it. The bottom nylon bearing normally used is removed. The sample tube is kept from sliding down any further after it is positioned by a tight fit in the spinner rotor. The optimum position for the sample tube is found by trial and error. (The dimensions on the figure are for the 40 mc probe in use here.) There is very little adverse effect on resolution even with very small sample volumes. Satisfactory spectra can be obtained on samples of a few hundredths of a cc in ideal cases. The bottom bearing is no longer used even for conventional samples.

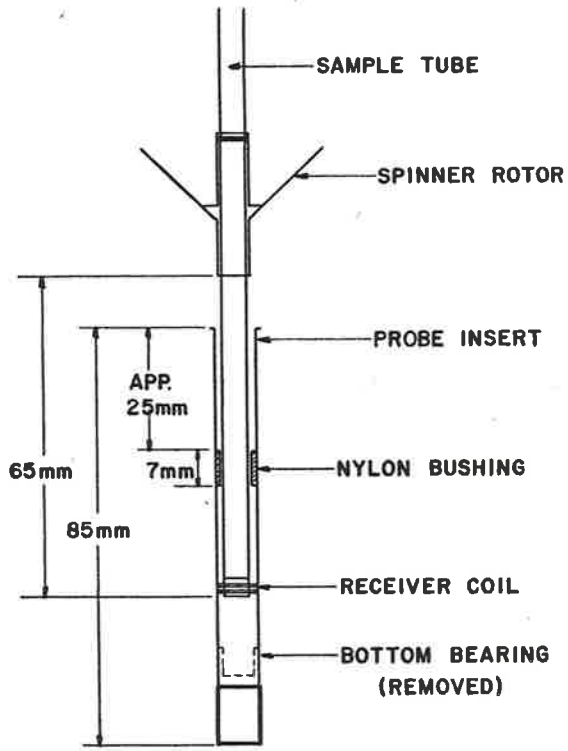
We have installed the field gradient coils described by Dr. Bothnerby in Mellon NMR No. 9 with excellent results.

Very truly yours,

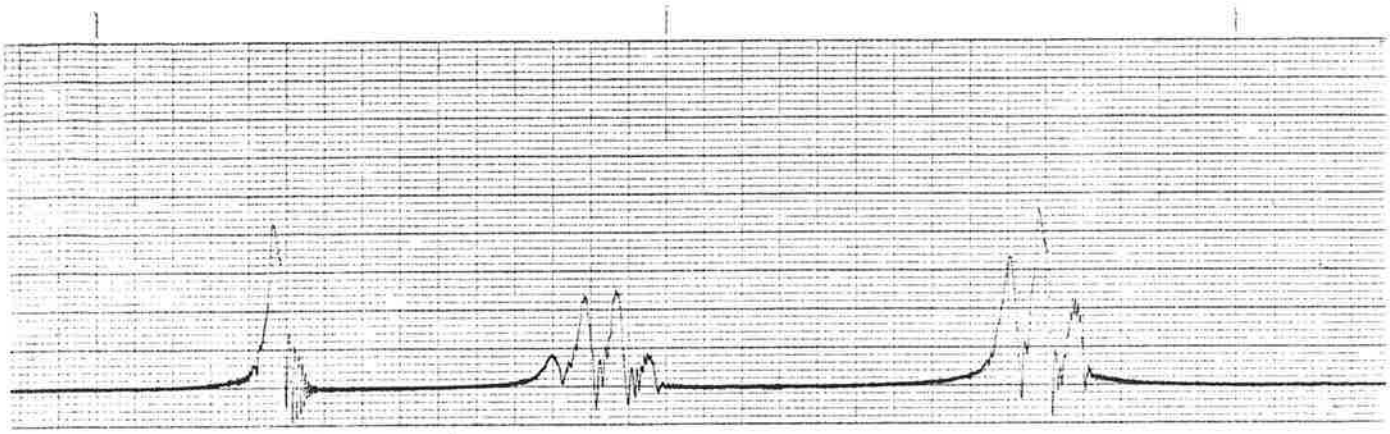
Robert J. Martin

Robert J. Martin

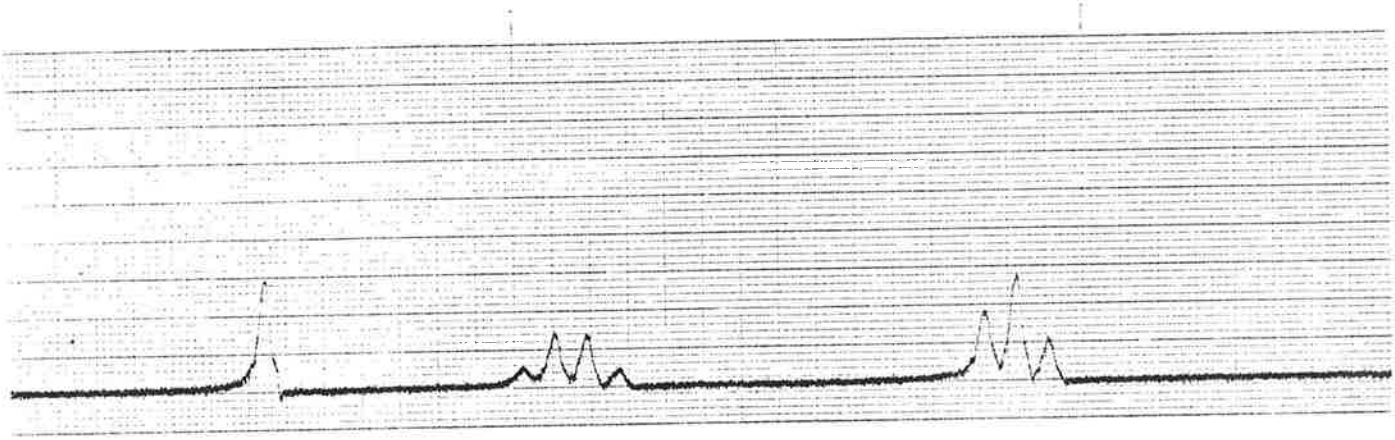
GFC
RJM:st



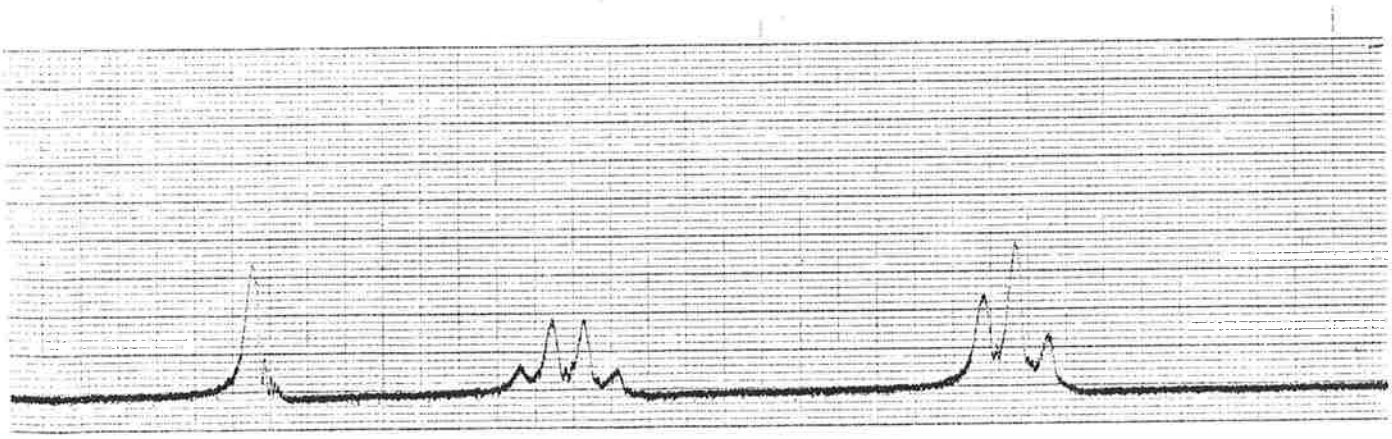
40 MC PROBE INSERT WITH BUSHING FOR MINIMIZING SAMPLE REQUIREMENTS



1. Sample volume greater than 0.3 ml with sample tube in normal position.



2. Sample volume equals 0.03 ml. Sample tube raised. Recorder gain 5 times that of 1.



3. Sample volume equals 0.05 ml. Recorder gain same as 2.

Spectra of ethanol + HCl obtained using nylon bushing to minimize sample requirements. Sample is not degassed. The magnetic field was not readjusted for any of the spectra.

R. J. Martin
Gulf Research & Development Co.

HARVARD UNIVERSITY

DEPARTMENT OF CHEMISTRY

12 Oxford Street
Cambridge 38, Massachusetts, U.S.A.

August 25, 1959

Dr. Bernard L. Shapiro
The Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Barry:

Please forgive this rather tardy contribution to M.E.L.L.O.N.M.R., but my recent marriage has put me somewhat behind in my correspondence.

Users of deuterochloroform may be interested in a method we have developed for the preparation of this peerless nmr solvent. It is a modification of the method of Lord, Nolin, and Stidham, J. Am. Chem. Soc., 77, 1365 (1955).

In a 500 cc three-necked reaction flask fitted with two dropping funnels, a Dean-Stark moisture trap, and a condenser connected to a vacuum line, are placed 15 g. analytical grade calcium carbonate and 15 g. analytical grade sodium carbonate. The solids are dried for twenty hours at 145° C. and 100 μ pressure. The flask is cooled and dry air admitted. The vacuum connection to the condenser is replaced by a calcium chloride drying tube, and 33 g. (30 cc) of deuterium oxide (99.8 per cent deuterium) are run into the flask through one of the dropping funnels. The flask is immersed in a heating bath held at 115° C, and 70 g. (40 cc) of hexachloroacetone* are added dropwise to the carbonate mixture over a period of 1.5 hours. The temperature is held at 115° for an additional 1.5 hours, then raised to 160°, and held there until no more deuterochloroform distills into the trap (about four hours). The product is withdrawn from the trap, dried over Drierite, and purified by a bulb-to-bulb vacuum distillation. The yield is 50 g. (80 per cent based on hexachloroacetone) deuterochloroform of 99.6 per cent deuterium content (mass spec).

*Hexachloroacetone was obtained as a gift from Baker and Adamson. The material as supplied was purified by fractionation at reduced pressure through a 68 x 1.5 cm vacuum jacketed column packed with 1/8 inch glass helices. Those fractions showing negligible nmr absorption were used in the preparation.

By evacuation of the reaction flask about 20 g. deuterium oxide may be recovered.

As a parting shot I might mention that we find it somewhat more convenient to use hexamethyldisiloxane as an internal reference rather than tetramethylsilane for two reasons: the former is considerably less volatile than the latter, making it easier to handle and measure out; and the siloxane needs no purification to remove ether as does the silane. The single sharp peak of the siloxane falls 2.0 cycles (wiggle-beat method) to the low field side of the silane at 40 mc.* Incidentally, the ether impurity in tetramethylsilane can be most simply removed in an apparatus consisting of two flasks connected together through a wash bottle containing concentrated sulfuric acid. The silane is placed in one flask and allowed to distill at room temperature through the sulfuric acid into the other flask which is cooled in a methanol-dry ice bath and is protected from moisture by a calcium chloride drying tube.

Yours sincerely,

Tom

Thomas J. Curphey

D

* Determined on a sample containing 5vol.% each of hexamethyldisiloxane and tetramethylsilane in carbon tetrachloride (not degassed)--estimated accuracy plus or minus .1cps. This value is in good agreement with that of Tiers, M.E.L.L.O.N.M.R. #6, Page 5.

CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA

GATES AND CRELLIN LABORATORIES OF CHEMISTRY

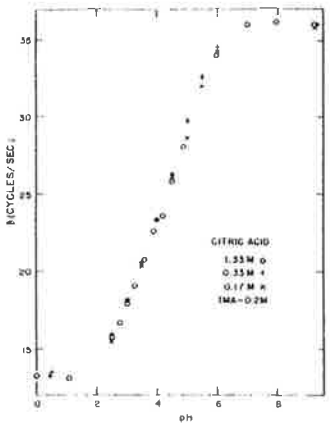
September 2, 1959

Dr. Aksel A. Bothner-By
Mellon Institute
440 Fifth Avenue
Pittsburgh 13, Pa.

Dear Aksel:

You and your MELLONMR readers may be interested in a NMR study completed here by Dr. A. Loewenstein (Weizmann Institute) of the ionization of citric acid. The problem was to determine the sequence of loss of the ionizable protons with increasing pH in aqueous solution and was originally posed to us by Dr. Donald L. Glusker. So far as I am aware the NMR method is almost unique in its ability to handle this problem.

Dr. Loewenstein measured the chemical shift of the methylene hydrogens (which appear as an AB quartet) in citric acid as a function of pH concentration at 60 Mc. On the assumption that all ionizable

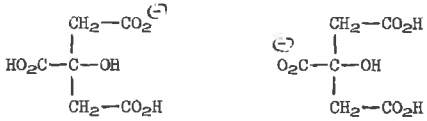


and ionized species are rapidly interconverted in aqueous solution and with the aid of the known ionization constants, it was possible to compute the chemical shift associated with each ionization step using a set of simultaneous equations of the type

$$\delta = x_1 \delta_1 + x_2 \delta_2 + x_3 \delta_3 + x_4 \delta_4$$

where x_n represent the mole fractions of non-, mono-, di- and tri-ionized citrates and δ is the overall chemical shift of the methylene hydrogens. Tetramethylammonium bromide was used as an interval standard.

The results were as follows. The first ionization causes a chemical shift of 9.2 cps; the second, 20.2 cps; and the third, 22.6 cps. Since the chemical shift of the methylene resonances associated with the



A B

ionization at the outside carboxyl (A) is larger than for ionization at the central carboxyl (B), the finding of two successive large chemical shifts followed by a smaller one argues for the first two ionizations occurring mainly at the ends of the chain.

Strong support for this conclusion was obtained from a study of the pH dependence of the methylene resonances in the symmetrical and unsymmetrical monomethyl esters of citric acid. Since the methylene resonances in $-CH_2-CO_2H$ and $-CH_2-CO_2-CH_3$ were found to be practically identical ($\pm$1cps) in those citrate species which could be compared directly, we were able to assign apparently reliable δ_n values for each citrate species and calculate the percentages of each present at different pH values. The results indicate formation of 81% of A and 19% of B in the first ionization and exclusively the symmetrical form in the second ionization.

At this time, I should like to put in a very strong plug for Jim Shoolery's point of view regarding publication of NMR data (cf. MELLONMR Nos. 10 and 11). As a chemist who regards NMR as a means to obtain chemical information, I maintain that no one should be required to get more or better spectral data than needed for the problem at hand. Furthermore, if a figure is the most revealing way of displaying the data so obtained, then the figure should be published. Certainly, minor resonance lines of possible chemical importance can be displayed in a figure which might be regarded as too time- or space-consuming to be worth measuring accurately for a table. Of course, if one wants to set up a catalog of NMR spectra, he can require any set of standards he thinks is appropriate but let us hope that the chemical journals eschew fulfilling cataloging functions lest they become even bigger and more indigestible than they are now.

Finally, I hope you will continue as best you can to list in your bibliographies all articles using NMR even as an adjunct to synthetic or structural studies. These are often extremely useful.

With all good wishes,

Very truly yours,

Jack

J. D. Roberts

R:w

[CONTRIBUTION 1578 FROM THE STERLING CHEMISTRY LABORATORY AT YALE UNIVERSITY]

Molecular Orbital Approximation to Spin Coupling of Vicinal Protons

BY HAROLD CONROY

RECEIVED

A simple molecular orbital approximation is shown to give good results in the prediction of the order of magnitude and the form of angular dependence of the coupling constant, $J_{HH'}$, involved in the high resolution NMR spectra of vicinal proton pairs. The results are compared with a number of experimentally determined coupling constants from the spectra of rigid molecular systems.

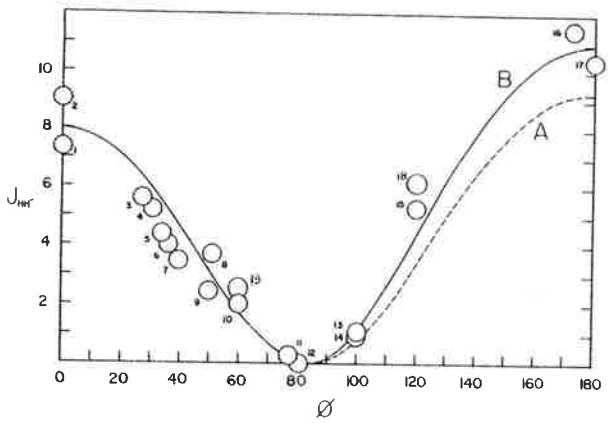


FIG. 2

Footnote to Fig. 2

Spectra were determined at 60 mc/sec with a Varian Associates High Resolution NMR Spectrometer equipped with field stabilizer; the solvent was ordinarily deuteriochloroform but in a few instances deuterioacetone was used. The experimental points are identified as follows: (1) endo 5,6 protons in 1-methyl-7-oxabicyclo[2.2.1]-2,3-heptene-exo-5,6-dicarboxylic acid anhydride; (2) 7,8 protons in 1-methyl-2,3:5,6-dibenzobicyclo[2.2.2]-2,5-octadiene-7,8-cis-dicarboxylic acid anhydride; (3) 2,3 protons in β-bromopicrotoxinin; (4) 4,5 protons in β-bromopicrotoxinin; (5) 4,5 protons in picrotoxinin; (6) (Average of four close points) a. 11b,12 protons in diacetylapopicrotoxininic dilactone; b. 4,5 protons in methyl acetyl-β-bromopicrotoxininate; c. 2,3 protons in acetylneopicrotoxinin; d. 2,3 protons in picrotoxinin; (7) 11a, 12 protons in diacetylapopicrotoxininic dilactone; (8) 3,4 protons in β-bromopicrotoxinin; (9)(Average of two close points) a. 2,3 protons in methyl β-bromopicrotoxininate; b. 2,3 protons in methyl acetyl-β-bromopicrotoxininate; (10) 2,3 protons in methyl picrotoxate; (11) 2,3 protons in diacetylapopicrotoxininic dilactone; (12)(Average of two close points) a. 11b,12 protons in diacetylapopicrotoxininic dilactone; b. 4,5 protons in 1-methyl-7-oxabicyclo[2.2.1]-2,3-heptene-exo-5,6-dicarboxylic acid anhydride; (13) 3,4 protons in methyl β-bromopicrotoxininate; (14) 3,4 protons in methyl acetyl-β-bromopicrotoxininate; (15) trans 5,6 protons in dimethyl 1-methyl-7-oxabicyclo[2.2.1]heptane-trans-5,6-dicarboxylate; (16) 4,5 protons in methyl picrotoxate; (17) 3,4 protons in diacetylapopicrotoxininic dilactone; (18) 7,8 protons in dimethyl 1-methyl-2,3:5,6-dibenzobicyclo[2.2.2]octadiene-7,8-trans-dicarboxylate; (19) 4,8 protons in dimethyl 1-methyl-2,3:5,6-dibenzobicyclo[2.2.2]octadiene-7,8-trans-dicarboxylate.

NMR Spectra of Methyl Thiophenes

by Irving Weinberg

SOCONY MOBIL OIL COMPANY, INC.
Research Department, Paulsboro Laboratory
Paulsboro, New Jersey.

We recently have been interested in the 60 megacycle spectra of several methylated thiophenes. During the course of this work it became necessary to obtain approximate values for chemical shifts and coupling constants. These are destined for eventual use as starting parameters in the exact calculations. In particular, approximate methods result in a reasonably good fit for the case of 3- methylthiophene. The ring proton spectrum for this compound is shown in Figure 1, together with the theoretical spectrum. Considering only this portion of the spectrum, the relative positions were calculated using second order pertubation theory, while the relative intensities are obtained to first order. The methyl group couples to all three ring protons but is ca 280 cps removed from them. Thus its effects on the ring proton spectrum can be adequately treated to first order. The results, using positive values for all coupling constants, are tabulated in Table 1. Incidentally, since the smaller splittings in the four low field quantities is 0.4 cps, this compound is useful in checking spectrometer performance.

Further comments on this and other methylated thiophenes are scheduled to appear as a note, by Paul Corio and myself, in the August J. Chem. Phys. This will no doubt have appeared in print by the time your current newsletter is in the mails.

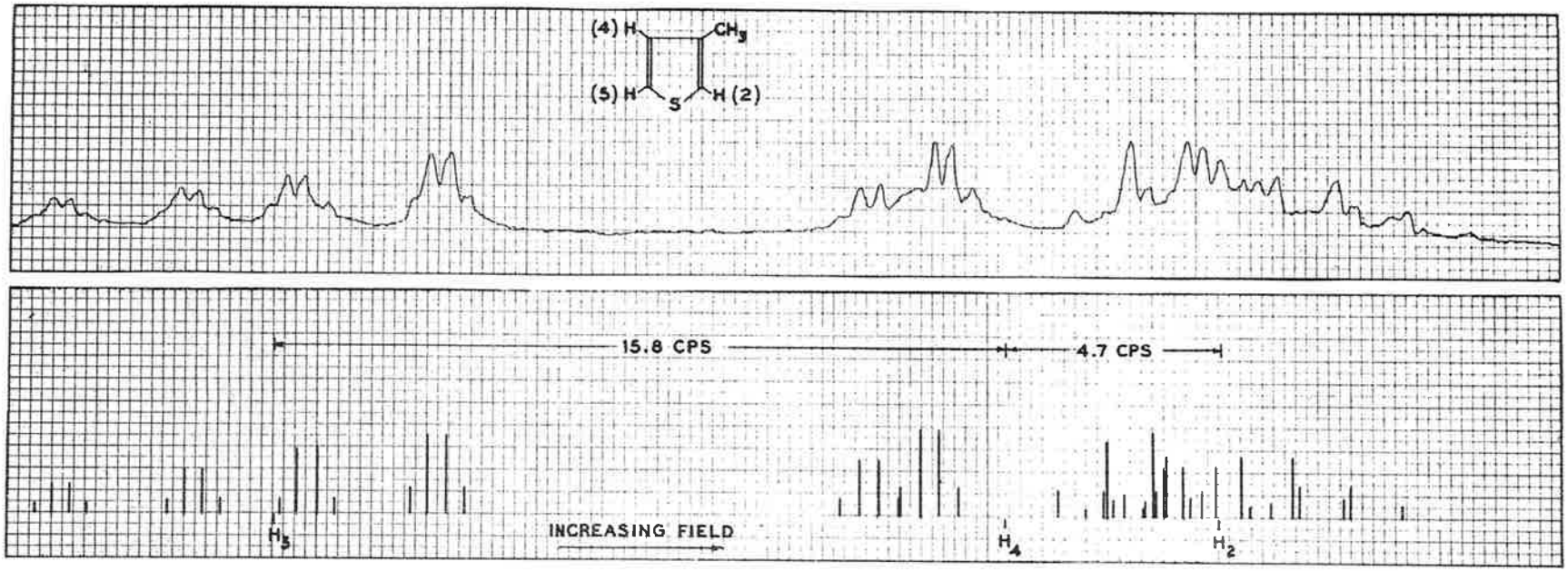
TABLE I

Coupling Constants and
Chemical Shifts for 3-Methyl Thiophene*

Coupling Constant	Measured Value
J_{54}	5.3 ± 0.1 cps
J_{52}	2.9 ± 0.1
J_{24}	1.3 ± 0.2
$J_{CH_3 \rightarrow 5}$	0.38 ± 0.03
$J_{CH_3 \rightarrow 4}$	0.42 ± 0.1
$J_{CH_3 \rightarrow 2}$	1.1 ± 0.1

Chemical Shift	Measured Value
δ 54	15.8 ± 0.8 cps
δ 52	20.5 ± 1
δ 42	4.7 ± 0.7

* Table does not include ring-methyl proton chemical shifts.



3-METHYL THIOPHENE, THEORETICAL AND EXPERIMENTAL SPECTRUM (RING PROTONS)

Frequency 60 Mc
Source API-USBM Standard Sample 12-5s
I. Weinberg : Mobil Oil Company R&D
Paulsboro, N. J.

PROTON N. S. R. SPECTROSCOPY. XI. A CARBON-13 ISOTOPE EFFECT.

By George Van Dyke Tiers

Contribution No. from the Central Research Dept.,

Minnesota Mining & Mfg. Co., St. Paul 9, Minnesota

Received

(Abstract)

High-precision measurement techniques are employed to demonstrate a very small carbon-13 "isotope effect" upon proton N. S. R. shielding values for $CHCl_3$, CH_2Cl_2 , and $(CH_3)_4Si$. The shift in position of the doublet center for protons attached to C^{13}, relative to the single peak for protons attached to C^{12}, is in the direction of increased shielding by the heavy isotope. Such has been observed previously in N. S. R. spectral studies of the effect of C^{13} upon attached fluorine, and of the effect of deuterium upon adjacent protons and fluorine atoms. The proton N. S. R. shielding shift, produced by the heavy isotope, in both cases is about one-fortieth of that for the corresponding fluorine compound. Some variability in the C^{13} proton shift is noted, but no simple correlation with spin-spin coupling constants, with relative shieldings, or with structure, is apparent.

*****

Recently a nuclear spin resonance (N.S.R.) "isotope effect" of C^{13} upon attached fluorine atoms has been discovered.[1] The rather unexpectedly large shifts were always found to be in the direction corresponding to greater shielding by C^{13} than by C^{12}. Though no shift was found for protons, the much smaller effect anticipated by analogy with the deuterium shifts[2] would not have been detected.

As both the sign and the relative magnitude of such a C^{13} effect might prove theoretically interpretable, a more elaborate experimental procedure has been used in the present work.

Experimental

The compounds studied were examined neat in the customary 5 mm. O.D. sample tubes, from which air had been swept by means of a brisk stream of bubbles of prepurified nitrogen; however, air-saturated $CHCl_3$ and $(CH_3)_4Si$ were found to give the same results. The C^{13} isotopic isomers were present at their natural abundances.

The N.S.R. spectrometer and measurement techniques have been described.[3] For the present study separate reference compounds were not employed, the exceedingly strong "parent-peak" from the normal compound being used instead. "Image" peaks (also called "side-bands") are readily produced from it by audio-oscillator modulation of the magnetic field. When C^{13} is present, the "parent peak" is split into a doublet, the coupling constant being ca. 100 to 250 c/s. The positions of these two weak C^{13} peaks are measured, separately, relative to the strong C^{12} central peak by use of the "image" peaks.[3]

(1) P.C. Lauterbur, private communication; also

I am indeed grateful for this advance information, without which it is unlikely that the present work would have been begun.

(2) G.V.D.Tiers, J.Am.Chem.Soc. 79, 5585 (1957), J.Chem.Phys. 29, 963 (1958).

(3) G.V.D.Tiers, J.Phys.Chem. 62, 1151 (1958).

The small but reproducible difference found in each case results from the isotopic shift, as otherwise the high- and low-field C^{13} components would be equally spaced from the C^{12} central peak.

Errors random in nature were counteracted by multiple repetition; all data has been used and weighted equally. Measurements were made over a three-week period. At each session six sweeps were run on each of the two C^{13} peaks for each of the compounds studied. In addition to the routine alternation of sweep direction[3], which virtually eliminates errors due to differential saturation or to "ringing" of the peaks, in most cases care was taken in the magnet cycling to obtain a "flat" field and hence very symmetrical peaks for both directions of sweep; sweep rates also were controlled to be equal (within 10%) in both directions. Subsequent examination of the data failed to reveal any significant effect of over- or under-cycling or of unequal sweep rates, or of the degree of resolution upon the magnitude or direction of the C^{13} effect. It should be emphasized that optimal resolution was not attained, nor was bad resolution tolerated. "Ringing" was never observed for any of the image peaks, or for the C^{13} peaks of $(CH_3)_4Si$, but was attained at the C^{13} peaks of the other compounds in about half of the measurements. The widths of the image peaks at half-maximum were 0.70 to 0.85 c/s. in nearly all cases, while the C^{13} peaks (when not ringing) were, if anything, narrower than the corresponding C^{12} images, except for $(CH_3)_4Si$, for which they averaged ca. 0.12 c/s wider. The effect of sweep direction is fairly large, the C^{13} isotope effect appearing to be larger by 0.002_2 ppm. when the sweep is toward decreasing field, or smaller by the same amount when the opposite sweep is used exclusively. Although such error was avoided, it would not have concealed the isotope effect. Other possibilities for directed error may be present but if so they have not been recognized.

Table I

The Excess N.S.R. Shielding, $\Delta\tau$, Produced by C^{13}, Relative to C^{12}, in Several Compounds.

Compound	No. of Meas.	$\Delta\tau$, ppm.[a] ($C^{13}-C^{12}$)	$J(C^{13}H)$ c/s[b]	Shielding Value, τ[c]
$(CH_3)_4Si$	18	+0.0042	118.20	10.000
CH_3I	18	+0.0012	151.17	7.843
CH_2Cl_2	12	+0.0042	178.24	4.720
$CHCl_3$	18	+0.0059	209.17	2.75

(a) Standard deviation of the averaged value was ±0.0012 ppm. in each case. (b) Standard deviation of the averaged value was ±0.09 c/s in each case. (c) Measured in dilute solution in CCl_4, as described in ref. 3.