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Monthly
Editorial
Letters from
Laboratories
Of
N - M - R
No. 43

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UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
PITTSBURGH 13, PENNSYLVANIA

Pittsburgh Coal Research Center

April 6, 1962

Dr. A. A. Bothner-By and
Dr. B. L. Shapiro
Mellon Institute
Pittsburgh 13, Pa.

Dear Friends:

Although we have in the past done a considerable amount of proton resonance work on coal derivatives, the many possibilities of carbon-13 spectroscopy now occupy our main interest. Using the Varian 15.085 mc/sec. R.F. unit we are able to obtain resolution of 1 ppm under rapid passage dispersion mode conditions.

One of our chief interests has been the study of carbon atoms that are completely substituted and which, therefore, cannot be investigated directly by proton resonance. We have investigated a series of non-hydrocarbon tertiary butyl derivatives and have in all cases found the single peak for the completely substituted carbon atom (figure 1). The differing effects of the hetero atoms α to the carbon atom are partly attributable to differences in electronegativity as shown by Lauterbur, Schneider, and others. Tertiary butyl groups can sometimes be identified in saturated hydrocarbons; however, the peak is often lost in the fine structure of the other aliphatic carbon atoms. We are now successfully using the spin-decoupling unit of NMR Specialties to unravel complex fine structure patterns.

Our principal endeavors have involved olefins and diolefins, and to some extent, acetylenes. We have examined a large number of terminal, internal, and branched olefins (figure 2). Fine structure obtainable with olefins, such as the triplet, doublet, and singlet for $>\text{CH}_2$, $-\text{CH}$, and $-\text{C}-$ groups respectively, provide easy identification. The completely substituted olefins are of interest because of the difficulties encountered by methods such as infrared and proton NMR in detecting such olefins. In C^{13} NMR the single peak for the completely substituted olefinic carbon atoms is easily detected. For mono-substituted internal olefins the doublet and singlet for the olefinic carbons are easily identified. The C^{13} method may become useful for functional-group type-analyses.

The unsaturated compounds of most interest are the diolefins, both conjugated and cumulative. There is little or no effect on the chemical shift of terminal olefins due to conjugation. The peaks appear in practically the same regions. For example, butadiene will have an olefinic spectrum very similar to that of 1-hexene and also 1,5-hexadiene.

For the cumulative diolefins, on the other hand, there is a striking difference. The 1 and 3 carbon atoms in methylallene are shifted upfield from the ordinary olefinic region, whereas the No. 2 carbon atom, completely substituted, will be shifted extremely far downfield by paramagnetic deshielding (figure 3). In the allenes that we have investigated the chemical shift of the central carbon atom is nearly constant and is several parts per million below that of CS_2 .

Compared with the spectra of diolefins, the acetylenic carbon atoms produce a shift quite far upfield, to the same position as that of the outside carbon atoms of the allene structure, $-\text{C}=\text{C}=\text{C}-$. As in H^1 NMR, the absorption for acetylenic carbons lies in between the absorption regions for alkyl and olefinic carbons. While investigating the acetylenes we have found a spin-spin splitting involving non-adjacent atoms, similar to that reported by Lauterbur at the recent NMR Conference. Coupling of the proton on the terminal carbon atom and the second carbon of the acetylene bond, $-\text{C}\equiv\text{CH}$, produce a J value of 47 cps, which is nearly the same as that reported by Shoolery from proton spectra, 50 cps.

We are engaged in extensive correlation studies of hydrocarbons and oxygenated compounds. The C^{13} method will be particularly useful for studying the carbonyl structures in complex carbonaceous substances.


R. A. Friedel


H. L. Retcofsky

Shoolery, J. N., Johnson, L. F., Anderson, W. A., Jour. of Molecular Spectroscopy, vol. 5, 1960, pp. 110-117.

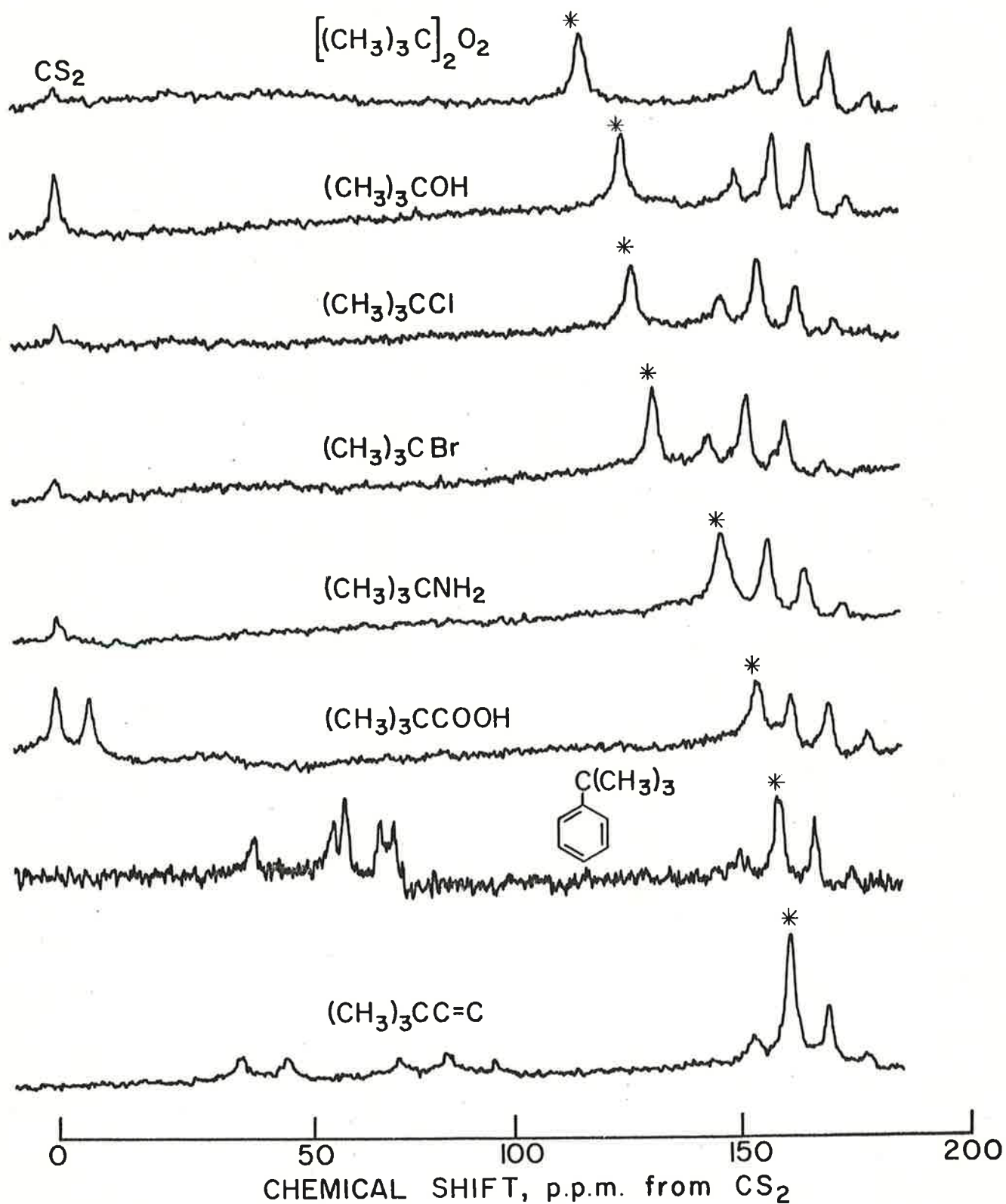


Figure 1.- C^{13} NMR spectra of compounds containing t-butyl groups.

* denotes t-butyl carbon resonance.

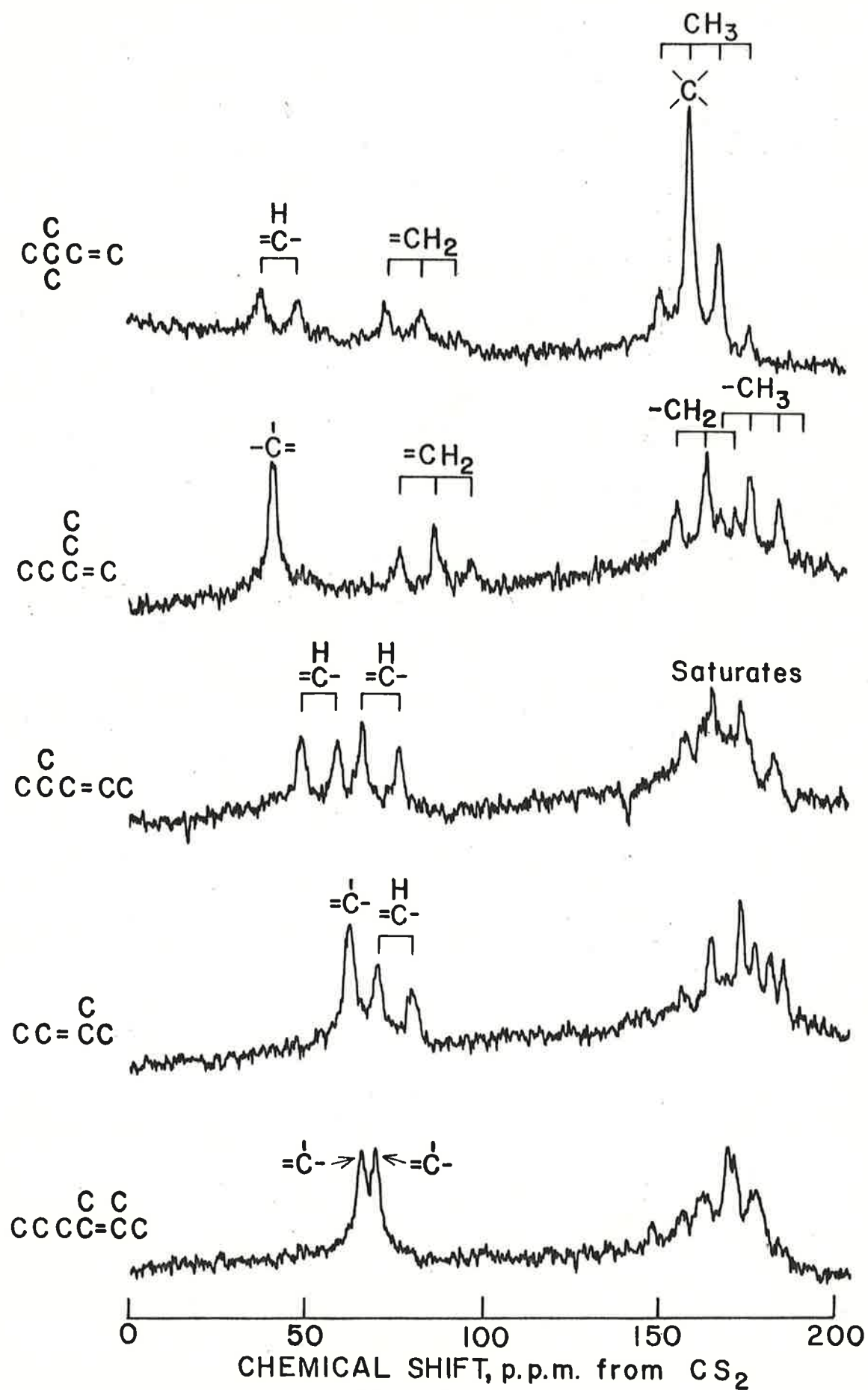


Figure 2.- ^{13}C NMR spectra of olefins.

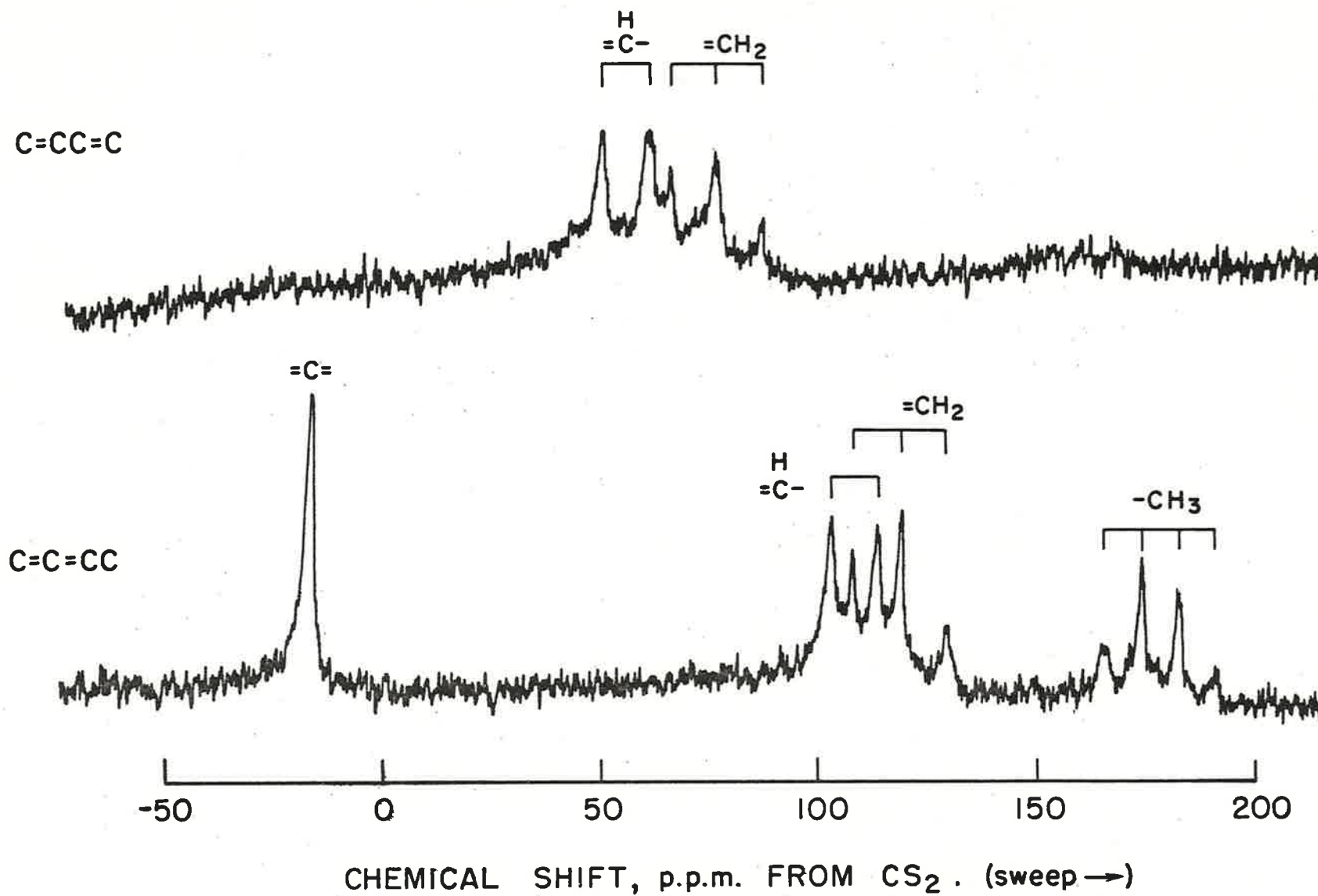
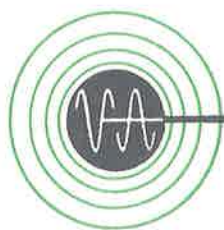


Figure 3.- C^{13} NMR spectra of 1,3-butadiene and 1,2-butadiene.



VARIAN associates

611 HANSEN WAY • PALO ALTO, CALIFORNIA • DAVENPORT 6-4000

April 9, 1962

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

Dear Barry,

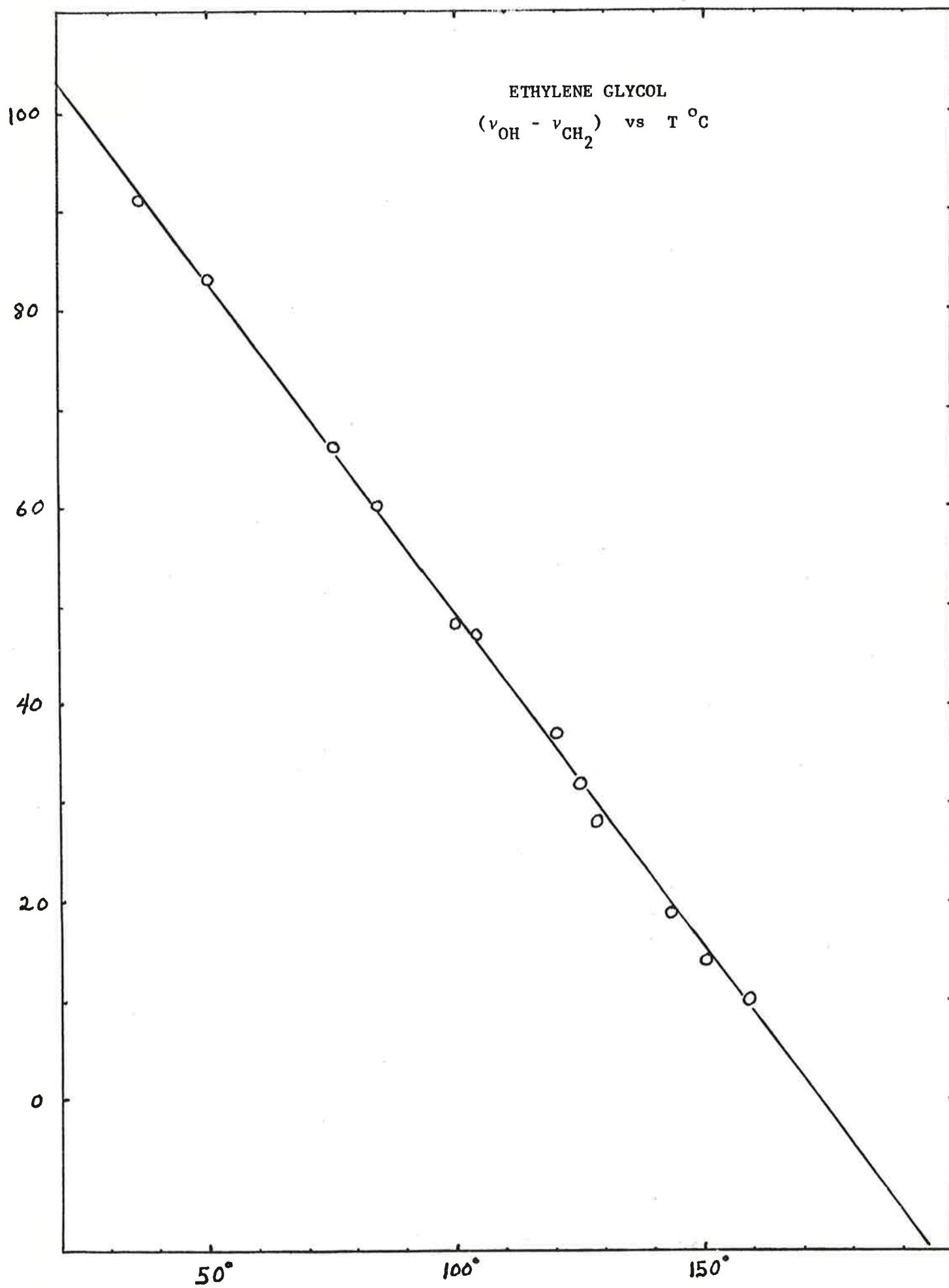
I would like to pass on some information which may be useful to MELLONMR readers. In the development of the variable temperature accessory for the A-60, the need became apparent for a sample with a temperature dependent resonance that could be used to calibrate the temperature controller. For this purpose dry ethylene glycol was found suitable from room temperature to about 200° C.

Ethylene glycol has two proton resonances: the CH₂ peak which is essentially independent of temperature, and the OH peak which shifts about 0.67 cycles per degree. At room temperature the OH resonance is about 100 cycles down field from the CH₂ peak. As the temperature of the sample is raised the OH peak moves closer to the CH₂ peak, and at 173° C the resonances cross. Plotted on the graph are data obtained using an A-60 to measure the peak separations and a thermocouple to measure the temperatures. The data may be represented by the equation $T = 173 - 1.483\Delta\nu$ to an accuracy of about two degrees. This sample also may be used for estimating thermal gradients, for these cause obvious distortions of the OH peak.

Yours truly,

Harmon Brown

HB:iw





U. S. NAVAL ORDNANCE TEST STATION
CHINA LAKE, CALIFORNIA

IN REPLY REFER TO:

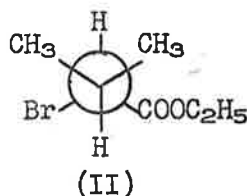
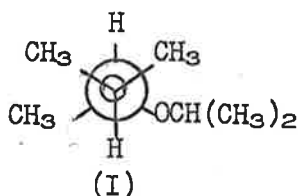
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17 Apr 1962

Dr. Aksel A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Bothner-By:

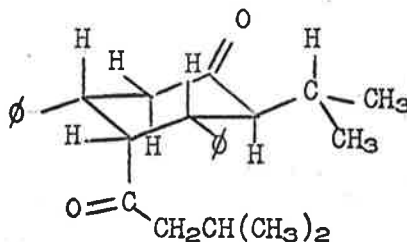
The appearance of some unexpected splittings in NMR spectra of isopropyl methyl signals in a series of cyclohexanone derivatives led us to re-investigate what a number of other NMR workers had already observed - that an isopropyl group on an asymmetric carbon will show two methyl doublets.

To reassure ourselves, and get some idea of the magnitudes of such "structural splittings", we ran proton spectra of diisopropyl acetal (for comparison with Robert's work on the diethyl compound) and ethyl 2-bromo-3-methyl butyrate. Axial projections of these molecules are shown below.



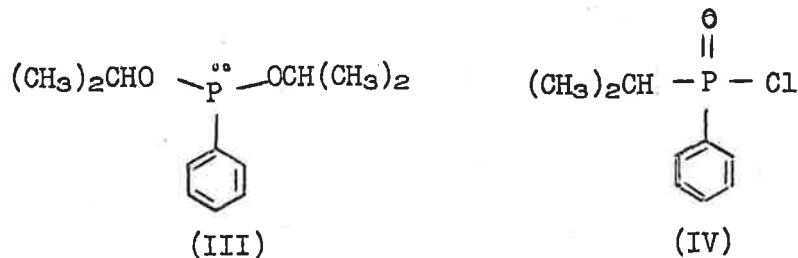
The gem-methyls of (I) are split 2.0 cps and of (II), 4.0 cps. In the acetal, of course, the asymmetric carbon is separated by an ether link from the groups which show the splitting. (Incidentally, I realize it is unfair to misuse the classic concept of molecular asymmetry in this sense, but is there a better term?)

Typical of the cyclohexanone derivatives which showed this effect is the compound below:



The isopropyl group on the asymmetric carbon shows an 8.5 cps structural splitting.

The recent supplement to the M. C. A. catalog of NMR data contains several examples of this type of splitting in which the asymmetric atom is phosphorus:



In (III) the methyls are split 3.0 cps. The splitting in (IV) is apparently equal to the proton-proton coupling constant, about 7.0 cps, resulting in an otherwise unexplainable triplet.

Problem for the student: Now that we have identified two dissimilar methyls, how do we tell which is which?

Sincerely yours,

Donald W. Moore

Donald W. Moore
Code 5058



VARIAN associates

611 HANSEN WAY • PALO ALTO, CALIFORNIA • DAVENPORT 6-4000

April 19, 1962

Dr. A. A. Bothner-by
Director of Research
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Bothner-by:

CHEMICAL SHIFTS BY DOUBLE IRRADIATION

There was a discussion some time ago (Cotton and Klapper, Newsletter No. 28) about the correction which must be applied to modulation sideband responses because of the presence of a strong centerband radiofrequency field. When observed by sweeping the magnetic field, the sideband signals are seen to be separated from the centerband response by slightly less than the modulation frequency.¹ This correction is unlikely to be important in most cases of calibration of spectra by the sideband method (except for those who make immoderate claims to accuracy) but may often be significant in proton spin-decoupling experiments where much stronger radiofrequency fields are employed. It would therefore seem natural to apply the same correction when using the 'optimum decoupling' criterion to measure chemical shifts (or relative signs of coupling constants) by the double irradiation method.

On looking into the details of spin decoupling behavior more closely² we found that this was not the whole story. Introducing the convention that X represents the proton group which experiences the strong radiofrequency field of amplitude H_2 and frequency ω_2 , and that A represents the group whose transitions are being stimulated by the weak radiofrequency field H_1 at ω_1 , we find that the conventional correction yields the condition:

$$(\omega_1 - \omega_2)^2 = (\omega_A - \omega_2)^2 + (\gamma H_2)^2$$

or by expansion, the approximate condition:

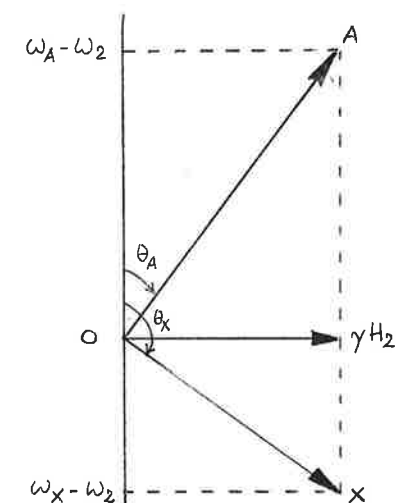
$$\omega_1 - \omega_2 \approx \omega_A - \omega_2 + (\gamma H_2)^2 / 2(\omega_A - \omega_2)$$

The point we would like to make here is that the detailed theoretical treatment indicates that the condition $\omega_2 = \omega_X$ does not produce optimum



(W. A. Anderson and R. Freeman)

decoupling—this in fact occurs when ω_2 is slightly displaced from ω_X towards ω_A . This second correction is approximately twice the magnitude of the first and in the opposite sense. It can perhaps be understood most easily by considering the effective fields seen by nuclei A and X in a



reference frame rotating about OZ at ω_2 (See figure). If

$$\gamma H_2 / 2\pi \gg |J|$$

the spins are quantized along the effective fields, vectors OA and OX respectively. The condition for optimum decoupling is that the axes of quantization be at right angles ($\theta_X - \theta_A = \pi/2$). With this

condition, $\tan \theta_A = \gamma H_2 / (\omega_A - \omega_2) = (\omega_2 - \omega_X) / \gamma H_2$ and therefore,

$\omega_2 - \omega_X = (\gamma H_2)^2 / (\omega_A - \omega_2) \approx (\gamma H_2)^2 / (\omega_A - \omega_X)$. Thus, for a field sweep experiment the total correction is given by the condition,

$$\omega_1 - \omega_2 \approx \omega_A - \omega_X - (\gamma H_2)^2 / 2(\omega_A - \omega_X).$$

We have verified this relation experimentally on a sample of 1,1,2-trichloroethane. This work forms part of a general treatment of spin-decoupling experiments² which extends the work mentioned in Mellon Newsletter No. 40 to cover any molecules of the type $A_n X_m$ where $n, m \leq 3$.

Yours sincerely,

W. A. Anderson

W. A. Anderson
Ray Freeman
R. Freeman

Instrument Division

1. W. A. Anderson, Phys. Rev. 102, 151 (1956); "N.M.R. and E.P.R. Spectroscopy", Pergamon Press, (1960), p. 164.
2. W. A. Anderson and R. Freeman, J. Chem. Phys., to be published.



VARIAN associates

611 HANSEN WAY • PALO ALTO, CALIFORNIA • DAVENPORT 6-4000

April 20, 1962

Dr. Aksel Bothner-by
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania

Dear Aksel:

The interest displayed in proton-proton spin decoupling at the Third Conference on Experimental Aspects of NMR has prompted us to try some experiments along these lines using the existing Varian integrator. The following describes a simple modification in the system which has allowed us to obtain 60 mc. decoupled spectra such as those shown in figures 1 and 2. The modification is easily removed so that operation as a normal integrator is not hampered. The method is similar to that described by Freeman and Whiffen, Mol. Phys. 4, 321 (1961).

As you know, the integrator operates in conjunction with a 2Kc field modulator using a modulation index of 1.8, an optimum amount for centerband work. It is possible to operate in a sideband mode by attenuating the modulation level and shifting the audio phase 90° . This is done conveniently by breaking connection between the modulator output and the probe sweep coils and inserting a 0.01 μ fd capacitor. In our system this reduced the 2Kc voltage at the sweep coils from 9v r.m.s. to 0.035v r.m.s. Since the effective H_1 in the sideband is a function of $J_1 H_1$, H_1 must be increased approximately 40 db at this new low level of modulation compared to the centerband method. Ordinary absorption spectra, differing only in sign, are then obtained by using either the upper or lower 2Kc ($\pm \omega_1$) sideband.

Since the new modulation index is very small there is a large H_1 power level at the centerband frequency (however, signals at the centerband are not detected because of the 90° phase shift). Additional field modulation at a variable frequency, ω_2 , can make a portion of this H_1 power available for selective nuclear saturation and hence spin-spin decoupling. The modulation index at ω_2 is much larger than that used for ω_1 but is still small enough so that the centerband component and hence the 2Kc sideband components are not greatly reduced. In our system the variable frequency voltage at the sweep coils, when set near 2Kc,



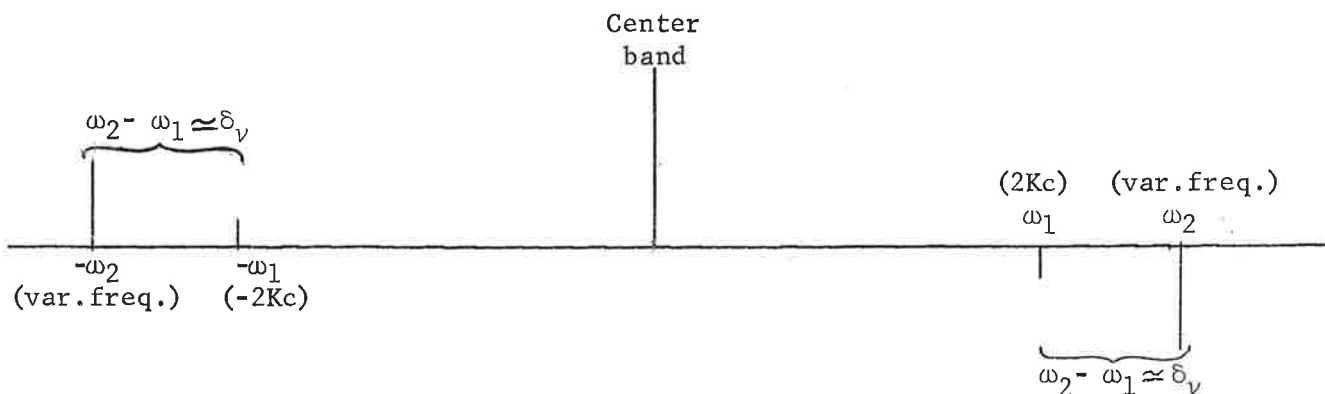
(Roy Johnson)

- 2 -

is 5.0v r.m.s.

When operating on the lower 2Kc sideband protons whose chemical shifts are at higher applied field than those to which they are coupled may be decoupled by setting $\omega_2 - \omega_1$ equal to the chemical shift (or whatever frequency difference near this value that gives the best decoupled spectrum). This produces a spectrum such as that shown in figure 1a. To record a decoupled low field group the upper 2Kc sideband is recorded after reversing the leads to the sweep coils to obtain an upright spectrum. Alternately, the low field 2Kc sideband may be used if $\omega_1 - \omega_2$ is set approximately equal to the chemical shift. The former method was used for figure 1b.

The following diagram should serve to illustrate the method; note that the intensities are not drawn to scale. The audio phase detector operates with reference voltage at 2Kc so that signals are detected only at $\pm 2Kc$.



Figures 2a and 2b show that the system is capable of producing acceptable spectra using moderately weak solutions as well as neat liquids. No difficulties were encountered in recording these spectra.

For those who are interested I will soon have available a more detailed write-up on this method including some comments on operating technique. A letter to me will insure receipt of this information.

Sincerely yours,

Roy Johnson

L. F. Johnson
Applications Laboratory
Instrument Division

*unperfected
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LFJ:jl

ETHANOL

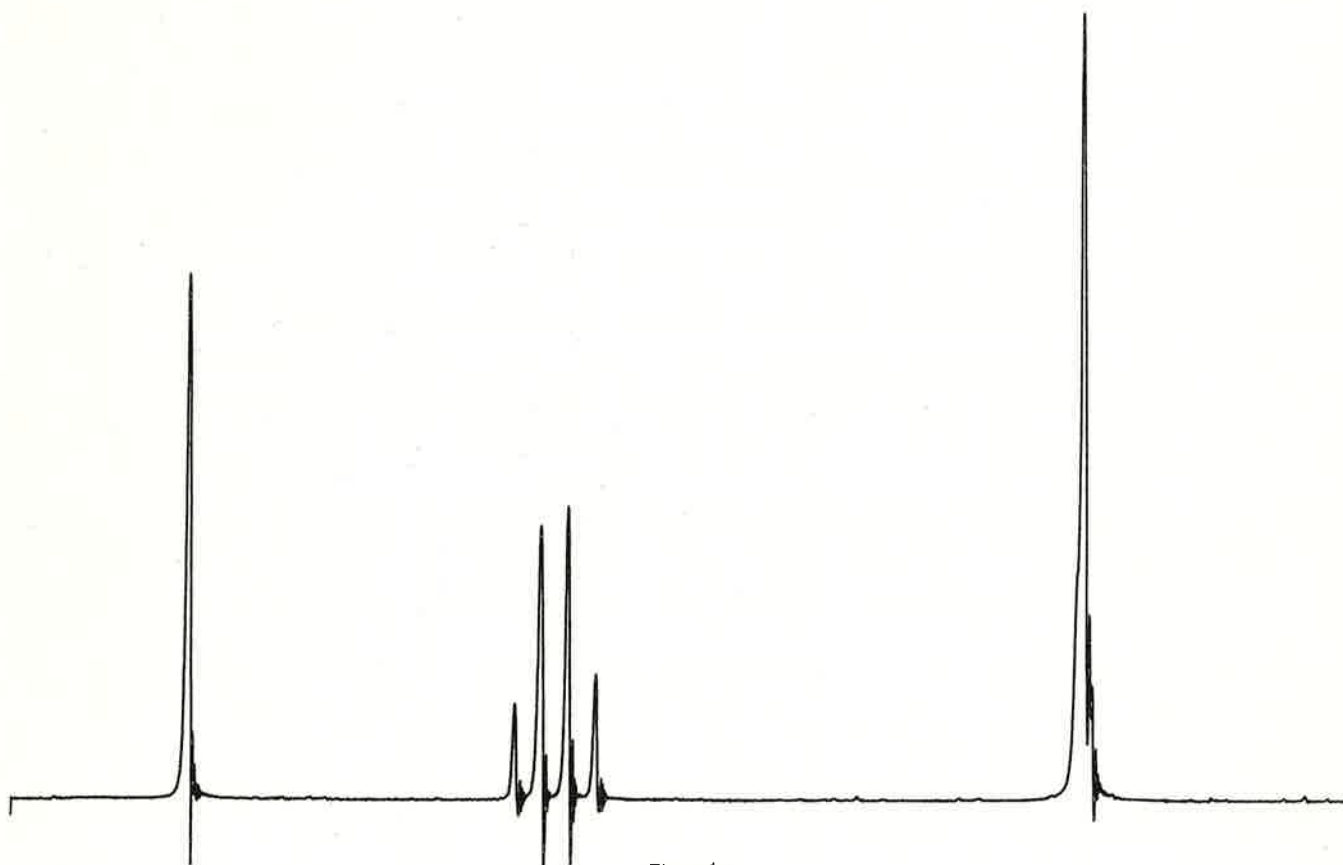


Figure 1-a

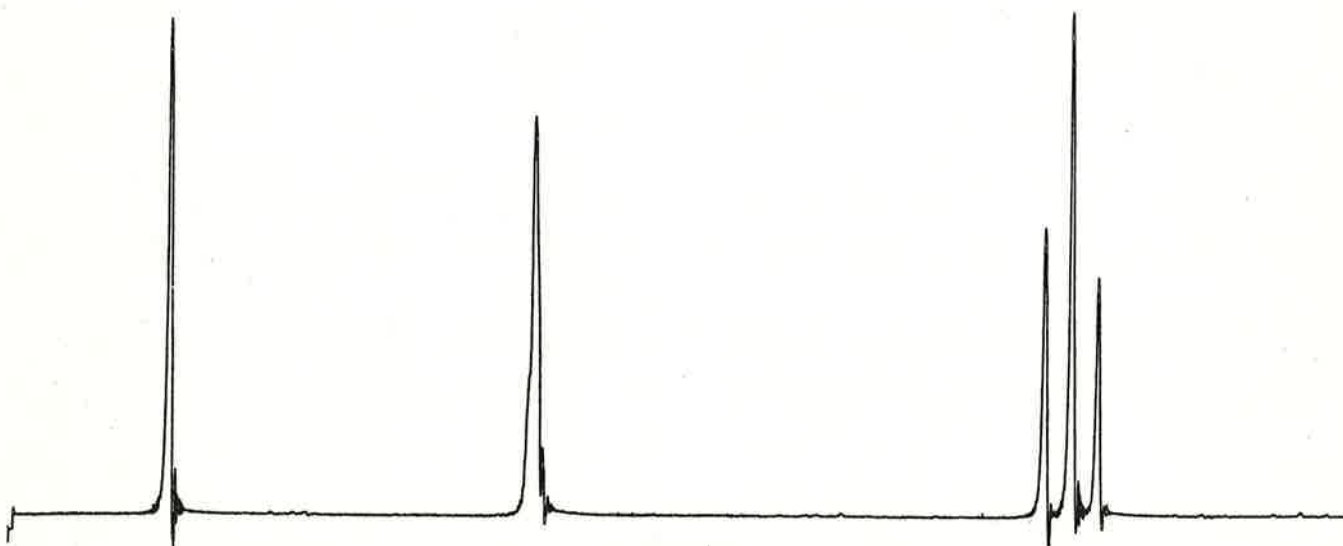


Figure 1-b

2% ETHYL BENZENE
(ethyl group only)

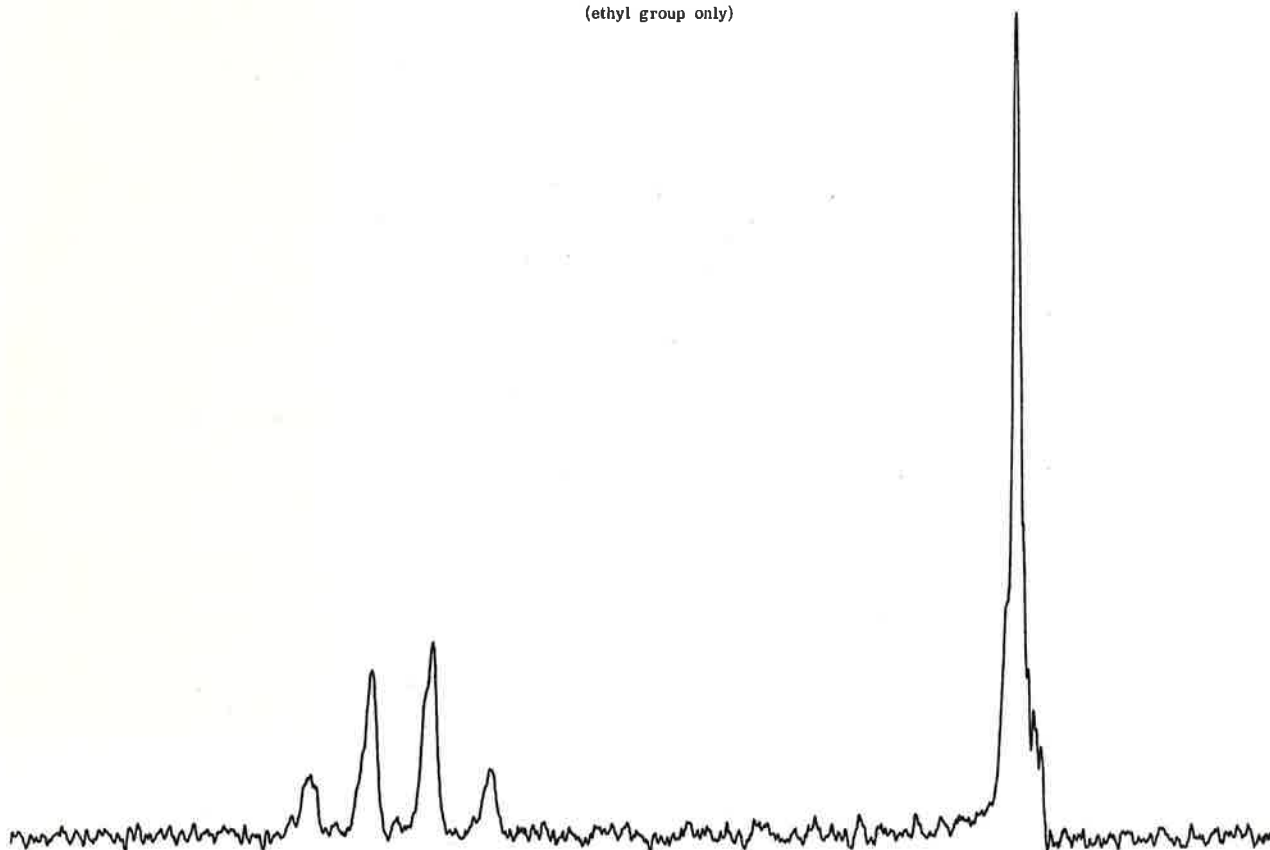


Figure 2-b

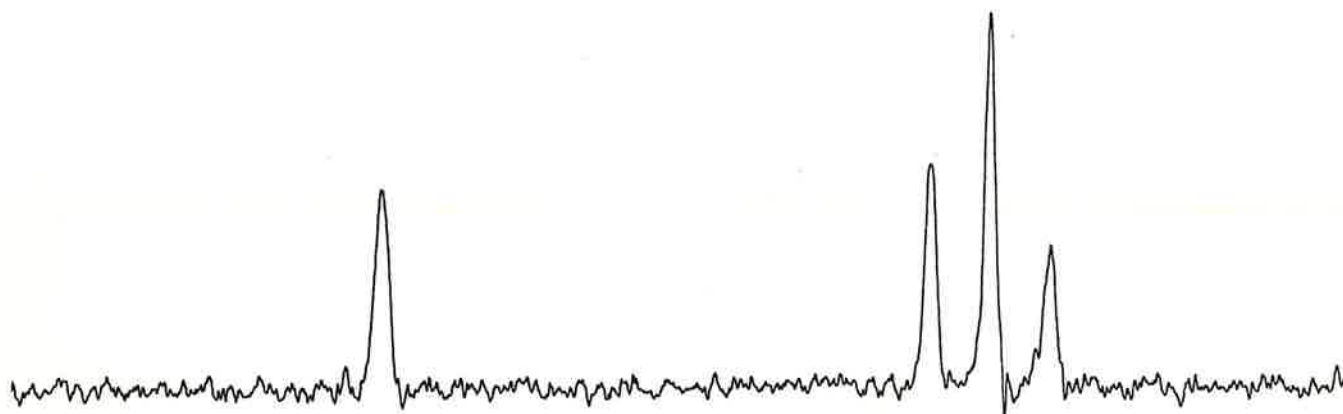


Figure 2-a



**Laboratorium
für organische Chemie**
Eidg. Technische Hochschule
Zürich

Dr. D. Mesche

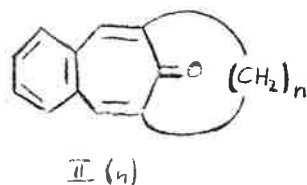
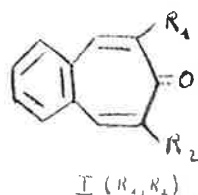
ZÜRICH,
Universitätstr. 8

March 22nd 1962

Dr. A. Bothner-By
Nelson Institute
4400, Fifth Avenue
Pittsburgh 15 pa

Dear Dr. Bothner-By,

We have recently investigated the NMR-spectra of 4,5-benzotropone of types I and II.



R_1, R_2 : CH_3 -(Me), CH_2CH_2 -(Et), $\text{CH}_2(\text{CH}_2)_4$ -(Pr),
 $\text{CH}_2(\text{CH}_2)_6$ -(Hx) and $(\text{CH}_2)_7$ -(I-Hx)

These substances had been prepared in connection with investigations being carried out on the electronic structure of tropone¹⁾. Other physical properties (UV, IR, dipole moment,...) of II(n) have shown that when n is small, the benzene and tropone rings are not coplanar. The lowest value of n for which a Stuart-Hirschfelder model of a planar tropone ring can be built is 9, but it is only with $n = 12$ that can be done without strain.

The spectra of II ($n = 12$) and of I (Hx, Hx) (compare table and Fig.) are quite similar indicating an undistorted structure for II($n = 12$). In the spectra of II(n) where $n = 7$ and 9 the signals of the tropone ring protons are considerably shifted to higher field, whereas the position of the signals of the benzene ring protons are only slightly changed. The four α -methylene-protons of II ($n = 12$) are equivalent and their free rotation is not hindered. Their δ -values (2.75 ppm) are slightly



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für organische Chemie**
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Zürich

ZÜRICH,
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larger than that of I (Hx, Hx) (2.61 ppm) or of exaltol (2.33 ppm). In the spectra of II, where $n = 9$ and 7 there are broad signals at $\delta = 2.31$ ppm and 3.01 ppm resp. corresponding to only two protons. They belong probably to that proton of the α -methylene group which is more strongly deshielded by the carbonyl group. The δ -values of the benzene ring protons in 4,5-benzotropone are of the same magnitude as the average δ -value of α - and β -protons in naphthalene. The δ -values of the α - and β -protons in the tropone ring are comparable with those of the double bond protons in cinnamic aldehyde ($\delta = 7.36$ ppm, 6.64 ppm). This indicates that in 4,5-benzotropone the tropone ring does not have much "oxy-tropylium" - character. This result is consistent with the information which gave especially the UV spectra and show that the large dipole moment and the low $\text{C}=\text{O}$ - stretch frequencies of 4,5-benzotropone may not be overestimated.

We are working now on the spectra of 4,5-benzazabenzone, 2,3-dihydro-4,5-benzazabenzone and some homologous oxybenzotropylium- and benzotropylium-cations, which should give useful information concerning the problem of their aromatic character.

The enclosed spectra you may copy, if they are of general interest.

With best regards,

Doris Mesche

Dr. D. Mesche

Not mentioned

1. E. Kloster-maggen, H. Tölg, A. Schenker and G. Heilbrunn, *Helv. 39, 789*

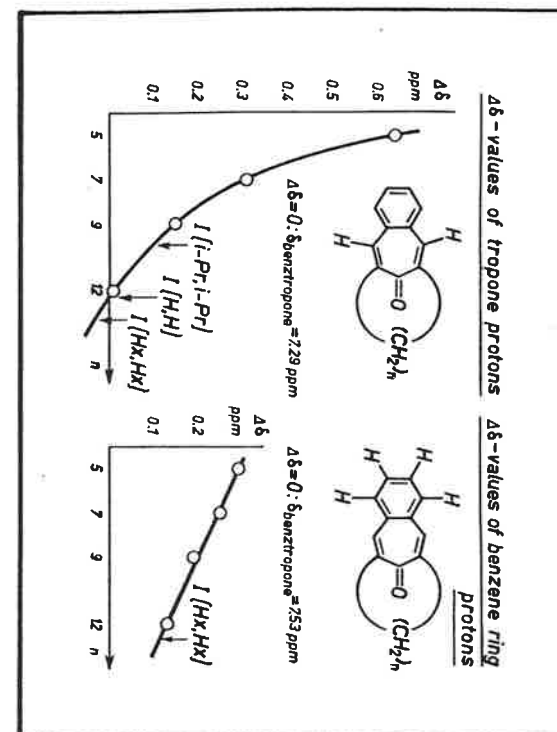
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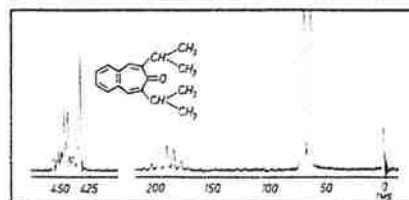
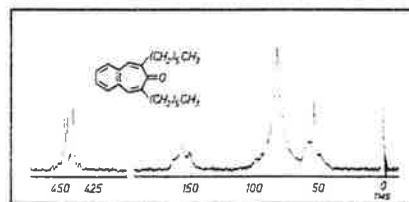
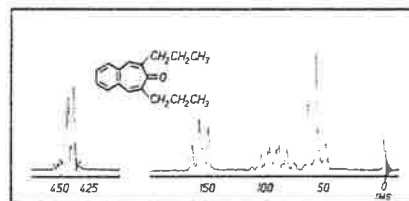
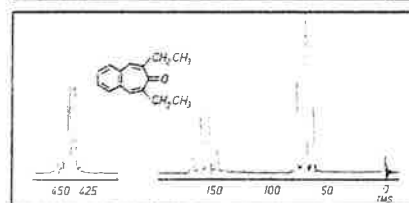
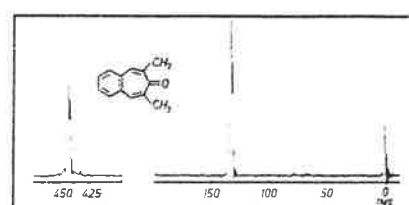
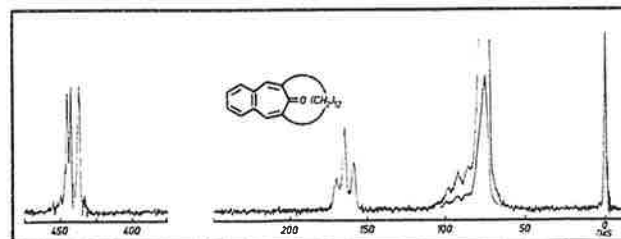
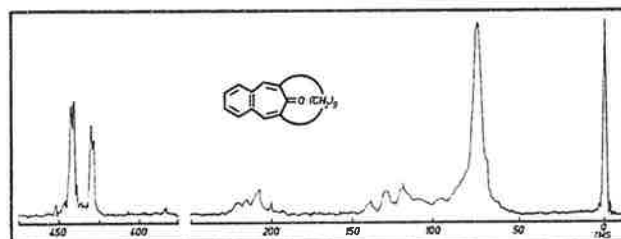
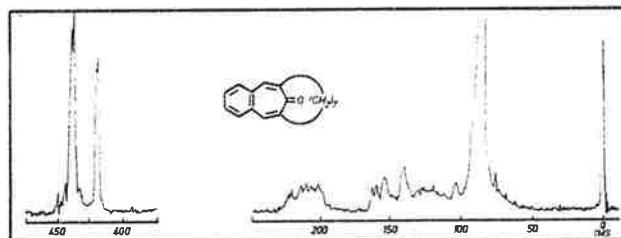
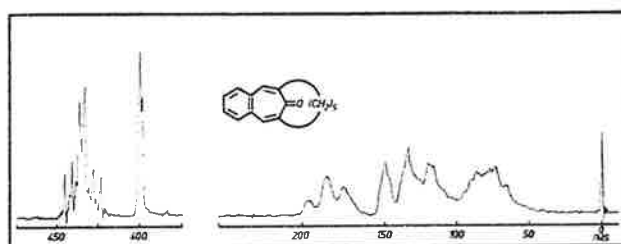
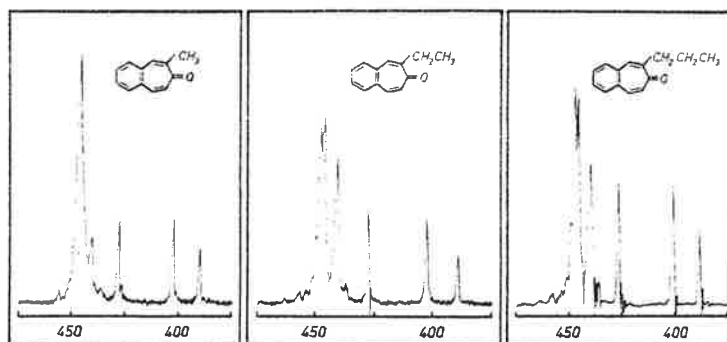
Tabelle I

 δ -values of ring protons (ppm) *)

Substituent	Protons			
	R_1 resp. n	R_2		
	on benzene ring	on tropone ring in α -position in β -position to the benzene nucleus		
		A B	J_{AB} (cps)	
I H H	7.53	7.29 6.61	12.3	
I Me H	7.43	7.24 6.60	12.6	
I Et H	7.45	7.33 7.22 6.58	12.9	
I Pr H	7.44	7.33 7.22 6.58	13.1	
I Me Me	7.41	(7.39)		
I Et Et	7.39	7.30		
I Pr Pr	7.41	7.32		
I Hx Hx	7.42	7.32		
I i-Pr i-Pr	7.41	7.19		
II n = 5	7.24	6.65		
II n = 7	7.28	6.98		
II n = 9	7.34	7.14		
II n = 12	7.40	7.28		

*) The spectra were measured with a Varian HA 60 Spectrometer at the Varian Research Laboratories Zürich. (We thank Dr. A. Melzer for his kind introduction in the technique of NMR) The frequencies were determined with the usual side-band technique (± 1 cps) on 5-10% non degassed solutions in CCl₄. (TMS internal reference: $\delta = 0$ ppm). These compounds had already been measured, on a TRUP-TM 25 MHz, by Prof. H. Primas and P. Bommer. The chemical shift values agree well with those obtained on the Varian Spectrometer. The given values of $I(H, n)$ are measured at 25 MHz.





UNIVERSITY OF CALIFORNIA

Bio-Organic Chemistry Group
LAWRENCE RADIATION LABORATORY
BERKELEY 4, CALIFORNIA
1557 Life Sciences Building

March 30, 1962

Dr. A.A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Bothner-By,

For one reason or another our n.m.r. work has been virtually at a standstill for the past several months. We do have two projects under way which I can briefly describe. Neither is sufficiently far along to yield even preliminary results.

We are pursuing our study of the S-S bond (MELLONMR no. 22 and J.A.C.S. 83, 4357 (1961)) by studying the internal conversion of the seven membered ring compound 1,2-dithiane. This will yield an independent number for the barrier height for rotation about the S-S bond. Aside from this, the study of the conformation of the molecule is of some interest in itself. The n.m.r. spectrum of the molecule is split into two groups of lines; contributions from the protons coming at $\tau \sim 7.23$, and contributions from the remaining protons at $\tau \sim 8.07$. These spectra are too complicated for internal conversion analysis through observation of the collapse of a simple n.m.r. doublet, so compounds which are methyl substituted in these positions are being synthesized.

The other project has to do with the n.m.r. spectrum of highly pure chlorophyll a which has been extracted from plant materials and purified in our laboratory. We are investigating the exchange properties of the bridge protons as well as the C₁₃ proton in the isocyclic ring of the chlorophyll a molecule. Sample concentration is somewhat of a problem, so we are having a larger spinner made.

We should have some numbers to quote soon; hopefully before you have to turn us.

Yours truly,

G.M. Andrews

G.M. Andrews

GA/LRB

CYANAMID

AMERICAN CYANAMID COMPANY
STAMFORD RESEARCH LABORATORIES
1937 WEST MAIN STREET, STAMFORD, CONN.
FIRESIDE 8-7331

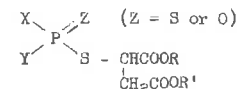
April 10, 1962

Dr. B. L. Shapiro
MELLONMR News Letter
Mellon Institute
Pittsburgh 19, Pennsylvania

Dear Barry:

Recently Kuntz, Schleyer, and Allerhand (J. Chem. Phys. 35, p. 1533) reported long-range N¹⁴-H¹ couplings in isocyanates, where the coupling, normally broadened by quadrupole relaxation, is rendered visible by high electric field symmetry at the N¹⁴ nucleus. They stated that they had not observed long range N¹⁴-H¹ couplings in other molecules. We have observed this, however, in the quaternary salts (C₂H₅)₄N⁺Br⁻, C₂H₅(CH₃)₃N⁺I⁻, and (CH₃)₂CH(CH₃)₃N⁺I⁻ in both D₂O and dimethyl sulfoxide solution. In these cases it is not surprising that the electric field gradient is near zero, but it is interesting to note that the only coupling observed is with the hydrogens on the α carbon atom. Thus the methyl 1-2-1 triplet of the ethyl groups is further split into a 1-1-1 triplet with $|J| = 3.3$ cps, and the isopropyl methyl doublet is similarly split with $|J| = 2.1$ cps. The α -hydrogen coupling is evidently near zero. Thus it appears that this nitrogen case is similar to those already noted for Pb, Hg, P, etc., where coupling to the α hydrogens of attached ethyl groups was found to be larger than to the β hydrogens. We also noted that in the compound (C₂H₅)₃NCH₂I⁺I⁻, the symmetry was apparently destroyed sufficiently to wash out the extra splitting.

We have observed that the methoxy groups (X and Y) in several compounds with the structure



have an observable non-equivalence. The methoxy doublets (the doublets arise from coupling to the phosphorus) are separated by 0.13 ppm when

43-19

INSTITUT FÜR ELEKTROWERKSTOFFE

GEMEINNÜTZIGES FORSCHUNGsinstitut DER FRAUNHOFER-GESELLSCHAFT

Dr. B. L. Shapiro

- 2 -

April 10, 1962

observed in 10% chloroform solution. The possibility that this extra doubling arose from a long range spin coupling to the succinate CH was disproved by observations of both the CH resonance and the solvent dependence of the splitting. The non-equivalence is evidently produced by the asymmetry at the succinate CH carbon. This is well removed in terms of the number of intervening bonds, but the major contribution to the shift probably arises from the anisotropy of the C=O groups, which may actually approach rather closely to the methoxy groups. A compound in the series with only one OCH₃ group (X was OCH₃, Y was S-C₂H₅) showed the splitting also. Since now the phosphorus atom is also now an asymmetric center, the two separate resonances would be due to molecules having dd' (or ll') or ld' (or dl') arrangements.

Very truly yours,

John E. Lancaster
John E. Lancaster

Maria T. Neglia
Maria T. Neglia
Magnetic Resonance Group
Research Service Department

lmb

INSTITUTSDIREKTOR:
PROF. DR. R. MECKE

Dr. Aksel A. Bothner-By
Mellon Institute
4400, Fifth Avenue,
Pittsburgh 13, Pa.
U S A

FERNRUF NR. 5514

FREIBURG I. BR.
ECKERSTRASSE 4

April 10, 1962

Ihre Zeichen: Ihre Nachricht vom: Unser Zeichen:

Dear Dr. Bothner-By:

Some time ago, POPLÉ et al. (Mol.Phys. 3, 547 and 557 (1960) = Ref. 1) have made the very useful suggestion to treat spectra of the type $A_mB_nR_pX_q$ as a superposition of simpler spectra by introducing "effective" LARMOR frequencies.

On this basis we have analysed A_2B_2X spectra (B. DISCHLER and G. ENGLERT, Z. Naturforsch. 16a, 1180 (1961) = Ref. 2) and as a further point we have tried to determine the relative signs of the spin-coupling constants J_{AX} and J_{BX} in a case where no information from the X-spectrum can be derived and no spin decoupler is available (see e.g. FREEMAN, MELLONMR 40, 2 (1962)).

The general idea is demonstrated in Fig. 1 for a simple ABX spectrum. The centers of the two superimposed AB-spectra are separated by exactly $\frac{1}{2} |J_{AX} + J_{BX}|$. These centers are observable by multiple quantum transitions, which occur under saturation conditions (W. ANDERSON, Phys. Rev. 104, 805 (1956)). Depending on the relative signs of J_{AX} and J_{BX} spectra like Fig. 1b or 1c may be observed. In an A_2B_2 system 21 multiple quantum transitions are possible (16 for $\Delta F_2 = 2$, 4 for $\Delta F_2 = 3$ and 1 for $\Delta F_2 = 4$). Again there is a strong signal at the center position, which results from the superposition of three lines.

In the actual case of liquid pyrrole, the complete analysis²⁾ of the normal spectrum yielded $|J_{AX}| = 2.6$ and $|J_{BX}| = 2.3$ c.p.s. The two possible patterns under saturation conditions are given in fig. 2c and 2d. In several recordings we observed the pattern of fig. 2c with $|J_{AX} + J_{BX}| = (2.4 \pm 0.1)$ c.p.s., giving evidence for like signs. (Most of the multiple quantum transitions are buried under the single quantum spectrum).

Since our latest publication¹⁾ on A_2B_2 -spectra²⁾ we have completed the analysis for about 30 further compounds. Our main interest is in the study how the proton coupling constants in the benzene ring are influenced by substituents.

We hope to present the results in a future contribution to

MELLONMR.

Sincerely yours,

B. Dischler
Bernhard Dischler

43-22

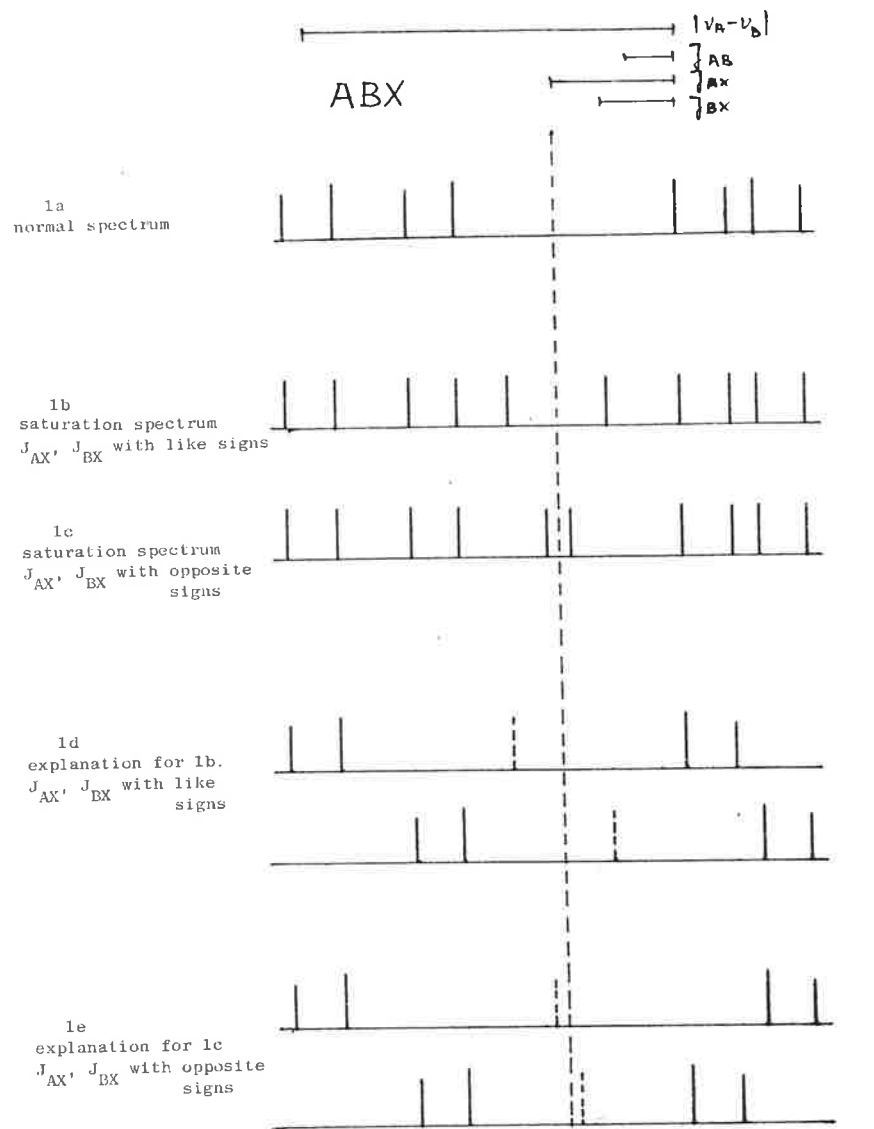
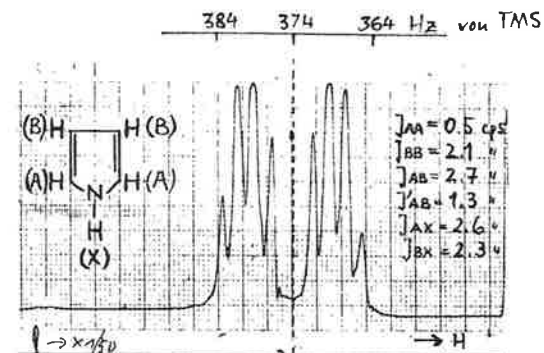


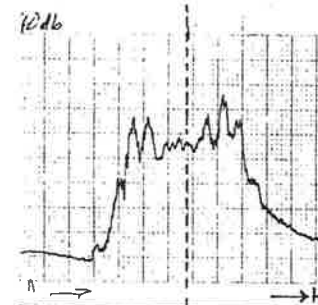
Fig. 1

Determination of relative signs of coupling constants for ABX by multiple quantum transitions (schematic).

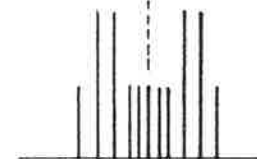
2a
pyrrole (liquid)
normal spectrum
at 60 Mc.



2b
pyrrole (liquid)
spectrum with multiple
quantum transitions
(H_1 -field increased
by 22 db)



2c
saturation pattern
expected for J_{AX}, J_{BX}
with like signs



2d
saturation pattern
expected for J_{AX}, J_{BX}
with opposite signs

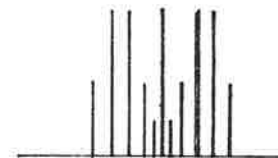


Fig. 2

Determination of the relative signs of $J(\text{NH}-\text{H}_\alpha) = J_{AX}$ and $J(\text{NH}-\text{H}_\beta) = J_{BX}$ by multiple quantum transitions.

(Contribution from Research and Development, Humble Oil and Refining Company, Baytown, Texas)

CARBONIUM ION REARRANGEMENT IN THE CATIONIC POLYMERIZATION OF BRANCHED ALPHA OLEFINS

by

W. R. Edwards and N. F. Chamberlain

ABSTRACT

The polymerization of olefins of the series (n-1)-methyl-1-alkenes through carbonium ion intermediates appears to involve a rearrangement from a secondary to a tertiary carbonium ion.



The structure of the final polymer, as determined by NMR, depends on the relative rates of rearrangement and polymerization. At low temperatures the repeating unit



investigated, the rate of rearrangement decreases with increasing length of the monomer, and is comparable to the rate of polymerization for 4-methyl-1-pentene.

The resonances of the methyl groups in the repeating polymer units appear as distorted first order spin-spin multiplets, and can be readily attributed to $\text{CH}_3\text{-CH}_2\text{-}$, $\text{CH}_3\text{-CH-}$, or $\text{CH}_3\text{-C-}$ groups. When mixtures of the groups are present, the complex but stable patterns produced are characterized by comparison with spectra of known compounds. For this series of polymers, the ratio of intensities of the methyl to methylene resonances decreases with increasing length of the monomer chain, as is required by the proposed polymer structures.

NMR CONDITIONS
SOLVENT: CCl_4
CONCENTRATION: <5%, ESTIMATED
INTERNAL REF.: TETRAMETHYLSILANE
SAMPLE TEMP.: 32° C.
INSTRUMENT: VARIAN A-60
FREQUENCY: 60 Mc
SCAN RATE: 1 CPS/SEC.
R. F. AMPLITUDE: 0.3 mG (DIAL READING)

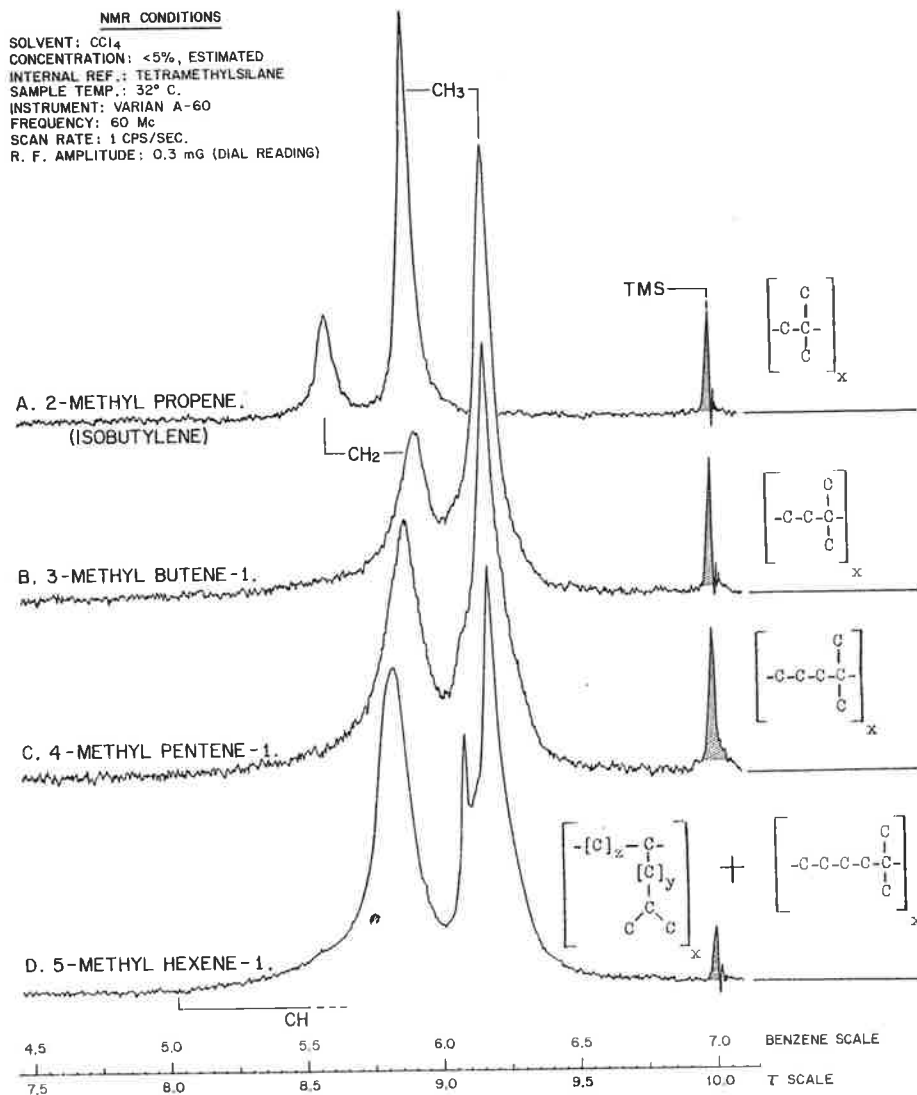


FIG. 1. NMR SPECTRA OF ACID CATALYZED POLYMERS OF THE SERIES (n-1)-METHYL ALKENE-1. AlCl_3 POLYMERIZED AT -73° C.

43-22

NMR CONDITIONS

SOLVENT: CCl₄
 CONCENTRATION: < 5%, ESTIMATED
 INTERNAL REF.: TETRAMETHYLSILANE
 SAMPLE TEMP.: 32° C.
 INSTRUMENT: VARIAN A-60
 FREQUENCY: 60 Mc
 SCAN RATE: 1 CPS/SEC.
 R. F. AMPLITUDE: 0.3 mG (DIAL READING)

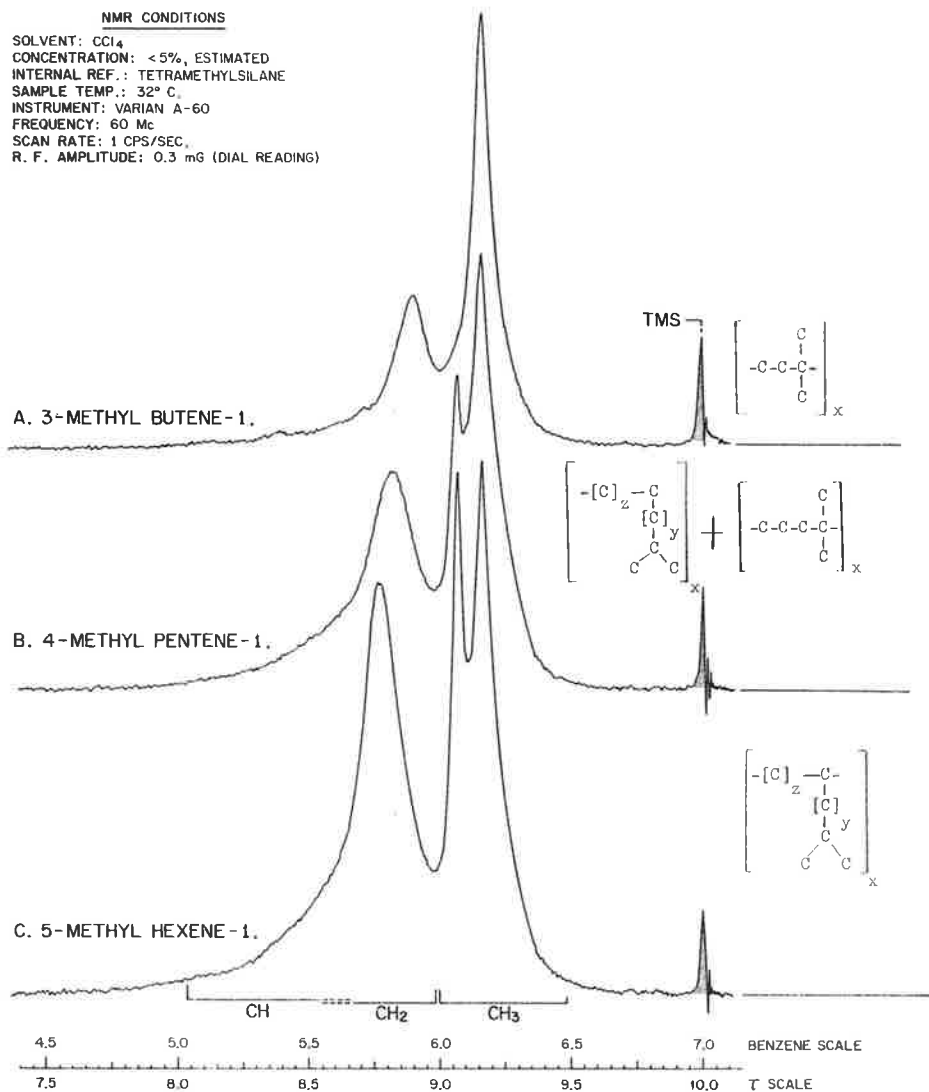


FIG. 2. NMR SPECTRA OF ACID CATALYZED POLYMERS OF THE SERIES (n-1)-METHYL ALKENE-1. AlCl₃ POLYMERIZED AT 0° C.

NMR CONDITIONS

SOLVENT: 2-CHLOROTHIOPHENE
 CONCENTRATION: < 5%, ESTIMATED
 INTERNAL REF.: HEXAMETHYLDISILOXANE
 SAMPLE TEMP.: 120° C.
 INSTRUMENT: MODIFIED VARIAN V-4300 WITH PROTON SIGNAL CONTROL OF FIELD
 FREQUENCY: 60 Mc
 SCAN RATE: 2 CPS/SEC.
 R. F. AMPLITUDE: 0.06 mG (EQUIV. TO 0.2 mG DIAL READING ON A-60)

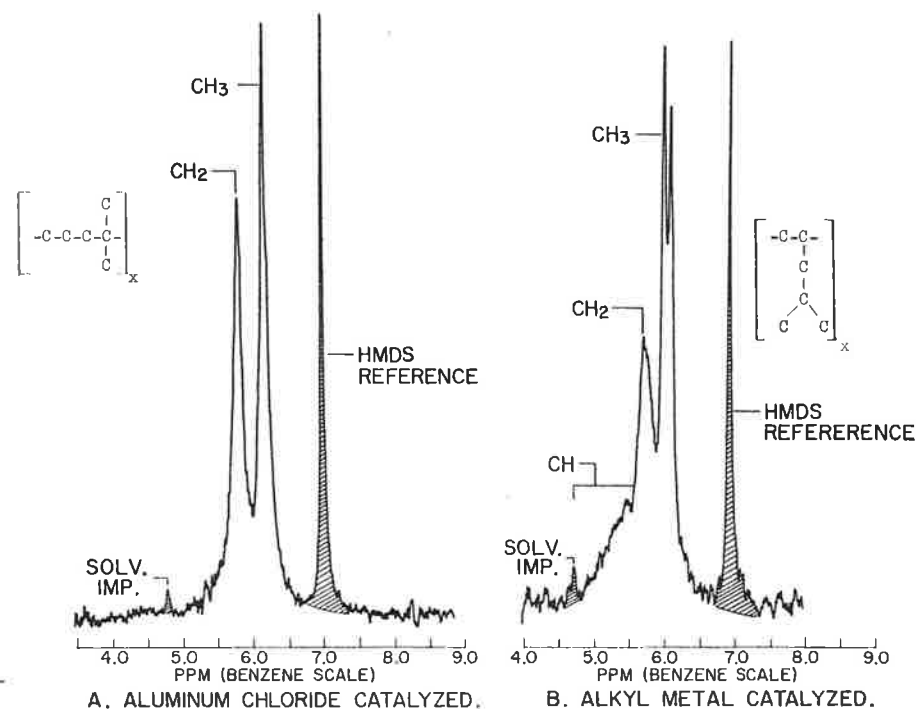


FIG. 3. NMR SPECTRA OF POLYMERS OF 4-METHYL-1-PENTENE.

COMMENTS ON THE SIGNS OF PROTON COUPLING CONSTANTS

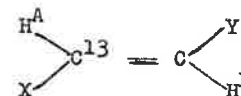
Sir:

A number of recent papers¹ concerned with spin-spin coupling of non-bonded protons have contained experimental results that are inconsistent with certain quantitative aspects of the approximate valence-bond theory for these systems.² The essential point is that in the compounds studied the relative signs of the geminal (1,1) and vicinal (1,2) proton coupling constants were determined to be of opposite sign,³ while the simple theory indicates that the constants should be of like sign if reasonable values for the bond angles are assumed.

Although a detailed comparison of theory and experiment is complicated by a number of factors (e.g., effect of substituents with lone-pair electrons, lack of knowledge of bond angles, question of uniqueness of the assignments), the most important problem is that only relative signs are provided by the available data in contrast to the absolute signs obtained from the calculations. Thus, the observed difference in relative signs for the geminal and vicinal couplings does not show which of the theoretical results are in error. In this Communication, we wish to suggest a method for obtaining an indication of the absolute sign of the proton coupling constant and to present some comments on what might be significant approximations in the theory.

It is known that the absolute signs of coupling constants in molecules can be determined, in principle, by a low temperature

measurement of relative populations in different nuclear spin states.⁴ However, the difficulty in finding suitable conditions for such experiments has thus far discouraged all attempts. As an alternative to such direct measurements, it is of interest to consider the following somewhat indirect approach. The theoretical results for the sign of the spin-coupling constant between directly-bonded atoms are considerably more straightforward than those for nonbonded species. From the detailed calculations⁵ for H₂ and the more approximate treatments of the contact interaction in complex systems (e.g. C-H, B-H)⁶ it is very probable that the sign of the coupling constant is positive. (Here the positive sign is taken to signify that an antiparallel nuclear spin orientation corresponds to a more stable state than the parallel orientation.) This result suggests that an "absolute" sign determination could be made by a measurement of the sign of a non-bonded proton-proton coupling constant relative to the coupling constant between a proton and a directly-bonded carbon 13. By means of the double-irradiation technique⁷ that was first applied to relative sign determinations by Evans and Maher⁸ and has been effectively exploited more recently by Freeman and Whiffen,⁹ Manatt¹⁰, and others, the required experiment should be feasible. For illustration, we consider the first-order spectrum of the substituted ethylene:



3.

where X and Y are non-magnetic nuclei. For such a system, available data¹¹ indicate that the approximate coupling constants are $J(C^{13}, H^A) \approx 160$ cps, $|J(C^{13}, H^B)| \approx 2.5$ cps, and $|J(H^A, H^B)| \approx 20$ cps. The C^{13} spectrum consists of two $J(C^{13}, H^B)$ doublets separated by 160 cps, due to $J(C^{13}, H^A)$. Correspondingly, the H^B spectrum consists of the two $J(C^{13}, H^B)$ doublets separated by the 20 cps. splitting of $J(H^A, H^B)$. If one irradiates at the appropriate frequency to collapse the up-field doublet in the C^{13} spectrum, the up-field doublet in the H^B spectrum will be affected if $J(H^A, H^B)$ and $J(C^{13}, H^A)$ are of the same sign and the down-field doublet will be affected if $J(H^A, H^B)$ and $J(C^{13}, H^A)$ are of opposite sign [independent of the sign of $J(C^{13}, H^B)$]. Thus, one obtains an "absolute" sign determination of $J(H^A, H^B)$. Exactly comparable arguments can be applied to more complex systems (e.g. appropriate substituted ethanes) to obtain the sign of the vicinal coupling relative to that of a directly-bonded C^{13} -H coupling.

A corresponding experiment can be done to obtain the sign of the geminal hydrogen coupling by use of a system such as $HD\ C^{13}X_2$ with X an appropriate substituent (e.g. CN). By looking at the D resonance while irradiating the C^{13} resonance so as to affect one or the other of the $J(D, C^{13})$ doublets, the sign of $J(H, D)$ relative to $J(D, C^{13})$ could be determined. Thus, the "absolute" sign of $J(H, D)$ and, consequently, of $J(H, H)$ for geminal hydrogens would become available.

Until the appropriate measurements have been carried out, no absolute comparison between experiment and theory is possible.

4.

However, the presently available results show that, while the theory is qualitatively correct, it may yield values for the coupling constants that are quantitatively in error. Although there are a large number of approximations in the valence-bond method, the inadequacy being considered here can probably be traced to the sensitive dependence of the sign and magnitude of the geminal and vicinal constants on the differences between a number of effective exchange integrals. As is evident from Eq. (7) of Ref. 2(b) for the geminal couplings, a cancellation of terms occurs and rather minute changes in the contributing integrals can significantly alter the result. Certain cancellations also are found in the vicinal coupling (particularly for the dihedral angles close to 90°), which may therefore deviate somewhat from Eq. (11) of Ref. 2(a).¹² However, a comparison of the two calculations indicates that, because of their greater sensitivity, the geminal coupling results are more likely to be of the wrong sign over an extended range of angles.¹³ Confirmation of this suggestion will have to await experimental measurements corresponding to those outlined here, as well as applications of the theory to more refined molecular wave functions.

Martin Karplus
Department of Chemistry
and Watson Laboratory
Columbia University, New York, New York

43-25

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- ¹R. R. Fraser, R. V. Lemieux, and J. D. Stevens, J. Am. Chem. Soc. 83, 390(1961), C. A. Reilly and J. D. Swalen, J. Chem. Phys. 35, 1522(1961). F. Kaplan and J. D. Roberts, J. Am. Chem. Soc. 83, 4668(1961).
- ²(a) M. Karplus, J. Chem. Phys. 30, 11(1959); (b) H. Gutowsky, M. Karplus, and D. M. Grant 31, 1278(1959); (c) S. Alexander, J. Chem. Phys. 34, 106(1961).
- ³The opposite relative sign is in agreement with that found for the coupling between an atom X(X = Sn, P, Hg, etc) and geminal or vicinal protons. See, for example, P. T. Narasimhan and M. Rogers, J. Chem. Phys. 31, 1430(1959); for X=F, the constants apparently have been shown to be of the same sign by S. L. Stafford and J. D. Baldeschwieler, J. Am. Chem. Soc. 83, 4473(1961).
- ⁴See also H. Shimizu and S. Fujiwara, J. Chem. Phys. 34, 1501(1961).
- ⁵E. Ishiguro, Phys. Rev. 111, 203(1958); M. Stephens, Proc. Roy. Soc. London A243, 274(1958); T. P. Das and R. Bersohn, Phys. Rev. 115, 897(1959).
- ⁶M. Karplus and D. M. Grant, Proc. Nat. Acad. Sci. 45, 1269(1959), N. Muller and D. E. Pritchard, J. Chem. Phys. 31, 768, 1471(1959).
- ⁷F. Bloch, Phys. Rev. 93, 944(1954).
- ⁸D. F. Evans and J. P. Maher, Proc. Chem. Soc., 208(1961).
- ⁹R. Freeman and D. H. Whiffen, Mol. Phys. 4, 321(1961); R. Freeman, Mol. Phys. 4, 385(1961).
- ¹⁰S. Manatt, private communication.
- ¹¹J. A. Pople, W. G. Schneider, and H. J. Bernstein, High Resolution Nuclear Magnetic Resonance (McGraw-Hill Book Company, New York, 1959), R. Truscott and N. Sheppard, private communication.
- ¹²However, non-nearest-neighbor integrals were neglected in the vicinal coupling calculation. More recent estimates indicate that this approximation is not completely justified because of the magnitudes of the integrals involved (Shavitt and Karplus, unpublished calculations).
- ¹³The more complete cancellation involved in geminal couplings is probably responsible for the fact that $|J_{HX}^{gem}| < |J_{HX}^{vic}|$ for the X atom results mentioned in Ref. 3.

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TELEPHONE: ROYAL 6022



DEPARTMENT OF ORGANIC CHEMISTRY

13th April, 1962.

Dr. A. A. Bothner-By,
Mellon Institute,
4400 Fifth Avenue,
Pittsburgh 13, Pa.
U.S.A.

Dear Dr. Bothner-By,

Mellon readers may be interested in some work which Dr. McLauchlan (of the N.P.L.) and I have just completed on the P.M.R. spectra of hydroxy L-proline and allo hydroxy L-proline in D_2O .¹ These spectra can be analysed to give all the coupling constants between adjacent CH-CH protons in the ring, from which the precise conformations of these molecules can be determined by means of the Karplus eqtn. relating vicinal couplings to the dihedral angles (eqtn. 1).

$$J = \begin{matrix} k_1 \cos^2 \phi - C & 0 \leq \phi \leq 90^\circ \\ k_2 \cos^2 \phi - C & 90^\circ \leq \phi \leq 180^\circ \end{matrix} \quad 1.$$

In these molecules, we have the coupling constants for three CH-CH fragments in the ring. Only two of the dihedral angles derived from these couplings are necessary to determine the conformation of the ring, thus a convincing test of this eqtn. is to determine whether all three are consistent with a single conformation.

Also if we make the assumption that chemically similar CH-CH fragments in different molecules have the same values of the coefficients in 1, then these coefficients can be experimentally determined merely by inserting the observed coupling constants in 1. and solving for ϕ , k_1 , k_2 and C . In order to obtain these results, it is necessary to calculate the dihedral angles in a five membered ring as functions of the amount of buckle of the ring. This has been done for the two symmetric deformations of the ring (the C_2 and C_5 modes). Also it is necessary to assign the couplings to the individual protons of the C_3 and C_5 methylene

/cont.

¹ A part of this work was mentioned previously in Mellon No. 33. This gave less accurate J values and an incorrect molecular confirmation.

groups, again this can be done. However, to cut a long story short, the coupling constants and assignments are:-

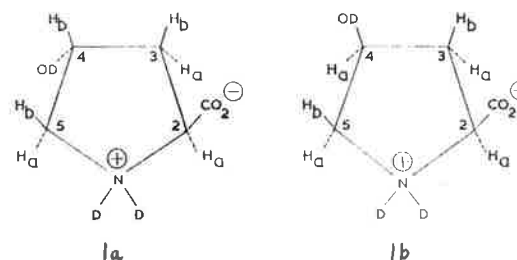
a. For hydroxy L proline (fig. 1a)

$$\begin{aligned} J_{2a-3a} &= 7.66 \text{ c.p.s.} & J_{3a-4b} &= 1.41 \text{ c.p.s.} & J_{4b-5a} &= 1.22 \text{ c.p.s.} \\ J_{2a-3b} &= 10.44 \text{ c.p.s.} & J_{3b-4b} &= 4.31 \text{ c.p.s.} & J_{4b-5b} &= 4.09 \text{ c.p.s.} \end{aligned}$$

b. For allo hydroxy L proline (fig. 1b)

$$\begin{aligned} J_{2a-3a} &= 10.48 \text{ c.p.s.} & J_{3a-4a} &= 4.71 \text{ c.p.s.} & J_{4a-5a} &= 0.94 \text{ c.p.s.} \\ J_{2a-3b} &= 3.84 \text{ c.p.s.} & J_{3b-4a} &= 2.09 \text{ c.p.s.} & J_{4a-5b} &= 4.57 \text{ c.p.s.} \end{aligned}$$

where a and b refer to protons on the opposite and the same side respectively of the ring as the carboxylate group.



The dihedral angles obtained from these assignments are

- a. For hydroxy proline $\phi_{2-3} = 31.25^\circ$, $\phi_{3-4} = 51.0^\circ$, $\phi_{4-5} = 50.4^\circ$
b. For allo compound $\phi_{2-3} = 2.0^\circ$, $\phi_{3-4} = 49.0^\circ$, $\phi_{4-5} = 72.25^\circ$

and the experimentally determined values of the coefficients in 1. are

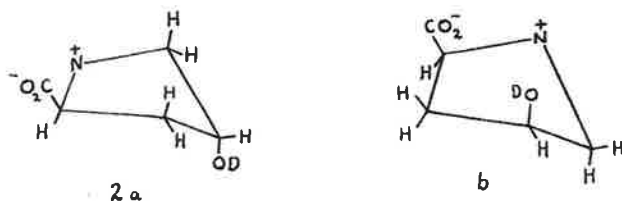
C_2-C_3	$k_1=10.5$	C_3-C_4	$k_1=10.9$	C_4-C_5	$k_1=10.1$
	$k_2=13.7$				
	$C = 0$		$C = 0$		$C = 0$

/cont.

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(the value of $C=O$ was obtained from the C_4-C_5 fragment and assumed in the other fragments).

The calculated dihedral angles for the C_5 or envelope conformations shown in fig. 2 are a. for hydroxy proline (with an angle of buckle of 53°) 31.25, 51.0 and 51.0 res. and b. for the allo compound (with an angle of buckle of 77°) 0, 43.3 and 72.0° res.



A number of interesting conclusions emerge. Firstly the agreement between the observed and calculated dihedral angles, especially in the case of hydroxy proline, is excellent. This constitutes a quantitative verification of the form of the Karplus eqn. 1. Also $k_2 > k_1$ for the only fragment for which k_2 can be measured, again in agreement with the predictions of Karplus. The fact that the theoretical values of these coefficients (8.5, 9.5 c.p.s. res.) differ from the above values is not surprising in view of the approximations necessarily involved in such quantum mechanical calculations. Also of interest are the conformations obtained for these molecules, especially with regard to the angle of buckle. In hydroxy proline, a molecule in which no specific interactions occur (as distinct from the allo compound in which intramolecular hydrogen bonding may be present), the angle of buckle is 53° , demonstrating conclusively the predominant influence of the one two interactions over the C-C angle strain in determining the conformation of five membered rings. In the allo compound the angle of buckle is even greater, suggesting considerable ring strain, and it may be significant in this connection that there is not such good agreement between the observed and calculated dihedral angles in this compound.

My apologies for this rather lengthy contribution. I enjoy reading Dr. Sutcliffe's M.E.L.L.O.N., and wish your news letter every success.

Yours sincerely,

Roy Abraham
(R. J. Abraham)

MONSANTO CHEMICAL COMPANY

INORGANIC CHEMICALS DIVISION
RESEARCH DEPARTMENT
300 NORTH LINDBERGH BOULEVARD
BOX 528
ST. LOUIS 68, MISSOURI

April 16, 1962

Dr. A. A. Bothner-By
Mellon Institute
4400 Fifth Ave.
Pittsburgh 13, Pa.

Dear Dr. Bothner-By:

I would like to vie for a position on your MELLON-M-R mailing list. As a down payment on my subscription, I am enclosing two items which may be of interest to readers of your commendable newsletter.

The first is a sample of the 8-1/2" x 11" charts which we find useful for direct recording of routine A-60 NMR spectra. We simply use the A-60 recorder on the 1000 c.p.s. Sweep Width and scan from -500 c.p.s. to 0 c.p.s. Filing and reproduction of recorded spectra are much easier with these smaller sheets. Overall precision is reduced by a factor of two, of course, but results are adequate for most routine samples.

The second item is a description of a special combination sample tube and probe insert which we have found useful for quantitative P^{31} NMR measurements. The compromise between signal to noise and resolution is somewhat more favorable than with standard Varian inserts and separate sample tubes.

Sincerely yours,

M. M. Crutchfield
M. M. Crutchfield

Encl.

mac

43-28

A SPECIAL SAMPLE CELL FOR QUANTITATIVE P^{31} NMR MEASUREMENTS

M. M. Crutchfield and R. R. Irani

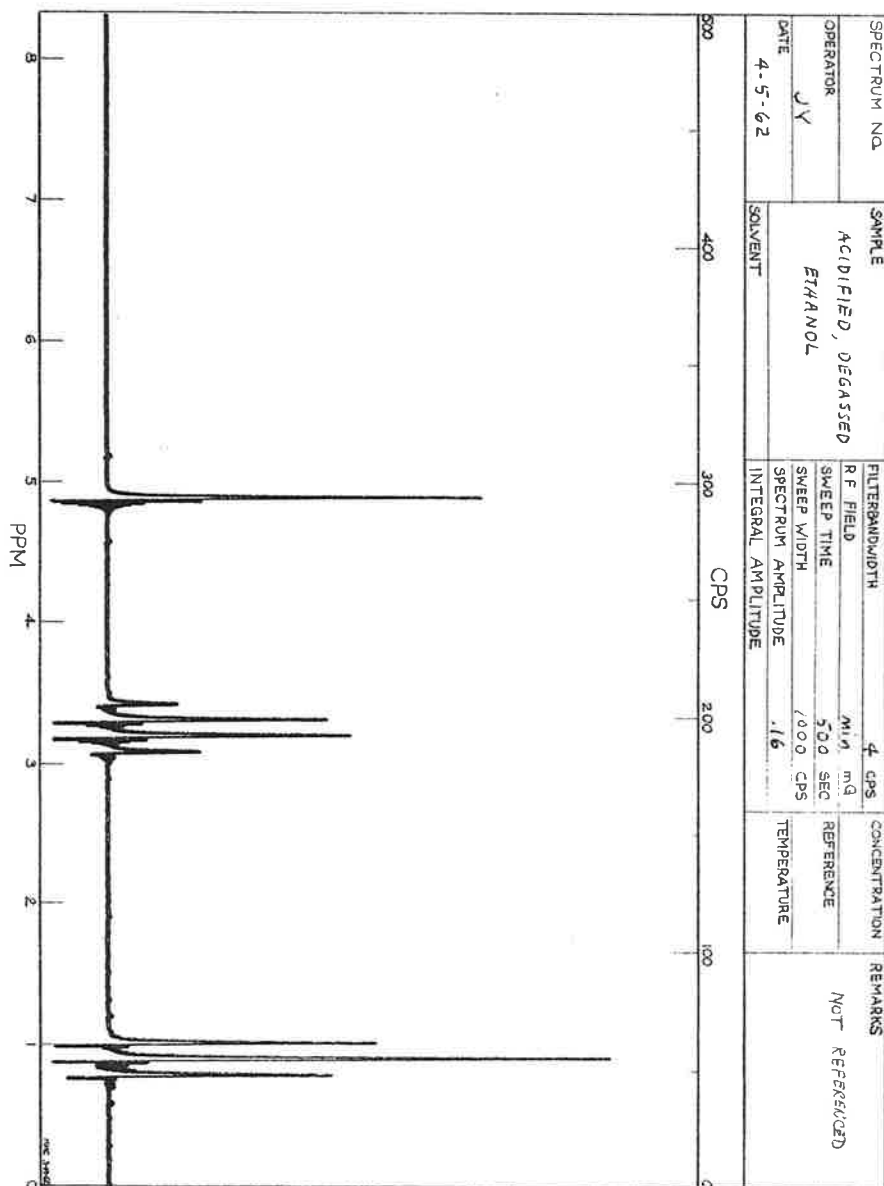
Monsanto Chemical Company
Inorganic Research Department
St. Louis, Missouri

Due to low sensitivity to the phosphorus nucleus, the accuracy of quantitative P^{31} high resolution nuclear magnetic resonance measurements is frequently limited by a small signal to noise ratio. Since signal intensity increases with the number of P^{31} nuclei in the region of the receiver coil, signal to noise can be increased by the use of large samples. However, this is usually accomplished only at the expense of decreased resolution of spectral details, for it becomes increasingly difficult to maintain a homogeneous polarizing magnetic field over the entire volume of large samples. The problem becomes critical for closely spaced peaks.

Common practice is to use 5 m.m. O.D. spinning sample tubes for optimum resolution, and 15 m.m. O.D. nonspinning sample tubes for optimum signal to noise. We have recently constructed a combination "sample-cell receiver coil" probe insert which is somewhat better than a compromise between these two. By eliminating the separate sample tube and placing the liquid sample directly in a specially wound probe insert with an all glass bottom and an inside diameter of 6 m.m., the filling factor of the receiver coil was improved to the point where signal to noise equivalent to that obtained with 15 m.m. O.D. sample tubes was achieved with considerably better resolution. The cell, shown in Figure 1, was used in a standard Varian Associates Model V-4331A Probe operating at 24.3 Mcps in a typical Varian HR-60 magnet system.

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A-60 NMR SPECTRUM



The cell construction was quite simple. An Amphenol[®] No. 31-003 connector^① was cut off 1.4 cm. from the open end, and the locking pins on the side of the connector were filed off. One end of a length of No. 30 gauge Nyclad[®] copper wire was soldered to the center pin of the connector^② and the wire brought out through a notch filed in the top. Epoxy cement^③ was used to bond the connector to the flat-bottomed Pyrex[®] tube^④. After the cement had hardened, a seven-turn coil^⑤ was wound around the tube. The coil was coated with clear expoy resin and the entire assembly cured at 100°C. The loose end of the coil was dressed down the side of the tube, parallel to the other wire and then soldered to the outside of the connector^⑥.

In use, liquid samples are placed directly in the cell up to the indicated mark^⑦. The cell is supported in the probe by a snug fitting Teflon collar. Since the cell must be removed from the probe for cleaning between samples, this requires mechanical re-balancing of the insert for a detector null point each time and a few extra minutes per sample.

Typical results are compared in Figure 2 for a sample of undiluted trimethyl phosphite in three different probe inserts. All measurements were made under as nearly equivalent conditions as possible, with magnetic field homogeneity shim coils adjusted for optimum homogeneity for each sample. The sweep rate was approximately one cps per second. The signal to noise ratio for the combination cell-insert is equivalent to that obtained with the standard Varian insert used with 15 m.m. tubes, but the resolution is considerably improved, due to the smaller sample diameter.

Although resolution is not quite as good as that obtained with the standard 5 m.m. spinning samples, it is sufficient to give essentially complete resolution of the peaks

in the trimethyl phosphite multiplet. These peaks are approximately 10 cps apart. In fact, the slight inhomogeneity broadening which results with the nonspinning 6 m.m. sample facilitates nonelectronic peak integration, since it eliminates the wiggles which are obtained under spinning conditions.

The degree of resolution obtainable with a cell of the given dimensions may depend to some extent on the individual magnet with which it is used, since field gradients vary. Some experimentation may be desirable to establish an optimum cell diameter for a given magnet. Thinner glass might also provide some additional improvement, but some compromise must be made for adequate strength.

Attachments

43-30

FIGURE 1.

COMBINATION SAMPLE CELL AND
RECEIVER COIL INSERT FOR
PHOSPHORUS NMR - 24.3 Mcps

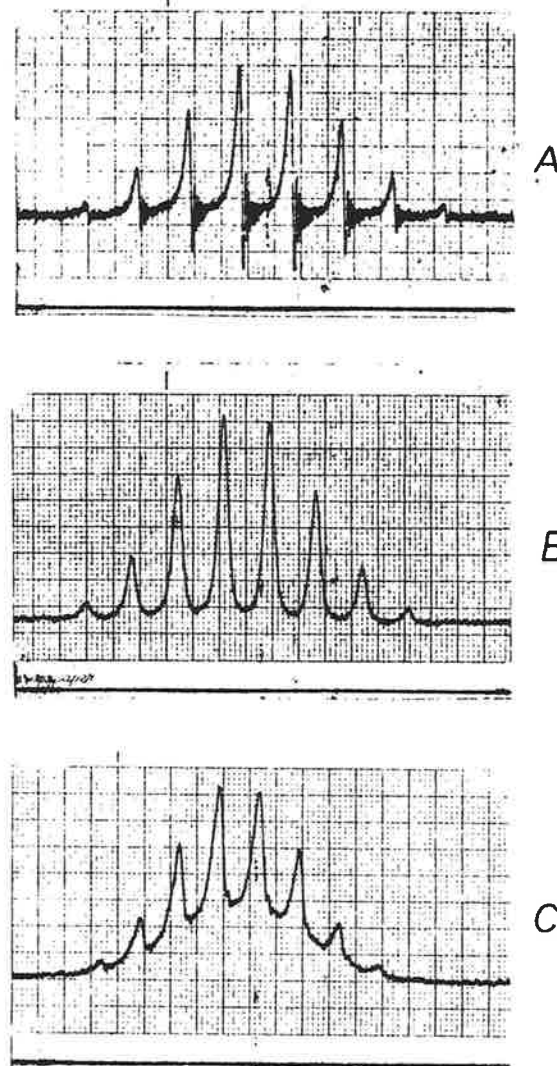
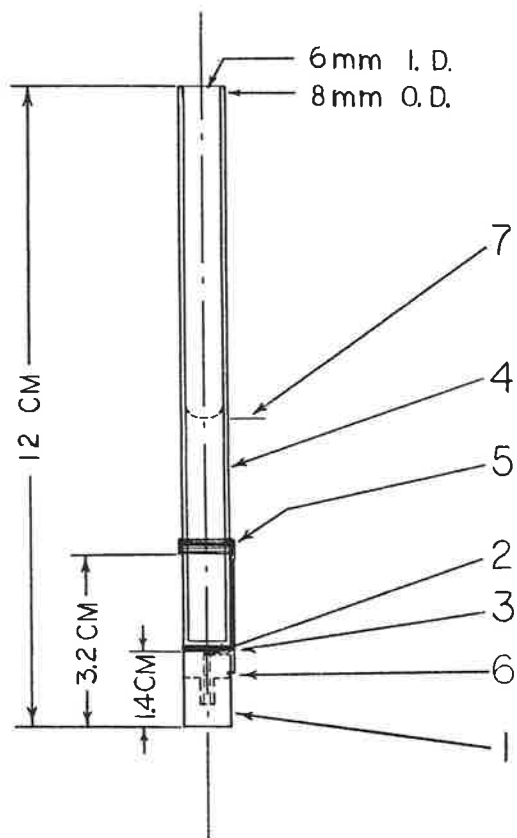


Figure 2. Phosphorus NMR Spectra at 24.3 Mcps for Trimethyl Phosphite in different Probe Inserts.

- a. Standard Insert with a separate 5 mm O.D. thin-wall spinning sample tube.
- b. Special combination insert without a separate sample tube. Holds a 6 mm O.D. non-spinning sample.
- c. Standard insert with a separate 15 mm O.D. non-spinning sample tube.



Department of Scientific and Industrial Research
NATIONAL PHYSICAL LABORATORY

TEDDINGTON, Middlesex

Telegrams: Physics, Teddington Telephone: Teddington Lock 3222, ext. 199

Please address any reply to
THE DIRECTOR
and quote: R.A.L.H.
Your reference:

BASIC PHYSICS DIVISION

16th March, 1962.

Dear Professor Bellamy,

Relative signs of coupling constants from double-quantum spectra

In Letter No. 41, Roy Freeman, Jeremy Lusher, Klaus Pachler and I reported that we had observed that the geminal and vicinal coupling constants in 1,2-dibromopropionic acid are of opposite sign. This conclusion was reached by two separate methods, accurate analyses of spectra at 15,086 Mc/s and 60 Mc/s and double irradiation, which both require specialised equipment and considerable effort. I now wish to report how David Whiffen and I have obtained the same information in an extraordinarily simple manner by observing the double-quantum spectrum.

Let us consider a 3-nuclei system, A B C, with chemical shifts ν_A, ν_B and ν_C and coupling constants J_{AB}, J_{BC} and J_{AC} . A typical double-quantum transition is between the state $m = -\frac{1}{2}$ for A and B and $m = +\frac{1}{2}$ for C and the state with $m = +\frac{1}{2}$ for all three nuclei. If we neglect second-order terms, the energies of these states are $(-\nu_A - \nu_B + \nu_C)/2 + (J_{AB} - J_{BC} - J_{AC})/4$ and $(\nu_A + \nu_B + \nu_C)/2 + (J_{AB} + J_{BC} + J_{AC})/4$, and the transition frequency between the two states is a half the energy difference, i.e. $(\nu_A + \nu_B)/2 + (J_{BC} + J_{AC})/4$. For the corresponding transition with C in the $m = -\frac{1}{2}$ state throughout, the frequency is $(\nu_A + \nu_B)/2 - (J_{BC} + J_{AC})/4$. Consequently the double-quantum spectrum in this region consists of two lines of approximately equal intensity centred on $(\nu_A + \nu_B)/2$ with a separation of $|J_{BC} + J_{AC}|/2$. Interpretation of the regular spectrum readily gives $|J_{AC}|$ and $|J_{BC}|$ and hence the relative signs of J_{AC} and J_{BC} are simply obtained from the measured separation of the double-quantum lines.

The figure shows the normal 60 Mc/s single-quantum spectrum of 1,2-dibromopropionic acid in benzene solution obtained with $\nu_{\text{HBr}}/\nu_{\text{H}} \approx 0.04$ q/s above the double-quantum one obtained with $\nu_{\text{HBr}}/\nu_{\text{H}} \approx 2.1$ q/s. In the latter the normal lines are broadened by saturation but sharp double-quantum lines are seen. The central pattern (lines 15, 16, 17 and 18) is complex since it represents the double-quantum transitions observed whilst nucleus B is subject to a strong stirring field. However the complete sign information can be obtained from lines 13, 14, 19 and 20.

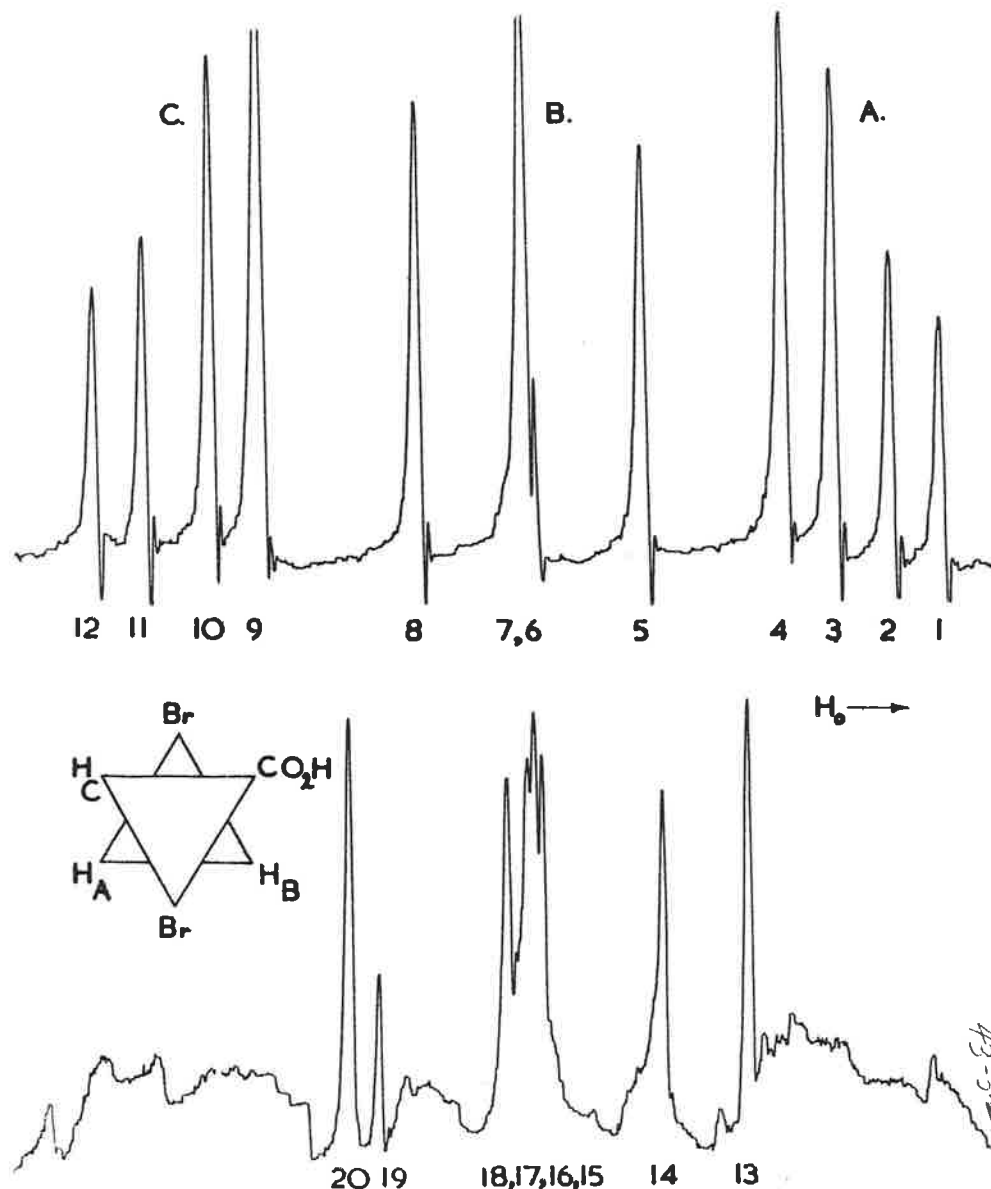
I should stress that this is a very simple method of obtaining such information which can be applied without any equipment additional to the normal high-resolution spectrometer.

A more full account will appear in Proc. Chem. Soc.

Yours sincerely,

R.A.L.H.
R.A. Lusher
Basic Physics Division

Prof. A.L. Bellamy,
Director of Research,
Mellon Institute,
4400 Fifth Avenue,
Pittsburgh 15, Pa.,
U.S.A.



STEVENS INSTITUTE OF TECHNOLOGY

HOBOKEN, NEW JERSEY

Department of
Chemistry and Chemical Engineering

April 19, 1962

Dr. Aksel A. Bothner-By
Director of Research
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Bothner-By:

Up to the present time attempts to correlate proton magnetic resonance spectra with electronegativity have been restricted to monosubstituted methanes and ethanes. A general empirical equation, which applies to compounds of the type CHXYZ, has been observed in this laboratory, namely,

$$\delta E = 13.39 - 0.5561 \delta - 0.01313 J_{CH}$$

In this equation δ is the chemical shift of the proton bonded to the carbon atom, J_{CH} is the C^{13} -proton spin-spin coupling constant, and δE is the sum of Huggins' electronegativities of the substituents X, Y and Z bonded to the central carbon atom.

As one can see from the accompanying table concerning poly-halogenated methanes, the agreement between Huggins' electronegativities and those calculated from n.m.r. data is excellent. This is quite surprising since the empirical equation does not, in any way, take into account effects such as bond diamagnetic anisotropy. Apparently the anisotropy correction for a carbon-halogen bond must be proportional to one or more of the factors in the empirical equation.

Further calculations and discussion of the above equation will follow in subsequent mail.

Sincerely yours,

Edmund R. Malinowski

Edmund R. Malinowski

ERM/jk
enclosure

Electronegativities Calculated from N.M.R. Data

Compound	δ^a (ppm)	J_{CH} (cps)	δE (calcd)	δE (Huggins)
CH ₃ F	5.74	149 ^b	8.24	8.30
CH ₃ Cl	6.95	150 ^b	7.46	7.55
CH ₃ Br	7.32	152 ^b	7.32	7.35
CH ₃ I	7.84	151 ^b	7.05	7.05
CH ₂ Cl ₂	4.67	178 ^b	8.45	8.50
CH ₂ Br ₂	5.06	185 ^c	8.15	8.10
CH ₂ I ₂	6.10	173 ^b	7.73	7.50
CH ₂ ClBr	4.84	179 ^d	8.35	8.30
CH ₂ ClI	5.01	178 ^d	8.27	8.00
CHCl ₃	2.75	209 ^b	9.12	9.45
CHBr ₃	3.18	206 ^b	8.91	8.85
CHCl ₂ Br	2.80	206 ^d	9.13	9.25
CHClBr ₂	2.94	206 ^d	9.05	9.05

a. G. V. D. Tiers, "Tables of Values for a Variety of Organic Compounds" (1958) (privately circulated).

b. N. Muller and D. E. Pritchard, J. Chem. Phys., 31, 1471 (1959).

c. Observed in this laboratory by Richard Magee, National Science Foundation Undergraduate Research Participant, 1961.

d. Calculated from zeta values, E. R. Malinowski, J. Am. Chem. Soc., 83, 4479 (1961).



OTTAWA 2, CANADA

DÉPARTEMENT DE CHIMIE

DEPARTMENT OF CHEMISTRY

April 19th, 1962.

Dr. A.A. Bothner-By,
Director of Research,
Mellon Institute,
44 W. Fifth Avenue,
Pittsburgh 13, Pa.
U.S.A.

Dear Dr. Bothner-By,

We have recently found abnormal chemical shifts in certain phenols and have traced the cause to a previously unrecognized type of hydrogen-bonding resulting in unusually stable dimers (e.g. I).

The effect was discovered during analysis of the nuclear magnetic resonance spectrum (60 Mc./sec.) of methyl 3-hydroxy-4-isopropylbenzoate (II) in carbon tetrachloride (not deuteriochloroform) solution (0.27M). The bands of the aromatic protons were assigned (see Figure) on the basis of the expected coupling constants ($J_{ortho} = 6-8$, $J_{meta} = 1.5-2$, $J_{para} < 1$ c./sec.), and analysis of the spectrum as an ABX system. However, the relative chemical shifts thus found for the aromatic protons were quite unexpected. From the effects of substituents, it was expected that H2 and H6 would have very similar chemical shifts, with H2 at perhaps very

..... 2

slightly higher field than H6, whereas the assignments made on the basis of coupling constants placed H2 at much lower field than H6.

This anomaly was resolved when it was found that the chemical shift of H2 was strongly concentration dependent, although only at such extremely low concentrations that the limit of the dilution shift could not be observed. A more satisfactory way of breaking the self-association of II was by the addition of acetone or methanol. The addition of about one molar proportion of methanol (concentration ca 1% vol. by vol.) resulted (see Figure) in a dramatic upfield shift in the position of H2, with little shift in H6 and practically no shift in H5. The phenolic hydroxyl proton became broad because of exchange with the methanol hydroxyl proton and was shifted to low field because of the basicity of methanol. With the addition of a little more methanol, H2 became practically coincident with H6.

These effects are most simply explained if two molecules of II are involved in a hydrogen-bonded dimer of structure I. In I, each H2 experiences the ring current effect of two benzene rings, whereas in the monomer (or approximately so in a non-cyclic dimer) H2 is affected by only one benzene ring. Whether I is planar or not, the ring current effect is of the required magnitude and direction.

..... 3

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The infrared spectrum of II was studied in carefully dried carbon tetrachloride solution at a path length of 5 cm. Except at concentrations below $10^{-4}M$, two bands (3455 cm^{-1} and 3613 cm^{-1}) were observed. By application of the treatment of Liddel and Becker, the equilibrium constant ($K = [\text{dimer}]/[\text{monomer}]^2$) was calculated to be $463 \pm 10\text{ mole/l.}$ and was constant over a ten-fold concentration range. By comparison, K for phenol in carbon tetrachloride has the value of about 1 mole/l.

For methyl m-hydroxybenzoate, K was equal to $544 \pm 10\text{ mole/l.}$ In the case of m-nitrophenol, hydrogen bonding also persisted to low concentrations but K was not calculated. The n.m.r. spectra of these compounds were too complicated for simple analysis, although marked changes were observed on addition of small amounts of methanol.

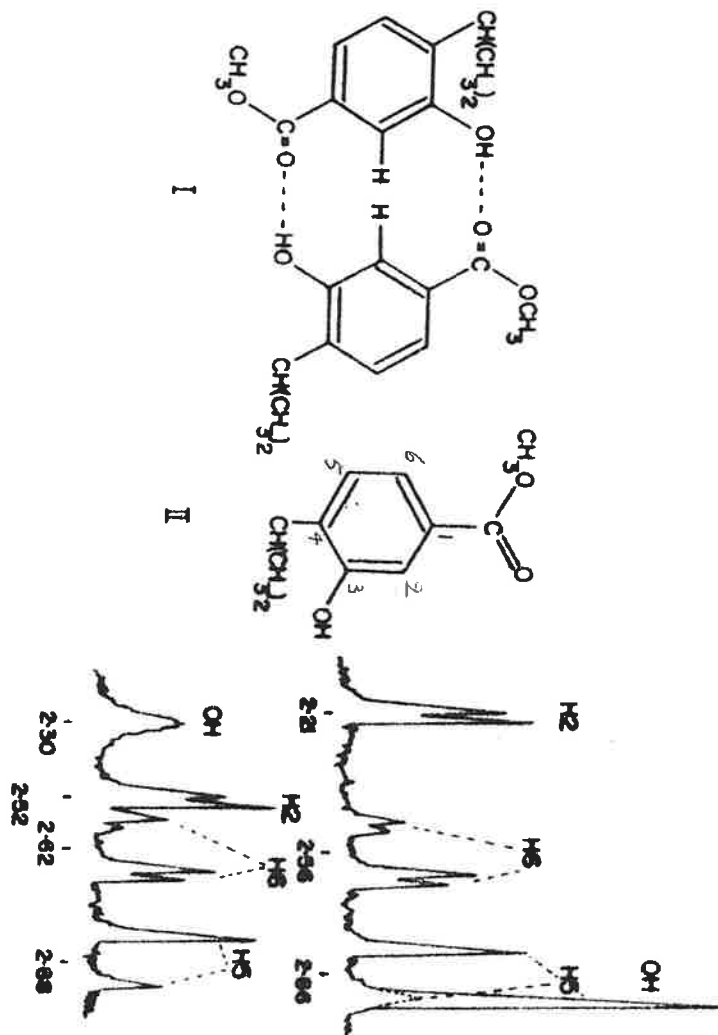
Yours sincerely,

F. A. L. Anet

F. A. L. Anet

FALA/cb

Nuclear magnetic resonance spectra of methyl 3-hydroxy-4-isopropylbenzoate. Top, in carbon tetrachloride. Bottom, in carbon tetrachloride containing 1% by volume of methanol. The chemical shifts in both cases are in p.p.m. with internal tetramethylsilane at 10.00. The OH bands were located by O-deuteration. The high-field regions of the spectra are not shown.



PURDUE UNIVERSITY
DEPARTMENT OF CHEMISTRY
LAFAYETTE, INDIANA

April 19, 1962

Dr. Aksel A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Aksel:

We have just submitted to the Journal of Chemical Physics a paper called "Anomalous Chemical Shifts in the Proton Magnetic Resonance Spectra of the Dimethylcyclohexanes and Related Hydrocarbons," by N. Muller and W. C. Tosch.

As the title implies, we have discovered a number of rather puzzling things. For your own use, I am enclosing a preprint which tells the whole story, but perhaps you might want to present to the readers of *Mellon* the following brief description of two of our rather surprising findings.

1. In the dimethylcyclohexanes the ring protons, whether axial or equatorial, occur at or below -1 ppm from TMS with one exception. The enclosed figure 7, from Bill Tosch's thesis shows the spectrum of the exceptional compound, *cis*-1,3-dimethylcyclohexane. Some of the ring resonances lie well upfield from the methyl signals. Anisotropy calculations do not explain this; in fact we have no explanation at this time.

2. The occurrence of the ring-proton signals as a single, relatively narrow band does not necessarily mean that the ring is undergoing rapid inversion. This is shown by the spectra of the two, conformationally "frozen" isomers of 1-4 methyl-*t*-butylcyclohexane. The *trans* isomer has a ring spectrum consisting of two regions of resonance one of which overlaps the methyl signals. These are about 1/2 ppm apart, as is "normal" for axial vs equatorial resonances. In the *cis* isomer these signals appear to be coalesced, as though ring inversion were taking place, but the presence of the bulky *t*-butyl group rules out any possibility of inversion between two, equivalent conformations.

I shall be reporting on some of these puzzles at the Mid America Spectroscopy Symposium in Chicago on May 2 and hope to see you there.

With best regards,

Sincerely,

Norbert Muller
Norbert Muller

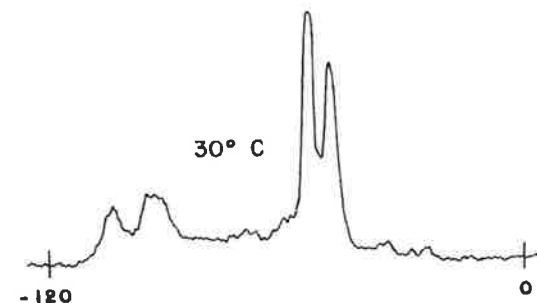
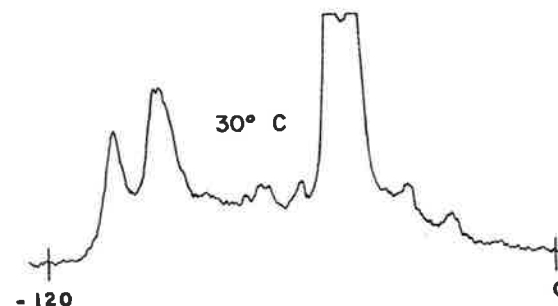


FIGURE 7

NMR Spectra of *Cis*-1,3-dimethylcyclohexane

P.S. Reprints you recently
requested also enclosed.



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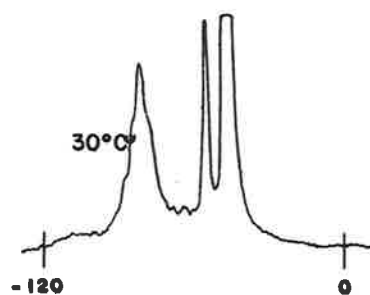


FIGURE 13
NMR Spectrum of Cis-1,4-methyl-t-butylcyclohexane
at 56.4 Mc

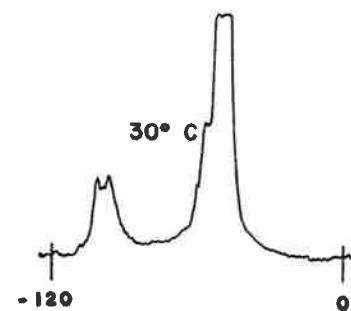


FIGURE 14
NMR Spectra of Trans-1,4-methyl-t-butylcyclohexane
at 56.4 Mc

NMR STUDY OF PYRAZOLE AND IMIDAZOLE AT ROOM TEMPERATURE

In our study of the hydrogen-bond strength of pyrazole and imidazole in chloroform solution at room temperature, using a Varian V-4300 High Resolution NMR Spectrometer with a 12-inch electromagnetic system operated at 14,100 gauss and 60 MC, we have found that only monomers and dimers of the compound exist in the solution of pyrazole, while this is definitely not true for imidazole.

Since the ranges of our data were limited by the weak signal-to-noise ratio for solutions of low concentration at one end, and by the low solubility of these compounds in chloroform at the other, the usual technique of extrapolation was rendered infeasible in obtaining NMR characteristic shifts for either the monomer or the dimer. It thus becomes impossible to obtain the equilibrium constants for the association equilibrium directly from the relation formulated by Huggins,¹ Pimental, and Shoolery. To overcome such difficulty, the method of least squares was then employed to estimate simultaneously the NMR characteristic shifts and the equilibrium constants from the sets of experimental data of NMR shifts. ($K = 50.830465$ for pyrazoles at 24.1°C)

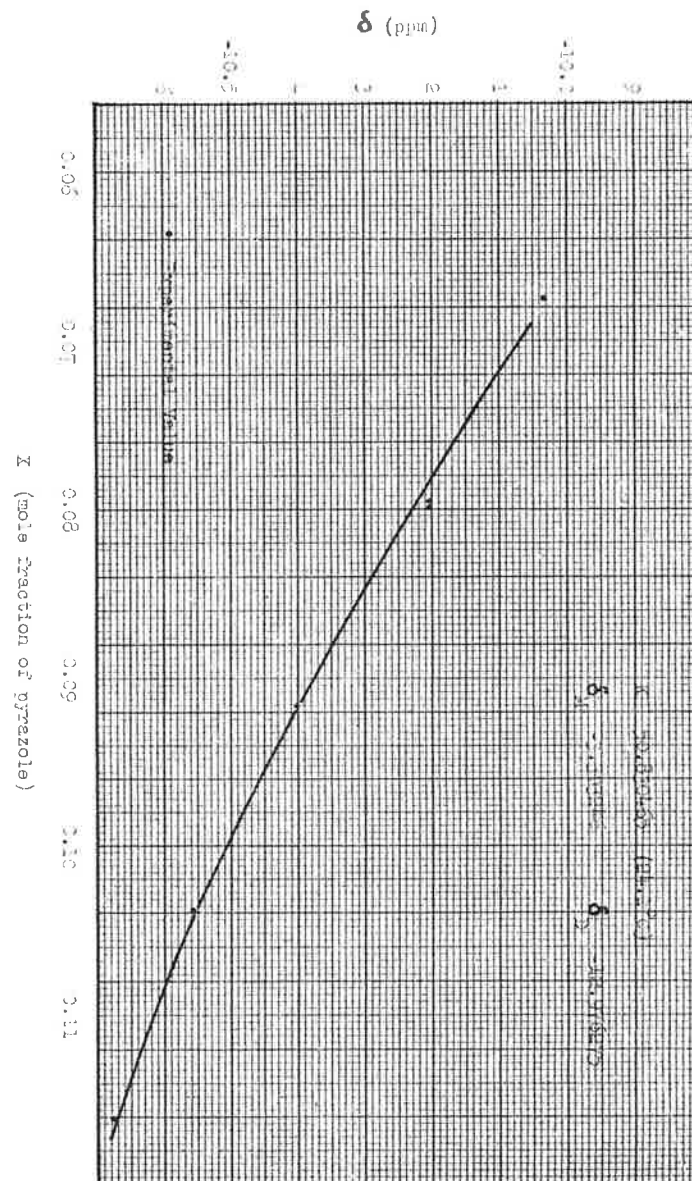
The theoretical NMR shifts, obtained from the equation derived by Huggins, Pimental, and Shoolery, based on these estimated parameters, are shown here in good agreement with the experimental NMR shifts for pyrazole at room temperature. Further studies at lower temperature and of other compounds of the same families are in process and will be reported at a later date.

¹ C.M. Huggins, G. C. Pimental, and J. N. Shoolery: J. Phys. Chem., 60, 1311 (1956).

Narl C. Hung

David J. Wilson

Proton Resonance Measurements of the NH Group of Pyrazole in Chloroform with Chloroform as Internal Reference



43-38