

12. 10-61

Private

Mailed: Sept. 29, 1961

Monthly
Ecumenical
Letters from
Laboratories
Of
N - M - R
No. 36

Author Index

| | | |
|-------------|--|----|
| Zurcher | - Steroids | 1 |
| Moore | - N,N-dimethyltrifluoroacetamide | 2 |
| Chamberlain | - 304TL's | 5 |
| Brownstein | - Inositol Hexa-acetates | 7 |
| Brey | - Polysubstituted Benzenes | 7 |
| Manatt | - Chemical Shifts by Double Resonance | 10 |
| Waugh | - Σ J (vinyl) | 13 |

A monthly collection of informal private letters from laboratories of nmr.
Information contained herein is solely for the use of the reader. Quotation
is not permitted, except by direct arrangement with the author of the letter,
and the material quoted must be referred to as a "Private Communication."

Basle, September 5, 1961

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

Dear Dr. Bothner-By:

I shall try to stick to your call for brevity. At least you cannot complain that I am flooding you with letters. You even had to remind me of this one, for which I apologize.

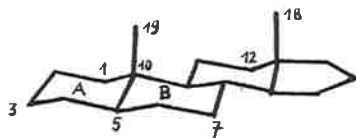
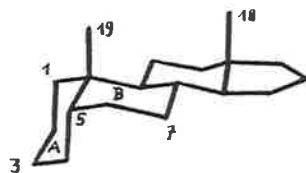
CALCULATION OF THE CHEMICAL SHIFTS OF THE C-19-METHYL PROTONS OF UNKNOWN STEROIDS.

Working in a steroid-producing company, it is quite natural to take a closer look at these molecules. Prof. T. Reichstein (University of Basle) and our chemists were kind enough to provide me with their collections of steroids with a known structure. The spectra obtained as 0.1 molar solutions in CCl_4 with SiMe_4 as reference showed that the effects of the various substituents and double bonds on the angular methyl groups are virtually additive.

One of the results of this investigation, namely the position of the C-19-methyl signal as a function of the various substituents at the various positions, has been published in *Helv. Chim. Acta* 44, 1380 (1961). When I was submitting it, I saw in *MELLONMR* No. 31 that Dr. Slomp is working in the same field and applies the additivity rule with equal success. The calculation of the position of the C-19-methyl signal starts from two basic substances:

5 α -androstande: 19-H signal $\delta = 46.5$ cps (at 60 Mcps) = 0.775 ppm

5 β -androstande: 19-H signal $\delta = 55.5$ cps (at 60 Mcps) = 0.925 ppm

5 α -androstande5 β -androstande

The "additional (incremental) chemical shifts" originating from different substituents have to be added to or subtracted from the δ value of the basic compound. These additional chemical shifts due to the more common substituents at the more common positions have been tabulated in the work quoted. In this way the position of the C-19-methyl signal can be calculated with an accuracy of ± 1 cps for most substances. The additional chemical shifts caused by the various substituents with regard to the C-18-methyl signal and other related work will soon be published.

The C-18-methyl group is probably not parallel to the C-19-methyl group, but to a first approximation the effects of equivalent substituents and double bonds on it are roughly the same as in the case of the C-19-methyl protons. E.g. a 12-keton causes about the same additional chemical shift of the 18-H-atoms as does a 1-keton (of a 5 α -H-steroid) with the 19-H-atoms. In the case of the C-19-methyl protons of 5 α -H-steroids it can be seen that, by the same token, all equal substituents or double bonds placed symmetrically relative to a plane through carbon atoms 3,10,19 or 5,10,19 or 7,10,19 should cause approximately the same chemical shifts. This feature could also be valuable in connection with an estimate of the additional chemical shifts of methyl groups in other cyclohexane derivatives as caused by various substituents.

THE DIAMAGNETIC ANISOTROPY OF THE C-C SINGLE BOND.

Steroids are rewarding substances in still another regard. Because their rings A and B are practically strain-free, they have a well defined geometry. This fact can be used to calculate the anisotropy of the diamagnetic susceptibility of various kinds of bonds. Our first result in this direction is an estimate of the diamagnetic anisotropy of the C-C single bond. 5 α - and 5 β -androstande (see above figure) differ only with respect to the geometry of ring A. This fact can be used to express the difference in the chemical shifts of the C-19-methyl protons as a function of the diamagnetic anisotropies of the C-C and C-H bonds, which are sterically different in the two molecules. With that one gets the following expression for the molar diamagnetic anisotropy of the C-C single bond:

$$\Delta\chi_{\text{mol}}^{\text{CC}} = +1.95 \cdot 10^{-6} + 1.19 \cdot \Delta\chi_{\text{mol}}^{\text{CH}}$$

If $\Delta\chi_{\text{mol}}^{\text{CH}}$, the molar diamagnetic anisotropy of the C-H bond, is assumed to vary between 0 and $+1.50 \cdot 10^{-6}$, this gives for $\Delta\chi_{\text{mol}}^{\text{CC}}$ a range from $1.95 \cdot 10^{-6}$ to $3.72 \cdot 10^{-6}$. Further details will be found in *Helv. Chim. Acta* 44, fasc. VI (to be published shortly). Other work along these lines (diamagnetic anisotropy of the $>\text{C}=\text{O}$ bond, etc.) is in progress.

With many thanks for the steady flow of *MELLONMR* I remain,

Sincerely yours,

R. Fürcher.

R. F. Zürcher



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

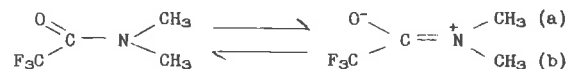
IN REPLY REFER TO
5058/DWM:ijb
16 August 1961

LIND-NO15-2700/4 (12-58)

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

Dear Dr. Bothner-By:

NMR studies of rotational isomerism have almost been done to death, yet I think we have come across one case which is of sufficient interest to deserve some mention in the newsletter. The 60 mc. proton spectrum of N,N-dimethyltrifluoroacetamide (Fig. 1-a) is a pair of quartets separated by a chemical shift of 7.5 cps. These correspond to the two methyl group positions in the resonance-stabilized planar structure:



The novelty in this case is the long-range spin-coupling between methyl protons and the F^{19} nuclei. The observed coupling constants of 1.7 and 0.8 cps presumably represent the trans- and cis-interactions, respectively, but I am hard put to prove this and would welcome any comments which might help substantiate it.

Heating the sample causes the two quartets to coalesce as the frequency of rotational transitions is raised. At temperatures above 80°C the spectrum is a single quartet (Fig. 1-b) with a time-averaged coupling constant of 1.2 cps.

In this instance a unique method of estimating the rotational energy barrier is possible. The collapse of the two quartets is preceded at lower temperature by the coalescence of the narrowly separated spin multiplet lines. Since this occurs at a temperature where protons are being exchanged between non-equivalent sites at a rate proportional to the peak separation (in cycles per second) we can obtain a simple relationship

$$\Delta E_{\text{rot}} = \frac{2.303 R \log J_A/J_B}{1/T_B - 1/T_A}$$

where J is multiplet separation at zero exchange rate, and T the coalescence temperature as indicated by the disappearance of the central minimum in each quartet. The narrower quartet collapsed at 43.5°C and the larger

one at 63.0°C., giving an activation energy of 8.5 ± 0.5 kcal.

The behavior of the F^{19} spectrum for this system is also noteworthy. The room temperature spectrum (Fig. 2-a) is a 10-line multiplet as would be predicted if one coupling were twice the other. The resulting overlap of quartets gives a series of lines whose predicted intensities are 1:3:6:10:12:12:10:6:3:1. Upon heating, this structure collapses and a simple 7-line multiplet (Fig. 2-b) emerges, as would be expected for coupling to six identical protons with an intermediate J-value of 1.2 cps.

Enclosed as a copy of a sample A_2B_2 spectrum which was produced indirectly by our IBM 7090 computer using the Wiberg modification of the Mellon Institute NMR program and a tape-reading x-y plotter. The plot represents 3000 computed intensity values at intervals of .05 cps. The data were obtained by a slight modification of Dr. Wiberg's PLOT routine to provide a tape output compatible with the input requirements of the Electronics Associates plotter.

If you plan to include this note in the next MELLON-M-R, please tell the circulation manager not to discard my addressograph plate. Sorry I didn't get my renewal in sooner.

Sincerely,
Donald W. Moore
Donald W. Moore

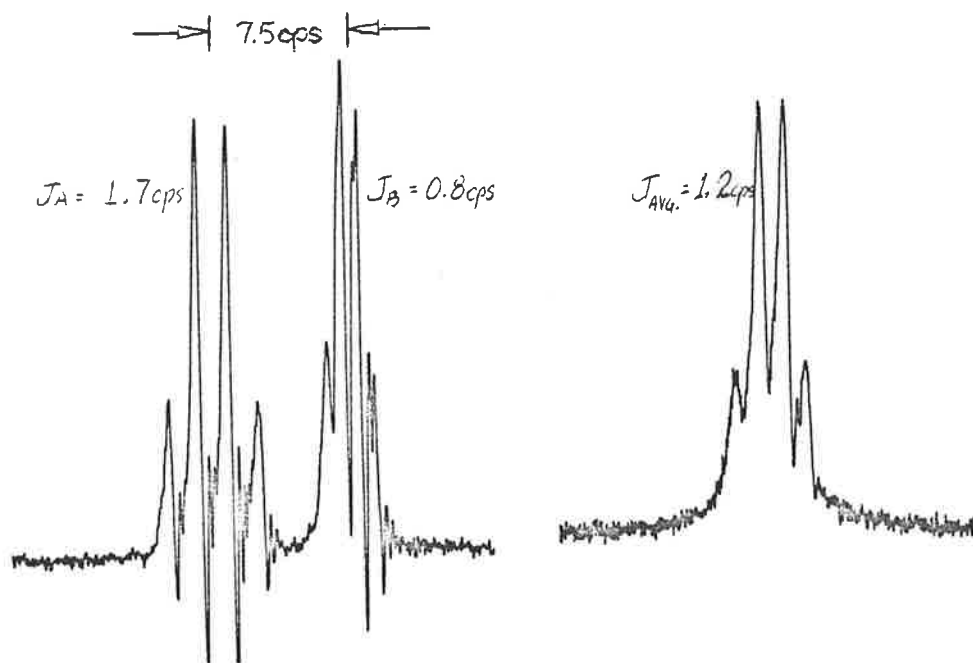


Fig. 1 Proton spectrum (60 mc.)
of N,N-dimethyltrifluoroacetamide.
(a) 30°C (b) 130°C.

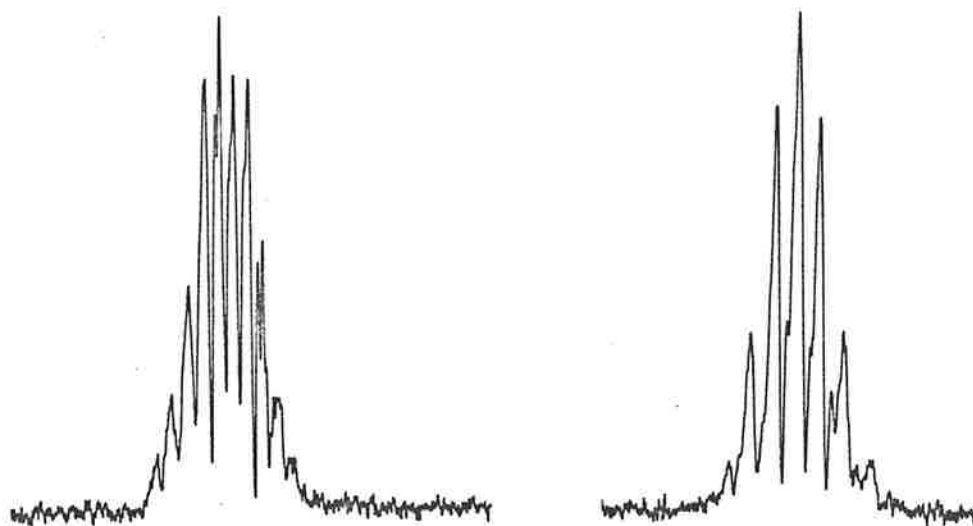
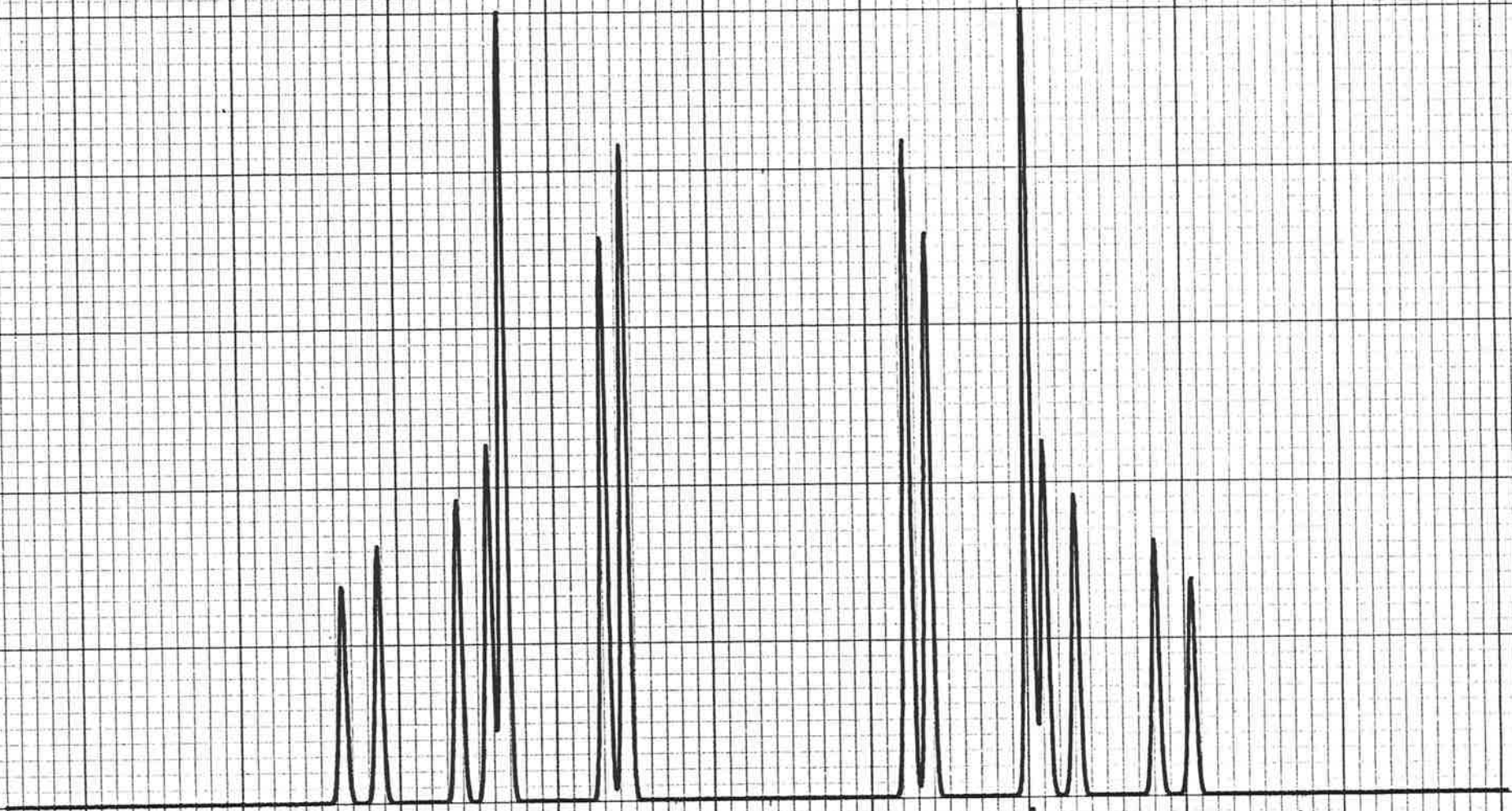


Fig. 2 F^{19} spectrum (60 mc.)
N,N dimethyltrifluoroacetamide
(a) 30°C (b) 85°C.

15.5



A_2B_2 $\omega_1 = 10 \text{ cps}$, $\omega_2 = 30 \text{ cps}$ $J = 5.0 \text{ cps}$ half-width 0.3 cps

36-4

HUMBLE OIL & REFINING COMPANY

BAYTOWN, TEXAS

RESEARCH AND DEVELOPMENT

August 28, 1961

Monitoring 304TL Pass
Tubes in Magnet Power
Supply

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

Dear Barry:

This letter is in reply to your recent request to Rollie Williams for information concerning our rig for testing 304TL tubes and the procedure for grading these tubes. At the time this special tube checker was constructed we were using surplus 304TL's which varied widely in their mutual conductance. It was thought that improved tube life would result from the use of sets of tubes selected for uniformity of conductance. The tube checker itself worked well and was capable of matching 304TL conductances to a satisfactory degree, but the tubes did not stay matched very long in service. The aging characteristics could not be matched by this procedure.

Consequently, it is the opinion of myself and Walter A. Morgan, of our Analysis Instrumentation Group, that the work involved in matching 304TL's with a tube checker is greater than the benefits derived. We do not recommend construction and use of the tube checker at this time.

A better system for determining the actual status of each 304TL is one which, to my knowledge, was first employed by Dr. R. E. Swarbrick and Mr. E. C. Rearick of Esso Research and Engineering Company. Periodic readings of the plate current of each tube are plotted on a chart as illustrated in the attachment. These readings may be made with a single meter which is switched from plate circuit to plate circuit, or by a separate meter permanently mounted in each plate circuit. We are currently using small (1") inexpensive meters mounted on a single plastic strip which in turn is attached to the outermost filament bus bar of the 304TL assembly. The entire assembly is mounted inside the cabinet and is viewed through the louvers. Reversing the bank plate conveniently turns the louvers inward so that the meters can be observed with ease. As the meters are at a potential of some 2,000 volts above ground, it is necessary to insulate them from the chassis and to isolate them from the operator. The possibility of unequal loads resulting from deterioration of the plate and screen suppressor resistors in the 304TL circuits can be reduced by replacing the composition carbon resistors with suitable wire-wound resistors.

The attached chart shows the history of a set of new 304 TL's. Except for

Dr. Bernard L. Shapiro - 2

tube No. 2, the plate currents were reasonably close together at the start. Although the meters were calibrated before they were installed, and the recorded currents are derived from the calibration curves, it is assumed that meter No. 2 has gone off calibration and is giving an erroneously high reading. The changes in plate current with time and the general pattern of tube deterioration are clearly shown by the chart. It is easy to replace each tube as it weakens or to determine when an entire set has deteriorated beyond satisfactory use. When a set has deteriorated to the state indicated for April, 1961, the magnet current usually becomes noisy, necessitating replacement of the entire set.

The plate current readings do not correlate precisely with the plate colors. This has been found to result in part from unequal circulation of air around the tubes. Unequal conductances among the four sections of a tube and possibly unequal thermal emissivities of the plates or surroundings also contribute.

If you consider this to be of sufficient interest we will be happy for you to place it in the MELLONMR.

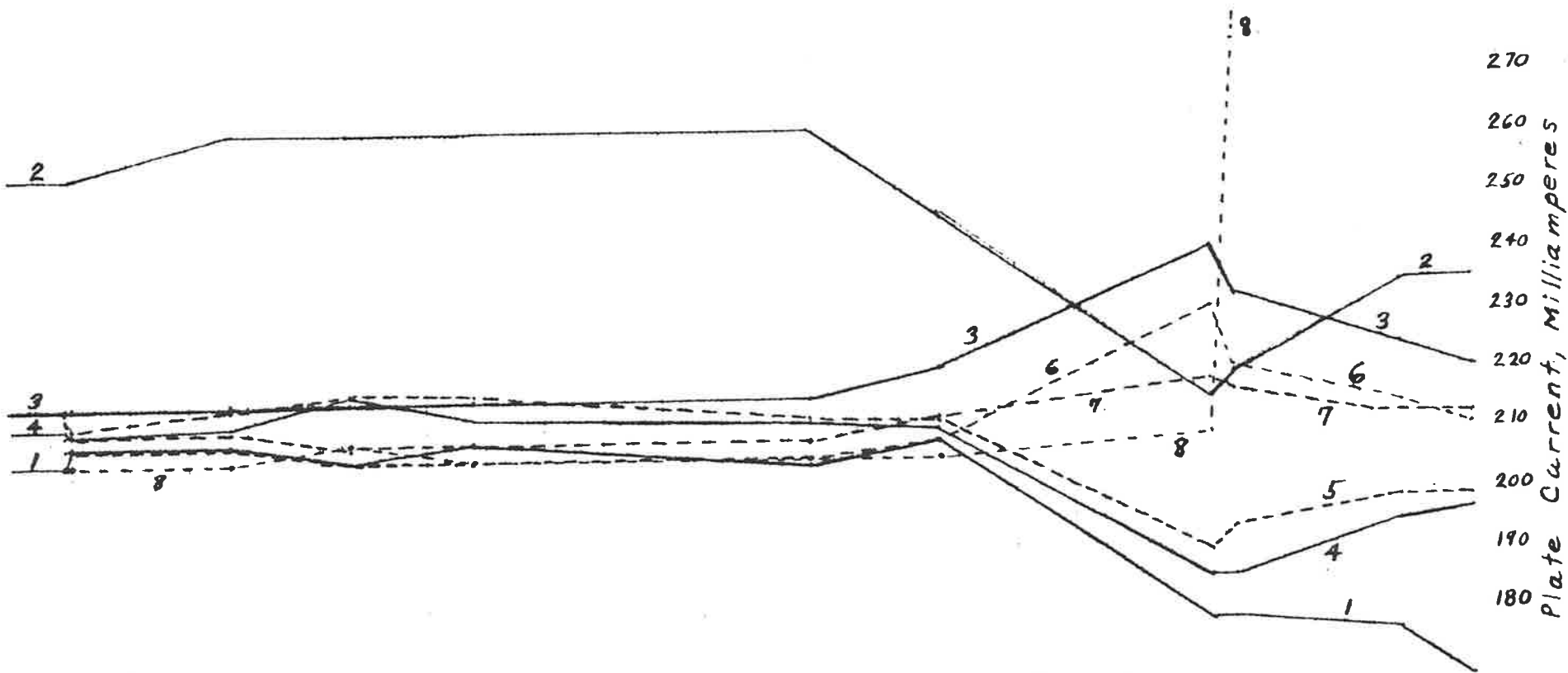
Sincerely,

N. F. Chamberlain

N. F. Chamberlain

NFC:vt
Attachment

36-5



Record of Plate Currents of Individual 304TL
Regulator Tubes in a Varian V2100 Magnet Power Supply

10 20 30 10 20 30 10 20 30 10 20 30 10 20 30 10 20 30 10 20 30 10 20 30 10 20 30 10 20 30
 Sept. Oct. Nov. Dec. Jan. Feb. Mar. April May 36-96
 1960 | 1961



NATIONAL RESEARCH COUNCIL
CANADA

DIVISION OF APPLIED CHEMISTRY

OTTAWA 2,
14 Sept., 1961.

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

Dear Dr. Bothner-By:

Your excellent bibliography seems to have missed one journal which contains papers on magnetic resonance. This is "Journal of Structural Chemistry" USSR which is available in English translation from Consultants Bureau. The first two issues (1960) have several papers on magnetic resonance, but more important is the list of papers on magnetic resonance, submitted or published in the U.S.S.R. which is to be presented periodically. The first compilation is located at the back of the second issue of the journal. It appears to be the Russian equivalent of the MELLONMR bibliography.

Recently we have been looking at the proton resonance spectra of substituted cyclohexanes as a function of temperature. The following data on some inositol hexa-acetates might be of interest to the readers. One unusual feature is the low Arrhenius factors obtained for the ring inversion. It also appears that the *muco* isomer is in the boat form.

| Isomer | ΔH^* | $\log 10 A$ |
|-------------|-----------------|-------------|
| <i>cis</i> | 6.60 ± 0.05 | 6.24 |
| <i>allo</i> | 5.48 ± 0.05 | 6.26 |
| <i>muco</i> | 20.2 ± 2 | 11.2 |

Yours truly,

Syd Brownstein
S. Brownstein

SB/jcf

CABLE ADDRESS "RESEARCH"

IN YOUR REPLY PLEASE QUOTE

FILE NO. _____

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF FLORIDA
GAINESVILLE

September 19, 1961

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

Dear Aksel:

Recently there has been much interest in the chemical shifts of ring hydrogens in mono- and poly-substituted benzenes. As our subscription to your invaluable publication, some results in this area may be worth reporting. A number of compounds have been run, either in cyclohexane or in carbon tetrachloride solution, and the chemical shifts extrapolated to infinite dilution. An external reference (in Wilmad coaxial tubes) was used and side-bands were recorded ten or more times. The averaged results are expressed as shifts from the position of unsubstituted benzene at infinite dilution in the same solvent. Complex spectra were analyzed by the method of moments, or exactly for AB , A_2B_2 , AB_3 , and AB_2X systems.

The accompanying Table I shows the values we assign for the contributions to the chemical shifts of a ring hydrogen made by the respective substituent group in the ortho, meta, or para position relative to the hydrogen. For many polysubstituted benzenes, the chemical shift of a ring proton may be predicted within ± 0.02 ppm. It is striking that shifts in compounds containing several methyl or ethyl groups, or alkyl in addition to other groups, may be better correlated in terms of ortho, meta, and para contributions which are not identical, although in compounds such as toluene, the lines are too narrow to allow

of appreciable chemical shifts between the various ring hydrogens. Table I^f shows results for the observed average shifts of some polymethyl benzenes, compared with values calculated in several ways, always assuming additivity.

Our results differ from those of Diehl (Helv. Chim. Acta 44, 829 (1961); MELLON-M-R No. 29) in several ways. Firstly, although we include an entry for Cl effects, chlorine compounds do not behave at all well and there are large deviations from additivity. It appears that iodine compounds show satisfactory additivity, while bromine occupies an intermediate position. In the second place, meta-disubstituted compounds show considerable deviation, although ortho-disubstituted compounds behave satisfactorily unless the groups are quite large. Ortho xylene shows a single sharp peak, for example, while meta xylene has a broad peak with some structure. Table I^{if} illustrates the better agreement for a trisubstituted methoxy compound than for the meta-disubstituted compound.

* Other compound types which deviate markedly from additivity are pentasubstituted compounds and 2,6-disubstituted phenols. The latter case is not surprising, for there may be specific effects of the hydroxyl group in relation to the ortho groups, but what is surprising is that deviations appear to be decreased by further substitution in the ring, as indicated in Table IV.

The contributions in polysubstituted benzenes may be compared with chemical shifts in the monosubstituted compounds. The latter are available for some groups in the paper of Spisecke and Schneider (J. Chem. Phys. 35, 731 (1961)) and we have analyzed some of the same compounds as well as some others by the moment method. There are appreciable discrepancies for the groups I, ClO, OH, and OCH₃; the source and nature of these differences remains to be explained.

We hope to publish in detail the data obtained for something over one hundred compounds.

Cordially yours,

Wallace S. Gray, Jr.
Wallace S. Gray, Jr.

Kenneth V. Lawson

Kenneth V. Lawson

TABLE I-ORBITAL SHIFT CONTRIBUTIONS OF SEVERAL SUBSTITUENTS

| Substituent | Contributions (ppm) | | |
|---|---------------------|-------|---------|
| | Ortho | Meta | Para |
| H ₃ | 0.23 | 0.09 | 1.13 |
| CH ₃ CH ₃ | 0.20 | 0.05 | 0.18 |
| CH ₃ CH ₂ CH ₃ | 0.21 | 0.06 | 0.15 |
| CH(CH ₃) ₂ | 0.13 | 0.03 | (0.23) |
| Cl | -0.24 | -0.17 | |
| CH ₃ | -0.52 | -0.32 | |
| NH ₂ | 0.78 | 0.17 | |
| NO ₂ | -0.93 | -0.25 | |
| OH | 0.98 | 0.16 | 0.36 |
| OCH ₃ | 0.50 | 0.03 | 0.31 |
| I | -0.05 | 0.06 | 0.15 |
| Br | -0.11 | 0.03 | (-0.07) |
| F | -0.22 | 0.19 | -0.32 |

36-8

TABLE II-AROMATIC CHEMICAL SHIFTS (PPM TO HIGH FIELD FROM BENZENE)
OF RING PROTONS IN METHYL-SUBSTITUTED BENZENES
IN CARBON TETRACHLORIDE

| | Observed | Calculated | | |
|---------------------|----------|------------|------|------|
| | | (1) | (2) | (3) |
| Toluene | 0.19 | 0.19 | 0.15 | 0.15 |
| 1,2-dimethyl | 0.27 | 0.38 | 0.30 | 0.27 |
| 1,3-dimethyl | 0.33 | 0.38 | 0.30 | 0.34 |
| 1,4-dimethyl | 0.33 | 0.38 | 0.30 | 0.32 |
| 1,2,3-trimethyl | 0.42 | 0.57 | 0.45 | 0.40 |
| 1,2,4-trimethyl | 0.47 | 0.57 | 0.45 | 0.47 |
| 1,3,5-trimethyl | 0.60 | 0.57 | 0.45 | 0.59 |
| 1,2,4,5-tetramethyl | 0.54 | 0.76 | 0.60 | 0.64 |
| Average deviation | | 0.09 | 0.05 | 0.02 |

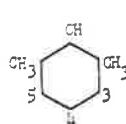
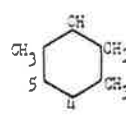
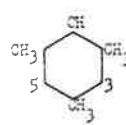
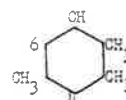
- (1) Chemical shift equals 0.19 x number of methyl groups
 (2) Chemical shift equals 0.15 x number of methyl groups
 (3) Chemical shift for each hydrogen equals 0.19 for each ortho methyl plus 0.09 for each meta methyl plus 0.13 for each para methyl

TABLE III-HEMIOXY COMPOUNDS

| Substituents | Position | Observed | Calculated |
|--|----------|----------|------------|
| 1-OCH ₃ , 3-OCH ₃ | 2 | 0.833 | 1.00 |
| | 5 | 0.050 | 0.05 |
| | 4,6 | 0.750 | 0.81 |
| 1-OCH ₃ , 4-OCH ₃ | 2,3,5,6 | 0.53 | 0.53 |
| 1-OCH ₃ , 4-OH | 2,6 | 0.62 | 0.64 |
| | 3,5 | | 0.51 |
| 1-OCH ₃ , 4-Br | 2,6 | 0.60 | 0.58 |
| | 3,5 | -0.03 | -0.08 |
| 1-OCH ₃ , 4-I | 2,6 | 0.70 | 0.59 |
| | 3,5 | -0.22 | -0.19 |
| 1-OCH ₃ , 2-OCH ₃ , 3-OCH ₃ | 5 | 0.41 | 0.37 |
| | 4,6 | 0.80 | 0.84 |

Average deviation, not including the first compound, is 0.029

TABLE IV-CHEMICAL SHIFTS IN PHENOLS

| | Ring Position | Observed | Calculated |
|---|---------------|----------|------------|
|  | 3,5 | 0.35 | 0.50 |
| | 4 | 0.53 | 0.54 |
|  | 5 | 0.53 | 0.59 |
| | 4 | 0.75 | 0.77 |
|  | 3,5 | 0.69 | 0.73 |
|  | 6 | 1.00 | 1.03 |
| | 4 | 0.85 | 0.91 |

THE USE OF A PROTON-PROTON SPIN DECOUPLING METHOD FOR THE
DETERMINATION OF NMR CHEMICAL SHIFTS

Sir:

The complexities of high-resolution NMR spectra of molecules can in many cases be drastically simplified by the use of double resonance spin decoupling techniques.¹ Until recently the application of spin decoupling techniques to

-
- (1) See J. A. Pople, W. G. Schneider and H. J. Bernstein, High-resolution Nuclear Magnetic Resonance, McGraw-Hill Book Co., New York, N. Y., 1959, pp. 160-161, 229-230, 298-305 and 370-371 for discussions and leading references.

proton-proton systems was limited due to the complexity of the required instrumentation.² A new technique for accomplishing proton-proton spin decoupling

-
- (2) W. A. Anderson, Phys. Rev., 102, 151 (1956).

with relatively simple instrumentation has recently been described by Kaiser³

-
- (3) R. Kaiser, Rev. Sci. Instr., 31, 963 (1960).

and Freeman⁴; this is the audio side band phase detection technique.⁵ We now

-
- (4) R. Freeman, Molecular Phys., 3, 435 (1960).

-
- (5) J. Itoh and S. Sato, J. Phys. Soc. Japan, 14, 851 (1959), previously described an audio side band technique without phase detection; the decoupled signals were observed by their de-component. The disadvantages of this method have been discussed in reference 3.

describe a new application of this technique for the determination of certain proton chemical shifts which could not be unambiguously or accurately measured heretofore.

There are many molecules whose high-resolution proton NMR spectra have one proton or group of equivalent protons which are chemically shifted considerably downfield from most of the other protons. As is usually the case for only moderately complex molecules, the signals from the latter protons may form a very complex fingerprint region. Any multiplet structure of the downfield protons can not generally be completely analyzed to give the relevant coupling constants and chemical shifts.

In order to spin decouple two groups of chemically shifted protons, it is necessary that the condition $\frac{\gamma H_1}{2\pi} > J$ (γ = gyromagnetic ratio, H_1 = rotating magnetic rf. field, J = spin-spin coupling constant in cps.) must be met.⁶ If a

-
- (6) A. L. Bloom and J. N. Shoolery, Phys. Rev., 97, 1261 (1955)

resonance signal occurs at frequency ν (cps.) and a weak audio frequency ω (cps.) is applied to the sweep coils of the spectrometer, the first side bands will occur at $\nu \pm \omega$ if H_1 is small.^{3,6} However, for large H_1 , as required in the spin decoupling of two groups of chemically shifted protons, the first side bands do not occur at $\nu \pm \omega$.^{3,6} If δ is the position of the first side band (measured in cps. from the center band) then:

$$\delta = \pm (\omega^2 - \gamma^2 H_1^2 / 4\pi^2)^{1/2} \quad (1)$$

In the audio side band phase detection method for proton-proton spin decoupling, δ is the chemical shift between the two groups of protons being decoupled.

Since in a decoupling experiment all the parameters on the right of eq. 1 are known, the chemical shifts can easily be computed.

To test this technique, we studied the NMR spectrum of acetaldehyde at 60 Mc. (Fig. 1a). The chemical shift determined in the usual manner by a side band technique⁷ was 455.7 ± 0.2 cps. The value determined by

- (7) The first side band of one group was symmetrically superimposed on the center band of the other group; the audio frequency (ω) was measured by counting its period with a Hewlett-Packard Model 524-C frequency counter.

optimizing ω and minimizing $\frac{Y_{H_1}}{2\pi}$ was 455.7 ± 1.0 cps. This agreement seems excellent. This technique was applied to the NMR spectrum of α -bromo camphor⁸ in order to determine the unknown chemical shift between the 3- and

- (8) The high-resolution NMR spectrum of this molecule at 40 Mc. was previously reported by W. D. Kumler, J. N. Shoolery and F. V. Brucher, THIS JOURNAL, 80, 2533 (1958).

4-protons. Fig. 1b summarizes our results. The chemical shift was determined as 137.0 ± 0.5 cps. (at 60 Mc.). As is evident from Fig. 1b the resonance signal due to the 4-proton can be unambiguously assigned to the downfield end of the complex fingerprint region.

We have also applied this technique to the determination of the chemical shift between the vinyl protons and the α -methylene group protons of cyclohexene and the results are summarized in Fig. 1c. The signals of the two types of methylene protons in cyclohexene give two broad (about 20 cps. wide), very complex assymmetrical regions approximately two hundred cps. up field from the vinyl protons (at 60 Mc.). The shape and overlap of this multitude of lines make it unsafe to assume that the visual center of gravity of these two broad

bands corresponds to the chemical shift positions of the α - and β -methylene protons. By the double resonance technique we have determined the chemical shift between the α -methylene protons and the vinyl protons as 225 ± 1 cps.

The application of the audio side band phase detection decoupling technique to the determination of chemical shifts as described by us should be an extremely valuable means for the analysis of the NMR spectra of many molecules.

PHYSICAL SCIENCE DIVISION

STANLEY L. MANATT

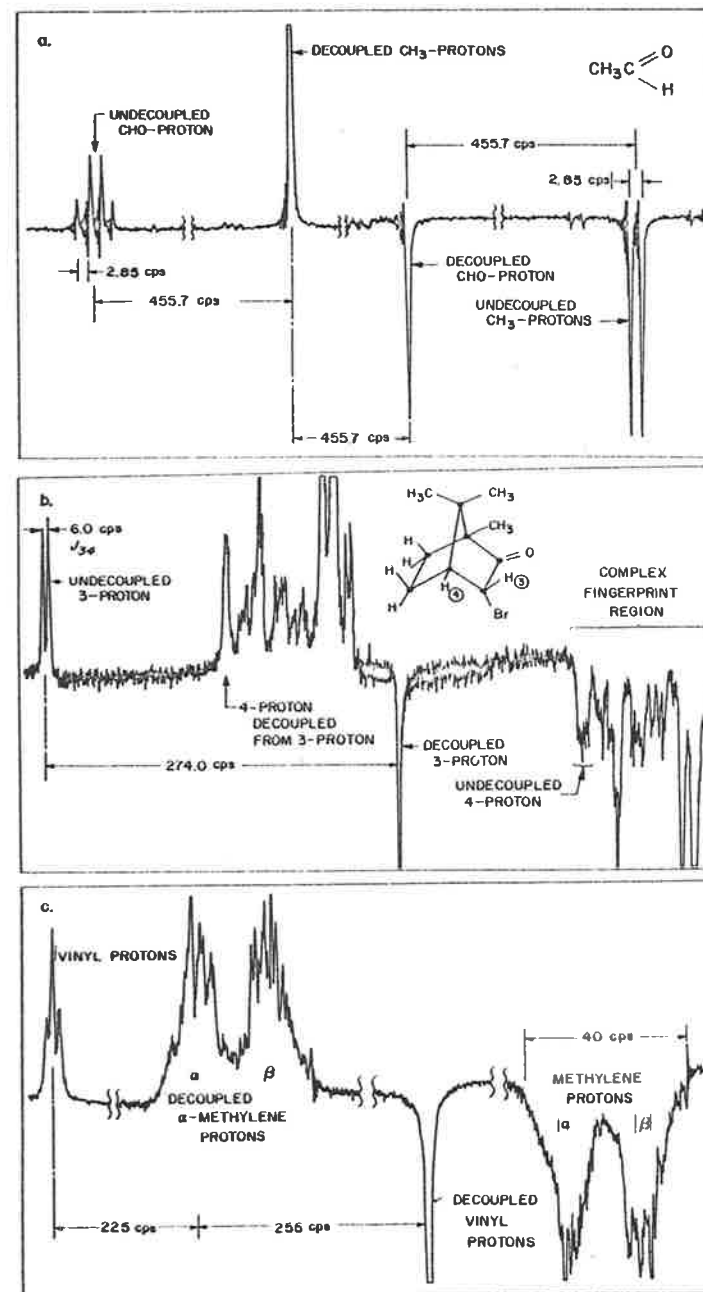
JET PROPULSION LABORATORY

DANIEL D. ELLEMAN

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA

Fig. 1.—Audio side band phase detection decoupled nuclear magnetic resonance spectra: **a**, protons of acetaldehyde (neat), $\gamma_{H_1}/2\pi = 13$ cps. and $\omega = 455.7 \pm 1.0$ cps., δ from decoupling = 455.7 ± 1.0 cps.; **b**, protons of α -bromocamphor (nearly saturated solution in $CDCl_3$), $\gamma_{H_1}/2\pi = 6$ cps. and $\omega = 137.0 \pm 0.5$ cps., δ from decoupling = 137.0 ± 0.5 cps.; **c**, protons of cyclohexene (neat), $\gamma_{H_1}/2\pi = 20$ cps. and $\omega = 225 \pm 1$ cps., δ from decoupling = 225 ± 1 cps. Increasing field in all cases from left to right.



MASSACHUSETTS INSTITUTE OF TECHNOLOGY

DEPARTMENT OF CHEMISTRY
CAMBRIDGE 39, MASSACHUSETTS

13th September, 1961.

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4400 Fifth Avenue,
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Penna.

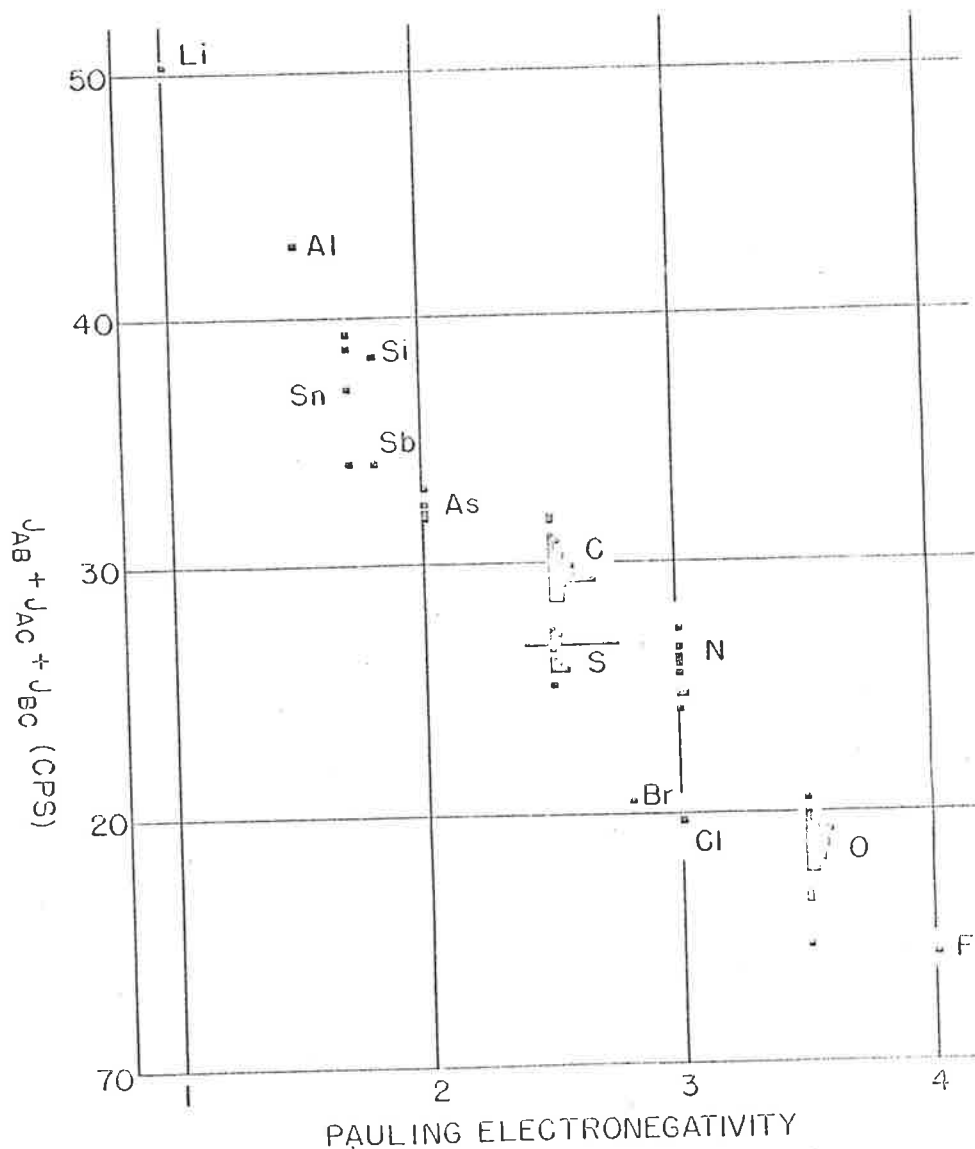
Dear Axel,

Bunwell and Shepard [Mol. Phys. 3, 351 (1960)] pointed out some time ago an apparent correlation between each of the coupling constants of a vinyl group and the electronegativity of the attached atom. We [Johnson, Weiner, March and Seyferth, J. A. C. S. 83, 1306 (1961)] observed that a log extrapolation of their correlation agrees with the results for vinyl lithium (electronegativity 1.0). In the attached figure I have extended the correlation to include 117 different vinyl compounds, the coupling constants having been gathered from many sources, principally the exhaustive paper of Brügel, Ankel and Kruckeberg [Z. f. Elektrochem. 64, 1131 (1960)]. The correlation is indeed strikingly good and the immediately attached atom dominates the substituent effect to a great degree.

You will note that I have plotted the sum of the coupling constants rather than their individual values. This is partly to make the plot simpler but mainly to enable me to make the point [cf. Castellano and March, J. Chem. Phys. 34, 195 (1961)] that $\sum J_{ij}$ is obtainable directly from the spectrum (it is the sum of the three repeated spacings with properly chosen signs) whereas a full analysis is required to obtain the J_{ij} individually. This property was in fact used to obtain the point for Si. Dr. R. Arndt ran a spectrum of $\text{Si}(\text{VI})_2$ on the A-60, from which it could quickly be deduced that $|\sum J_{ij}|$ must have one of the following values: 9.5, 10.7, 18.3, 20.1, 25.7, 38.5, 47.9, 47.9, 55.3, 84.3 cps. Only the value 38.5 cps is consistent with the figure, and it was therefore chosen. The usefulness of the correlation with electronegativity from the point of view of a spectral analyst is then that it permits a considerable narrowing down of the possible assignments (for vinyl compounds) from which an analysis, either by our method or by iteration, must proceed.

As a corollary, it also provides a convenient check of previous analyses. In the present instance it was found that the results of Brügel et al. for $\text{Si}(\text{VI})_2$, Me VI ketone, Et VI ketone, acrylyl fluoride, and 1-vinylcyclohexene-1 are completely inconsistent with the figure.

But the most important feature of this really excellent correlation seems to me to be its apparent conflict with the theory [Gutowsky, Karpus and Grant, J. Chem. Phys. 31, 1278 (1959)] which relates proton coupling constants to bond angles without any explicit allowance for the effects of pushing electron density into or out of the molecular fragment considered.

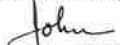


36-13

It would seem particularly remarkable to me that such a theory could predict the fact that all three coupling constants in the vinyl group apparently vary with electronegativity with the same slope. This seems to suggest that the electron density in the delocalized π system may have some importance. In any case, you will understand that I was most interested in the contributions of Barfield and Grant and of Kaplan and Roberts in MELIOMR No. 39.

In conclusion, mention might be made of the note by Reddy and Goldstein [J. Chem. Phys. 35, 300 (1961)], in which they discover a tendency for ΣJ_{ij} to fall into one or the other of two narrow ranges, centered around 20 and 30 cps, respectively. This feature clearly amounts to nothing more than the fact that most easily available substituents begin with either an oxygen or a carbon atom.

Yours sincerely,


J. S. WAUGH

JSW/MMB

DEADLINE NEXT ISSUE

Wed., October 25
