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1-dechlket p. 35-4
Anisotropie p. 35-7

Mailed: Sept. 5, 1961

Reinz

Monthly Ecumenical Letters from Laboratories Of N - M - R

No. 35

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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."

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE BETHESDA 14, MD.
NATIONAL INSTITUTES OF HEALTH

August 14, 1961

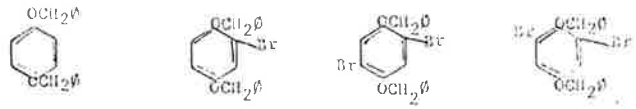
Dr. Aksel A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Aksel:

Here are two items involving recent work at NIH that might interest readers of MELLONMR.

Dr. Alex Robertson, of the Laboratory of Chemistry, has been using a novel technique to identify the NMR lines of OH or other exchangeable protons by deuteration. After obtaining the spectrum of the original sample (usually in $CDCl_3$ solution), he returns the sample to the vial in which it was prepared, adds one or two drops of D_2O, shakes briefly, allows the layers to separate, and withdraws the sample layer for a repeat spectrum. Sufficient D_2O evidently dissolves in $CDCl_3$ to effect rapid exchange in most cases (complete in less than one minute). The rapidity and simplicity of this method encourage its use on almost a routine basis. However, there are still some problems. Alex has found one class of alkaloids where there is virtually no exchange of an OH proton (presumably strongly intra-molecularly hydrogen banded), and in some cases spurious peaks appear after treatment with D_2O. We have not yet determined the cause of this difficulty or the limitations of the technique. Incidentally, Alex adapted this technique from a similar method used by Dr. Henry Fales, of the Heart Institute, for IR studies.

We have also been interested in the NMR spectra of some bromine derivatives of the dibenzyl ether of hydroquinone, which Dr. Herman Ziffer, of our laboratory, has prepared as intermediates in the synthesis of deuterated quinones. Specifically the point of the spectra that attracted his attention is the pattern of chemical shifts for the CH_2 protons in the benzyl groups. The shifts (in cps from internal TMS) are summarized as follows:



I	II	III	IV
298	303 298	303	297

The spectra of I, II, and III are subject to a consistent assignment of the peak at 298 cps to the benzyl group at an unsubstituted end of the molecule and that at 303 cps to the benzyl group when a single Br is ortho to it. The spectrum of IV was at first suprising, since one might have expected two peaks even further separated. I believe that this anomoly can be interpreted in terms of the ring current effect in the hydroquinone ring. Molecular models indicate that the two bulky bromine atoms force the benzyl group out of the plane of the hydroquinone ring, probably into a region of diamagnetic shielding. An upfield shift of 10-15 cps from this cause seems reasonable and compensates the downfield shift probably associated with an inductive effect of the bromines.

Best wishes for continued success with MELLONMR.

Sincerely,

Ted

Edwin D. Becker
Laboratory of Physical Biology
National Institute of Arthritis
and Metabolic Diseases

35-1

GEMINAL SPIN-SPIN COUPLING CONSTANTS

Geminal H-H coupling constants for a number of substituted methanes were determined from the deuterium substituted compounds. These are listed in Table I. Coupling constants of compounds for which the H-C-H bond angles are known are plotted in Figure 1, along with the theoretical curve of Gutowsky, Karplus and Grant[a] which portrays the angular dependence of geminal coupling constants. In compounds containing adjacent π electrons significantly larger coupling constants are observed.

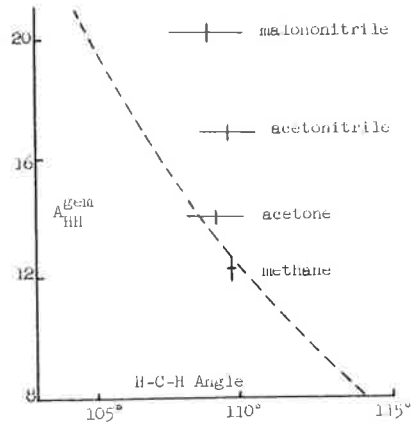


Figure 1. Geminal H-H coupling constants as a function of the H-C-H bond angle. The dashed line is the theoretical curve of Gutowsky et al.[a]

By describing a molecule of the type $XYCH_2$ with a four electron valence-bond treatment, the previous work did not consider possible interactions of the methylene group with the X or Y substituents. Such effects are evidently important, and the larger coupling constants are explained in terms of hyperconjugation of the adjacent π electrons with a methyl or methylene group.

It is to be noted that in the case of nitromethane, valence structures which correspond to hyperconjugation, place like charges on adjacent atoms. Such structures violate the adjacent charge rule, contributing little to the ground state wave function and thereby explaining the more normal coupling in nitromethane.

Michael Barfield

David M. Grant

Department of Chemistry

University of Utah

Table I. Geminal H-H coupling constants and H-C-H bond angles for some substituted methanes.

Compound	A^{gem}_{HH}	HCH Angle
1. malononitrile	20.3 ± 0.3[a] cps	108.7° ± 1.3°[b]
2. ethyl cyanoacetate	18.7 ± 0.6	
3. acetonitrile	16.9 ± 0.3	109.3°[c], 109.1°[d]
4. acetic acid	15.2 ± 0.5	
5. acetone	14.9 ± 0.3[a]	108.5° ± 1.0°[a,e]
6. nitromethane	13.2 ± 0.2	
7. methane	12.4 ± 0.6[f]	109.5°

[a] H. S. Gutowsky, M. Karplus and D. M. Grant, J. Chem. Phys., 31, 1278 (1959).

[b] E. Hirota and Y. Morino, Bull. Chem. Soc. Japan, 33, 158 (1960). Gutowsky et al used the value 105.5° for the H-C-H angle, based on the work of N. Muller and D. E. Pritchard, J. Am. Chem. Soc., 80, 3483 (1958). Several parameters were assumed in the latter study in order to calculate the structural values. As Hirota and Morino made an almost complete analysis based on isotopic substitution in the malononitrile molecule, it is felt that the larger value for the H-C-H angle is more reliable.

[c] L. F. Thomas, E. I. Sherrard and J. Sheridan, Trans. Faraday Soc., 51, 619 (1955). No error was reported.

[d] M. Kessler, H. Ring, R. Trambarulo, and W. Gordy, Phys. Rev., 79, 54 (1950). Due to zero-point energy effects the error was estimated as about one percent.

[e] The H-C-H angle can be calculated from the results reported by J. D. Swalen and C. C. Costain, J. Chem. Phys., 31, 1562 (1959). In a private communication Dr. Swalen indicated that the error in the H-C-H bond angle of acetone would be as large as ± 1°.

[f] M. Karplus, D. H. Anderson, T. C. Farrar, and H. S. Gutowsky, J. Chem. Phys., 27, 597 (1957).

35-2

Dr. P. Diehl

PHYSIKALISCHES INSTITUT
DER UNIVERSITÄT BASEL
KLINGELBERGSTRASSE 82 TELEFON 430422
VORSTEHER: PROF. DR. P. HUBER

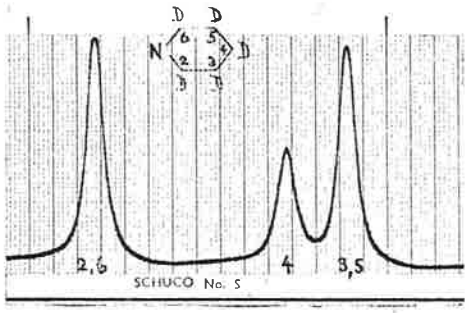
Basle, 31st July 1961

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

Dear Dr. Shapiro,

It is well known that all the contributions to a spin coupling constant $J_{NN'}$ are proportional to the product of the magnetogyric ratios $\gamma_N \gamma_{N'}$. If therefore a D-NMR spectrum of a fully deuterated molecule is compared with the proton-spectrum of the same molecule, all the coupling constants will be found reduced by a factor of 42,5 ($\gamma_D/\gamma_H = 0{,}1535$). At the same time the chemical shifts are reduced by a factor of 6,5. So one is left with a gain in δ/J by a factor of 6,5. This factor does in many cases considerably simplify the spectra.

As an example I present a high resolution D-spectrum of pyridine-d_5 :



$\delta_4 - \delta_2 = 1{,}160 \pm 0{,}005$ p.p.m.
$\delta_5 - \delta_4 = 0{,}306 \pm 0{,}005$ p.p.m.

There are of course no coupling constants observable. The largest J_{DD} should be 0,18 cps. The observed line width is 0,8 cps. I do not know whether this is the natural line width due to quadrupole relaxation as I have so far not been able to find narrower D-resonance lines.

The spectrum has been taken with a Varian fixed frequency unit at 7,65 Mc/s. The sample had a diameter of 1 cm and was rotated with a spinner of our own construction. The active volume of the sample was about 1 cc.

It is interesting to compare the D-shifts with the H-shifts measured by Schneider et al.[1]. They have found the following values by means of a complex AB_2X_2 analysis

$$\delta_4 - \delta_2 = 1{,}114 \pm 0{,}005 \text{ p.p.m.}$$
$$\delta_5 - \delta_4 = 0{,}375 \pm 0{,}005 \text{ p.p.m.}$$

The differences between these shifts and the values given above may be due to isotope effects. Schneider et al. have found for ($\delta_5 - \delta_4$) values of 0,372 and 0,390 in the proton spectra of 2,6-pyridine-d_2 and 3-pyridine-d_1.

I am indebted to Dr. H.G. Leemann from Sandoz AG in Basle for providing the sample.

Yours sincerely,

P. Diehl

P. D i e h l

1) W.G. Schneider, H.J. Bernstein and J.A. Pople, Ann. N.Y. Acad. Sci. 70, 806, 1958

35-3

CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA

GATES AND CRELLIN LABORATORIES OF CHEMISTRY

August 14, 1961

Dr. A. A. Bothner-By
Department of Chemistry
Mellon Institute
Pittsburgh, Pennsylvania

Dear Aksel,

In company with many others, we have been analyzing the NMR spectrum of diethyl sulfite. We now think we have the answer and perhaps our results are of general interest.

Although the spectrum of diethyl sulfite might be expected to offer only a more or less trivial example of an ABC_3 type, the manner of its sensitivity to solvent changes turned out to be at first baffling and then illuminating. The methylene resonances of 50% diethyl sulfite—50% benzene are shown in Fig. 1. A series of iterative calculations demonstrated that this spectrum could be fitted to within experimental error by assigning a 1.09 cps (J_{AC} = 7.69 cps and J_{BC} = 6.60 cps) difference between the spin-spin coupling constants for the different methylene hydrogens and the methyl hydrogens. The other parameters had unexceptional values, thus, $\nu_B - \nu_A$ = 5.77 cps, $\nu_C - \nu_A$ = 168.6 cps, J_{AB} = 10.45 cps and J_{CC} = 12.50 cps. (The calculated spectra were insensitive to J_{CC} or its sign over the range, 1-15 cps.)

With neat diethyl sulfite, the chemical shift between A and B is smaller (Cf. Fig. 2) but, we were not able to compute a satisfactory theoretical spectrum by varying the chemical shifts and keeping the coupling constants constant. Matters were considerably improved when the J_{AC} and J_{BC} coupling constants were set about 2 cps apart along with a smaller $\nu_A - \nu_B$ but, even after more than a hundred trials, the overall agreement could not quite be brought to within experimental error.

The difficulties appeared to be resolved when (following a suggestion from Dr. Marjorie C. Caserio) we explored the possibility of assigning coupling constants of opposite signs. Complete success was obtained with J_{AB} having an opposite sign from J_{AC} and J_{BC} (see Fig. 1). With these relative signs, the theoretical spectra agreed within experimental error with the experimental spectra when J_{AC} was taken as equal J_{BC}. Furthermore, the change between diethyl sulfite in benzene solution and neat liquid could be ascribed as only due to changes in chemical shifts with no changes in the coupling constants. We believe that it is a considerable simplification to have these couplings equal and constant.

Complete agreement between the computed 40 Mc and observed 40 Mc spectra of diethyl sulfite in benzene solution was achieved only with the coupling constants of opposite signs. The spacings between the lines shown in Fig. 1 at 241.7 and 243.7 cps and 221.9 and 220.7 cps (Fig. 1) were reduced to 1.4 and 0.1 cps respectively at 40 Mc. With coupling constants of the same sign, the computed spacings for these lines were 0.8 and 0.9 cps respectively.

On the basis of these results, we believe that the relative signs of J_{AC} and J_{BC} must be taken as being indeed different from J_{AB}. Interestingly, this conclusion could only have been reached by treatment of the spin system as ABC_3, not as the ABX_3 approximation in which a change in the sign of J_{AB} relative to J_{AC} and J_{BC} does not effect the theoretical spectrum.

The results can be regarded as disquieting in two connections. First, the difference in sign between the geminal and vicinal H-H couplings runs directly counter to the theoretical predictions of Karplus and Gutowsky and, if found to be general, may well vitiate confidence in their approach. Second, in analogy with the findings of Castellano and Waugh [J. Chem. Phys., 34, 295 (1961)] for ABC systems, rather different sets of spin-coupling and chemical-shift parameters were found to give nearly identical theoretical spectra for diethyl sulfite in benzene and each of these corresponds amazingly well to the experimental spectram at 60 Mc. Indeed, the previously mentioned excellent agreement between theoretical and experimental spectra obtained for acetaldehyde diethyl acetal has now been duplicated with $\nu_B - \nu_A$ = 9.23 cps, $\nu_C - \nu_A$ = 146.3 cps, J_{AB} = 9.30 cps, and J_{AC} equal to J_{BC} = 7.03 cps with J_{AB} opposite in sign to J_{AC} and J_{BC}.

Clearly, caution and judgement must be exercised in use of the iterative method of obtaining spin-spin coupling constants since there seems to be no assurance that a "final" solution is truly unique. Certainly, in doubtful cases, assigned parameters should have to stand the test of a frequency change.

We are deeply indebted to Dr. Stanley L. Manatt and the Computing Center of the Jet Propulsion Laboratory for the IBM 7090 calculations of the theoretical spectra.

With all good wishes,

Very truly yours,

Fred Kaplan
Fred Kaplan
Jack Roberts
John D. Roberts

35-4

FK/JDR:jmm

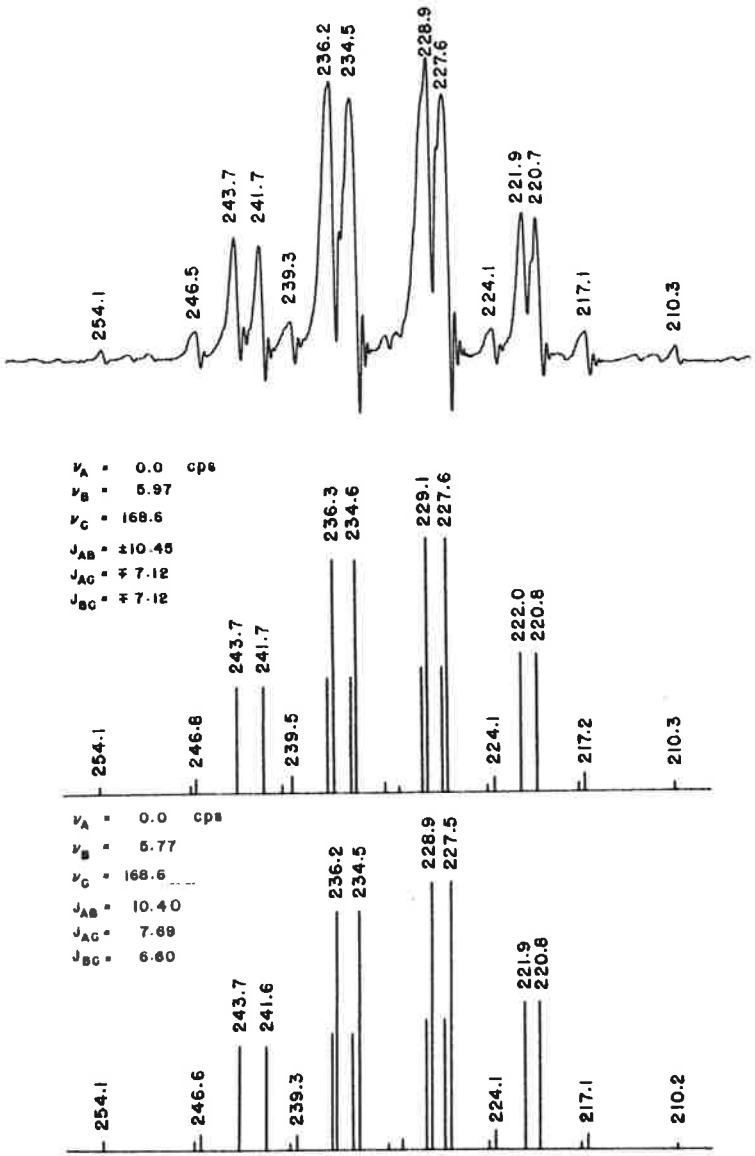


Fig. 1. — Observed and calculated n.m.r. spectra of a 50% (volume) solution of diethyl sulfite in benzene at 60 Mc with tetramethylsilane as an internal reference taken as zero.

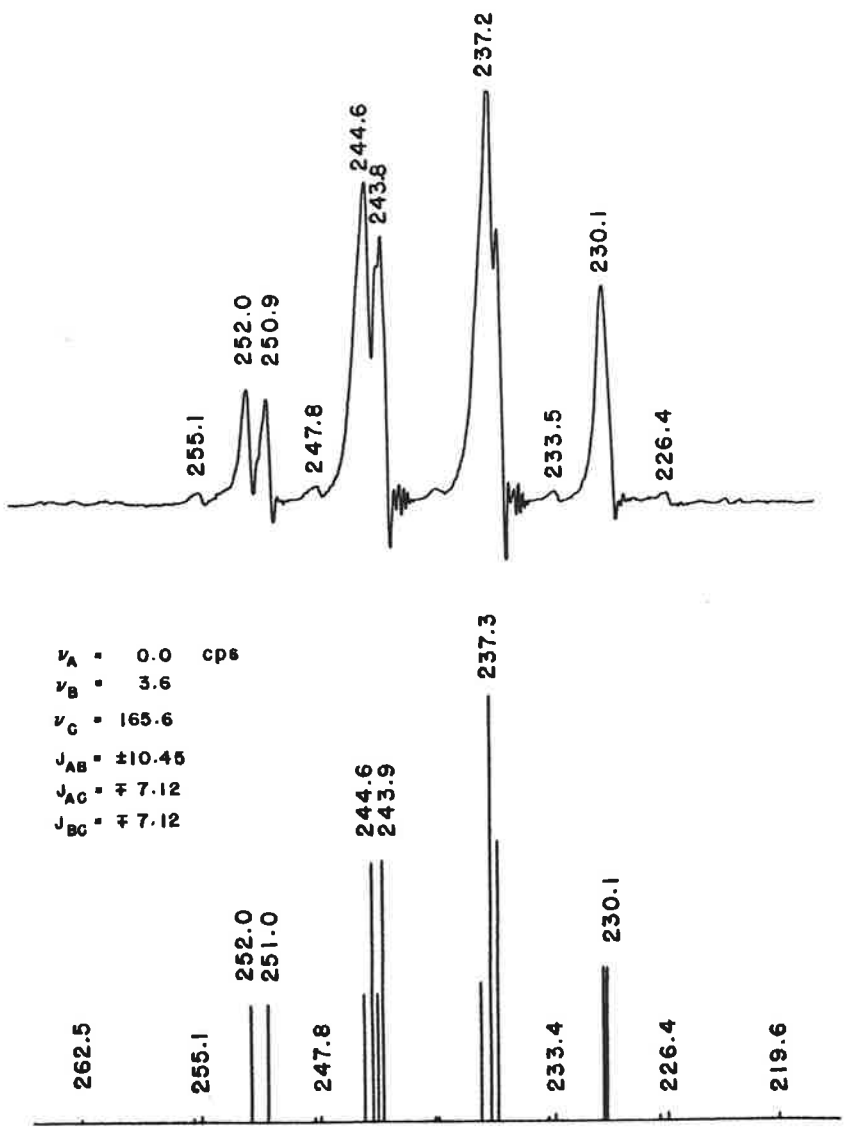


Fig. 2. — Observed and calculated n.m.r. spectra of neat diethyl sulfite at 60 Mc with tetramethylsilane as an internal reference taken as zero.

UNION CARBIDE CORPORATION

P. O. BOX 278, TARRYTOWN, N. Y.

UNION CARBIDE
RESEARCH INSTITUTE

August 23, 1961

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

Dear Doctor Bothner-By:

We were preparing to send you the attached spectrum of 1-chlorobutadiene 1-2 before receiving your last issue in which Dr. Snyder reported a closely corresponding value for the coupling constant $J_{BX} = +2.5$ cps across the four carbon system. Karplus' theory for the π-electron contribution preducts a value positive in sign and about one-fourth the magnitude of the allenic coupling, $J_{AB} = 5.8$ cps (unknown sign).

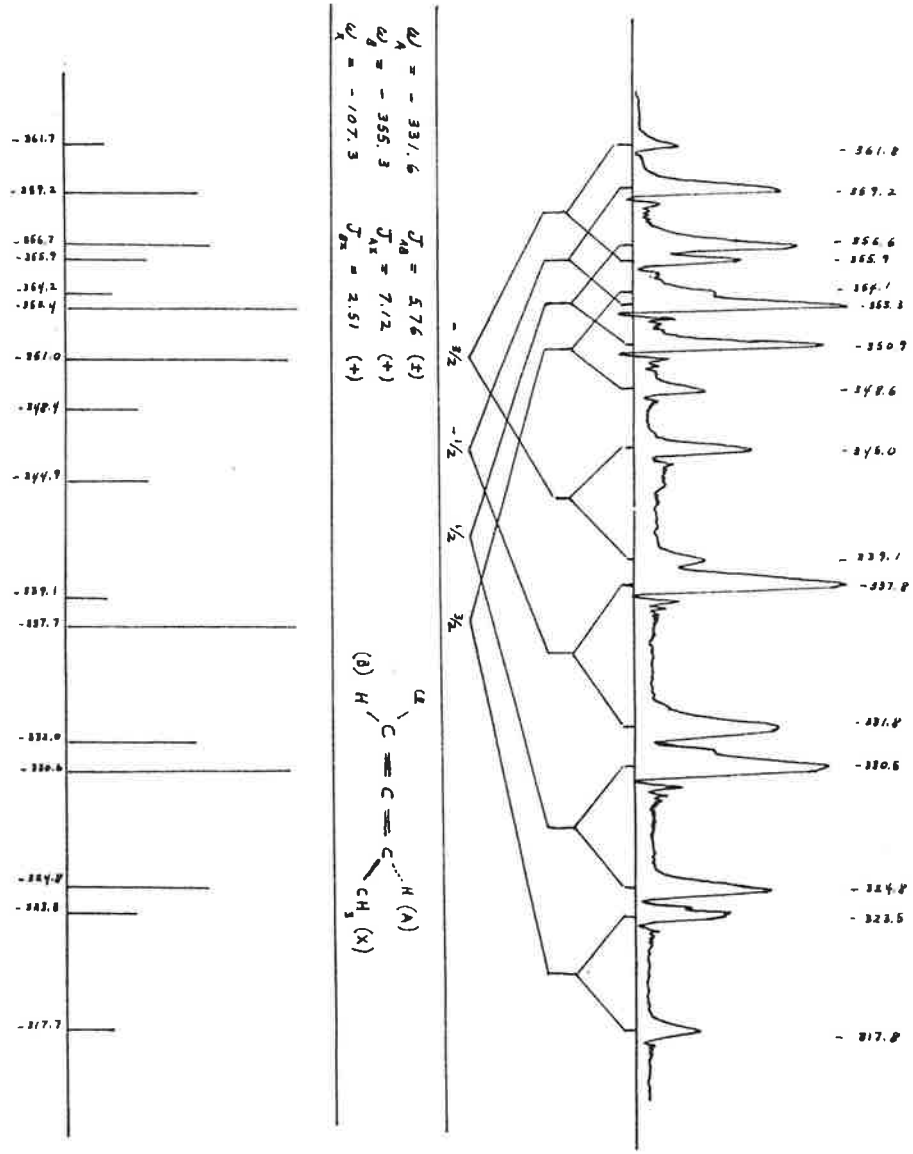
Our frequencies are in cps from an internal TMS reference in carbon tetrachloride solution, obtained at an operating frequency of 59.997 mc. They are determined by interpolation between sidebands and averaged over eleven scans. The sweep is rather non-linear on the figure I chose for reproduction.

We had hoped our payment would be more original than it turned out to be.

Sincerely yours,

Y. Chiang
E. B. Whipple

YC/EBW:pma



35-5

THE UNIVERSITY OF WESTERN ONTARIO
UNIVERSITY COLLEGE

DEPARTMENT OF CHEMISTRY

LONDON, CANADA

August 25, 1961.

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

Dear Dr. Bothner-By :

One of the projects underway in our laboratory is a study of the long range shielding effects of anisotropic groups with particular emphasis on the >C=C< and >C=O groupings. Some preliminary observations might be of interest to MELLONMR readers, since there is some disagreement in the literature concerning the shielding effect of the olefinic linkage, (for example, cf. Jackman, "Applications of NMR in Organic Chemistry", Pergamon, p. 129, and Conroy, "NMR in Organic Structural Elucidations", in Advances in Organic Chemistry, Vol. 2, Interscience, p. 285-6).

I have examined a series of compounds having the carbon skeleton of Figure 1. The parent compound for this series is the Diels-Alder adduct of levopimaric acid ester and maleic anhydride. All of the compounds studied were kindly supplied by Dr. W. A. Ayer, University of Alberta. The various members of this series were of three types : A, B, and C, as indicated in Figure 1. All spectra were run at 60 Mc./sec.

The methyl group on Ring A (C_{16}) would not be expected to shift greatly in these structures. Furthermore, the side-chain methyl protons are easily distinguished as doublets in the A and C structures and by the characteristic shift for CH_3-C=C in B. Thus, one can readily identify the peak for the angular methyl protons (on C_{17}) in this series, and a comparison of its peak position with structure provides information about the spatial effect of the double bond.

In the examples so far studied, the C_{17} methyl protons absorb at 67 $\pm$1 c./s. (relative to internal TMS). The angular methyl peak shifts for the three types in the following way :

A, 35 $\pm$ 1 c./s. ; B, 45 $\pm$ 1 c./s. ; and C, 56 $\pm$ 1 c./s.

Therefore, it would appear that the double bond shields the protons above the plane of the trigonal carbons and that this effect decreases with increasing separation as expected. An examination of Dreiding models (as sketched in Fig. 2) shows that in A, the angular methyl group is above the plane of the trigonal carbons and lying close to the centre of the double bond, while in B it is still above the plane but further removed from this bond. Thus, on the basis of the familiar point dipole approximation, the angular methyl protons are in a shielding position if the transverse susceptibility perpendicular to the plane of the trigonal carbons is larger than the transverse component

in this plane. This must be the case since the A structure has the most shielded angular methyl, the C structure the least shielded, and the B type is intermediate between these two.

Although this conclusion is not new, there has not been a great deal of support for it (Jackman, loc. cit.). These results provide more evidence as do the recent observations reported by Dr. R. R. Fraser from a study of Diels-Alder adducts having the bicyclo [2,2,1] heptene structure (paper presented at the 44th Annual Conference at the Chemical Institute of Canada, Montreal, Aug. 2-5, 1961). Further examples in the series discussed herein are currently being investigated, continuing our approach to the "mapping" of the long range effects of anisotropic groupings.

Sincerely,

J. B. STOTHERS
Assistant Professor

JBS/vl

Editor's Corner

DEADLINE NEXT ISSUE
Monday, Sept. 25

* * * * *

35-1

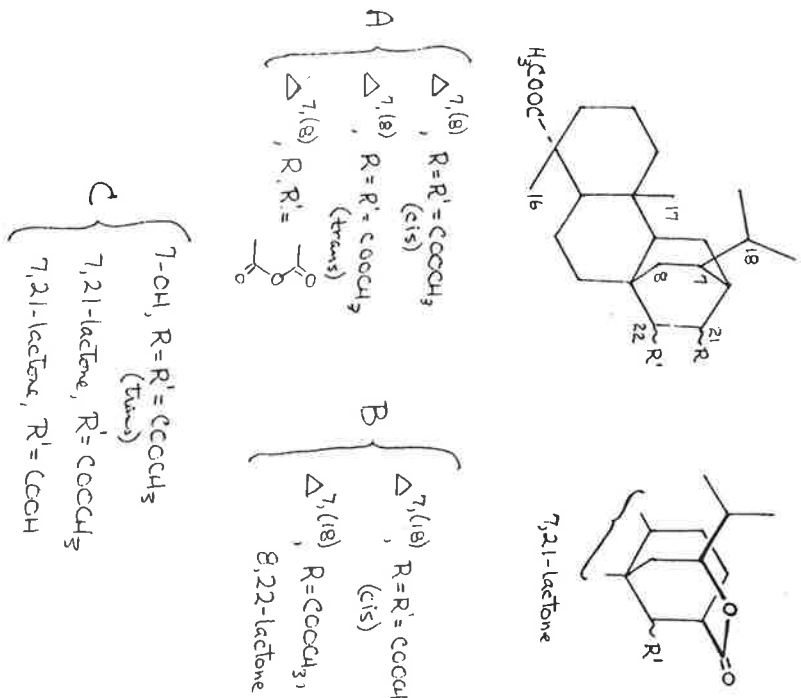


FIG. 1

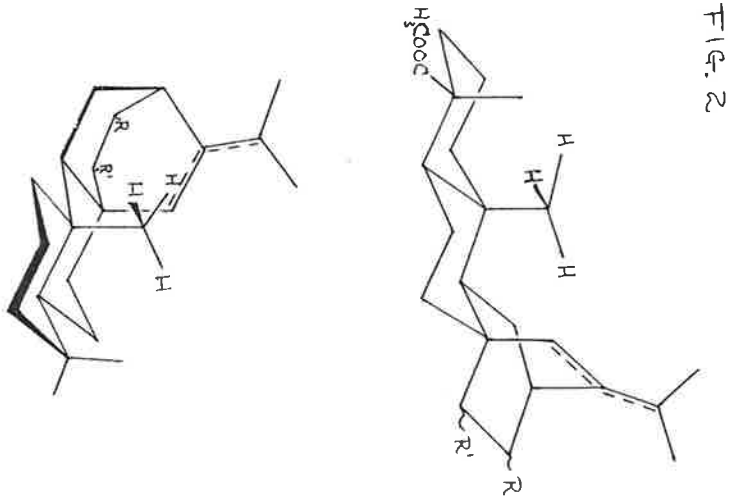


FIG. 2

MICHIGAN STATE UNIVERSITY EAST LANSING

KEDZIE CHEMICAL LABORATORY • COLLEGE OF SCIENCE AND ARTS • DEPARTMENT OF CHEMISTRY

Aug. 21, 1961

Dr. Aksel Bothner-By,
Director of Research,
Mellon Institute,
4400 Fifth Ave.,
Pittsburgh 13, Pa.

Dear Aksel:

We have recently examined the high-resolution proton magnetic resonance spectra of a number of cyclopropane derivatives selected to be of the AB, A_2B or ABX type. Since these are readily analyzed by exact methods we have been able to determine spin coupling constants between gem protons and between protons on adjacent carbon atoms which have both the cis and trans configurations. Values of the latter reported in the literature appear to be mostly in error as a result of assumptions made in attempting to interpret non-first-order spectra.

Our results are summarized below. In each case only the lowest and highest values observed in a series of four compounds are shown.

$$J_{gem} = 4.80 - 8.38 \text{ cps.}$$
$$J_{cis} = 7.90 - 9.33 \text{ cps.}$$
$$J_{trans} = 5.27 - 6.55 \text{ cps.}$$

Since the ranges for the cis and trans coupling constants do not overlap the assumption that $J_{cis} = J_{trans}$, occasionally made in interpreting the experimental spectra, is seen to be a poor one.

If J_{gem} is interpreted in terms of bond angles, using Karplus' theoretical results for the CH_2 fragment (with tetrahedral hybridization), $\angle HCH = 113 - 117.5^{o}$ for the four derivatives we studied. This range seems reasonable since values of $\angle HCH$ from microwave spectroscopy and electron diffraction have been in the range $114 - 118^{o}$. One may similarly compute the cis and trans coupling constants from Karplus' results for ethane-like molecules. One obtains in this way $J_{cis} = 8.2$ cps. (dihedral angle HCCH $= 0^{o}$) and $J_{trans} = 6.3$ cps. (dihedral angle HCCH $\cong 146.5^{o}$) compared with observed average values of 8.44 and 5.68 cps., respectively. It is interesting, and perhaps instructive, that for the three compounds which we studied in which all three coupling constants occur, $J_{cis} + J_{trans} + J_{gem} \cong 21.3$ cps.

A more detailed account of this work will ultimately appear in a more obscure spot.

Sincerely yours,

Max

Max T. Rogers
John D. Graham

MELLON INSTITUTE
4400 FIFTH AVENUE
PITTSBURGH 13, PA.

28 August 1961

Miscellany Concerning the A-60

Our experiences with the A-60 during the first month of its operation have been extremely good. Only recently have we had any of the troubles to which complex electronic gear is prone. Before mentioning a few small improvements and other things, it should be pointed out that we have had no trouble meeting or exceeding Varian's specifications without these minor changes, etc.

(1) In order to get the last, extra bit of resolution stability which the system seems to be capable of giving, we have found it helpful to keep the air temperature in the room as constant as possible. While this is of course much, much less critical than with the more classical high resolution systems, room temperature drifts and fluctuations do effect the A-60 magnet, too. Our A-60 is located in the same room as our HR-60, this room having a fairly good degree of room temperature control. The two magnets are ca. 10 feet apart (the field directions just happen to be at right angles) and they have not had bad effects on each other except when the field of one is being cycled or turned on or off.

(2) Another way to affect a small improvement in resolution stability of the A-60 is to leave a sample in the probe and the spinning air on at all times. In a single trial using a crude thermometer we found that the 'equilibrium' temperature of the business spot in the probe is 3-3.5°C. warmer when the spinning air is turned off.

(3) The optimum settings on the Curvature and Y-Gradient (fine) controls were so sensitive that we have replaced the single-turn pots with 10-turn pots of equal size making fine tuning much easier.

(4) With apologies to Varian's Sales Department: the sample tubes supplied by Varian are indeed excellent. However, the cost is simply prohibitive for applications such as ours in which it is necessary or desirable to keep several hundred sample tubes, filled and unfilled, on hand. We have therefore been using a cheaper variety of sample tube made by the Wilmad Glass Company. These tubes are also thin-walled and have an O.D. of close tolerance, albeit not quite as thin-walled or as precision ground as those Varian supplies. All these cheaper, Wilmad tubes have fitted properly into at least one of our nylon spinners and no difficulty has been encountered in their use in the A-60. These tubes

are simply designated as "semi-precision cells, 5 mm., 6 in. long" and cost $1.25 each in lots of 26 or more. They may be ordered from the Wilmad Glass Company, U. S. Route 40 and Oak Road, Buena, New Jersey.

(5) With further apologies to Varian's Sales Department, this time concerning chart paper for the A-60: for setting up, resolution trimming, integrating, and all rough work, we have been using blank chart paper first 'discovered' by Messrs. Dudek and Herrick of the Harvard Chemistry Department. This paper costs 1.01¢ per sheet (sic) in lots of 5,000 sheets, and has proved very satisfactory, as it inks well and is translucent enough to permit the blue grid of the ruled Varian paper to be seen through it readily. This is particularly handy for the exact positioning of the TMS line on the zero marker. This paper is sold by the Century Paper Company, Inc., 295 Congress Street, Boston 10, Massachusetts, and is designated as 5,000 sheets 11" x 26" Sub #9 white smooth quality manifold, punched 3 holes on 11" edge, 1/4" holes, 4'1/4" centers.

(6) Enclosed are samples of two very handy sample caps for NMR sample tubes. Both are sold by Protective Closures Company, Inc., Caplugs Division, 2207 Elmwood Avenue, Buffalo 23, New York. The red one is type K5 ($7.75/M), and the white one is type 3/16" SC Natural ($5.00/M). The white one is best cut off just above the second rib before attempting to get it on the very fragile thin-walled A-60 tubes.

We would appreciate hearing from other A-60 users about any problems, unusual techniques, gimmicks, particularly useful imprecations, etc.

B. L. Shapiro

35-6

EMORY UNIVERSITY
ATLANTA 22, GEORGIA

DEPARTMENT OF CHEMISTRY

August 11, 1961

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

Dear Aksel:

One of the studies that we have recently completed here involves the use of C^{13}-H spectra (in natural abundance) to provide a complete and unambiguous analysis of A_2B_2 systems, specifically furan in this case. The upper-field half of the β-proton C^{13}-H doublet and the lower-field half of the α-proton doublet are sufficiently displaced to permit a first-order treatment to be carried out in each case. In this way it is possible not only to obtain all four coupling constants but also to check the values of J_{AB} and $J_{AB'}$. Finally, the values so obtained are employed to calculate the spectrum of normal furan, which under the conditions of resolution employed here consists of two quartets.

From the C^{13}-H pattern, the values of the coupling constants are: J_{AB} = 1.75 cps (average), $J_{AB'}$ = 0.85 cps (average), J_{AA} = 1.4 cps, and J_{BB} = 0.3 cps. These may be compared with the corresponding values employed by Abraham and Bernstein who adopted the coupling obtained by averaging over a large series of substituted furans.[1] For J_{AB} and $J_{AB'}$ the two sets of values are essentially identical (within 0.1 cps), while the other two constants, J_{AA} = 1.55 and J_{BB} = 3.53 cps, differ from the present values by 0.15 cps and 0.23 cps respectively. Thus, it appears that, on the whole, the constants obtained by the averaging process are in reasonably good agreement with those provided by a complete analysis.

The use of C^{13}-H patterns to supplement or complete an analysis is to be recommended, particularly when the patterns are free of interference and are tractable by first-order theory.

Sincerely,

J. H. Goldstein

J. H. Goldstein
Professor of Chemistry

JHG:lt

1. R. J. Abraham and H. J. Bernstein, Can. J. Chem., 37, 1056 (1959).