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Newsletter

No. 137  
FEBRUARY, 1970

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Deadline Dates: No. 138: 2 March 1970  
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All Newsletter correspondence, etc., should be addressed to:

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(UNIVERSITY OF LONDON)

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DEPARTMENT OF CHEMISTRY



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PROFESSOR B. C. L. WEEDON,  
D.Sc., Ph.D., F.R.I.C.  
PROFESSOR D. C. BRADLEY,  
D.Sc.

2nd January 1970

Dear Barry,

N.m.r. Meeting, London, September 1970

Plans are being laid by the N.m.r. Discussion Group of the Chemical Society for a two day symposium to be held as one section of the Society's Autumn Meeting scheduled for September 29-31, 1970 at Imperial College, London.

The current idea of the Discussion Group Committee:

Jack Becconsall	I.C.I., Petrochemical & Polymer Division
Bill McFarlane	Sir John Cass College, London
Ernie Cummins	Perkin-Elmer Ltd,
Derek Shaw	Varian Associates
Les Sutcliffe	University of Liverpool

recently elected at the meeting of December 18th at Chelsea College, is to have two main themes: (i) the n.m.r. of large molecules and (ii) recent advances in techniques and instrumentation.

The programme will be kept flexible however, so that meritorious contributions not covered by these categories will be allowed. The form of the programme will probably be conventional: a large number of twenty minute talks and a small number of longer lectures.

The purpose of this letter is mainly to alert Fall visitors to Britain (and residents also) to the possibility of including a few hopefully useful days of scientific conviviality to whatever other European activities, frivolous, or otherwise, they had planned.

Suggestions for contributions are welcomed. They should be sent to Dr Eric F. Mooney, University of Birmingham, Post Box 363, Birmingham 15.

A more formal announcement will appear later when additional detail is evolved.

Yours sincerely,

Ed

Edward W. Randall

## MOLECULAR PHARMACOLOGY RESEARCH UNIT



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OLD PRESS SITE,  
MILL LANE,  
CAMBRIDGE.

Professor Bernard L. Shapiro  
Department of Chemistry  
Texas A&M University  
College Station, Texas 77843

10 . 12 . 1969

<sup>1</sup>H NMR Studies of Human Carbonic Anhydrase B

Dear Dr. Shapiro,

Sorry we needed reminding about our contribution. We have been continuing to study proteins by NMR, most recently human carbonic anhydrase B. This is a zinc metalloenzyme, molecular weight 30,000, with eleven histidine residues, only four of which are titratable in the native enzyme. A group with a pK of 7 - 7.5 is involved in the activity of the enzyme; this is thought to be either an imidazole or a zinc-bound water molecule.

By following the changes in chemical shift of the imidazole C2-H peaks of the histidine residues, we have obtained the titration curves shown in the figure. All four titratable histidines can be seen. The linewidth of the peaks ( 5-10 Hz ) indicates that these imidazole groups must be free to rotate at a greater frequency than the tumbling of the whole molecule, and must presumably be on the surface of the protein. Rough calculations give a value of 20-25 Hz for the linewidth of the buried histidines ( those which move only with the tumbling of the whole molecule ) - we would be unlikely to resolve peaks as broad as this under the conditions of our experiments. Unfortunately denaturation and precipitation of the protein prevents us from going to a low enough pH to complete all the curves, but peaks 1 and 4 have pK's of 7.08 and 6.98 respectively.

Figure B shows the titration curves for the apoenzyme ( lacking the zinc atom ). Curves 1-4 are essentially identical to those of the native enzyme. This, and the marked similarity of the aromatic region of the spectrum indicate that no gross unfolding of the molecule has occurred. Nevertheless, a further C2-H peak (5) is visible throughout the accessible pH range; the imidazole corresponding to this peak has become mobile and titratable on removal of the zinc. It is tempting to speculate that this may be one of the ligands to the zinc in the native enzyme, though of course there are a number of alternative possibilities. Peak 6 is a further imidazole C2-H peak which is visible only below pH 6.6. Measurement of areas indicates that above this pH it is not in either peak 1 or the pH-independent peak shown by a dotted line ( this may be a non-titrating imidazole C2-H or a non-exchanged NH peak ). The most likely explanation is that peak 6 represents a histidine which is buried in the native structure of the enzyme, and which only becomes mobile and titratable as the enzyme begins to unfold at low pH ( the apoenzyme is more readily denatured by acid than the native enzyme ).

The next step is obviously to try and identify these peaks with particular histidine residues in the protein, though the amino-acid sequence is not yet fully known.

Yours sincerely,

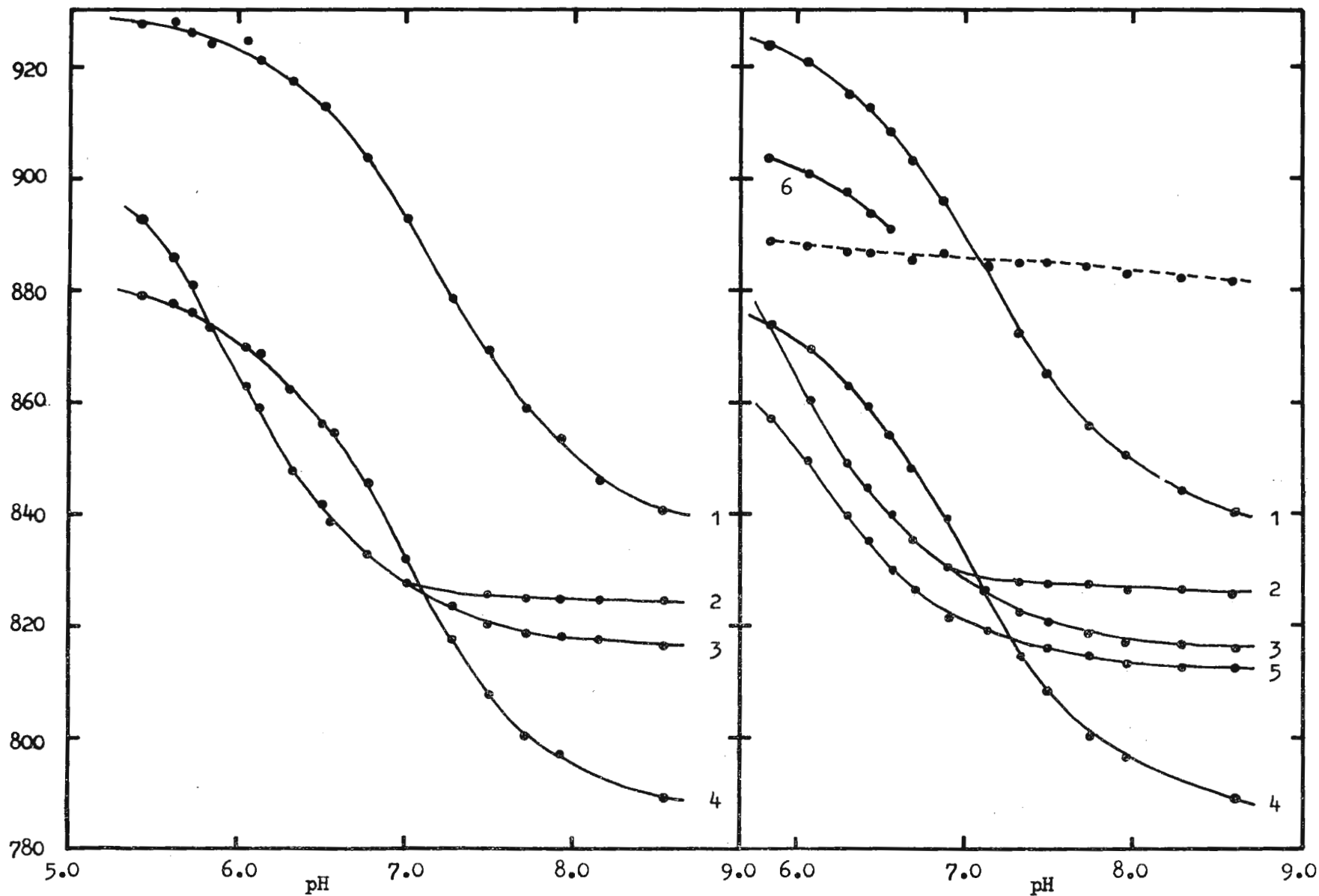
*R. W. King.*

R. W. King.

*Gordon Roberts*

G. C. K. Roberts.

( Subscription credit )



Native HCA-B in D<sub>2</sub>O / K<sub>2</sub>SO<sub>4</sub> I = 0.2

Apo HCA-B in D<sub>2</sub>O / K<sub>2</sub>SO<sub>4</sub> I = 0.2

Spectra obtained with Varian HA-100D and Biomac 'CAT', probe temperature 28°.

Ordinate: Chemical shift in Hz ( at 100 MHz ) downfield from external TMS.



LABORATORIUM  
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 ORGANISCHE CHEMIE  
 —  
 UNIVERSITEIT - GENT  
 LABORATORIUM v. DRG. SCHEIK.  
 PROF. M. ANTEUNIS  
 Krijgslaan 105 - S 4  
 GENT

GENT, 15th December 1969

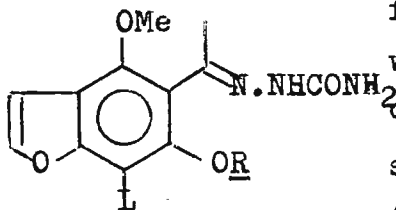
KRIJGSLAAN 105  
 (België - Europa)

Tel. (09) 22.60.95

Heterotopism Due to Slow N-Inversion in Semicarbazones

Dear Barry,

We recently obtained from prof. W. Tadros (Cairo-University-U.A.R.) a series of isomeric semicarbazones derived from khellinone (L=OMe) and visnagone (L=H), with R = Me, Et, i.Pr. Several isomeric pairs could be separated, i.e. in the khellinone series (R=Et and i.Pr) and the visnagone series (R=i.Pr). Their nmr spectra do differ not only



with respect to the line positions, but what is remarkable it turns out that the Me-groups in the i.Pr-derivatives are anisochronous (1).

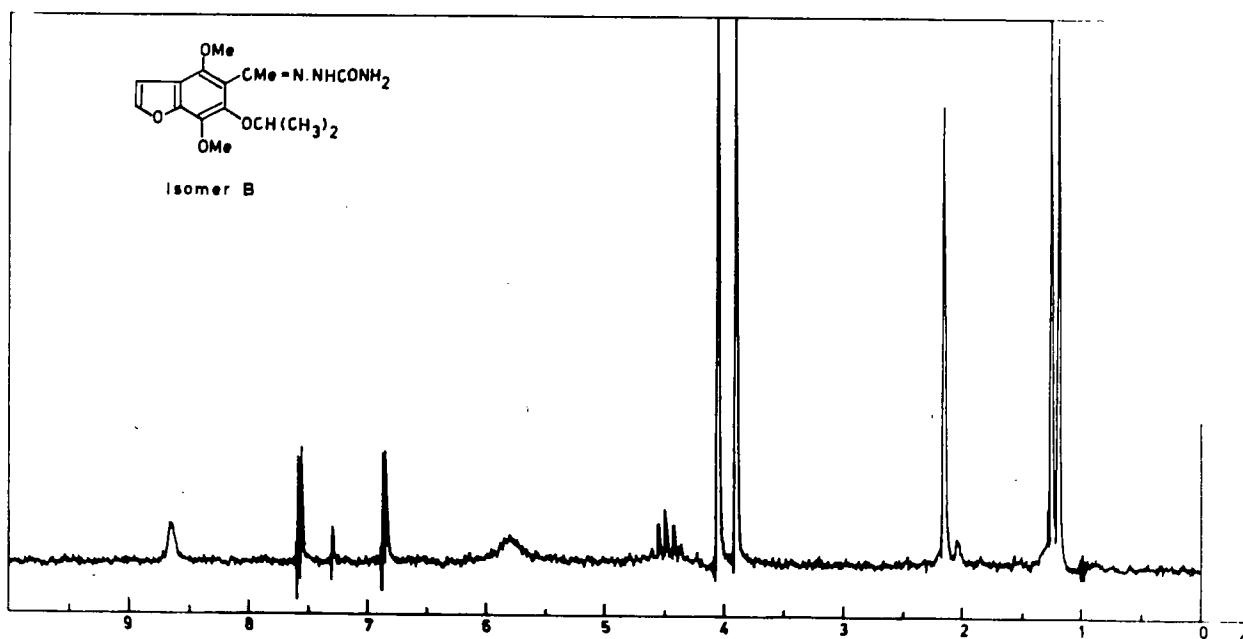
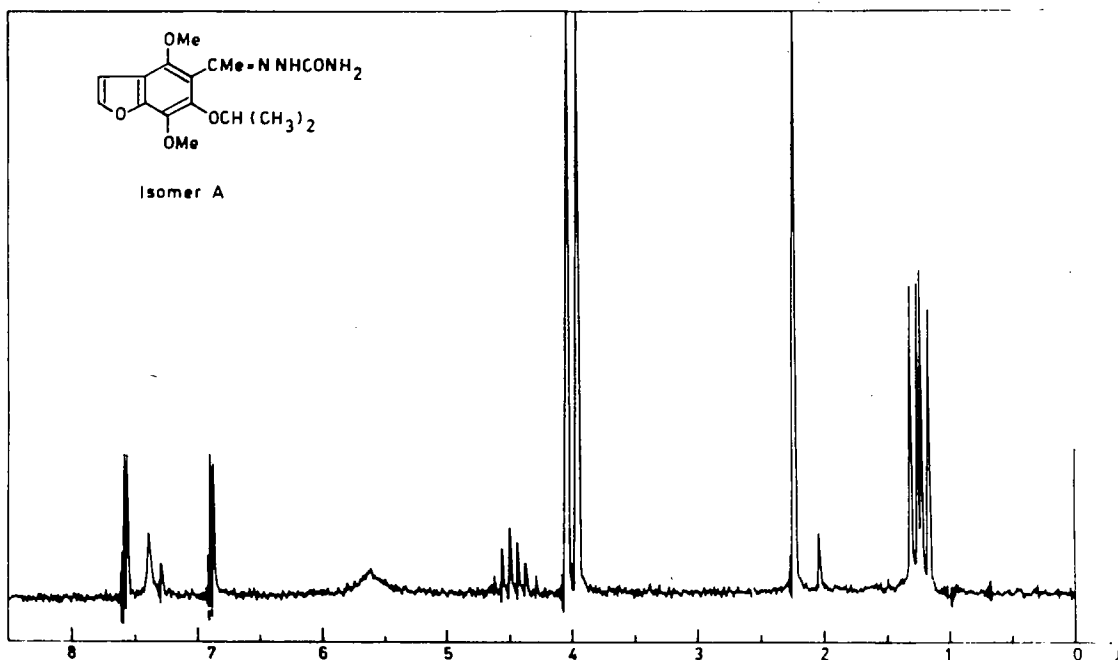
At the basis of the observed isomerism, a cis/trans relationship around the C=N bond might be accepted (although up to 135° no inter-conversion between isomers A and B (fig.) was observed).

More puzzling is the origin of the anisochronism. Strictly speaking both Me-groups are enantiotopic (1), thus being shift-equivalent. A relatively slow inversion of the =N-NH-CONH<sub>2</sub> nitrogen (slow on the nmr time scale of the observed separation of the -CHMe<sub>2</sub> peaks) would result in diastereotopic Me-groups. Although recently such slow inversion has been observed in negatively substituted azirines (2), we feel some doubt on the validity of such phenomena in semicarbazones, the more that in high temperature registration the anisochronism is not lacking. It is further not clear why this does not occur for the other isomer. Perhaps the semicarbazone moiety is forced in one of the isomers out of the plane of the aromatic nucleus, the influence of polarity being disrupted by non-conjugation, with a resulting changed

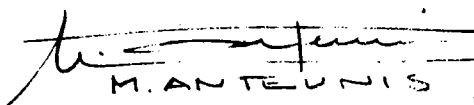
rate of N-inversion.

I should greatly appreciate if any of the readers could help me in solving the problem.

- (1) K. Mislow, M. Raban; Topics in Stereochemistry, vol. I pp. 1-37; Edit. E. L. Eliel, N. L. Allinger; Intersc. Publ., (1967).  
 (2) S. Brois; J. A. C. S., 90, 508 (1968); Tetr. Letters, 5997 (1968);  
 F. Montanari e. a., Chem. Comm., 1694 (1968); E. Eschenmoser; Angew., 80, 197 (68)



Sincerely yours

  
 M. ANTEVINIS



**JAPAN ELECTRON OPTICS LABORATORY CO., LTD.**  
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K-0089

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Professor Bernard L. Shapiro,  
 Department of Chemistry,  
 Texas A & M University,  
 College Station,  
 Texas 77843,  
 U.S.A.

23rd December, 1969.

Title: The NMR of Molten Polyethylene

Dear Dr. Shapiro,

It is well known that the existence of the methyl group and the olefinic group in the chain of polyethylene is confirmed by IR measurement. The amount of such irregular bondings in polyethylene varies according to the method of polymerization, and this variation defines the various properties of solid state polyethylene.

Using a molten sample, an NMR approach to investigate such irregular bondings of polyethylene was first attempted by A. Nishioka 1) and R. C. Ferguson. 2)

The results obtained were not very good, however, even though computer time averaging techniques were used. This was because they used rather low sensitivity instruments at 40 and 60 MHz. Recently, we obtained better results on molten polyethylene measured at 180°C. without accumulation, using a 100 MHz. instrument. One of the results is shown in Fig.-1.

There seems to be three types of olefinic groups in polyethylene, i.e. (a) vinyl  $\begin{matrix} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{R} & & \text{H} \end{matrix}$  (b) vinylidene  $\begin{matrix} \text{R} \\ | \\ \text{C}=\text{CH}_2 \end{matrix}$  and (c) trans vinylene  $\begin{matrix} \text{R} & & \text{H} \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{H} & & \text{R} \end{matrix}$ .

We assigned the spectrum shown in Fig.-2, by referring to the measurement results of the model compounds such as (a) octadecane-1  $\{\text{CH}_3(\text{CH}_2)_{15}\text{CH}=\text{CH}_2\}$  for vinyl, (b) 2-ethyl-butene-1  $\{(\text{CH}_3\text{CH}_2)_2\text{C}=\text{CH}_2\}$  for vinylidene and (c) elaidic acid  $\{\text{CH}_3(\text{CH}_2)_7 \begin{matrix} \text{H} \\ | \\ \text{C}=\text{C} \\ | \\ (\text{CH}_2)_7\text{COOH} \end{matrix}\}$  for trans vinylene. The ratio of the amount of these three olefinic groups was calculated from the integration results.

For example, the high density polyethylene, Fig.-1,2, which was polymerized by the Phillips method shows the ratio of (a) vinyl 81%, (b) vinylidene 1% and (c) trans vinylene 18%. Another example of low density polyethylene which was polymerized by I.C.I. method and seemed to be carrying 33 methyls among a thousand carbon atoms shows the ratio of (a) 66%, (b) 15% and (c) 19%.

The measurement of high resolution NMR spectrum of molten polymers has the advantages of high sensitivity and safety from contamination due to impurities in the solvent, so that this technique is suited for the detection of a very few irregularities in the polymer chain.

Continued...





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- 2 -

However, for obtaining a high resolution spectrum, it is necessary to prepare the sample carefully and use high temperatures for measurement, since the viscosity of polyethylene is reduced to a half value, each time the temperature is increased by 25 degrees. (However, the temperature should not exceed the destroying temperature).

Further study on this matter is in progress.

Please credit this to the JEOL subscription.

Yours sincerely,

A handwritten signature in cursive script that reads 'K. Goto'.

K. GOTO

Bibliography:

1. Y. Kato and A. Nishioka  
International Symposium on NMR Tokyo, (1965)
2. Ferguson, R.C.  
Kautschuk Gummi, 18, 723, (1965)

KG/sh



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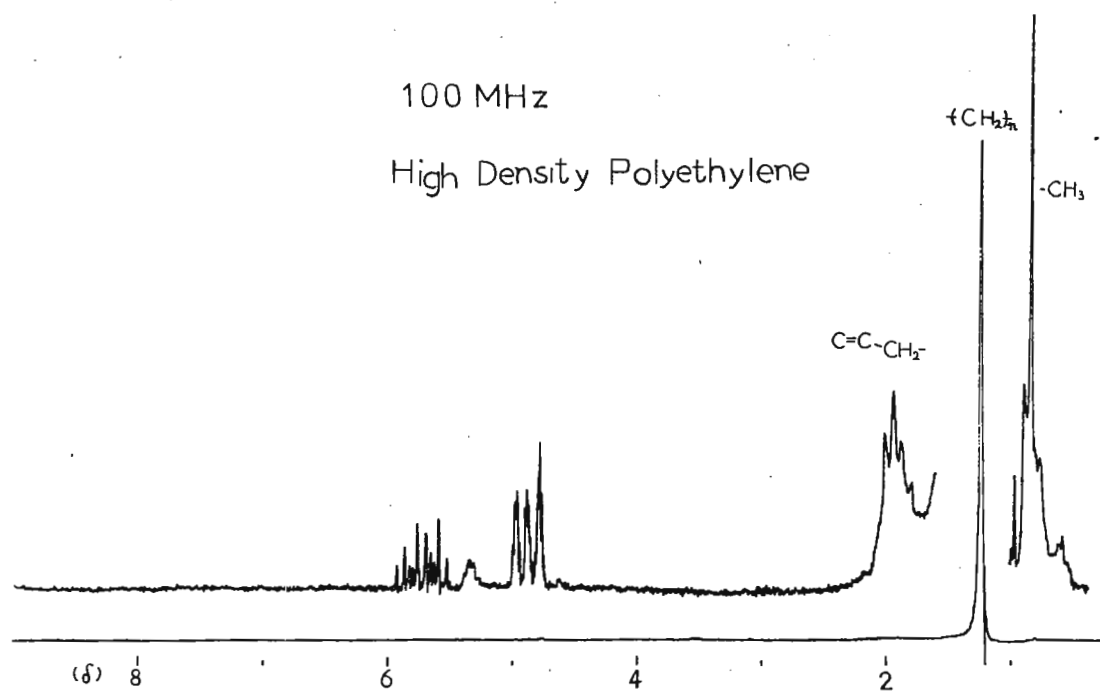


Fig.-1. NMR Spectrum of molten high density polyethylene measured at 180°C by JNM-4H-100 approximately 2% H.M.D.S. is added for internal locking.

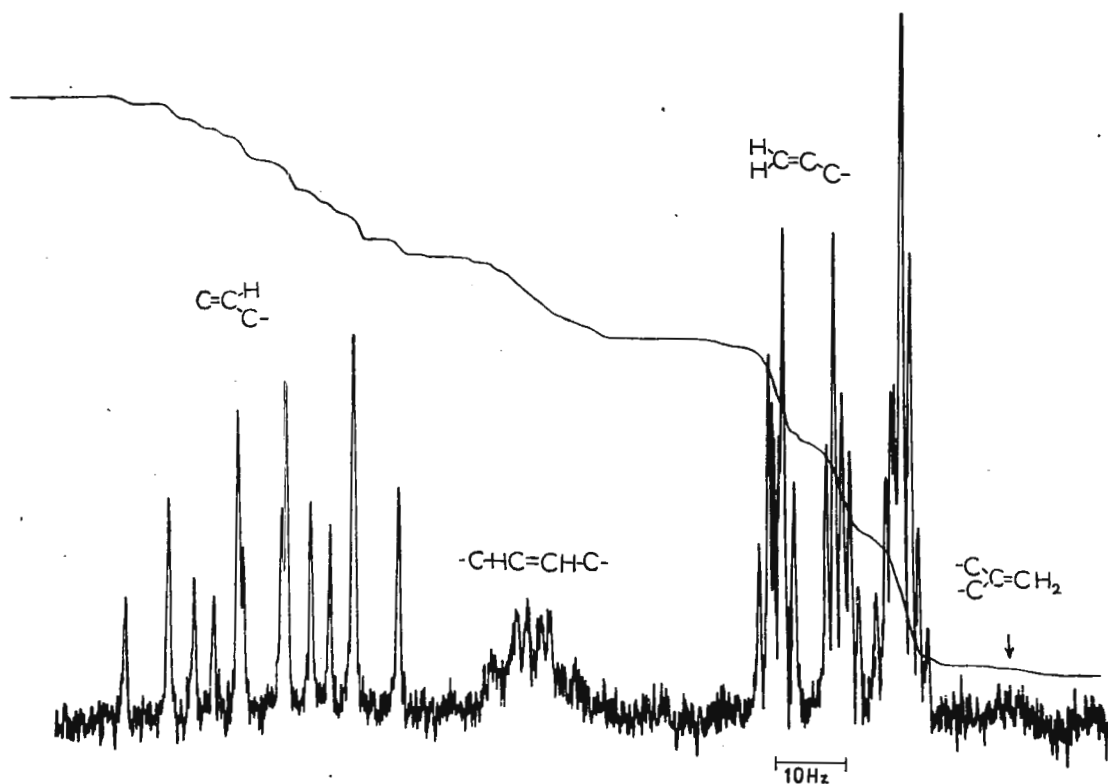
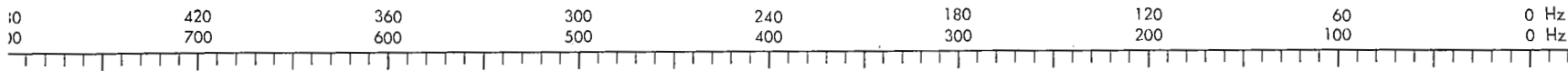
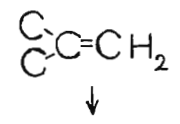
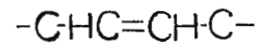
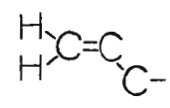
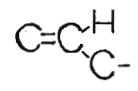


Fig.-2. Expanded spectrum of olefinic protons in polyethylene.



SPECTRUM No. \_\_\_\_\_  
 DATE Dec. 8 '69  
 FREQ. 100 MHz  
 NUCLEUS <sup>1</sup>H  
 SAMPLE polyethylene

Stiffness: High density.



SOLVENT neat  
 CONC. \_\_\_\_\_  
 REFERENCE \_\_\_\_\_  
 LOCK HMPD  
 TEMP. 18.5 °C  
 R. F. LEVEL -40dB  
 R. F. GAIN 3  
 A. F. LEVEL \_\_\_\_\_  
 FIXED FREQ. 4-8  
 VARI. FREQ. 5-5  
 A. F. GAIN 4-5  
 RESPONSE 4  
 SWEEP \_\_\_\_\_  
 WIDTH 9X 1/2 PPM  
 TIME 12 MIN.  
 OFFSET \_\_\_\_\_ PPM  
 \_\_\_\_\_ FREQ. / FIELD, \_\_\_\_\_ FREQ. / FIELD,

OPERATOR K. Ito  
 REMARKS;

10 Hz



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137-9

420 360 300 240 180 120 60 0 Hz  
 700 600 500 400 300 200 100 0 Hz

SPECTRUM No. 137-10  
 DATE Dec. 8 '69  
 FREQ. 100 MHz  
 NUCLEUS <sup>1</sup>H  
 SAMPLE polyethylen  
 Stapfen: High Density

(CH<sub>2</sub>)<sub>n</sub>

CH<sub>3</sub>

C=C-CH<sub>2</sub>

SOLVENT neat  
 CONC. \_\_\_\_\_  
 REFERENCE HMDS  
 LOCK "  
 TEMP. 180 °C  
 R. F. LEVEL -40 db  
 R. F. GAIN 3  
 A. F. LEVEL \_\_\_\_\_  
 FIXED FREQ. 4-10 (1-4)  
 VARI. FREQ. 5-6  
 A. F. GAIN 3-2 (2-2)  
 RESPONSE 2 (2)  
 SWEEP \_\_\_\_\_  
 WIDTH 9x 1 PPM  
 TIME 10 (5) MIN.  
 OFFSET \_\_\_\_\_ PPM  
 FREQ. FIELD/FREQ. FIELD,  
 OPERATOR K. Goto  
 REMARKS:

7 6 5 4 3 2 1 0



JAPAN ELECTRON OPTICS LAB.  
 TOKYO JAPAN



The University of Western Ontario, London, Canada

Faculty of Science  
Department of Chemistry

January 9, 1970.

Professor B.L. Shapiro,  
Dept. of Chemistry,  
Texas A. & M. University,  
College Station, Texas 77843  
U.S.A.

Dear Barry,

Some Long-range Couplings ( $J_{\text{HCCOCH}}$ ) in Bicyclic Esters

I now believe that your red letter exists and in response to it I would like to describe some long-range coupling constants exhibited by the carbomethoxyl protons in a number of 2-carbomethoxy bicyclo[2.2.1]heptenes and heptanes. For a series of 3-substituted 2-carboxylic esters, the coupling between the C-2 proton and the methoxyl protons is clearly resolved. Using the wiggle beat method these have been measured by Henry Brouwer for both the saturated and unsaturated series in which the substituents are Me, Cl, Br, I and OMe and certain regularities appear.

First these coupling constants depend on the relative orientation of the 2- and 3- substituents but not on the nature of the 3-substituent. In fact the couplings for the simple esters are the same as the 3-substituted cases. The magnitude of the coupling is also independent of the 5,6 bond ( $J$ 's are the same in the saturated and unsaturated series). For exo-carbomethoxyls  $J = 0.17 \pm 0.02$  Hz where the scatter indicated is the standard deviation for 21 examples. For the compounds having endo-carbomethoxyls this long-range  $J$  depends on the orientation of the 3-substituent; with endo-3-X,  $J = 0.18 \pm 0.02$  Hz (7 examples) and with exo-3-X,  $J = 0.25 \pm 0.03$  Hz (12 examples including the unsubstituted cases).

These results are similar to those found in acyclic systems by, for example, Riggs and Verma, Tetrahedron Letters 3767 (1968) and presumably the interactions occur primarily through planar extended W bond arrangements. In contrast to the lack of coupling in cyclohexyl acetates noted by Riggs and Verma, the cyclohexane carboxylic acid esters exhibit this coupling, with that for the axial ester ca. twice the  $J$  in its equatorial counterpart. Thus the present observations are consistent with the earlier ones and it is not necessary to invoke  $\alpha$ - $\pi$  interactions to account for these five-bond couplings.

I hope this restores my credit with the TAMU Newsletter.

Sincerely,

J.B. Stothers  
Professor of Chemistry.

JBS:sjc

School of Chemistry,  
University of Bristol,  
Cantock's Close,  
Bristol 8,  
England.

2nd January, 1970.

Professor Bernard L. Shapiro,  
Department of Chemistry,  
Texas A & M University,  
College Station,  
Texas 77843,  
U.S.A.

Dear Professor Shapiro,

AA'MM'X<sub>3</sub> Propyl Groups - A Tetrafluoroethylene Complex

I was interested to see Derek Shaw's letter in the September Newsletter as we have just come across some AA'MM'X<sub>3</sub> type propyl groups in 9,10 dipropylantracene and some of its 9,10 dihydro- derivatives from Dr. Macmillan's group. The  $\alpha$ -CH<sub>2</sub> resonances are not simple triplets but, at least in the case of the anthracene, resemble the AA'XX' pattern. Some others look more complicated and may indicate chemical inequivalence between the geminal protons although we might have a mixture of compounds as they are rather unstable and difficult to purify. I have not been able to complete the analysis as our computer is being moved and in any case we are missing the outside lines needed to get the geminal coupling. Because of the stability problem, I have only gone up to 60° but this produced no noticeable change so these are probably fixed conformers like OsCl<sub>4</sub>(AsPr<sub>3</sub><sup>n</sup>).

Instability and insolubility have long prevented us from getting a good spectrum from a tetrafluoroethylene complex. However, Messrs. Cooke and Green have now produced a ruthenium complex which gives spectrum shown. The almost first order spectrum of the C<sub>2</sub>F<sub>3</sub>Cl complex was used as a starting point for the analysis. As with C<sub>5</sub>H<sub>5</sub>Rh(C<sub>2</sub>F<sub>4</sub>)(C<sub>2</sub>H<sub>4</sub>) (R. Cramer, J.B. Kline and J.D. Roberts, J.A.C.S. 2519, 91, 1969) the relative signs of the three F-F couplings are found although the geminal coupling is not well determined and was set to 180 Hz.

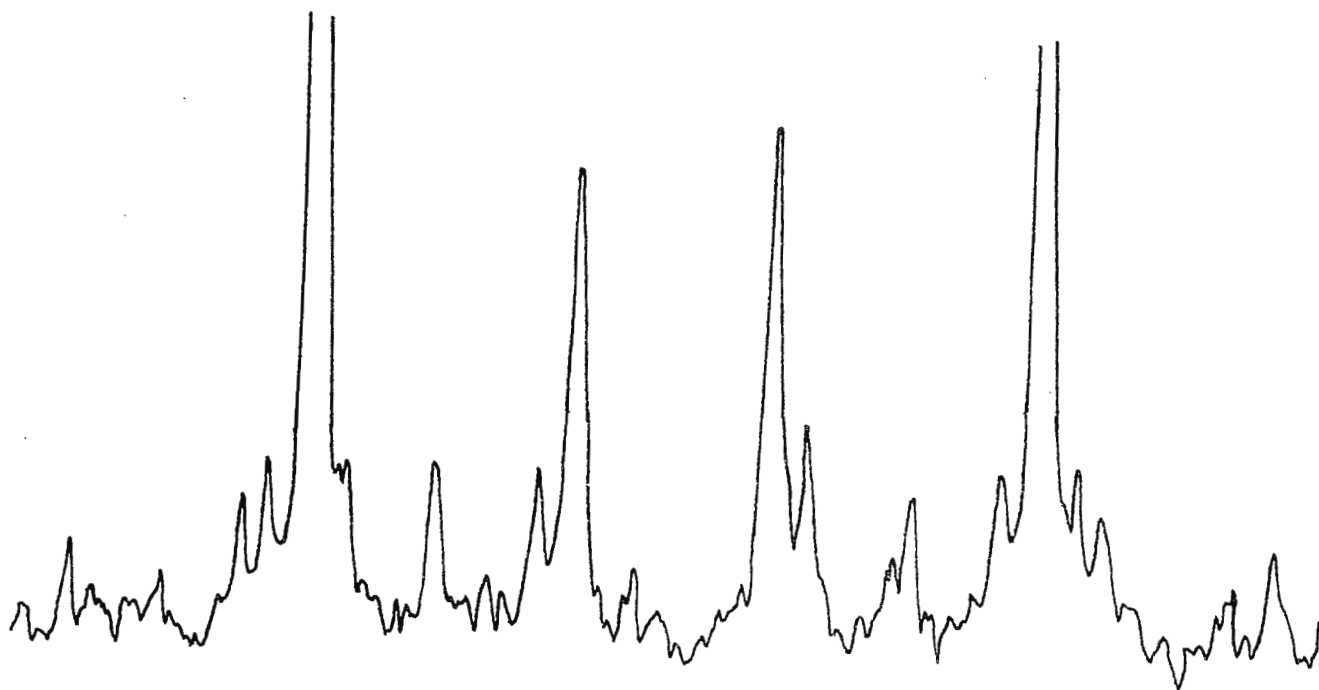
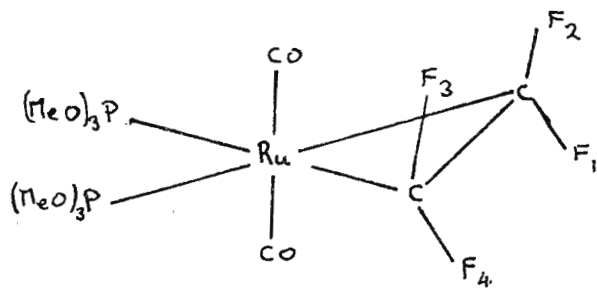
Complex	J <sub>f<sub>1</sub>F<sub>2</sub></sub>	J <sub>F<sub>1</sub>F<sub>3</sub></sub>	J <sub>F<sub>2</sub>F<sub>3</sub></sub>	J <sub>PF trans</sub>	J <sub>PF cis</sub>
C <sub>2</sub> F <sub>4</sub>	180+20	-39.6	10.0	59.0	12.2
C <sub>2</sub> F <sub>3</sub> Cl (Cl at 4)	163	44	7.5	61 61 46	14 14 7.5

These values suggest that the C-C bond is nearer to a single bond than in the rhodium complex. The cis and trans P-F couplings have the same sign but the relationship to the F-F couplings is not determined. I have not indicated this in the table above as I cannot think of a neat way of doing it - advice welcome. I am not very happy with the use of + and - even in simple cases as editors etc., seem to be able to 'correct' - to + faster than you can put it back again.

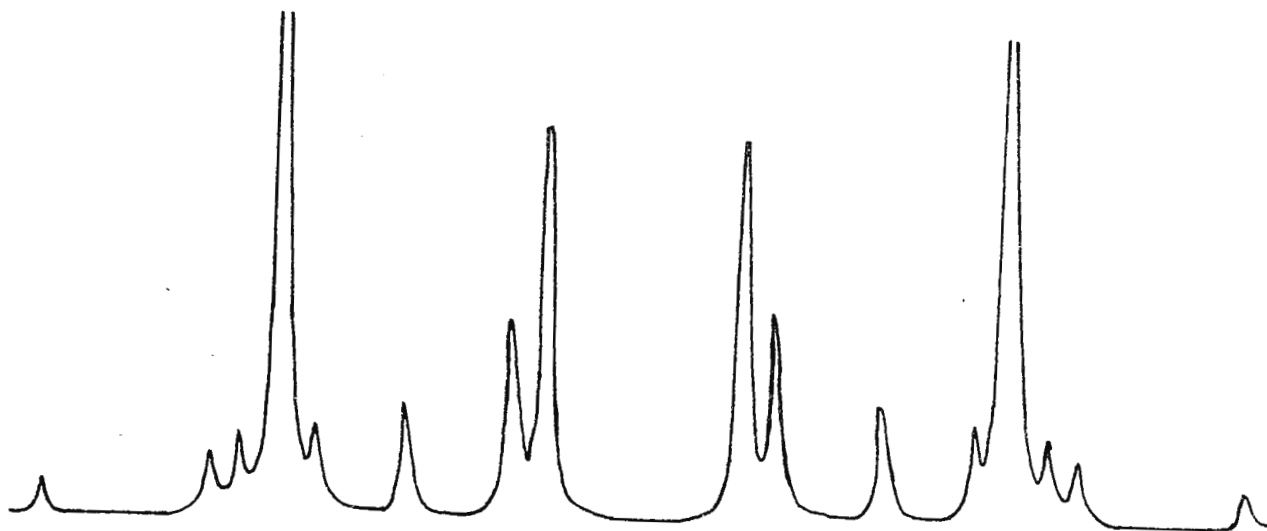
Yours sincerely,

*R.J. Goodfellow*  
R.J. Goodfellow.

$^{19}\text{F}$  NMR spectrum of



50 Hz





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7th January, 1970

Your Ref.

Our Ref. JKB/AR

Professor B.L. Shapiro,  
Chemistry Department,  
Texas A & M University,  
College Station,  
Texas 77843,  
U.S.A.

Dear Barry,

New approaches to magnetic susceptibility measurements

The various nmr methods that have been used for measuring magnetic susceptibilities of liquids [reviewed by K.D. Bartle, D.W. Jones and S. Maričić, *Croatica Chemica Acta*, 40, 227 (1968)] depend on comparing resonance positions in two geometrically dissimilar environments. Thus, the non-spinning coaxial cylindrical cell method [J.R. Zimmerman and M.R. Foster, *J. Phys. Chem.*, 61, 282 (1957); D.C. Douglass and A. Fratiello, *J. Chem. Phys.*, 39, 3161 (1963)] effectively compares resonances in the bisecting plane and at the periphery for an annular cross-section sample in a transverse magnetic field; the main disadvantage is a rather critical dependence on field homogeneity controls. The method using a spinning cell containing both a cylindrical and a spherical portion [K. Frei and H.J. Bernstein, *J. Chem. Phys.*, 37, 1891 (1962); L.N. Mulay and M. Haverbusch, *Rev. Sci. Insts.*, 35, 756 (1964)] is in principle absolute and of potentially high accuracy, but difficulties of making accurately shaped cells have usually forced the adoption of an empirical factor measured for the particular cell.

If one is in the fortunate position of being able to make measurements with two different magnet geometries, viz. (a) the conventional transverse field geometry, and (b) the longitudinal geometry adopted with a superconducting solenoid magnet, the difficulties of spherical cells can be avoided. Only a spinning coaxial double cylindrical cell of the Wilmad type is needed. Liquid media of susceptibilities  $\chi_A$  and  $\chi_B$  are compared by dissolving a common internal reference in both; provided that the usual "infinite" sample length condition is satisfied, the susceptibility difference can then be calculated as

Cont/.....



FROM: J.K. Beconsall

SHEET NO. 2

TO: Prof. B.L. Shapiro

DATE: 7.1.70

$$\chi_B - \chi_A = \frac{1}{2\pi} (\Delta_{AB}^{\perp} - \Delta_{AB}^{\parallel})$$

where  $\Delta_{AB}^{\perp}$  and  $\Delta_{AB}^{\parallel}$  are the relative shifts measured with transverse and longitudinal fields respectively (positive sense is upfield from A to B).

Where solvent susceptibility data are needed for making bulk susceptibility corrections in nmr, the difference  $\chi_B - \chi_A$  must be known quite accurately; published tables of susceptibilities are generally inadequate for this purpose. A table of accurate susceptibility differences for several solvent pairs, measured by the above method in collaboration with G. Doyle Daves, Jr. and W.R. Anderson, Jr., of Oregon Graduate Center, is in the press [J.K.B., G.D.D. and W.R.A., J. Amer. Chem. Soc.].

The possibility of using nmr for measuring magnetic susceptibilities of solids has had very little attention. We are currently experimenting here with cell designs for susceptibility determinations on paramagnetic solids (an application of importance in organometallic chemistry) by measuring the effect of a small specimen on the resonance of a nearby liquid reference.

Yours sincerely,



J.K. Beconsall



# AMERICAN OIL COMPANY

RESEARCH AND DEVELOPMENT DEPARTMENT 2500 NEW YORK AVENUE WHITING, INDIANA 46394

January 19, 1970

Subject: Microcells for Nuclear  
Magnetic Resonance Analyses

Professor Bernard L. Shapiro  
Chemistry Department  
Texas A & M University  
College Station, Texas 77843

Dear Barry:

Handling small amounts of substances for NMR analyses has led to the development of a number of different microcells. As far as we know several types of these cells are available commercially from:

JEOLCO, Medford, Mass.  
Kontes Glass Co., Vineland, J. J.  
NMR Specialties, New Kensington, Pa.  
Varian, Palo Alto, Calif.  
Wilmad Glass Co., Buena, N. J.

Other types have been developed. An excellent review by R. E. Lundin, et.al., in Applied Spectroscopy Reviews, vol. 1, 131 (1967), describes the various types of microcells developed prior to 1967. We wish to update their list of references for inclusion in the newsletter:

- 1967 R. A. Flath, et.al., Appld Spectry 21, 183 (1967)  
D. J. Frost, et.al., Chem and Ind (London), 116 (1967)  
S. C. Slaymaker, Appld Spectry 21, 42 (1967)
- 1968 L. R. Provost and R. V. Jardine, J. Chem Ed 45, 675 (1968)  
B. Milazzo, et.al., Appld Spectry 22, 574 (1968)
- 1969 E. M. Banas Appld Spectry 23 281 (1969)  
D. W. Mastbrook and E. P. Ragelis, Appld Spectry 23, 376 (1969)
- 1970 L. V. Haynes and C. D. Sazavsky, to be published in Appld Spectry(1970)

We also wish to point out the adaptability of our multicloistered cells (E.M.B., 1969 or IIT NMR Newsletter 118-48) to micro-sampling. Samples can be trapped from a chromatography column in one capillary tube and held immobile in the center by six empty outer capillary tubes, e.g., in the heptacloistered cell. Saves machining of special holders.

Sincerely,

R. A. DINERSTEIN

B. E. WENZEL

D. J. SLUPSKI

A. J. BUGAJSKI

E. M. BANAS

UNIVERSITÉ DE NANTES  
**FACULTÉ DES SCIENCES**  
 B. P. 1044 NANTES

Laboratoire de Chimie Organique-Physique  
 38, Boulevard Michelet - Nantes

Nantes, le 20.1.70

Use of magnetic non equivalence for  
 the determination of geminal allenic  
 spin-spin coupling constants.

Professor B.L. SHAPIRO  
 Department of Chemistry  
 COLLEGE OF SCIENCE  
 TEXAS A & M UNIVERSITY  
 College Station

TEXAS 77843

Cher Professeur SHAPIRO,

Dans les composés

$$\begin{array}{c} \text{(A) H} \backslash \\ \text{C} = \text{C} = \text{C} \text{ X Y} \\ \text{(B) H} / \end{array}$$

le couplage entre protons géminés ne peut pas être déterminé directement en raison de l'isochronie inhérente à la symétrie moléculaire. Cependant,  $^2J_{\text{HH}}$  est accessible par substitution de l'un des protons par un atome de deutérium et nous en avons déterminé le signe par examen du spectre à deux quanta<sup>2</sup>(1). Ce signe est d'ailleurs confirmé par étude des variations de  $^2J$  sous l'influence des solvants (2).

Nous avons pensé que l'introduction d'une dissymétrie moléculaire dans X ou Y, en levant l'isochronie de  $H_A$  et  $H_B$ , doit permettre la mesure directe de  $^2J_{\text{HH}}$ . Une non équivalence magnétique apparaît effectivement sur le spectre des composés R-CHBr-CO-C=C-CH<sub>2</sub> (3). Les protons alléniques donnent lieu par couplage avec le méthyle à un spectre ABX<sub>3</sub>. L'écart  $\nu_A - \nu_B$  dépend du solvant et de la concentration ; pour R = C<sub>6</sub>H<sub>5</sub>, il est de l'ordre de 1 Hz dans CCl<sub>4</sub> (fraction molaire  $c \approx 0,2$ )<sup>2,5</sup>. L'analyse conduit dans ce cas à  $|J_{\text{H-C-H}}|^4 = 14,25$  Hz (nous avons mesuré dans CH<sub>2</sub>COCH=C=CHD,  $c \approx 0,06$  dans CCl<sub>4</sub>,  $J_{\text{H-D}} = -2.10$  Hz soit  $J_{\text{H-H}} \approx -13,7$  Hz). [60 MHz]

- (1) MARTIN M.L., MARTIN G.J. et COUFFIGNAL R. - J. Chem. Phys. 49, 1985, 1968 -
- (2) MARTIN M.L., COUFFIGNAL R. et MARTIN G.J. - J. Molecular Spectroscopy, 1970 - sous presse -
- (3) Ces produits ont été préparés par MM. M. GAUDEMAR et R. COUFFIGNAL (Laboratoire de Synthèse Organométallique - Faculté des Sciences de PARIS).

Je vous prie d'agréer, Cher Monsieur SHAPIRO, l'expression de mes sentiments les meilleurs.

  
 M.L. MARTIN

  
 G.J. MARTIN

DEPARTMENT OF ORGANIC CHEMISTRY  
THE ROBERT ROBINSON LABORATORIES P.O. BOX 147 LIVERPOOL L69 3BX

TEL: 051 - 709 - 6022

Professor Bernard L. Shapiro,  
Department of Chemistry,  
Texas A and M. University,  
College of Science,  
College Station,  
Texas 77843,  
U.S.A.

21st January, 1970.

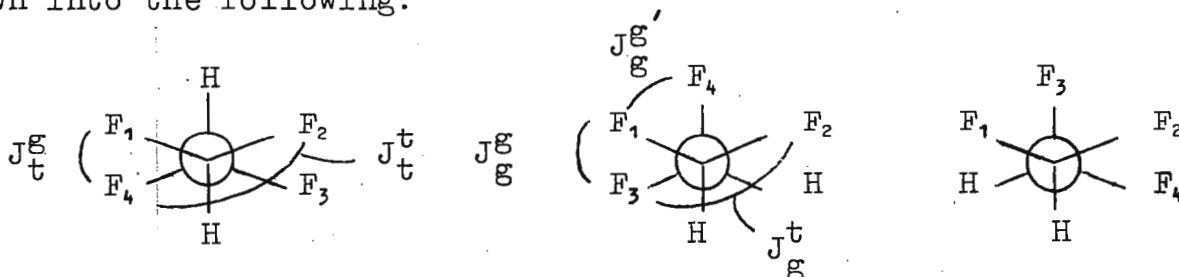
Dear Barry,

The N.M.R. spectrum and rotational isomerism of  
1,1,2,2 tetrafluoroethane.

In collaboration with Dr. L. Cavalli (Montecatini Edison S.P.A. Milan) we have just completed the detailed analysis of the  $^1\text{H}$  and  $^{19}\text{F}$  spectrum of  $\text{CHF}_2\cdot\text{CHF}_2$  and utilised the solvent dependence of the couplings to obtain the couplings in the distinct isomers and the energy difference between the isomers in the liquid and vapour states.

To cut a long story short, we obtain from this treatment the following results. For the trans isomer  $J_{\text{HH}}$  4.9,  $^3J_{\text{HF}}$  1.9,  $^3J_{\text{FF}}$  -5.4 and  $J_{\text{FF}}$  -0.6 Hz and for the gauche isomer  $^3J_{\text{HH}}$  1.6,  $^3J_{\text{HF}}$  5.3,  $^3J_{\text{FF}}$  -4.7 and  $^3J_{\text{FF}}$  -9.4 Hz. The energy difference between the isomers ( $E_{\text{g}} - E_{\text{t}}$ ) is 2.4 kcal/mole in the vapour, and 0.8 kcal/mole in the liquid.

Making the very crude assumption that the values of the gauche oriented  $^3J_{\text{HF}}$  and trans oriented  $^3J_{\text{FF}}$  couplings are similar in the two isomers, then these results can be broken down into the following:



...../

- 2 -

${}^3 J_{HH}$	$J_t^t$	4.9	;	$J_g^g$	1.6
${}^3 J_{HF}$	$J_t^g$	1.9	;	$J_g^t$	8.7
${}^3 J_{FF}$	$J_t^g$	-5.4	;	$J_g^g$	-9.2
	$J_t^t$	-0.6		$J_g^g$	-8.8

Changing the subject, I have recently heard that a very able post-doctoral fellow has been prevented from taking up an appointment with our group and I therefore have a P.D.F. position vacant.

Yours sincerely,



R.J. Abraham.

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**BROCK**  
University

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St. Catharines, Ontario

Glenridge Campus  
684-7201 Ext. 317

Jan. 23, 1970.

Dr. B.L. Shapiro,  
Dept. of Chemistry,  
Texas A & M University,  
College Station, Texas.

TRIPLE IRRADIATION WITH AN A-60

Dear Dr. Shapiro,

We have recently prepared a series of picoline adducts of the mixed boron trihalides. Complexation shifts are most apparent for the 2,6 protons, but the broad resonance which results from coupling with both boron and the 3,5 protons makes accurate measurement difficult.

We therefore have had to decouple both the boron and protons simultaneously. We did this on our A-60 by the simultaneous use of a Varian V-6058A proton decoupler and an NMR Specialties HD-60 heteronuclear decoupler. The audio modulation for the latter was provided by a GR 1310 oscillator for search purposes and a HP 4204 decade oscillator for accurate determination of the decoupling frequency. Both proton and boron decoupling frequencies were monitored with a frequency counter. We plan to use a voltage swept oscillator driven by the HP unit to pseudo-noise decouple in the boron region when we are dealing with solutions containing several adducts with different boron chemical shifts.

The two decouplers do not interfere with each other, rather the contrary, when tripple irradiating the improved S/N allows greater optimization of all parameters. For routine heteronuclear double irradiation we set the proton decoupler to Phase Lock mode for greater field stability.

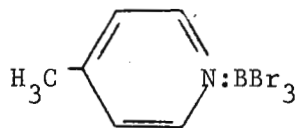
The attached figures show an example of our results for the single adduct, 4-picoline.BBr<sub>3</sub>, the 2,6 protons being shown with A; no decoupling, B; <sup>11</sup>B decoupling, and C; with both the 3,5 protons and the <sup>11</sup>B decoupled.

Yours Sincerely,

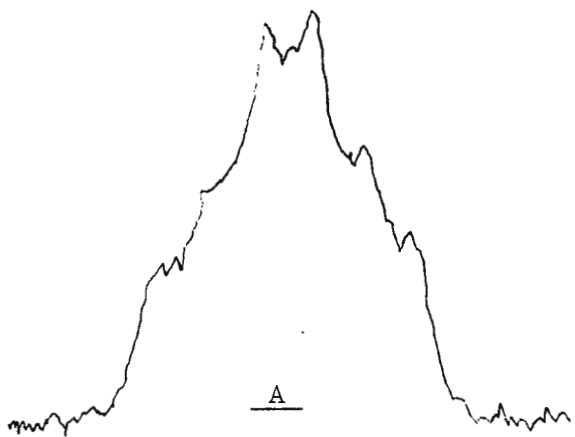
  
Jack M. Miller,

Assistant Professor.

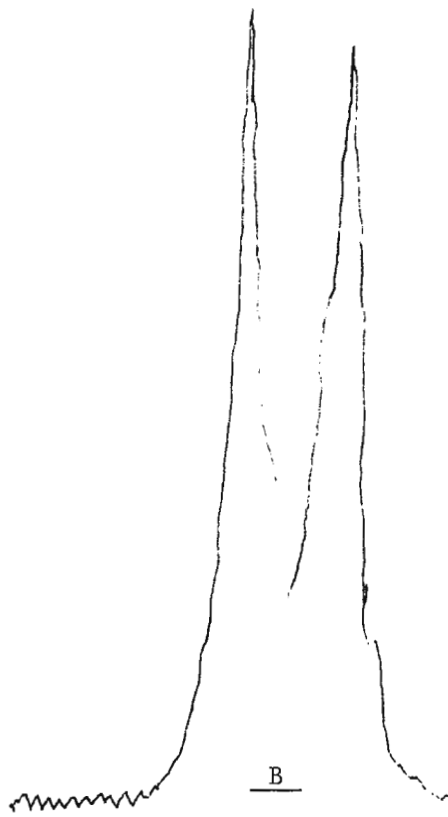
P.S. Please credit this contribution to the subscription of J.S. Hartman.



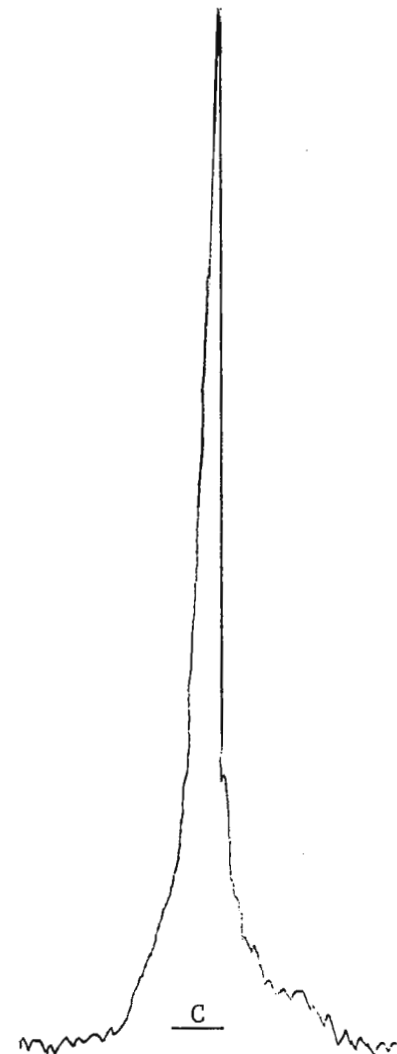
10 Hz



2,6 protons no decoupling



$^{11}\text{B}$  decoupled



$^{11}\text{B}$  and the 3,5 protons decoupled

FACULTÉ DES SCIENCES DE MARSEILLE - SAINT-JÉROME  
13 - MARSEILLE (13<sup>È</sup>)  
TÉL. : 50-31-61

DÉPARTEMENT DE CHIMIE ORGANIQUE  
LABORATOIRE DES ORGANOMÉTALLIQUES  
PROFESSEUR J. C. MAIRE

January 23 Th 1970

Professor Bernard L. SHAPIRO  
Department of Chemistry  
Texas A.M. University  
College of Sciences  
College Station, Texas 77843

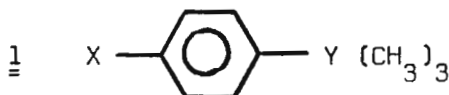
$J^{13}\text{C-H}$  IN p-SUBSTITUTED TRIMETHYLPHENYLSILANE  
AND GERMANES

---

Dear Professor Shapiro,

Thanks for your blue note. Apologies for tardy contribution. I hope that this missile will be found acceptable.

As you know, we have been working on problems involving aromatic derivatives of IVth group elements, on a pursuit of  $p\pi-d\pi$  interactions (1,2) between the phenyl ring and the empty d orbitals of the heteroatom. We have recently investigated the  $^{13}\text{C-H}$  coupling constant for the methyl protons in compounds of type 1.



The results for the two series of compounds so far studied (Y=Si,Sn) are given in table 1. Values are believed accurate to within  $\pm 0,4$  Hz.

The substituents X examined give in both cases a spread of  $^{13}\text{C-H}$  coupling constants of about 3 Hz and are roughly correlated with  $\sigma$  (3) (except for X =  $\text{NO}_2$ ).

We do believe as suggested in a recent paper (4) that, if  $J^{13}\text{C-H}$  is linearly related to the Hammett constant  $\sigma$  of the substituent X, the slope of such relations, should indicate the ability of Y to transmit the electronic effects of X. We hoped therefore that this study would prove of value in studying the interaction between Y and the aromatic ring. On the basis of the relative size of Si and Sn atoms a larger interaction was expected for Y = Si than for Y = Sn. Unfortunately the slope of J- $\sigma$  line, for the two series is almost the same so that no conclusion can be drawn about the overlap between d-orbitals and aromatic  $\pi$  system. We are investigating the germanium series.

Sincerely yours,

J.M. ANGELELLI

J.C. MAIRE

Y. VIGNOLLET

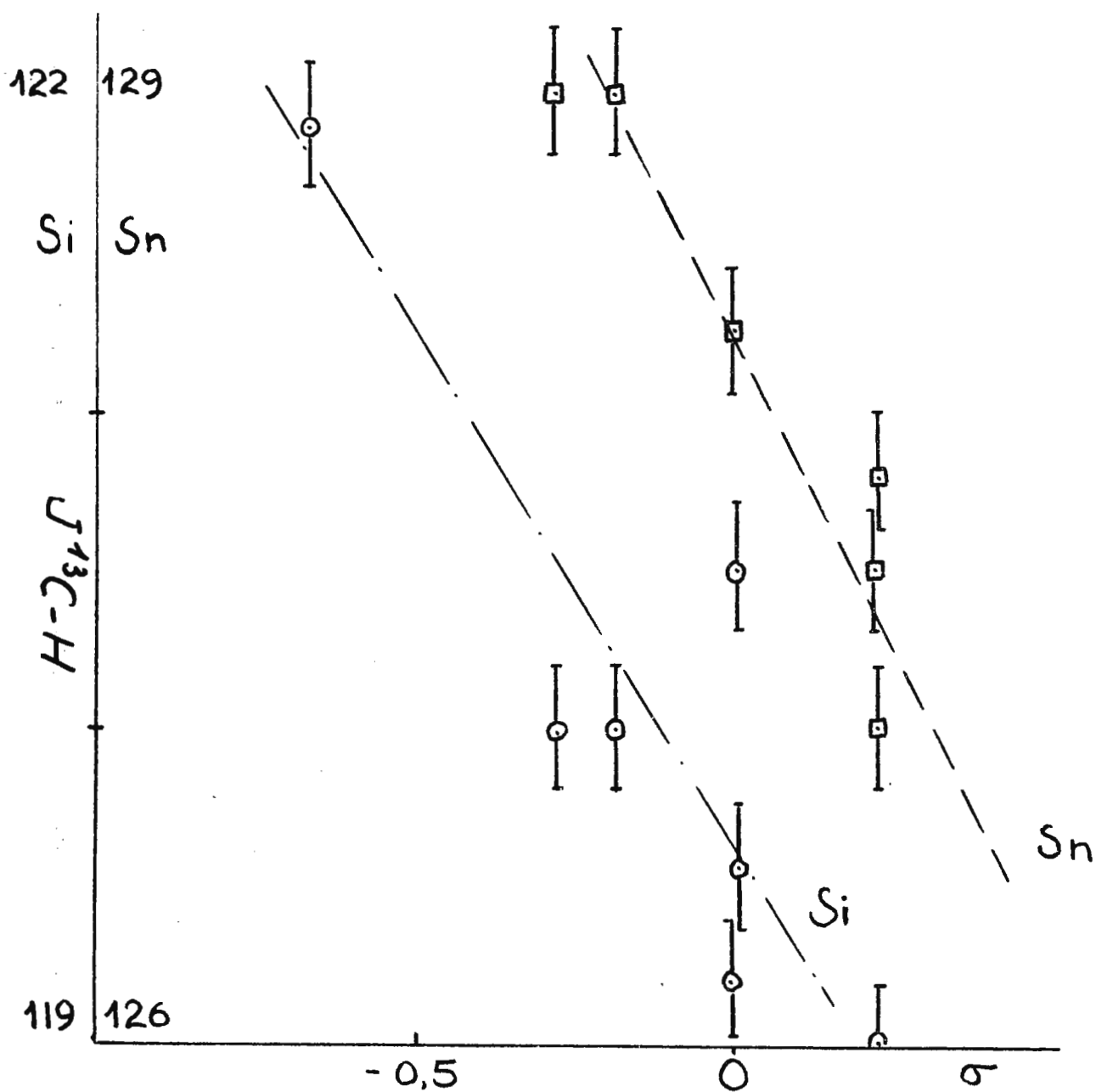
References

- (1) Y.VIGNOLLET, J.C.MAIRE, M.WITANOWSKI, Chem.Com. 1968, 1187.
- (2) Y.VIGNOLLET, J.C.MAIRE, A.D.BAKER, D.M.TURNER, J.Organometal.Chem.1969, 18, 349.
- (3) H.H.JAFFE, Chem.Rev. 1953, 53, 191.
- (4) C.H.YODER, R.H.TUCK, R.E.HESS, J.A.C.S., 1969, 91, 539.



X	$\sigma^*$	M = Si		M = Sn	
		$J^{13}\text{C-H (Hz)}$	$J^{13}\text{C-H (Hz)}$	$J^{119}\text{Sn-C-H (Hz)}$	$J^{119}\text{Sn-C-H (Hz)}$
NO <sub>2</sub>	0,778	120	-	-	-
Br <sup>2</sup>	0,232	119,1	127,8	35,7	
Cl	0,227	120,25	127,5	36,5	
F	0,062	119,5	127,5	35	
H	0	119,5	128,25	35,5	
Me	-0,17	120	129	36	
OMe	-0,268	120,1	129	35,7	
NH <sub>2</sub>	-0,660	121,9	-	-	

- Table 1 : \* ref.3



**DOW CORNING**

January 23, 1970

Professor B. L. Shapiro  
 Department of Chemistry  
 Texas A and M University  
 College Station, Texas 77843

Dear Barry:

Subject: Renewal of lapsed subscription.  
 Predicate: Interpretation of tin NMR shifts.

Regarding the NMR shift of group IV A nuclei, some workers have cited the remarkably large nonlinear shifts which have been observed in the various  $R_m MX_{4-m}$  [R=alkyl, aryl; X=halogen, oxygen; M=Si, Sn] series of compounds as reflecting (p→d)π bonding. (1) However, a lesser nonlinearity in the same direction has also been observed when M=carbon. If d orbital populations are neglected and only atom-localized terms are retained in the shielding equation, (2) one obtains

$$\sigma = -K \langle r^{-3} \rangle_p P / \Delta E$$

where P is given by the  $p$  orbital population,  $P_{ii}$ , in the principal axes system by

$$P = P_{xx}(1 - 1/2 P_{yy}) + P_{yy}(1 - 1/2 P_{zz}) + P_{zz}(1 - 1/2 P_{xx}).$$

P can be obtained for tetrahedral tin compounds of the above type from the  $^{119}\text{Sn}$  Mössbauer spectrum. (3) I have found that if one assumes that  $\Delta E$  is linearly dependent on the value of m, then deviations of  $\sigma$  from linearity in m can be accounted for by nonlinear changes in P. Although the errors involved in this procedure are substantial (mostly due to deviations from tetrahedral geometry), this analysis also enables the absolute paramagnetic shielding of  $\text{SnMe}_4$  to be evaluated to be -4400 p.p.m.

To a good approximation, the value of P is proportional to the value of the Mössbauer isomer shift and the total orbital population on tin. This is in agreement with the

Professor B. L. Shapiro  
Page 2  
January 23, 1970

large upfield NMR shifts which are observed when the process  $\text{SnX}_4 \rightarrow \text{SnX}_6^{-2}$  occurs, (1,4) and is also in agreement with the fact that NMR shifts are nearly linear in  $m$  for alkyl phenyl tin compounds. (5)

Very truly yours,

*Dwight E. Williams*

Dwight E. Williams  
Supervisor  
Molecular Spectroscopy

gb

- (1) B. K. Hunter and L. W. Reeves, *Canad. J. Chem.* 46, 1399 (1968).
- (2) M. Karplus and T. P. Das, *J. Chem. Phys.* 34, 1683 (1961).
- (3) D. E. Williams and C. W. Kocher, *J. Chem. Phys.*, in press.
- (4) A. G. Davies et al., *J. Chem. Soc.(C)*, 1136 (1969).
- (5) D. E. Williams, unpublished work.

P. S. Regarding the observations by Glasby and Gordon [NMRN 136-42], at high resolution we have observed only one SiMe NMR peak in each case which they cite. Our samples of trimethyl-acetoxysilane and -allylsilane were well characterized and quite pure.

CHEMISCHE LABORATORIA  
DER RIJKS-UNIVERSITEIT  
Afd.: Dr.H.R.Buys

Wassenaarseweg  
Postbus 75  
Leiden  
Telefoon 4 83 33  
Tst.

LEIDEN, January 27 19 70

Professor B.L.Shapiro  
Department of Chemistry  
Texas A&M University  
College Station, Texas 77843

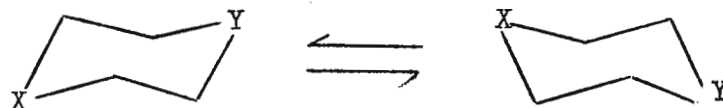
Dear Professor Shapiro,

220 Mc/s NMR spectrum and geometry of 2-phenyl-1,3-oxathiane

In 1967, the so-called "R-value method" was introduced by Lambert (1) for obtaining a qualitative picture of conformational effects in six-membered rings. For six-membered rings having two equivalent conformers (so that the conformer population ratio is 1:1, see Fig.1) and having a  $-\text{CH}_2-\text{CH}_2-$  moiety for which two vicinal proton coupling constants ( $J_{\text{trans}}$  and  $J_{\text{cis}}$ ) can be evaluated from the NMR spectrum, Lambert defined:

$$R = J_{\text{trans}}/J_{\text{cis}} = \frac{1}{2}(J_{aa} + J_{ee})/\frac{1}{2}(J_{ae} + J_{ea}) \approx \frac{1}{2}(J_{aa} + J_{ee})/J_{ae} \quad (1)$$

Fig.1



Quantitative extensions of this method have been developed as follows:

1. With the aid of the Karplus equation (2) relating vicinal coupling constants to the dihedral angle between the coupling protons, R could be related to the ring torsional angle  $\psi$  in the  $-\text{CH}_2-\text{CH}_2-$  moiety in compounds of the type defined above by (3):

$$R = J_{\text{trans}}/J_{\text{cis}} = (3 - 2\cos^2\psi)/4\cos^2\psi \quad (2)$$

The results for more than 20 compounds indicate (3) that the  $\psi$  values calculated from the experimental vicinal coupling constants with the aid of eq.(2) agree with the results from diffraction analyses within about  $2^\circ$ .

2. In heterocyclic systems as shown in Fig.2 the R-value method was applied by Anteunis et al.(4): The  $\text{C}_4-\text{C}_5$  part of the ring yields  $J_{aa}$  and  $J_{ae}$ , the  $\text{C}_5-\text{C}_6$  part yields  $J_{ea}$  and  $J_{ee}$ . Then:

$$(J_{aa} + J_{ee})/(J_{ae} + J_{ea}) = R = (3 - 2\cos^2\psi)/4\cos^2\psi \quad (3)$$

Of course, when  $\psi_{45} \neq \psi_{56}$  only an average value for  $\psi$  is obtained. The

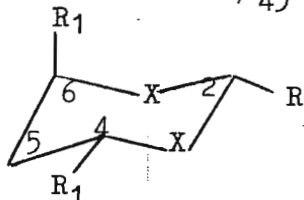


Fig.2 R = alkyl, R<sub>1</sub> = alkyl, X = O, S

system needs not be biased in one conformer as the chair-chair equilibrium constant drops out of eq.(3). However, again an average value for  $\psi$  is obtained if the dihedral angle in question has a different value in the two conformers.

3. In six-membered rings having a  $-\text{CH}_2-\text{CH}_2-$  moiety and not existing as an equilibrium mixture of two equivalent conformers (cf. 1), four vicinal coupling constants are obtained from the  $-\text{CH}_2-\text{CH}_2-$  fragment:  $J_{\text{trans}}$ ,  $J'_{\text{trans}}$ ,  $J_{\text{cis}}$  and  $J'_{\text{cis}}$ . For these systems(5):

$$(J_t + J'_t)/(J_c + J'_c) = R = (3 - 2\cos^2\psi)/4\cos^2\psi \quad (4)$$

As in the situation described in 2, the chair-chair equilibrium constant has no influence on the validity of eq.(4), but an average value for  $\psi$  is obtained if the dihedral angle differs in the two conformers.

A very good agreement of the results from eq.(4) with the dihedral angles obtained from X-ray analyses is found (5) for 2-p-chlorophenyl-1,3-dioxane, 2-phenyl-1,3-dithiane, trimethylene sulfite, trans-2,3-dichloro-1,4-dioxane and -oxathiane. In general the analysis of these types of NMR spectra is rather difficult, so rather few data for applying this variant of the R-value method are available.

We have studied the 220 Mc/s NMR spectrum of 2-phenyl-1,3-oxathiane (Fig.3). The analysis of this spectrum, taken from a 10% solution in  $\text{CCl}_4$ , was rather straightforward, as at this high field the chemical shifts between the 6 protons in the  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$  moiety were large with respect to the coupling constants.

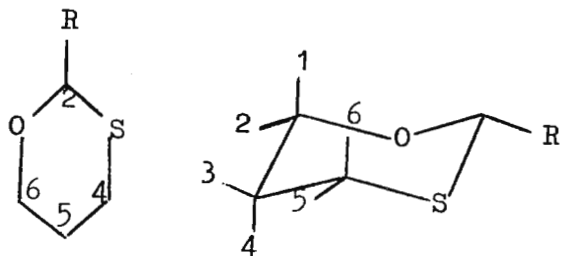


Fig.3 R = phenyl: 2-phenyl-1,3-oxathiane

The analysis was carried out with the aid of the iterative computer program LAME (6), the final results being collected in Table 1.

Table 1. NMR parameters of the  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$  moiety in 2-phenyl-1,3-oxathiane in  $\text{CCl}_4$ .

Chemical shifts (ppm from TMS)							
$\gamma_1$	$\gamma_2$	$\gamma_3$	$\gamma_4$	$\gamma_5$	$\gamma_6$		
3.57	4.16	1.59	1.95	2.64	3.02		
Geminal coupling constants (c/s)			Long-range coupling constant				
$J_{12}$	$J_{34}$	$J_{56}$	$ J_{25} $				
-11.9	-13.8	-13.1	1.9				
Vicinal coupling constants							
$J_{13}$	$J_{14}$	$J_{23}$	$J_{24}$	$J_{35}$	$J_{36}$	$J_{45}$	$J_{46}$
2.2	12.5	2.2	3.9	3.2	2.4	3.7	12.8


From the  $\text{C}_4-\text{C}_5$  moiety (S-side) it follows that  $R = 2.62 \rightarrow \psi_{45} = 61^\circ$ ; for the  $\text{C}_5-\text{C}_6$  fragment (O-side)  $R = 2.41 \rightarrow \psi_{56} = 59^\circ$ .

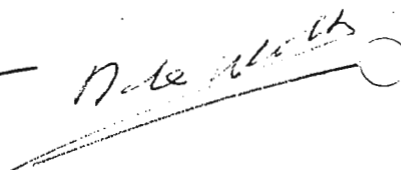
These figures are in excellent agreement with the angles obtained for the unsubstituted 1,3-oxathiane ring (7) by applying the R-value method according to eq.(2) (variant 1). It appears, therefore, that

- a. An equatorial substituent on C<sub>2</sub> does not influence the puckering in the C<sub>4</sub>-C<sub>5</sub>-C<sub>6</sub> moiety to a significant extent. In 2,2-disubstituted derivatives (dimethyl (7) and diethyl (8)) the C<sub>4</sub>-C<sub>5</sub>-C<sub>6</sub> moiety appears to be a little flattened.
- b. Like in the unsubstituted ring and its 2,2-disubstituted derivatives the S-side is more puckered than the O-side of the ring.

1. J.B.Lambert, J.Am.Chem.Soc. 89, 1836 (1967).
2. M.Karplus, J.Chem.Phys. 30, 11 (1959); J.Am.Chem.Soc. 85, 2870 (1963).
3. H.R.Buys, Rec.Trav.Chim. 88, 1003 (1969).
4. J.Gelan, G.Swaelens and M.Anteunis, Bull.Soc.Chim.Belges, in press.
5. H.R.Buys, Rec.Trav.Chim., in press.
6. A copy of this program was kindly placed at our disposal by Drs.J.A.den Hollander, who had obtained the listing of the program from Dr. C.W.Haigh (cf. this Newsletter, no.121, p.54 (1968)).
7. N.de Wolf and H.R.Buys, Tetrahedron Letters, in press.
8. N.de Wolf, A.H.D.Wepster and H.R.Buys, unpublished.

Yours sincerely,

  
H.R.Buys

  
N.de Wolf

College of Technology,  
Bolton Street,  
DUBLIN 1.

Dear Barry,

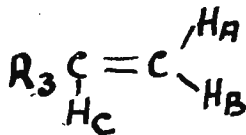
I was very happy to be invited by the ČSSR Academy to work in Prague during the Summer and am happy to report results obtained by Jan Schraml and myself as follows:

Tesla 60 Mhz with internal lock stabilisation and a Varian HA100 machines were used to obtain proton spectra which were analysed iteratively by means of programs due to Vladamir Spirko. Starting parameters, randomly generated, produced two sets of solutions for each problem - the usual methods were used to isolate the true solution. We are working on a comparison of our results with analogous Si compounds. There appears to be useful conclusions concerning  $d_{\pi} - P_{\pi}$  bonding.

Table 1 PMR Parameters in Hz with TMS internal referencing

Cpd. <sup>a</sup>	$\delta_{Me}$	$\delta_A^b$	$\delta_B^c$	$\delta_C$	$J_{AB}^d$	$J_{AC}$	$J_{BC}$
1*	60.5	293.4(-1.9)	287.5(-1.4)	347.6(-1.8)	1.37	17.33	10.68
2*	98.2	310.7(+.2)	297.7(+1.0)	361.8(-0.6)	0.69	17.08	10.57
3*	132.7	328.2(+.3)	307.7(+0.1)	371.8(+.3)	0.03	16.72	10.42
4*	-	345.2(+1.1)	316.1(+1.2)	383.1(+.4)	-0.49	16.06	10.07
1**	100.3	486.5	477.3	577.4	1.36	17.50	10.69
2**	164.6	518.1	497.6	602.6	0.79	17.20	10.62

a) Neat compound b)  $\delta$ 's  $\pm 0.5$  c) algebraically adding the numbers in brackets gives the shift at  $\infty$  dilution in  $CCl_4$  d) J's  $\pm 1\%$   
\*60 MHz \*\*100MHz 1)  $Me_3CVi$  2)  $Me_2ClCvi$  3)  $MeCl_2Cvi$  4)  $Cl_3Cvi$



Jan Schraml

Seán Cawley

Seán

Jan

title: PMR results for the vinyl group; alkenes.

Please credit SC



1

2



3

4





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