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Newsletter

No. 224

May, 1977

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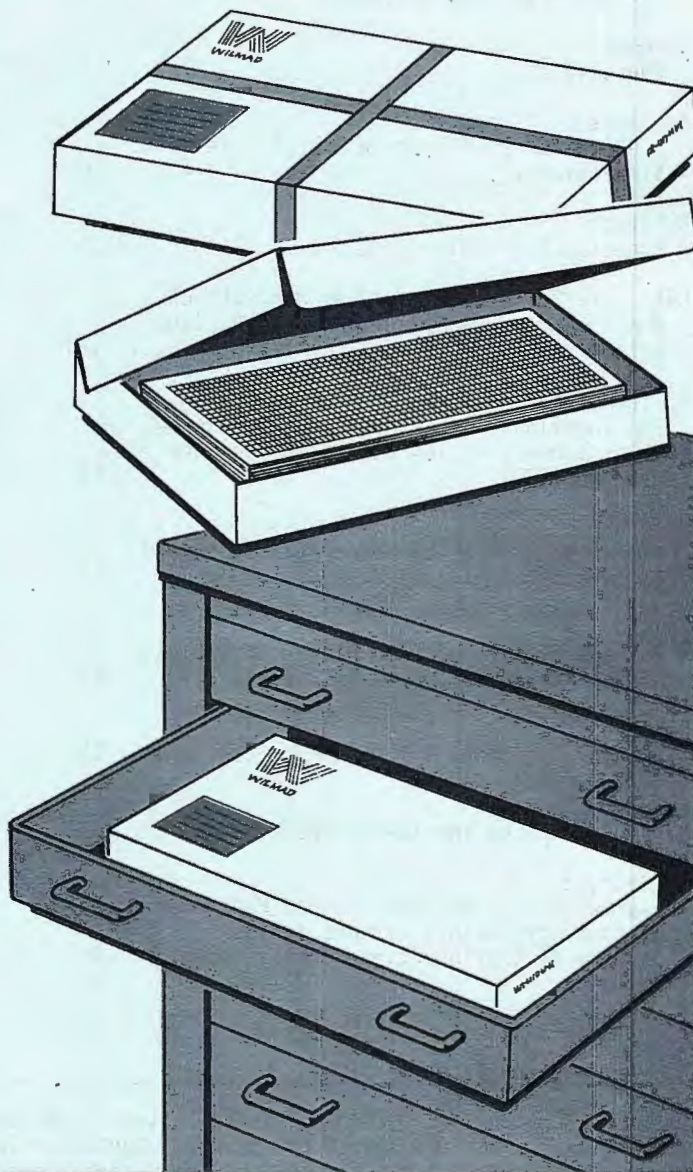
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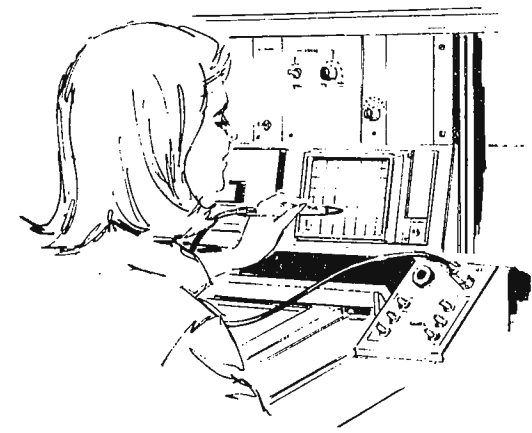
All Newsletter Correspondence, Etc. Should Be Addressed To:

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

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

Date 27 JAN 77

Dear Professor Shapiro

Proton FID's in Amorphous Silicate Hydrates

Drying down solutions of sodium silicate usually result, not in a crystalline product, but in an amorphous plastic solid containing variable amounts of water. Attempts to find out about the structure of these using I.R., X-ray diffraction or thermogravimetry have not proved very rewarding. Therefore we have examined the ^1H FID of these compounds to see if it is possible to gain some information that way. Work by Woessner [1] has indicated that in clays it is possible to distinguish "OH" and H_2O units.

At low total water contents ($\approx 10\%$), the FID shows two distinct components similar to those observed by Woessner. These can be resolved into a gaussian component and an oscillating part [Fig. 1].

At high water contents [$\approx 25\%$] the situation is less well resolved at room temperature, but on cooling to 200K [Fig. 2] the FID shows contributions from an oscillating component and can be deconvoluted. This presumably happens because at high water contents the solid is sufficiently plasticised to allow rapid exchange of water and hydroxyl protons.

The oscillating component has been assigned to water because 1) it seems unlikely that it could arise from hydroxyl units and 2) the dipolar splitting constant found for the oscillating part is very similar to that measured on $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in our spectrometer system.

The main problem with deconvoluting the data is that fitting the gaussian part relies heavily on the last 20 or 30 data points and thence on a lengthy extrapolation to find the relative intensity of the signal. Because of this and because the oscillating component needs extrapolation as well we can only obtain the ratio $\frac{\text{H}_2\text{O}}{\text{OH}}$ to about 20% accuracy.

Yours sincerely

PS Belton

P S Belton

Reference

1. D E Woessner and B S Snowden Jr. J Colloid and Interface Sci, 30, 54, 1969.

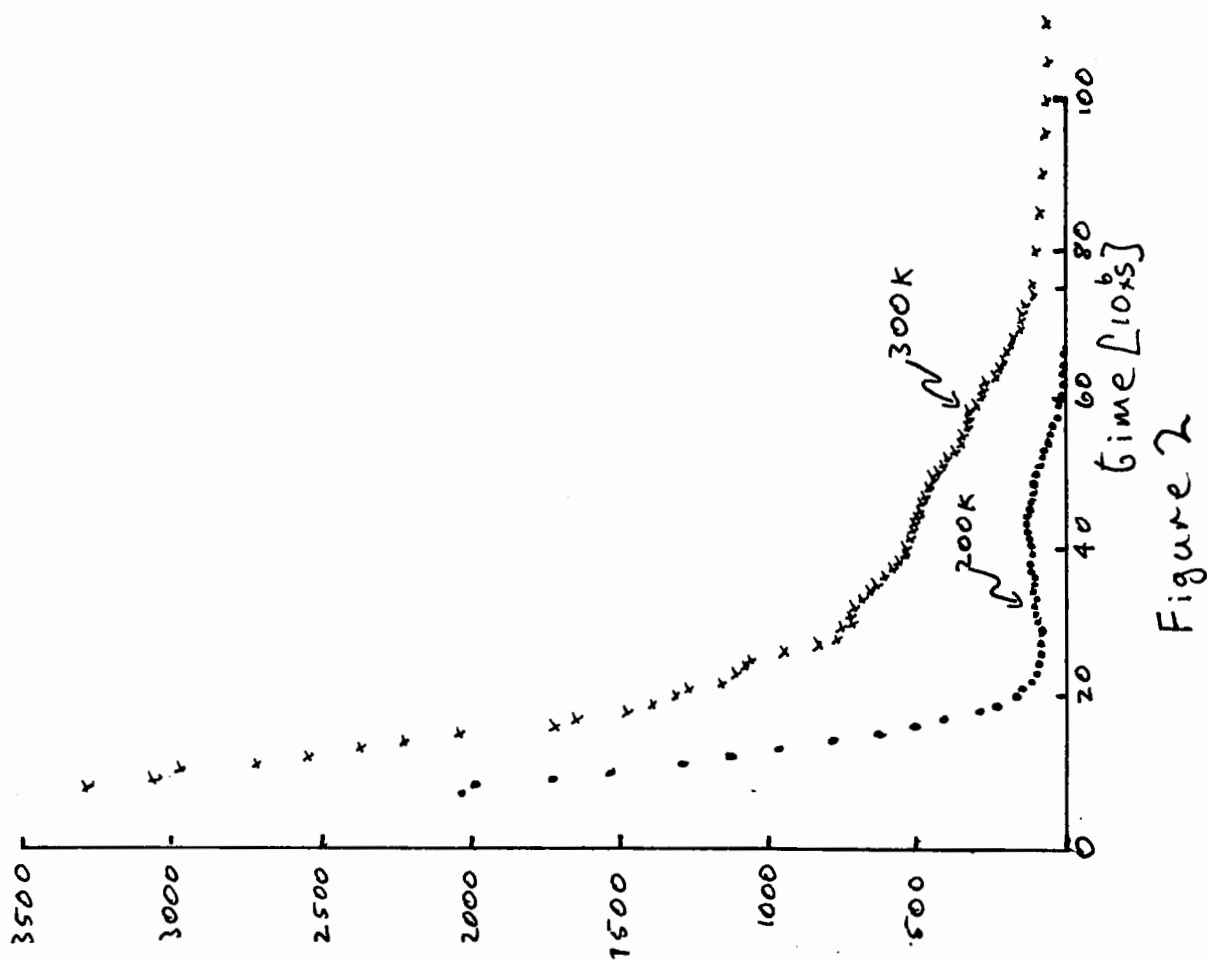
$m_{x,y}$ 

Figure 2

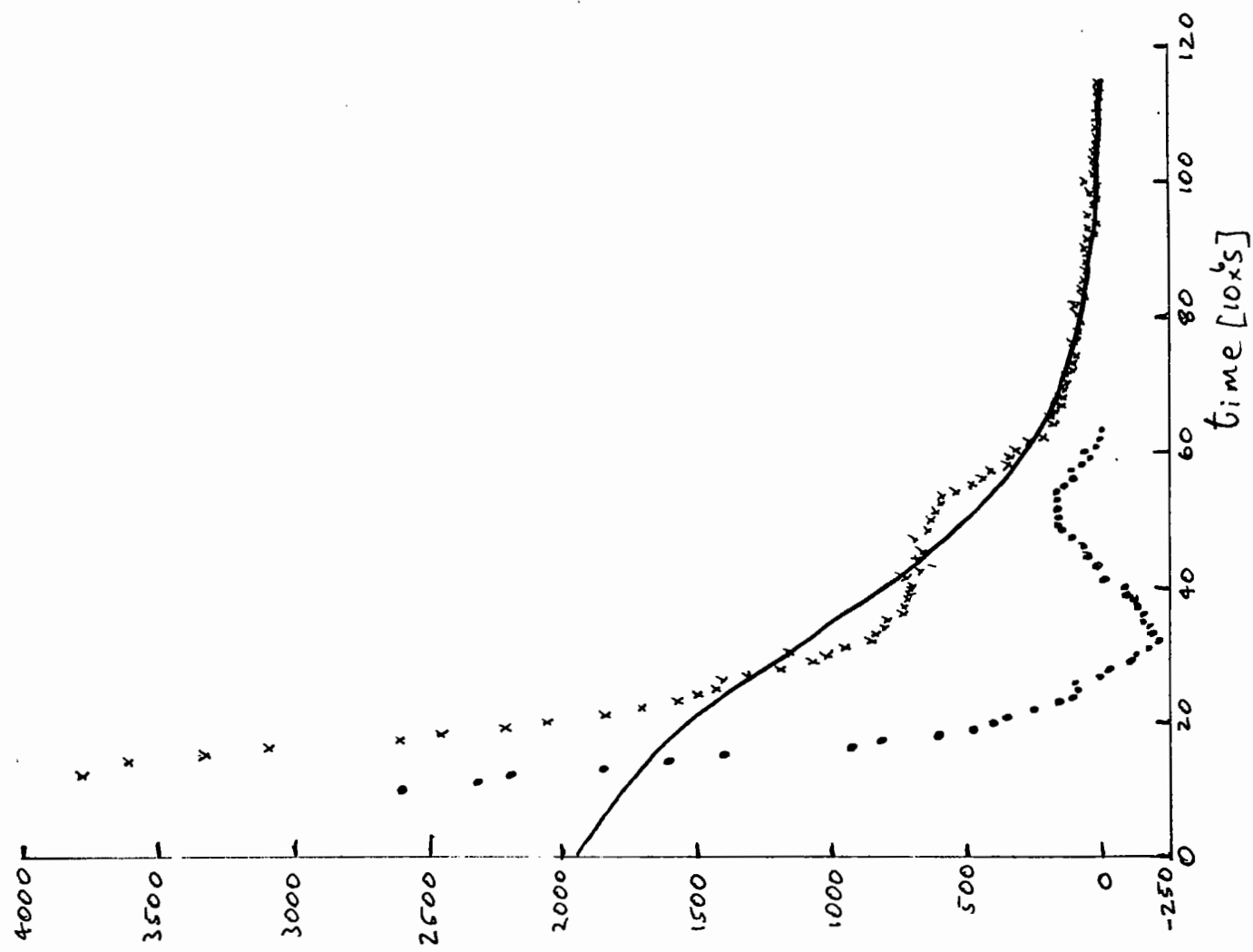
 $\eta_{x,y}$ 

Figure 1

C. N. R.

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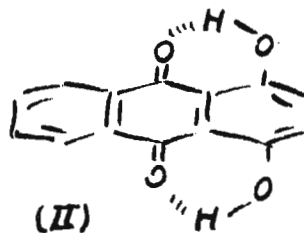
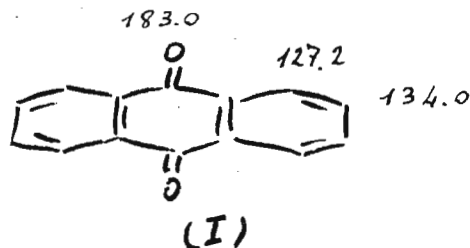
Milano, March 31st, 1977

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

¹³C-NMR ANALYSIS OF ANTHRAQUINONES AS MODELS FOR ANTHRACYCLINE
ANTIBIOTICS

Dear Barry,

we have recently completed a ¹³C study of 9,10-anthraquinone (I) and several derivatives which reproduce the substitution



patterns (oxygenated functions as OH, OMe, COMe, OCOMe) occurring in natural anthracyclines and anthracyclonones (A. Arnone, G. Fronza R. Mondelli and J. St. Pyrek, submitted to the J. Magn. Resonance).

We had intended to use these compounds as models for the ¹³C analysis of the antitumor antibiotics Daunomycin and Adriamycin. But the ¹³C signals in both antibiotics were in fact attributed independently. All the carbon atoms, including quaternary and carbonyl carbons, have been assigned uniquely by SFSD, with the aid of ¹H low power noise decoupling and "gated" decoupled spectra (A. Arnone, G. Fronza, R. Mondelli and A. Vigevani, Tetrahedron Letters 3349 (1976)).

Nevertheless we continued our investigation on anthraquinones and the conclusions of this work are the following:

- Incorrectly assigned values have been reported (St. Berger and A. Rieker in S. Patai, "The Chemistry of Quinonoid Compounds", Wiley, N.Y. 1974) for the parent compound 9,10-anthraquinone (I). The correct ones, obtained by SFSD, are given with the formula. The α and β benzenoid carbons show an opposite trend to what obser-

ved for the protons in the same positions. The upfield shift of the α carbons is most probably due to steric effects of the oxygen atoms in peri (γ) positions, whereas magnetic anisotropy and electric field factors are indeed more important for the proton shifts.

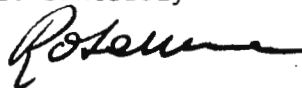
- On the basis of the new assignment of ^{13}C signal in (I), it appears that the side rings in 9,10-anthraquinone are benzenoid in nature and not dissimilar to an ortho-dicarbonyl substituted benzene, but the conjugation of the carbonyl groups with the aromatic system is enhanced in (I) with respect to 1,4-naphthoquinone and to p-benzoquinone.

- The effects of substituents such as OH, OMe, COMe on the ^{13}C shifts are roughly consistent with those of monosubstituted benzenes, with some exceptions for COMe and OH groups. The additivity rule is obeyed for some 1,5 and 1,8-di and tri-substituted derivatives. The long-range effects of the substituents, although small, are additive and noticeable especially for the OMe and COMe groups.

- When intramolecular H-bonding occurs, as in 1,4-dihydroxy-9,10-anthraquinones (II), a substantial contribution of tautomeric structures with the hydroxy proton on the oxygen atom in the chelated carbonyl 9 (or 10) can be excluded.

with best regards and wishes

yours sincerely



Rosanna Mondelli

PHYSICAL CHEMISTRY LABORATORY

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OX1 3QZ

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

Dear Barry,

"PHASE TWIST"

Recently we have been using double Fourier transformation (1,2) to generate NMR signals that are a function of two orthogonal frequency parameters (F_1 and F_2). Not surprisingly the procedures for phase adjustment are a little more complicated than for conventional Fourier spectroscopy. Even when the frequency-independent and frequency-dependent instrumental phase shifts are corrected in both dimensions, some interesting phasing problems remain.

The experiments of interest involve double Fourier transformation of carbon-13 spin echoes that are modulated by proton-carbon coupling through the application of a 180° pulse to protons in synchronism with the carbon-13 refocussing pulse (3). The resulting surface in three dimensions represents the conventional carbon-13 spectrum (coupled or decoupled) in the F_2 dimension, but a "J-spectrum" in the F_1 dimension. The latter (4,5) shows no chemical shifts but only proton-carbon splittings, and benefits from enhanced resolution. It has a true frequency zero and displays positive and negative frequencies (right and left handed precessions of multiplet components).

The interesting new feature is the shape of the three-dimensional response in a phase-sensitive display. It can be visualized as a sequence of parallel sections through the surface at regular increments of one of the frequency parameters, say F_2 . There is a progressive change in the mode of this signal as F_2 is varied through resonance. For example, the signal in the F_1 dimension might start out in the absorption mode, change smoothly to dispersion at exact F_2 resonance, and proceed to negative absorption in the tail on the far side. Alternatively it might follow the sequence: dispersion-absorption-negative dispersion. We call this effect "phase twist" and two simulated examples are shown in the Figure.

Phase twist poses some new problems for multiline spectra, since a linear phase correction cannot properly "correct" it. In some practical applications the effect can be masked by adjusting for absorption mode at exact resonance and by using coarse digitization in the F_2 dimension where resolution is not particularly critical. In certain situations it is possible to fold the spectrum about $F_1 = 0$

in such a way that two phase-twisted lines become exactly superimposed with the senses of the twist in opposition. Four possible line shapes may result: double absorption (the desirable form for high resolution), double dispersion, or an absorption profile in one dimension and dispersion in the other. This expedient cannot always be used since there are some experiments which require that positive and negative frequencies be discriminated.

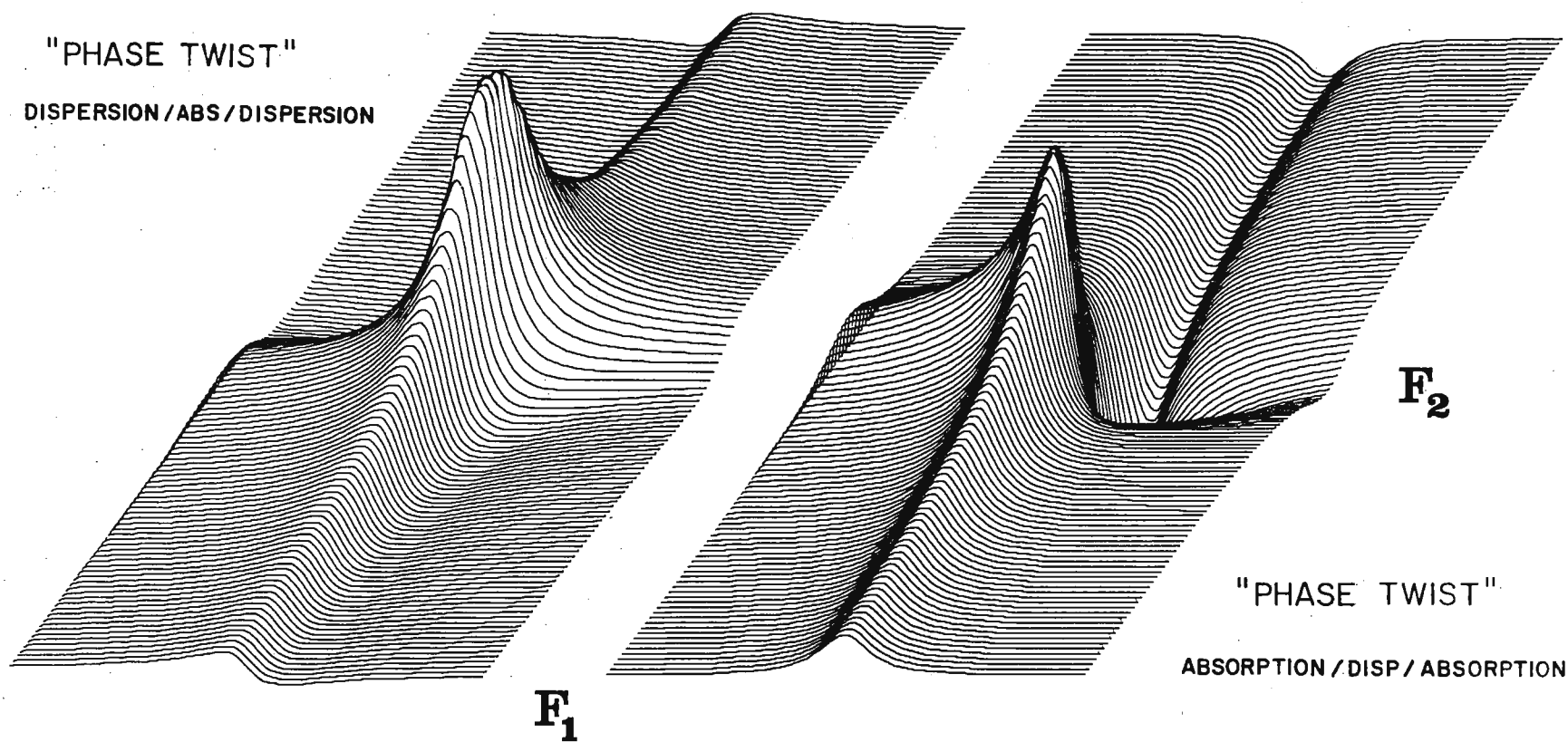
This work is part of an investigation of double Fourier transformation techniques by Geoffrey Bodenhausen, Reinhard Niedermeyer and David Turner, to be published in J. Magn. Resonance. David Turner made the simulations, and it is interesting to note that they represent analytical expressions programmed on the CFT-20 computer and drawn out on the recorder.

Kindest regards,

Ray

Ray Freeman

- (1) J. Jeener, Ampere International Summer School, Basko Polje, Poland (1971).
- (2) W. P. Aue, E. Bartholdi and R. R. Ernst, J. Chem. Phys. 64, 2229 (1976).
- (3) G. Bodenhausen, R. Freeman, R. Niedermeyer and D. L. Turner, J. Magnetic Resonance, 24, 291 (1976).
- (4) E. L. Hahn and D. E. Maxwell, Phys. Rev. 88, 1070 (1952).
- (5) R. Freeman and H. D. W. Hill, J. Chem. Phys. 54, 301 (1971).



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A ghosh for a fish or an exercise in spin simulation.

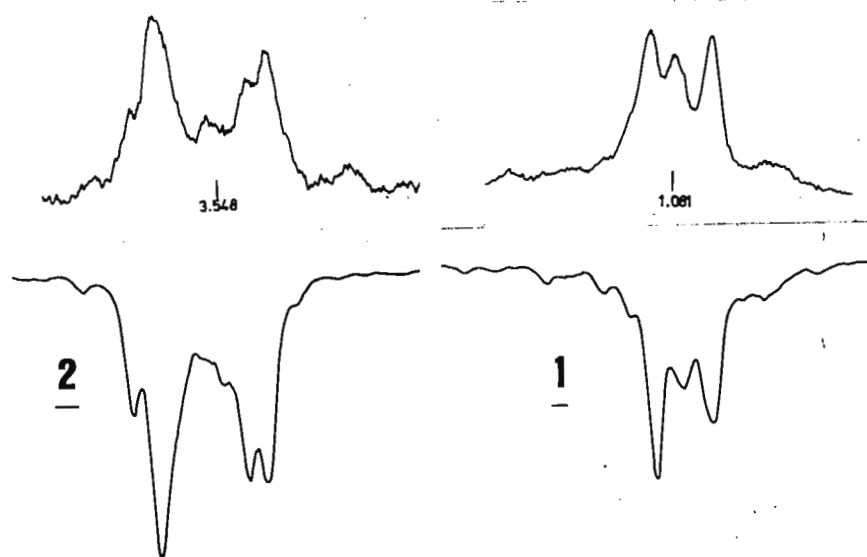
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KRIJGSLAAN 271 · S 4
(België · Europa)

Tel. 22 57 15

Dear Barry,

One may consider it an instructive amusement in calculating and/or simulating exotically-degenerated spin systems, such as the one build up by an ethyl fragment further coupled to another proton, but with one of the methylene protons being isochronous to the methyl protons. The experimental encounter of such a case offers nevertheless a somewhat puzzling situation, to be compared with the case that somebody has to spell the word ghosh as a fish (gh = f, cf. enough and o = i, cf. women). The ionophore Lysocellin- Na^+ offers¹ such a booby-trap when looking to its spectrum in $\text{C}_6\text{D}_6:\text{CD}_3\text{OD}$ (50:50) where the $\text{>C-CH(OH)CH}_2\text{.CH}_3$ fragment forms an $\text{A.MX.X}_3'$ spin system. At first glance an ethyl grouping is missing from the spectrum, showing instead a kind of doublet at δ 1.08 superimposed to another multiplet (1). The enigma is soon solved after inspecting spectra taken in other solvent systems. We have reproduced the experimental and simulated XX_3' part (see 1) constituting the methylsignal and the isochronous upfield methylene proton X and also the methine signal A, (see 2), resulting from $^3\text{J(A,M)} = 2.0$, $^3\text{J(A,X)} = 10.0$, $^3\text{J(X,X')} = 7.2$ and $^2\text{J(M,X)} = ^2\text{J(X',X')} = -12.5$ Hz.



(1) M. Anteunis; Bull. Soc. Chim. Belges, in press.

Yours truly,

Prof. M. ANTEUNIS.

Dear Barry:

224-11

I would like to advise the readers of TAMUNMR of the job opportunity described below. Interested parties may contact me for additional details, or apply directly to personnel.

Sincerely,

Tom
Thomas R. Krugh
Associate Professor of Chemistry
Telephone: 716-275-4224

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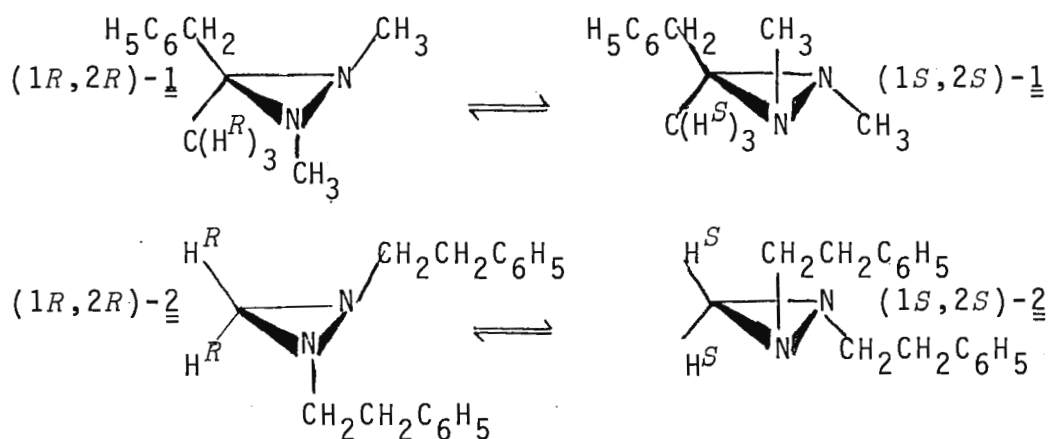
Professor B.L. Shapiro
Department of Chemistry
Texas A. and M. University
College Station, Texas, 77843

MONITORING OF RACEMIZATIONS BY NMR SIGNAL INTENSITIES?

Dear Professor Shapiro!

The ratio of enantiomers in a given mixture may be determined by nmr signal intensities in the presence of an optically active auxiliary compound¹⁾. Therefore, we thought it worthwhile to check whether this procedure might be useful to monitor racemizations. The latter job is normally done satisfactorily by polarimetry, although difficulties are encountered, e.g. if the angle of rotation is small.

As a first example we chose a chiral system, the racemization rate of which was known precisely from polarimetry. $(-)-1^{2,3}$, $[\alpha]_{436}^{22} = -85^{\circ}$, enantiomeric purity $P = 59\%$, prepared by liquid chromatography on triacetylcellulose, shows a barrier to *trans* \rightarrow *cis*²⁾ nitrogen inversion of $\Delta G^{\ddagger} = 27,57 \pm 0.02$ kcal/mol³⁾ (89.9°C, toluene).



Alternatively, from a solution of $(-)-\underline{1}$ ($P = 90\%$) in toluene- d_8 , racemizing at 89.9°C , eleven sample solutions were withdrawn at certain times, cooled to 34°C , and analyzed by ^1H CW nmr after the addition of 0.27 equivalents of $(+)$ -tris[3-(heptafluorobutyryl)- D -camphorato]europium(III). Under these conditions, $(\pm)-\underline{1}$ showed *two* C- CH_3 signals^{2,3)} at $\delta_{(+)} = 2.87$ and $\delta_{(-)} = 2.93$ (linewidths 1.5 Hz)⁴⁾, whereas the above sample solutions showed that racemization makes the intensity at 2.93 equal to the intensity at 2.87. Because of some overlap, the relative intensities were determined by cutting of diagrams and weighing the pieces. This procedure makes it difficult to determine the systematic error of the result $\Delta G^\ddagger = 27.6$ kcal/mol. Iterative computer fitting⁵⁾ of two calculated lines to the experimental signals yielded intensities similar to the ones obtained by weight, although we did not succeed in obtaining a complete fit to two Lorentzian lineshapes. Comments are welcome.

We plan to investigate the racemization of $(-)-\underline{2}$. In this case polarimetry will give a *less* precise result than above, because our sample ($P \approx 35\%$) shows $[\alpha]_{436}^{22} = -7.3^\circ(\text{EtOH})$ only. $(\pm)-\underline{2}$ in C_6D_6 at 24°C gives rise to *two* ring- CH_2 PFT nmr signals at $\delta_{(+)} = 1.91$ and $\delta_{(-)} = 1.95$ (linewidths 1.1 Hz) in the presence of 9.5 equivalents of $(+)-\text{H}_5\text{C}_6\text{CH}(\text{CF}_3)\text{OH}$. Therefore, the measurement of the racemization of $(-)-\underline{2}$ by ^1H nmr may well turn out to be more accurate than polarimetry.

Monitoring of a thermal racemization would become easier if it were carried out *in the presence* of the optically active additive⁶⁾. This was impossible for $(-)-\underline{1}$ which at 89.9°C is slowly decomposed by the europium complex. Automatic pulses after constant time intervals and storing of the corresponding ^1H free induction decays represent further experimental simplifications^{7,8)}. After Fourier transformation, the signal intensities are obtained by manual evaluation of conventional integral curves. Unfortunately, this non-automatic procedure seems to result in more precise relative intensities than do the routine computer programs for print-out of "intensities"⁹⁾. Comments are welcome concerning these remarks, too.

Moreover, we are continuing our work on non-planar anilines⁶⁾ and dienes¹⁰⁾.

Sincerely yours,

Harri Häkli

Harri Häkli

Thomas Burgemeister

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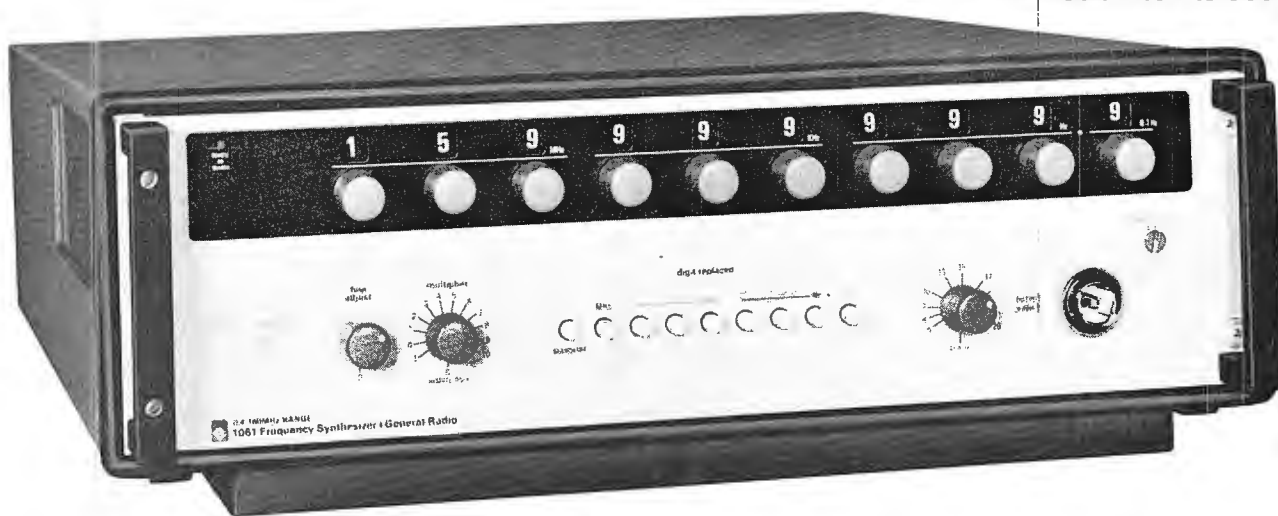
- 1) A.Mannschreck, Nachr.Chem.Techn. 23, 295 (1975).
- 2) Cf. A.Mannschreck and W.Seitz in: International Union of Pure and Applied Chemistry (ed.), XXIIIrd International Congress of Pure and Applied Chemistry, Vol.2, p.309, Butterworths, London 1971.
- 3) H.Häkli and A.Mannschreck, Angew.Chem., submitted for publication; preprints available.
- 4) These linewidths are partially due to the paramagnetic auxiliary compound. Diamagnetic additives did not generate sufficient shift differences.
- 5) A.Mannschreck and L.Ernst, Chem.Ber. 104, 228 (1971), p.246. This program was modified by R.Rauchschalbe.
- 6) Cf. F.Lefèvre, T.Burgemeister, and A.Mannschreck, Tetrahedron Lett. 1977, 1125.
- 7) D.A.Couch, O.W.Howarth, and P.Moore, J.C.S.Chem.Comm. 1975, 822, and papers cited therein.
- 8) T.Burgemeister, R.Jost, and A.Mannschreck, unpublished results obtained by semi-automatic monitoring of ¹H PFT nmr signal intensities.
- 9) Cf. B.Thiault and M.Mersseman, Org.Magn.Resonance 7, 575 (1975), p.576.
- 10) Cf. H.-O.Bödecker, V.Jonas, B.Kolb, A.Mannschreck, and G.Köbrich, Chem.Ber. 108, 3497 (1975).

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6 April 1977

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

Roche Products Limited PO Box 8 Welwyn Garden City Hertfordshire AL7 3AY Telephone Welwyn Garden 28128

Title: The Individual pKa Values for the cis and trans Isomers of Thyrotropin-Releasing-Hormone (TRH)

Dear Barry

We have been interested for some time now in the determination of pKa values by ^1H and ^{13}C n.m.r. We find the method useful in assigning values of dissociation constants in compounds with several ionisable groups where there is some dispute in assigning values to a particular ionisation. We read, with interest, the contribution of A.G. Marshall (TAMU, Dec. 1976) but so far we have found it of limited use in our experiments.

In earlier work¹⁻³, pH* (the pH meter reading in D_2O) has been taken as the effective pH, since it was assumed that an electrode correction factor of -.40 should be taken into account, thus negating the isotope effect of deuterium. This was shown by Markley¹ by measuring pKs by n.m.r. in H_2O and D_2O . Thus we take the pH meter reading as the effective pH, buffering against normal protonated pH 4.01 and 7.00 buffer solutions.

N.m.r. is one of very few methods available for determining the individual pK's of isomers equilibrating slowly on the n.m.r. time scale. We have examined the cis and trans isomers (IA and IB) of thyrotropin releasing hormone (TRH), since an earlier paper⁴ suggested that the physiological activity of analogues in promoting release of thyrotropin correlated with the pKa of the histidine residue. ^{13}C n.m.r. spectra were obtained at 13 pH values in D_2O solution. Changes in chemical shift were measured against internal dioxan reference using carbon nuclei, some of which though quite remote from the basic centre (cis Pro- δ - CH_2 and cis Pro- β - CH_2 and trans His-5-CH and trans His- β - CH_2), gave excellent ionisation curves. Previous spectra did not apparently demonstrate this curvature. The ionisation curves are shown in the figure. Non-linear and linear fits of the points using the Hill equation (II) led to values of pKa (trans) 6.09 ± 0.04 ; pKa (cis) 5.91 ± 0.06 .

Since TRH exists as 85% trans isomer in D₂O, the effective (weighted average) pK_a is 6.06 ± 0.04 . By potentiometric titration we find that the pK_a is 6.27 ± 0.05 (titration with acid and back titration with base). This gives a discrepancy of 0.2 pK units in the two methods. This anomaly is not explained by isotope effects since the equations of Marshall would predict a value by n.m.r. higher (6.4) than that measured by titration, not lower as found here. We have double-checked the results and are puzzled by the discrepancies, particularly since ¹³C measurements of other simple compounds, e.g. acetic acid, give pK_a values in agreement with standard potentiometric methods (± 0.05).

Although this discrepancy appears real for the absolute pK_a values measured by ¹³C, we believe that the relative values are significant, i.e. that the cis isomer has a consistently lower pK_a than the trans.

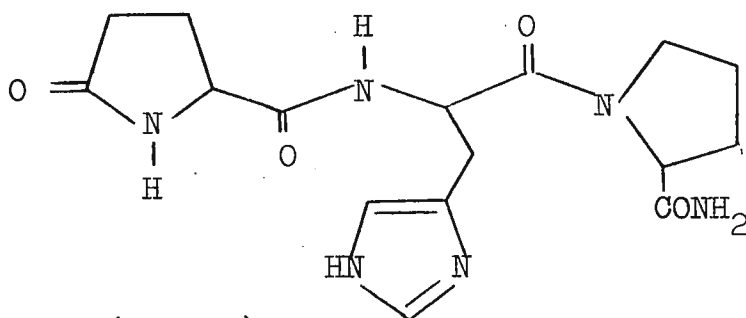
Yours sincerely

Tom

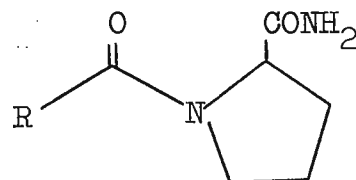
Ian Whitcombe

Dr W A Thomas and Mr I W A Whitcombe
Physical Methods Department

1. J.L. Markley, Acc.Chem.Res. 8, 70-80 (1974).
2. H.J.C. Yeh, K.L. Kirk, L.A. Cohen, J.S. Cohen, J.C.S. Perkin II, 9, 928-934 (1975).
3. J.L. Markley, Biochemistry 12(12), 2245-2250 (1973).
4. G. Grant, N. Ling, J. Rivier and W. Vale, Biochemistry 1972, 11, 3070.
5. R. Deslauriers, I.C.P. Smith, Topics in ¹³C Nmr Spectroscopy, Vol.2, Chapter 1, ed. G.C. Levy, Wiley-Interscience, 1976.

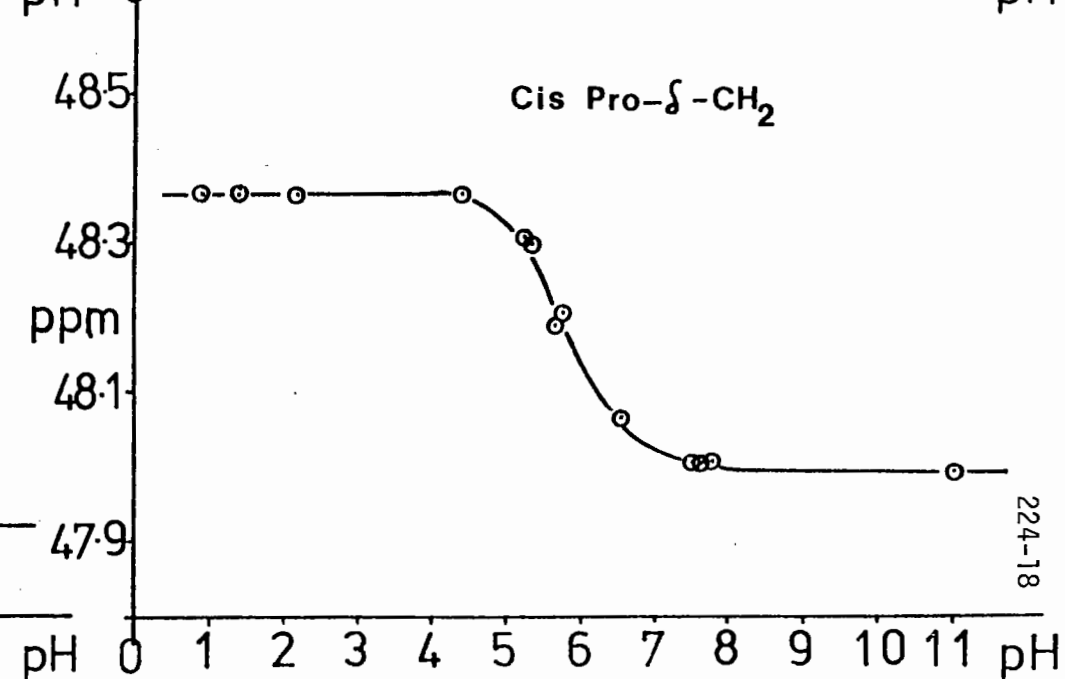
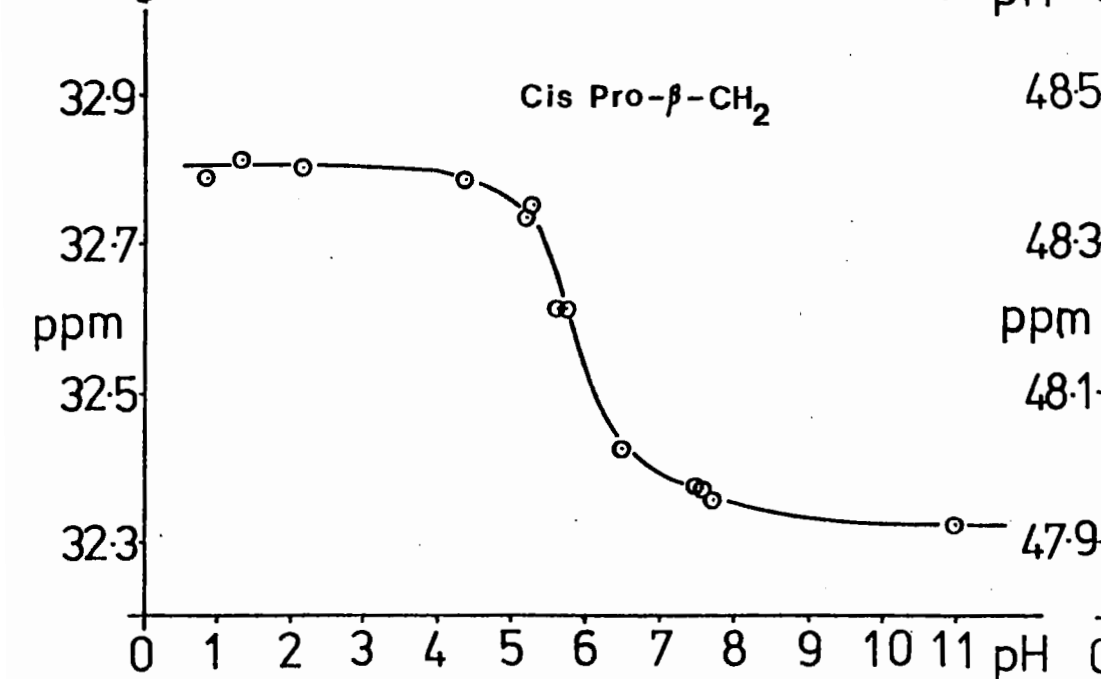
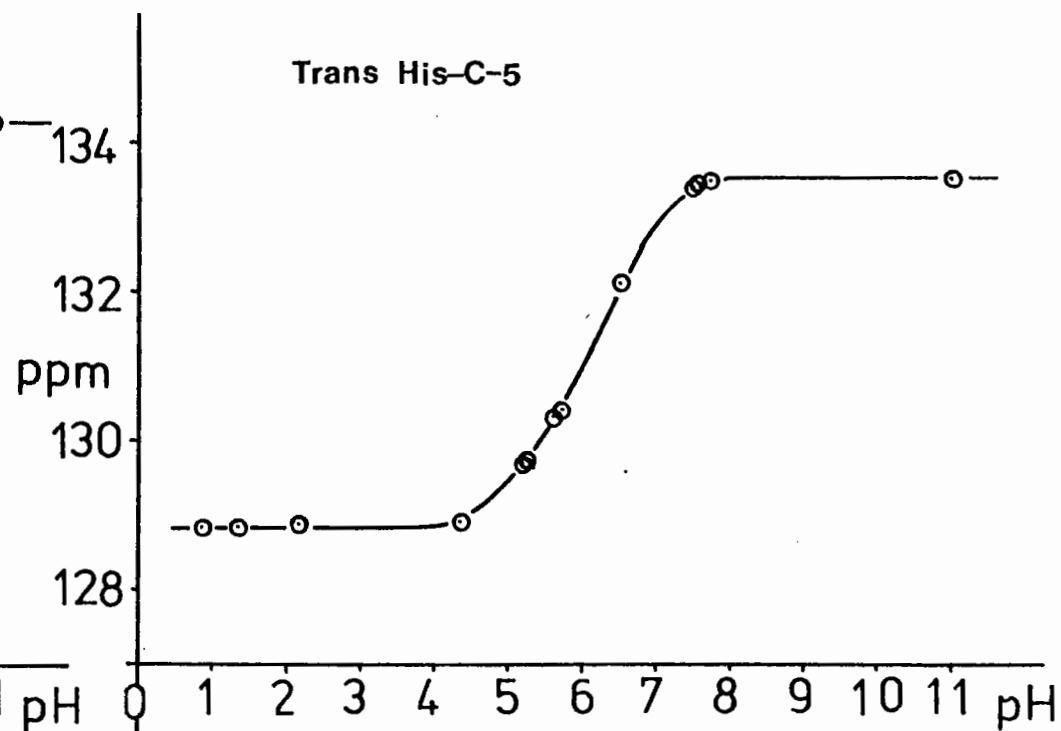
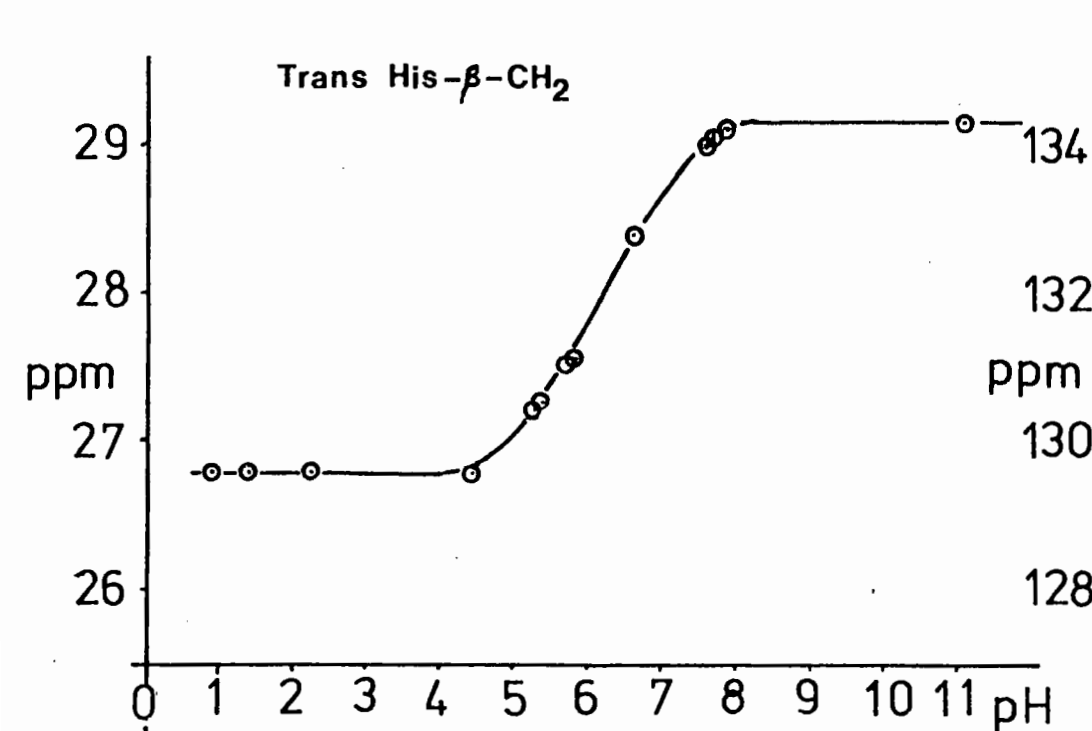


(IA cis)



(IB trans)

$$\frac{\delta H^+ - \delta_{\text{obsd}}}{\delta H^+ - \delta H^0} = \frac{K_a^n}{K_a^n + [H^+]^n} \quad (\text{II})$$





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DEPARTMENT OF CHEMISTRY

Professor V. Gold, F.R.S.
Head of Department

April 14th 1977.

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

Dear Professor Shapiro,

Alan Marshall's "Simple recipe for pH meter reading in D_2O " (December 1976, No.219) prompts the following words of caution to prospective users of the procedure.

(1) pH is not simply related to the concentration of H^+ in H_2O , nor is pD simply related to the concentration of D^+ as stated, pD in $D_2O = \log(1/[D^+])$, except in the limit of a solution of zero ionic strength. There is more to the interpretation of pH numbers read from a pH meter, even without deuterium oxide, than can be put into a brief letter. Anyone who would like to derive degrees of ionisation of solutes from pH numbers would be well advised to refer to an authoritative text, e.g. "pH Determinations, Theory & Practice" by R.G. Bates.

(2) The correlation between pK_H and $pK_D - pK_H$ is not as straightforward as was thought when the first edition of R.P. Bell's book "The Proton in Chemistry" was published (1959), a figure from which is reproduced in Alan Marshall's letter as basis for his recipe. If we turn to the second edition (1973), we find the following statement (p.234): "Early results for a number of weak acids suggested that the value of K^H/K^D decreased regularly with increasing acid strength, but when more extensive experimental data are considered there appears to be no real basis for this generalisation, except perhaps as an ill-defined qualitative trend. There is some evidence that such a relation holds approximately for a closely related series such as the phenols and alcohols or the thiols but not for the carboxylic acids, where the available pK range is rather small."

(3) To achieve the result that "a protein will have the same net charge in either solvent", brings in the further complication that some knowledge of K^H/K^D for the relevant ionisation of the protein is required, and not only that for the buffer acid.

In short, I do not believe that a short-cut to this problem exists. For dilute solutions, it requires thinking through in detail. In cases where high ionic strengths are employed, its a priori theoretical solution seems intractable at the present time.

Yours sincerely,


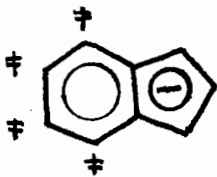
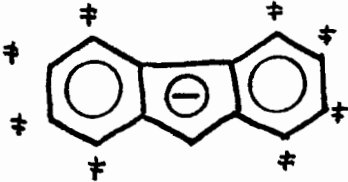
14th April 1977

Solvent Studies of Some Planar Carbanions Using ^{13}C NMR.

Dear Barry,

Only very few attempts have been made to obtain structural information from ^{13}C NMR chemical shifts of carbanions especially if we compare with the numerous and often successful carbocation studies.

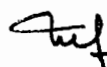
By varying solvent and temperature ^{13}C NMR studies of these species will be a powerful probe into the ion pairing mechanism especially if we have the possibility to combine these studies with NMR observations of the alkali cations. A few self-explanatory (?) results from a ^{13}C NMR investigation of some planar lithium carbanions are shown below. It should be mentioned that no significant solvent dependence of the chemical shift of the ^7Li nucleus has been observed for these ions in solvents where contact ion pairing was expected¹.

	δ		
	103.5		THF
	103.3		Diglyme
	103.7		DMSO-d ₆
	$\delta_{\text{av}}^{\#}$	$\delta_{\text{others}}^{\text{av}}$	
	118.5	110.6	Diethylether
	117.1	111.4	THF
	114.7	113.2	Diglyme
	118.2	118.0	Diethylether
	115.8	120.7	THF
	115.8	121.1	Diglyme

a. In ppm from internal TMS. The solvent dependence of the TMS signal was within ± 0.3 ppm in the ethereal solvents. Conc. 0.3M.

1. R. H. Cox and H. W. Terry Jr., J. Magn. Resonance 14, 317 (1976)

Best wishes



Ulf Edlund

UPPSALA UNIVERSITET
FYSIKALISK-KEMISKA INSTITUTIONEN
UPPSALA

Uppsala, April 4, 1977.

Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
COLLEGE STATION, Tx 77843, USA.

Dear Professor Shapiro,

As our first contribution to the TAMU NMR Newsletter we would like to submit a note concerning Fourier transform $T_{1\rho}$ -measurements. Usually $T_{1\rho}$ -values are uninteresting, since for most small molecules in nonviscous solution $T_2 = T_{1\rho} = T_1$ for all resonances, and T_1 can be measured instead. However, for nuclei subject to "fluctuating magnetic interactions" in the rate range up to 10^7s^{-1} this is no longer true (1). Examples of interactions of this kind are chemical exchange between nonequivalent sites and scalar coupling to rapidly relaxing nuclei. $T_{1\rho}$ -values can now be obtained in the FT mode on many pulse spectrometers and we have recently begun work in this area (2). Some problems and pitfalls we have found to date are:

- a) The measurements are quite time-consuming since the choice of pulse repetition rates should be based on the T_1 -values and not the $T_{1\rho}$ -values.
- b) For low values of the spin-locking field, only signals close to ω_0 will be properly spin-locked. In the rotating frame the misalignment between the nuclear magnetization after the initial 90° pulse and the spin-locking field will be $\arctan(2 \cdot PW(\pi) \cdot \nu(\text{DEV}))$ degrees, where $PW(\pi)$ is the necessary time for the spin-locking field to produce a π -pulse and $\nu(\text{DEV})$ is the deviation in Hz from the location of ω_0 in the spectrum. Typical minimum $PW(\pi)$ -values are in the 100 μs range, which restricts the accessible spectral range to a maximum of a few kHz around ω_0 . It is thus advantageous to use a spectrometer with a quadrature detection system, where ω_0 can be placed in the midpoint of signals of interest.
- c) As a rule of thumb it can be stated that unless the "fluctuating interaction" is significantly larger than 10 Hz, its contribution to $1/T_{1\rho}$ becomes vanishingly small, and $T_{1\rho}$ will be essentially equal to T_1 (1); (3).
- d) To detect small differences between $T_{1\rho}$ and T_1 , accurate evaluation procedures are needed. We have found that e.g. the on-line spectrometer computer readout from the JEOL Auto- T_1 program can not be trusted. Direct fitting

of line intensities to the respective exponential decay functions is recommended.

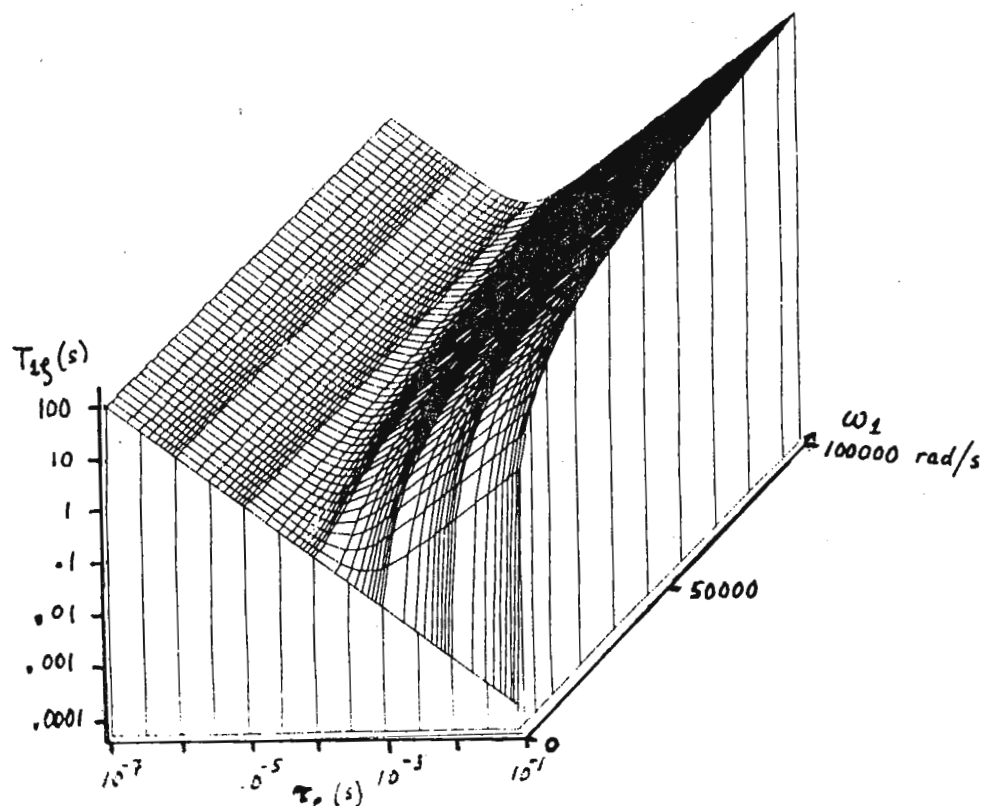
With best wishes,

Yours sincerely,

Peter Stilbs

(Peter Stilbs)

- (1) An excellent review of early $T_{1\rho}$ studies has been given by N. Boden in part 4 of "Determination of Organic Structures by Physical Methods", Eds. F.E. Nachod and J.J. Zuckerman, Academic Press, New York 1971.
- (2) We have recently submitted a communication concerning studies of chemical exchange to J. Magn. Resonance.
- (3) The following figure illustrates the theoretical exchange contribution to $T_{1\rho}$ as a function of ω_1 and τ_e for a two-site exchange with a shift difference ($\delta\nu$) of 100 Hz and equal populations. ω_1 is the resonance frequency in the rotating frame, and $1/\tau_e$ is the exchange rate. For $\delta\nu=10$ Hz, the vertical axis scale should be multiplied by a factor of 100 due to the inverse quadratic dependence of $T_{1\rho}$ (ex.) on $\delta\nu$. Note that the existing theory is valid only in the fast exchange limit, i.e. for τ_e below 10^{-3} s for $\delta\nu=100$ Hz.



FACHBEREICH CHEMIE DER PHILIPPS-UNIVERSITÄT

- Dr. Stefan Berger -

Fachbereich Chemie - Lahnberge - D-3550 Marburg 1

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Department of Chemistry
Texas A & M University
College Station

Texas 77843

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D-3550 MARBURG 1

Telefon (0 64 21) 28 5520

Telex: 4 82 372

den 4. April 1977

FAN Spectra on the XL-100 Spectrometer

Dear Dr. Shapiro,

Bock and Pedersen very recently published an elegant gated decoupling technique with noise decoupling during the pulse delay and single frequency decoupling during the acquisition time ¹⁾. They used a Bruker instrument and an additional frequency synthesizer as the required low power frequency source. Having no spare frequency synthesizer we found a very easy to employ and cheap method to carry out this experiment on a Varian XL-100 spectrometer.

The decoupler on / off gating line from the Computer station J-1 EE to the noise oscillator card (87-126-857, pin 13) ist interrupted by a switch S-1. The +21 Volt lead to the LOW/HIGH switch S-705 in the decoupler controller (87-126-859) is removed and connected to another switch S-2 which for the purpose of this experiment leads the 21 volts to a Reed relay as shown in our schematic. This relay lies in the collector line of a transistor switch the basis of which ist connected via S-1 to the computer station. Since wie use external square wave noise as proposed by Grutzner ²⁾ we have build an identical device to gate the output of our square wave generator.

To do an FAN experiment (single Frequency And Noise decoupling as we call it) one simply centers the decoupler frequency on the required proton position according to the method communicated by Ernst ³⁾ and sets the low dB output as needed. The computer will then switch the decoupler between the high power noise modulated and low power single frequency mode. So far our decoupler has stood all the relay switching involved.

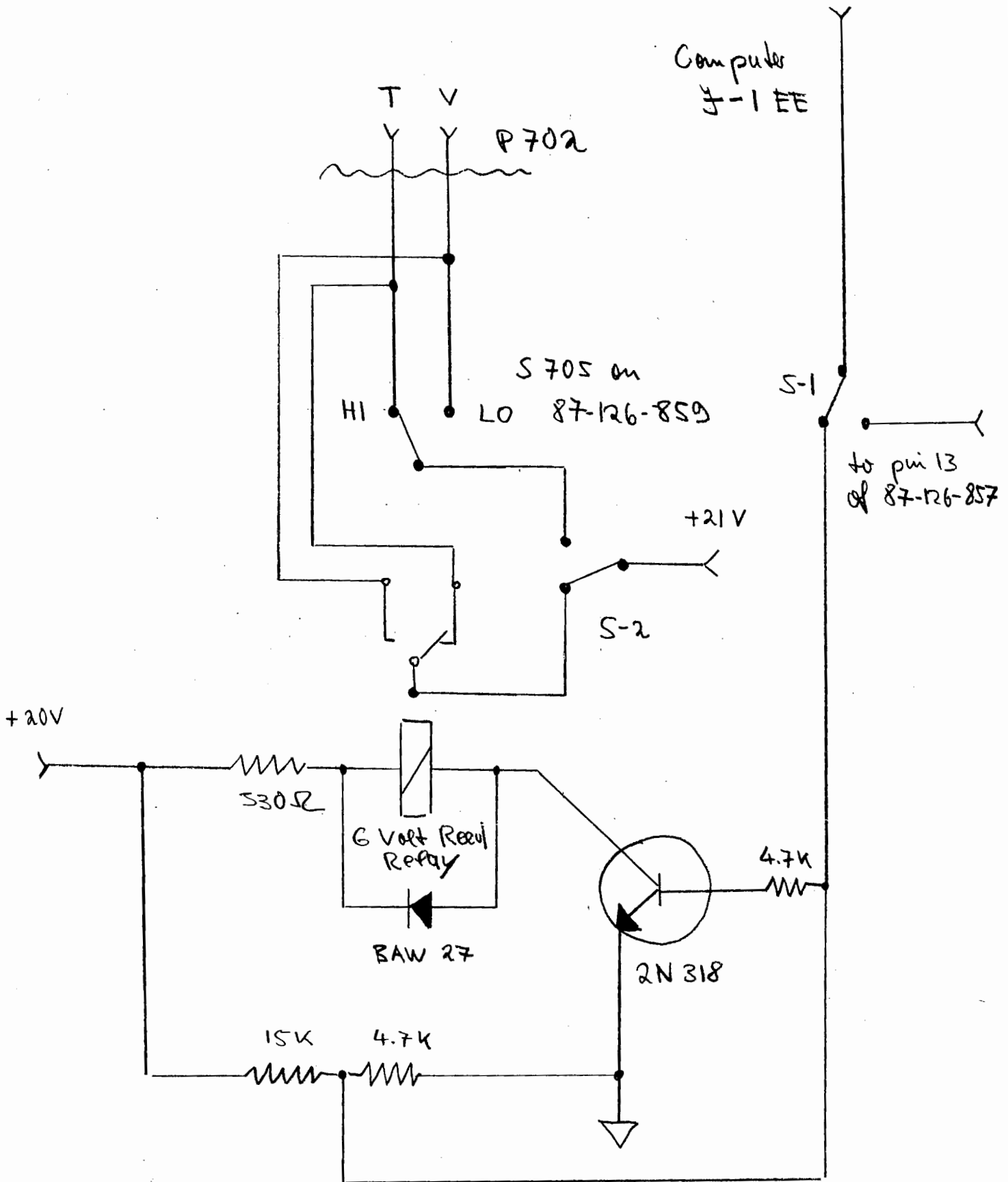
Sincerely yours

(Stefan Berger)

1) K. Bock and C. Pedersen, J. Magn. Res. 25 227 (1977)

2) J.B. Grutzner and R.E. Santini, J. Magn. Res. 19 173 (1975)

3) J. Ernst, J. Magn. Res. 100 10 (1975)



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DEPARTMENT OF CHEMISTRY

April 18, 1977

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

Title: Asymmetry Induced Magnetic Non-equivalence of Isopropyl Methyl Carbons in the Carbon-13 Spectra of Configurational Diastereomers.

Dear Dr. Shapiro;

This letter is to initiate my subscription to TAUM NMR Newsletter and/or relieve the effect of pink notes on the account of R.R. Fraser, also of this university.

Our interest in magnetic non-equivalence in carbon-13 nmr studies is the result of some observations made a few years ago, when I was associated with the University of Toronto, of acyclic and cyclic diastereoisomers containing at least one isopropyl substituent on an asymmetric carbon adjacent to a second asymmetric carbon.

The effect of interest can be clearly demonstrated for a series of E and Z epoxides (see Table 1). It can be seen that the differences in the methyl carbon chemical shifts $\delta_\alpha - \delta_\beta$ is generally larger for the Z isomer relative to the corresponding E isomer. A preliminary analysis suggests a conformational origin to the effect with variations in the absolute magnitude $|\delta_\alpha - \delta_\beta|$ of for example the Z series arising through proximity effects rather than variations in the conformer populations.

Much larger differences have been observed for threo and erythro diastereoisomers of the type $\text{RCH}_2\text{CHXCH}(\text{CH}_3)_2$. The degree of non-equivalence $\delta_\alpha - \delta_\beta$ (see Table 2) is found to be significantly larger for the erythro isomer relative to the corresponding threo isomer. Further as R is varied from methyl to isopropyl the difference is seen to increase monotonically for the erythro isomers for any constant X and Y. The threo isomers show a more erratic behaviour. Thus only the vicinal dichlorides show a constant decrease in $\delta_\alpha - \delta_\beta$ as R is varied from methyl to isopropyl. The presence of the bulkier trimethylsilyl groups lead to somewhat larger differences for the threo isomers than normally observed but still show large $\delta_\alpha - \delta_\beta$ for the erythro isomer.

An analysis of the factors giving rise to the above suggests a conformational origin; the large difference $\delta_\alpha - \delta_\beta$ in the erythro cases arising primarily as a result of $\delta_{\alpha\beta}$ interactions. We hope to solidify these hypotheses through studies utilizing wider variations in substituents. It is apparent, however, that irrespective of the origin, the large difference observed with respect to the degree of non-equivalence amongst threo and erythro isomers lends itself to making assignments of relative configuration.

Sincerely yours,



Dennis G. Garratt
Assistant Professor

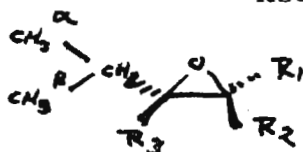
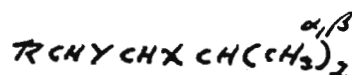


Table 1

Configuration	Compound			Chemical Shifts (δ , ppm)		
	R_1	R_2	R_3	δ_α	δ_β	$\delta_\alpha - \delta_\beta$
Z	Me	H	H	20.28	18.55	1.73
E	H	Me	H	19.03	18.45	0.58
Z	Et	H	H	21.22	18.77	2.45
E	H	Et	H	19.14	18.46	0.68
Z	iPr	H	H	20.41	19.12	1.29
E	H	iPr	H	19.20	18.47	0.73
	H	H	Me	18.05	17.09	0.96
Z	Me	H	Me	18.82	17.60	1.22
E	H	Me	Me	18.51	17.68	0.83

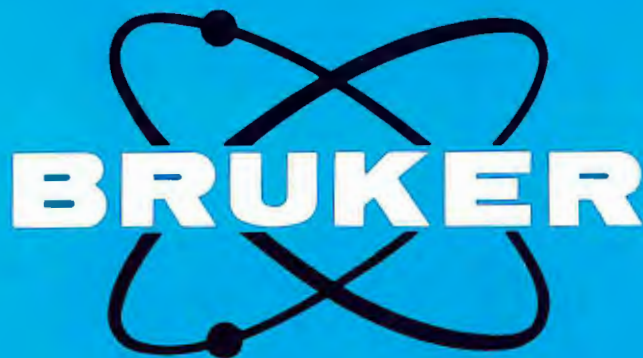
Table 2



Compound			Configuration	Chemical Shifts (δ , ppm)		
R	Y	X		δ_α	δ_β	$\delta_\alpha - \delta_\beta$
Me	Br	Br	threo	21.24	20.66	0.58
			erythro	22.39	15.87	6.52
Et	Br	Br	threo	21.73	20.36	1.37
			erythro	22.43	15.71	6.72
iPr	Br	Br	dl	21.43	20.45	0.98
			meso	22.70	15.37	7.33
Me S1	Br	Br	threo	21.68	20.02	1.66
			erythro	22.27	15.41	6.86
Ph S1	Br	Br	threo	21.70	19.73	1.97
			erythro	22.62	16.41	6.21
Me	Cl	Cl	threo	20.06	19.53	0.53
			erythro	20.94	15.11	5.83
Et	Cl	Cl	threo	20.24	19.97	0.27
			erythro	21.05	14.73	6.32

Table 2: continued

Compound			Configuration	Chemical Shifts (δ , ppm)		
R	Y	X		δ_α	δ_β	$\delta_\alpha - \delta_\beta$
iPr	Cl	Cl	dl	19.97	19.82	0.15
			meso	21.20	13.98	7.22
Me	PhS	Cl	threo	21.58	20.79	0.79
			erythro	20.69	17.66	3.03
Et	PhS	Cl	threo	20.96	20.07	0.89
			erythro	21.04	16.75	4.29
iPr	PhS	Cl	threo	21.12	20.93	0.19
			erythro	22.07	16.02	6.05
Me	PhSe	Cl	threo	21.62	20.79	0.83
			erythro	20.88	17.32	3.56
Et	PhSe	Cl	threo	20.56	20.50	0.06
			erythro	21.25	16.30	4.95
iPr	PhSe	Cl	threo	21.09	19.92	1.17
			erythro	21.84	14.74	7.10
Me	Cl	PhS	threo	21.58	20.42	1.16
			erythro	21.67	16.98	4.69
Et	Cl	PhS	threo	21.38	20.96	0.42
			erythro	21.74	17.03	4.71
iPr	Cl	PhS	threo	20.22	19.19	1.03
			erythro	21.77	15.05	6.72
Me	Cl	PhSe	threo	21.97	21.78	0.19
			erythro	22.55	17.73	4.82
Et	Cl	PhSe	threo	22.02	21.70	0.32
			erythro	22.60	17.73	4.87
iPr	Cl	PhSe	threo	21.84	20.66	1.18
			erythro	22.78	17.03	5.75



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Southern Illinois
University at Carbondale
Carbondale, Illinois 62901

Department of Physics and Astronomy

April 20, 1977

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

Dear Prof. Shapiro:

I would appreciate your including this letter in the next issue of the NEWSLETTER.

We are seeking an individual to head our Fine Instruments Research Shop. Responsibilities of the position include the design, fabrication, and development of instrumentation in support of faculty research on a campus-wide basis. While the position is not strictly dedicated to NMR research, NMR-related work will certainly constitute a significant portion of the responsibilities. Applicants should have a B.S. degree in electrical engineering or related field, and, as well, an M.S. degree or equivalent experience. Salary will be in the range \$17,000 - \$21,000 or commensurate with experience.

Individuals interested in the position may contact me by phone (618-453-3735) for further information or apply directly to Ms. Millie Powell, Personnel Section, Office of Research and Projects, SIU-C, Carbondale, IL 62901.

Thank you for your assistance.

Sincerely,

A handwritten signature in cursive script that reads "John D. Cutnell".

John D. Cutnell
Associate Professor of Physics

JDC:ks

GBF Mascheroder Weg 1 D-3300 Braunschweig-Stöckheim

Prof. Dr. Bernhard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, TX 77843
USA

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Abteilung

Physikalische Meßtechnik

Ihre Nachricht vom

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Datum
18 April 1977

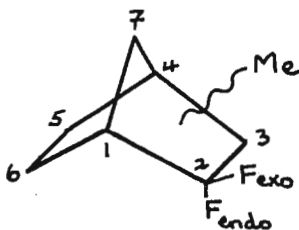
Karplus-type relationship for $^3J_{FC}$

Dear Professor Shapiro,

Recently we have been interested in the orientational dependence of, and the effects of substituents upon, $^nJ_{FC}^1$. The deoxyfluoropyranoses proved an interesting system in which long-range J_{FC} values could be determined. In particular INDO MO calculations on model compounds showed that J_{FC} have a Karplus-type orientational dependence, the maxima and minima of which were influenced by substituents attached to the carbons on the coupling pathway.

Further evidence for the angular dependence of $^3J_{FC}$ is shown in the figure where all the known literature data for this J in saturated systems are given. Dihedral angles were deduced from Dreiding models, while the curve was calculated for 1-fluoropropane by INDO MO theory, with Whiffen's atom values of the nuclear valence shell s electron densities for carbon and fluorine. Thus the general validity of a Karplus-type relationship for J_{FC} is established although deviations from the theoretical curve are expected due to the influence of substituents.

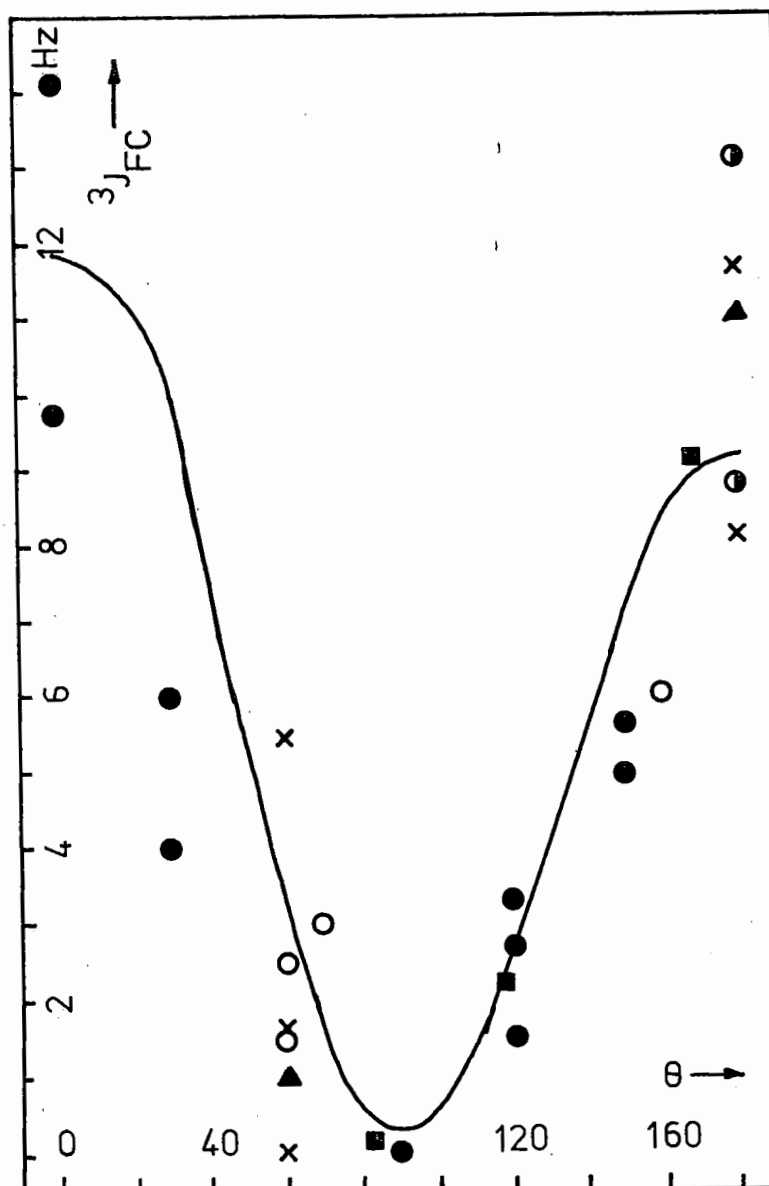
This relationship allows a rationalisation of the data observed for the methyl-2,2-difluoronorbornanes. Thus only one J_{FC} per compound is



reported for C7; there will only be a coupling to F_{endo} as the dihedral angles are $\sim 90^\circ$ to F_{exo} and $\sim 210^\circ$ to F_{endo} . Similarly only one coupling is observed to the 1-methyl compound as the dihedral angles are $\sim 330^\circ$ to F_{exo} and $\sim 90^\circ$ to F_{endo} . The larger of the two couplings to the 3-methyl compounds arise from coupling to F_{exo} in the 3-exo-methyl and with the F_{endo} in the 3-endo methyl compound.

Yours sincerely,

Victor Wray



Correlation of $^3J_{FC}$ and the θ dihedral angle in methyl-2,2-difluoronorbornanes³ (●), exo-2-fluoronorbornane⁴ (■), fluorocarbohydrates¹ (x), fluorocyclohexane⁶ (▲), 9-fluorocortisol⁵ (○) and 1-fluorobicyclo 3.3.1 nonane⁶ (⊙).

References

1. V. Wray, J.C.S. Perkin II 1598 (1976)
2. D.H. Whiffen, J.Chim.Phys. 41, 1589 (1964)
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6. H.J. Schneider and W. Ansorge, Tetrahedron 33, 265 (1977).



Medical Research Council

National Institute for Medical Research
The Ridgeway, Mill Hill
London NW7 1AA

telegrams Natinmed London NW7
telex 922666 (Natinmed London)
telephone 01-959 3666

reference

18th April, 1977.

Dear Barry,

Your readers will be interested in the details about the following meeting to be held in York, England 2-7th July 1978.

The Chemical Society - NMR Discussion Group
Fourth International NMR Meeting, York 1978

The meeting will deal with selected topics in high resolution NMR spectroscopy and will comprise seven consecutive symposia.

Symposium 1. NMR Conformational Studies

Chairman: Dr. H. Booth

Invited speakers: Professor F.A.L. Anet
Dr. I.O. Sutherland

Symposium 2. NMR Studies of Large Molecules

Chairman: Dr. R.K. Harris

Invited speaker: Dr. I.C.P. Smith

Symposium 3. NMR Studies of Biological Systems

Chairman: Dr. J. Feeney

Invited speakers: Professor A. Allerhand
Professor R.J.P. Williams

Symposium 4. Studies of Dynamic Processes

Chairman: Professor E.W. Randall

Invited speakers: Professor G. Binsch
Dr. R.E. Carter

Symposium 5. Relaxation Studies

Chairman: Dr. I.D. Campbell

Invited speakers: Professor D.M. Grant
Professor J.D. Hall

Symposium 6. New experimental Techniques and Applications

Chairmen: Dr. J.W. Emsley; Dr. K.J. Packer

Invited speakers: Professor R. Ernst
Dr. R. Freeman
Professor J.S. Waugh
Professor E.R. Andrews

Symposium 7. Review Lectures

Chairman: Dr. D. Shaw

Invited speakers: Dr. J.W. Emsley
Dr. K.A. McLauchlan
Dr. J.N. Shoolery

Contributed Papers

In addition to the Invited lectures there will be a number of short contributed papers included in the programme and in poster sessions. Anyone wishing to contribute a paper should submit (not later than Feb. 1st 1978) a title and synopsis (ca 250 words) to Dr. J. Feeney, National Institute for Medical Research, The Ridgeway, Mill Hill, London NW7 1AA, England, indicating the appropriate symposium.

Further details from Dr. J.F. Gibson,
The Chemical Society,
Burlington House,
London W1V 0BN

Yours sincerely,



J. Feeney,
Chairman, NMR Discussion Group.



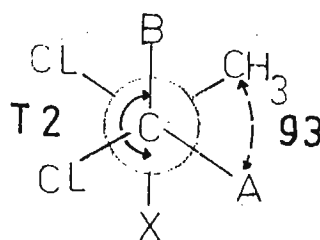
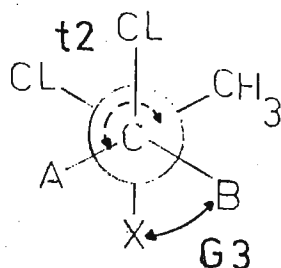
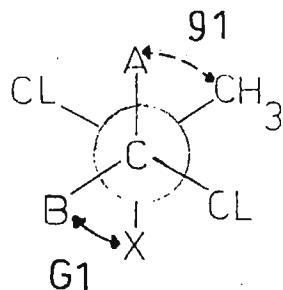
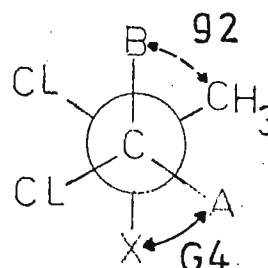
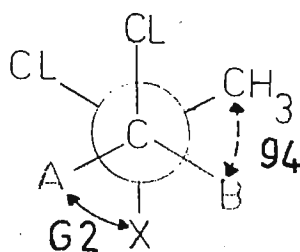
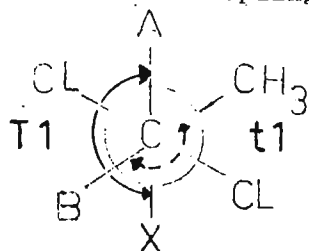
April 22, 1977

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

A pitfall in the conformational analysis of 1,2-dichloropropane

Dear Professor Shapiro,

I hope that this letter will avert the dreadful future spelled out in your last pink note. We are interested in the use of vicinal proton-proton and carbon-proton coupling constants for conformational analysis and therefore we study the magnitude of coupling constants as a function of substituent effects and the dihedral angle. In the past year we completed an extensive study on halogenated ethanes and propanes in order to establish some of these effects. In this study we performed also some solvent studies. From these studies we got the idea that it should be possible to perform a populational analysis of a compound, such as 1,2-dichloropropane, by varying the solvent. We measure four different vicinal coupling constants, two $J(\text{H-H})$ and two $J(\text{C-H})$ for each solvent studied. We have for each solvent two unknown populations and twelve contributing gauche and trans coupling constants.



I

II

III

Vicinal proton-proton and carbon-proton coupling constants (in Hz) in 1,2-dichloropropane

Solvent ^a	(CD ₃) ₂ CO	CD ₃ OD	C ₆ D ₆	CCl ₄	C ₆ D ₁₂	CCl ₄ ^b
AX	6.45	6.98	7.45	8.45	8.60	8.95
BC	3.62	3.91	4.22	4.76	4.78	5.07
BX	5.55	5.32	5.20	4.77	4.75	4.65
AC	2.36	2.22	2.13	1.97	1.95	1.91

We assume that the gauche and trans coupling constants are solvent independent, because in isopropyl halides the vicinal, the geminal and the one bond coupling constants are practically solvent independent. When we now measure the coupling constants in at least six solvents (see table) it should be possible to obtain all populations (12) and all contributing coupling constants (12) from the 24 equations for the coupling constants. The vicinal coupling constants are given by

$$J = p_I \cdot J(p_I) + p_{II} \cdot J(p_{II}) + p_{III} \cdot J(p_{III})$$

where p_j is the fractional population of rotamer j and $\sum p_j = 1$ and $J(p_j)$ is the coupling constant in rotamer j contributing to J . After some rearranging we get for each solvent i for the proton-proton (AX^i and BX^i) and the carbon-proton (AC^i and BC^i) coupling constants:

$$AX^i = G2 + p_I^i (T1 - G2) + p_{III}^i (G4 - G2) \quad (1)$$

$$BC^i = g4 + p_I^i (t1 - g4) + p_{III}^i (g2 - g4) \quad (2)$$

$$BX^i = T2 + p_I^i (G1 - T2) + p_{II}^i (G3 - T2) \quad (3)$$

$$AC^i = g3 + p_I^i (g1 - g3) + p_{II}^i (t2 - g3) \quad (4)$$

An unique solution can only be found when all these equations are independent. However, experimentally the following relation is found between AX^i and BC^i :

$$AX^i = 1.768 BC^i - 0.04 \quad (\text{the correlation coefficient is } .998)$$

$$\text{Thus: } p_I^i \{(T1-G2)-1.768(t1-g4)\} = p_{III}^i \{(G2-G4)-1.768(g4-g2)\} - 0.04 + 1.768g4 - G2$$

As it is not reasonable that p_I^i and p_{III}^i are linearly dependent we obtain:

$$T1 - G2 = 1.768 (t1 - g4)$$

$$G2 - G4 = 1.768 (g4 - g2)$$

$$\text{and } 0.04 + G2 = 1.768 g4 \approx G2$$

For all practical purposes we may then say that $T1 = 1.768 t1$, $G2 = 1.768 g4$ and $G4 = 1.768 g2$. This is reasonable: comparable proton-proton and carbon-proton coupling constants in the same rotamer are proportional! In that case also $G1 = 1.768 g1$.

As a result it is now impossible to perform the analysis we intended to do, but the result also indicates that Karplus relations found for vicinal proton-proton couplings might be transferable to carbon-proton couplings.

If a similar proportionality exists between BX^i and AC^i it can be shown that the results for $G1$, $G3$, $T2$, $g1$, $g3$ and $t2$ are quite out of line from the expectations. Therefore, any proportionality which might be observed in the latter case is fortuitous. It is customary in the literature¹ to state that $G2 = G4$. When we assume that the carbon-proton coupling constants $g3$ and $t2$ are related to $G3$ and $T2$ with the same proportionality factor as given above (an assumption which is doubtful because we are comparing different rotamers) and use values for $T1$, $T2$, $G1$, $G2$ and $G3$ calculated from the relations given by Abraham² we obtain for $t1$, $t2$, $g1$, $g2$ and $g3$ values of 6.9, 7.1, 3.1, 1.5 and 0.5 Hz respectively.

In conclusion, because of the proportionality between the observed coupling constants a populational analysis is not possible for 1,2-disubstituted propanes with equal substituents. However an analysis might be possible for different substituents.

Yours sincerely,

M.J.A. de Bie

T. Spoormaker

References (1) L. Ernst and T. Schaefer, Can. J. Chem., 51, 565 (1973)

(2) R.J. Abraham and G. Gatti, J. Chem. Soc. B, 961 (1969)



ISTITUTO CHIMICO

della

UNIVERSITÀ DI TORINO

10125 TORINO, 26 April 1977

CORSO MASSIMO D'AZEGLIO, 48

Tel. 65 2102 - 68 2892 - 65 5831 - 65 5832

Detection of the solution isomers of $\text{Fe}_3(\text{CO})_7\text{Se}_2[\text{P}(\text{n-C}_4\text{H}_9)_3]_2$ and their dynamic behaviour.

Dear Professor Shapiro,

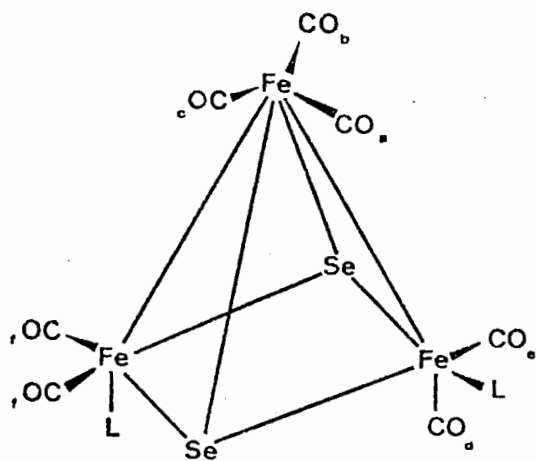
in the course of a ^{13}C -n.m.r. investigation on the dynamic properties of $\text{Fe}_3(\text{CO})_9\text{X}_2$ ($\text{X} = \text{NR}, \text{S}, \text{Se}, \text{Te}$), we have obtained a mixture of isomers for the bisubstituted derivative $\text{Fe}_3(\text{CO})_7\text{Se}_2[\text{P}(\text{n-C}_4\text{H}_9)_3]_2$. The mixture could not be separated in each individual component, but its variable temperature ^{13}C -n.m.r. spectra nicely show how it's possible by this technique to fully characterize positional isomers; Eight resonances are present in the -73°C spectrum. Their behaviour with the temperature and their integrated intensities show that each isomer gives four resonances and that one isomer is twice abundant than the other. The detection of two sets of resonances allows then the assignment of the solution structures of the isomers, 1 being the most abundant. The presence of two phosphorous atoms in the molecules, makes each carbonyl resonance the X part of an ABX system, the AB part of which is constituted by the two non equivalent phosphorous. The signal peak of intensity 3 within the set of the signals of 1 shows that at this temperature the carbonyls of the apical iron are still scrambling among themselves. A second distinct process occurs in 1 in raising the temperature: the resonances of $\text{CO}_{d,e,f}$ broaden, collapse and merge in a new signal whose chemical shift is in good accord with the calculated average. The delocalised scrambling requires carbonyl bridge formation via the chalcogen atoms, (in $\text{Fe}_3(\text{CO})_9\text{Se}_2$ the distance between the two basal iron is non bonding (3.51 \AA)¹). The multiplicity of the average peak indicates that at this stage the P atoms are not participating to the exchange; otherwise a triplet is expected. Carbonyl exchange occurs also in 2 upon raising the temperature: $\text{CO}_{d',e'}$ become equivalent on the n.m.r. time scale.

With best regards

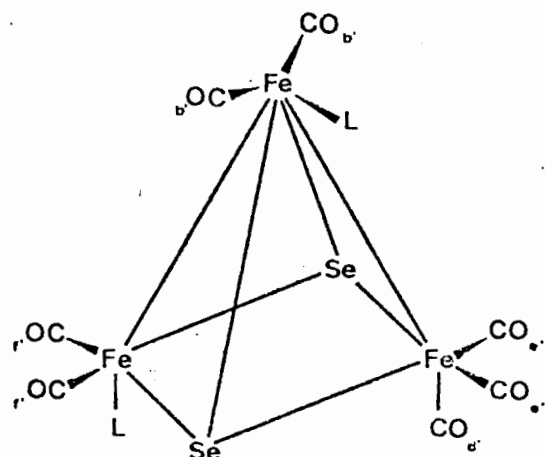
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(L. Milone)

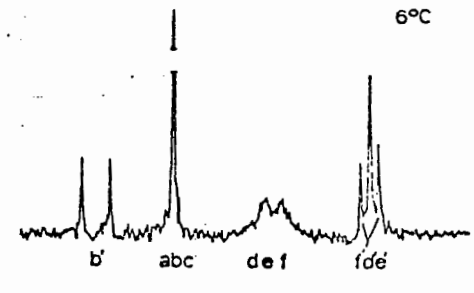
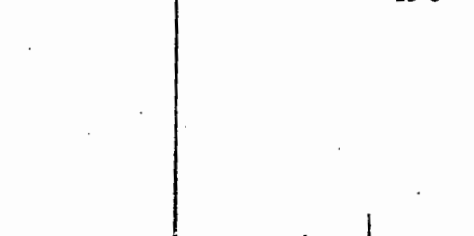
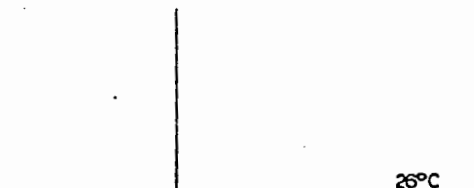
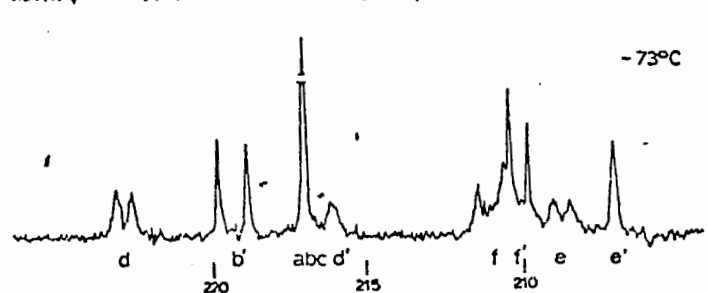
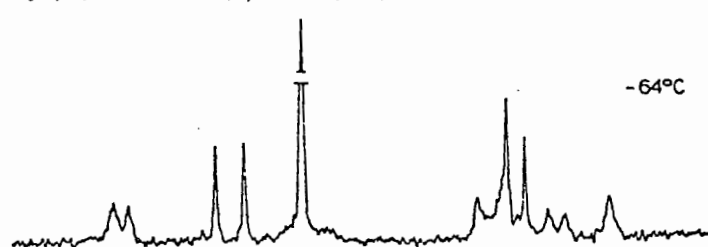
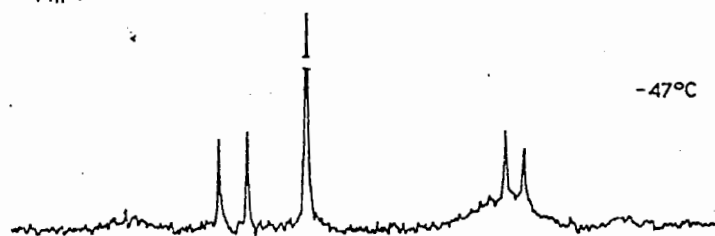
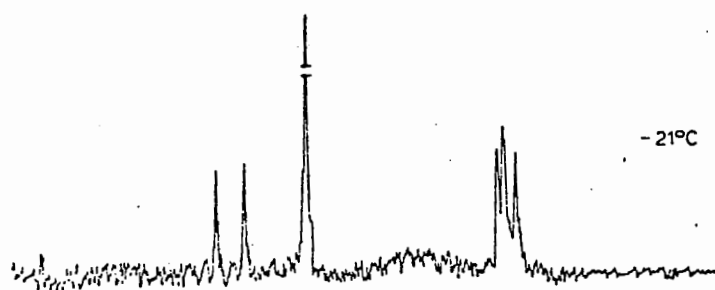
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1



2



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Department of Chemistry
713/749-2612



May 3, 1977

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

ONO, MONA, NTC-440 and Related Topics

Dear Barry:

Our Nicolet multi-nuclear probe (7-40.5 MHz at 2.3T) has been duly initiated except for a calling name. It is variously known as per the title. We have found the 12mm probe to be efficient, convenient and an unbelievable catalyst for the consumption of spectrometer time. So far we have observed about 25 nuclides with ease. Unfortunately, the chemical reasons for looking at them were nil; we used whatever was soluble, at hand and inexpensive. It is easily possible to perform all FT experiments on each nuclide without altering any of the FT software. It is necessary to verify the 180 pulse after each probe frequency change if you are doing T_1 experiments. These are typically 26-40 μ s and can be made reproducible if suitable care in tuning is taken. The combination of finding the 180 and then doing several relaxation experiments does require 168 hours/week.

One performance specification is certain. The ONO 12mm probe has double the ^{13}C nmr sensitivity of our V-4412 probe. There are a variety of reasons, but the longer receiver coil is probably the biggest factor. Performance for other nuclides is harder to specify. In fact, we still make such loose claims as ^{23}Na , ^{11}B , ^{10}B , and ^{119}Sn are "easy", ^{15}N is "hard", etc. We would enjoy hearing the TAMU nmr readers comments on their favorite samples for specification of performance for nuclides other than ^1H and ^{13}C nmr. If these suggestions could be sent to us at Houston, we would tabulate them and send them back to the newsletter for further comment.

With best regards.

Sincerely yours,

Bob Ruth

M. R. Willcott
R. R. Inners

P. S. I am seeking a post-doctoral fellow to study thermolysis reactions in the pinene series. The work will use, but not emphasize a variety of nmr techniques. Interested parties should write to MRW. The position is available as early as 1 June.



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April 22, 1977

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

Dear Professor Shapiro,

I am submitting this letter report so that I may be added to the list of TAMUNMR subscribers.

We recently acquired a CFT-20 to be used in the investigation of shale oils, tar sands, products from coal gasification processes, and petroleum crudes.

Preliminary carbon-13 studies were conducted on a petroleum crude (Fig. 1). Spin-lattice relaxation times and NOE's were measured for the aromatic and aliphatic envelopes. Shown in Figure 2 are the plots to obtain the spin-lattice relaxation times for the two types of carbons and Table I lists the data. Since the information is of a preliminary nature, a discussion of the results at this time would only be speculative.

Table I.

<u>¹³C-SPIN-LATTICE RELAXATION TIMES FOR A PETROLEUM CRUDE</u>				
CARBON TYPE	AVE T ₁ (SEC)	DD T ₁ (SEC)	OTHER T ₁ (SEC)	NOE
Aliphatic Envelope	0.29	0.39	1.18	1.5
Aromatic Envelope	1.3			0.05

Sincerely,

Daniel A. Netzel
Section Supervisor (Acting)
Division of Research Support

Enclosures
As stated above

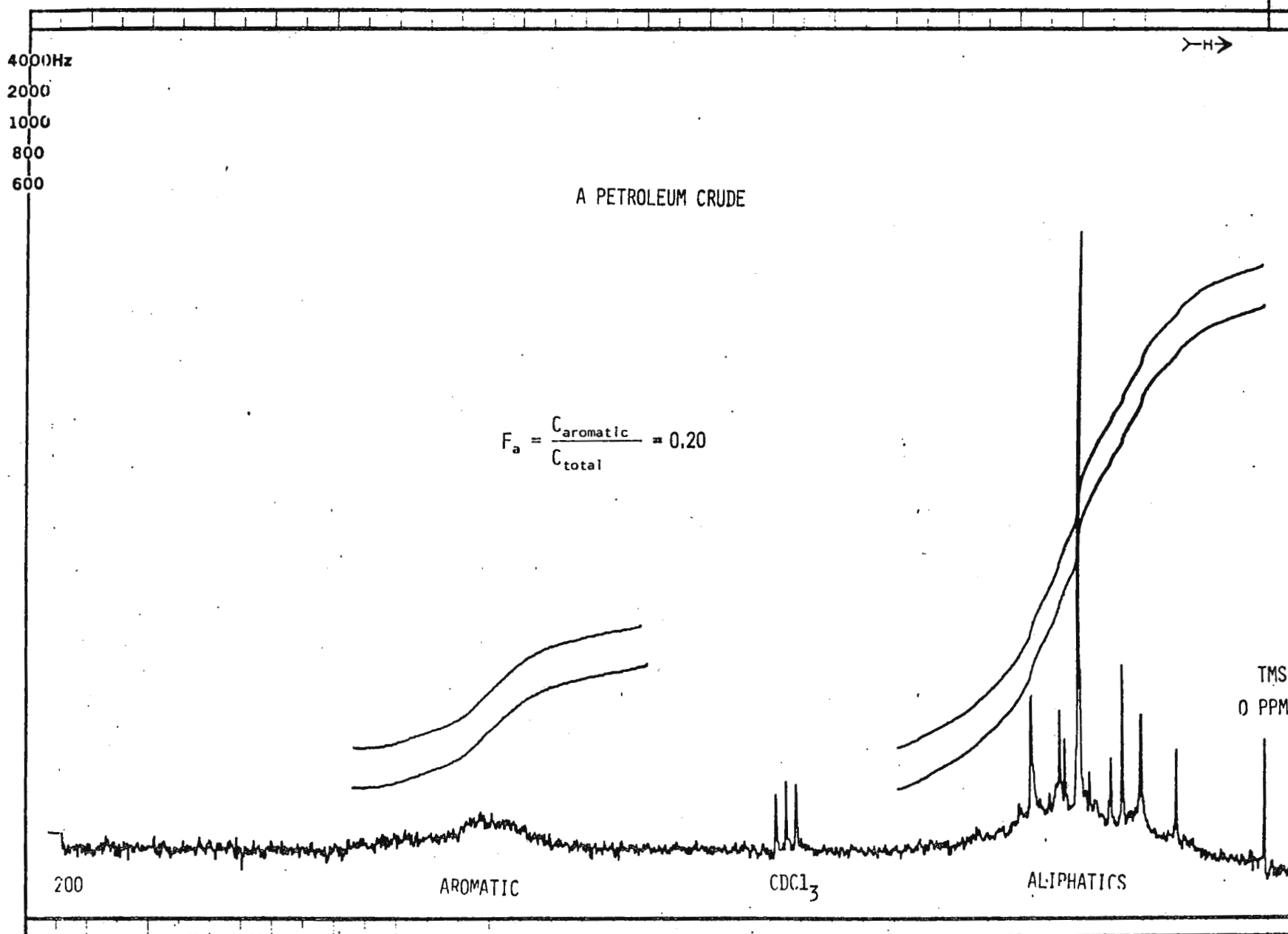


Figure 1.

SPIN-LATTICE RELAXATION TIME
SATURATE REGION OF A PETROLEUM CRUDE
 $T_1(\text{ave.}) = 0.29 \text{ sec.}$

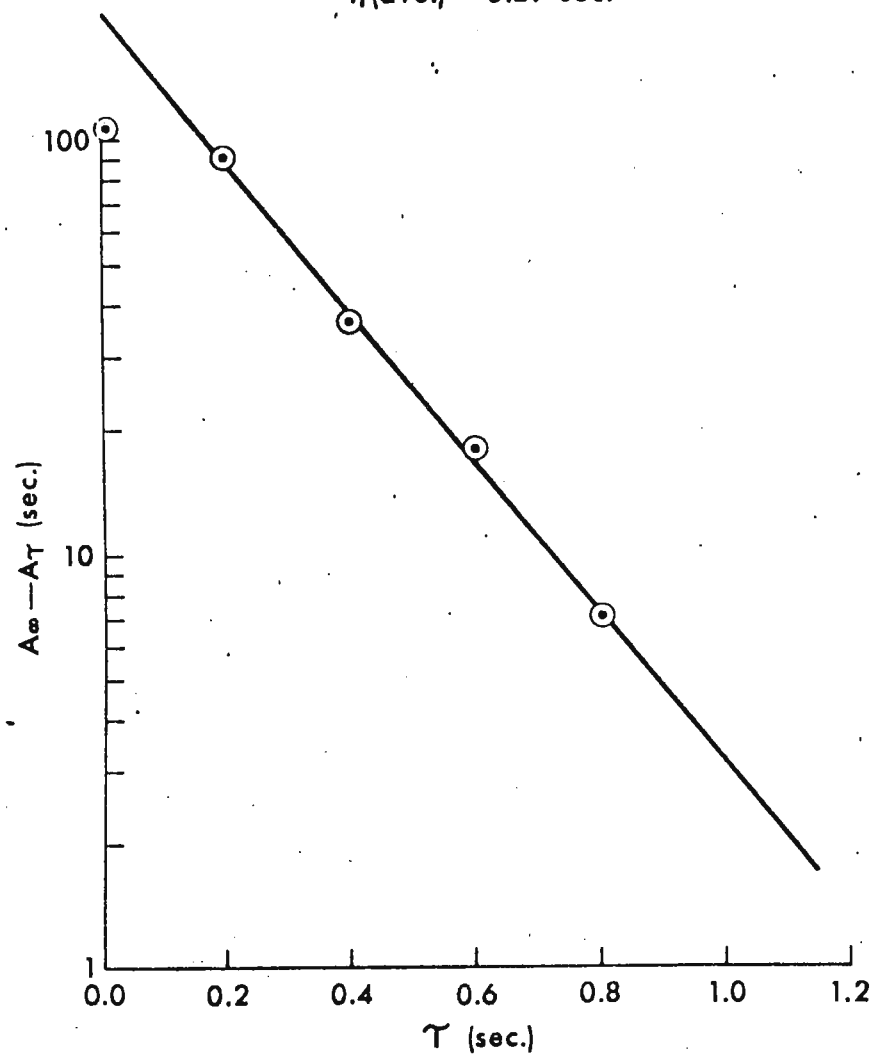
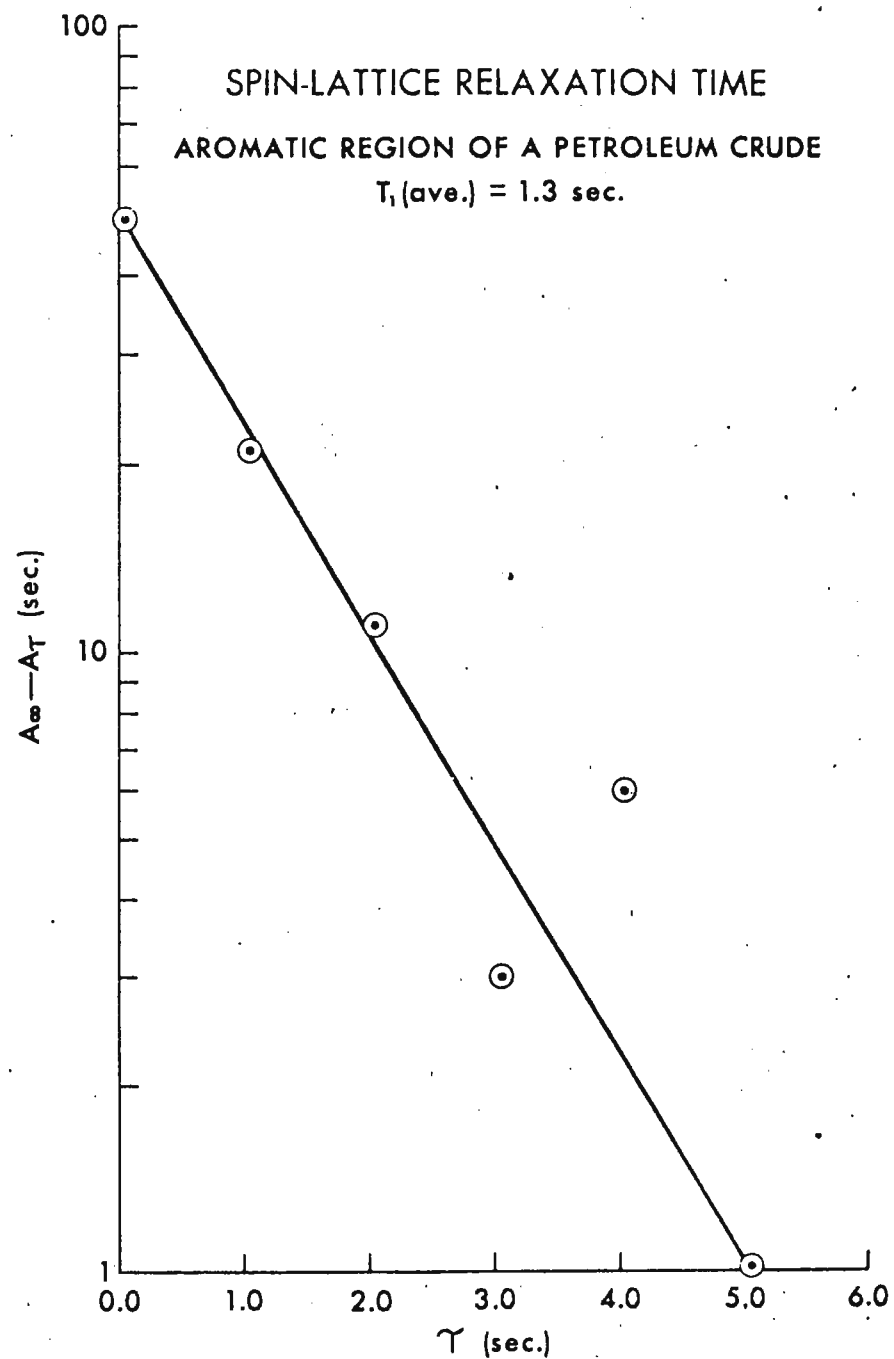


Figure 2.



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University of Melbourne

DEPARTMENT OF ORGANIC CHEMISTRY

Parkville, Victoria 3052
27th April, 1977.

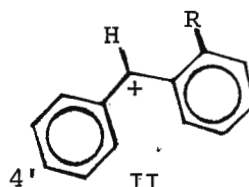
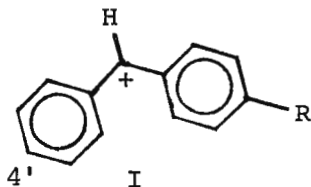
Prof. B. L. Shapiro,
Department of Chemistry,
Texas A&M University,
College Station, TX 77843,
U.S.A.

Dear Professor Shapiro,

σ_{ortho}^+ Constants from ^{13}C Shifts of Benzhydryl Cations

The idea of determining Hammett σ constants by simply measuring ^{13}C shifts of appropriate molecules is an attractive one and has been discussed previously in these newsletters (170-38, 180-21) and in the literature (JACS, 94, 3089 (1972); J.Chem.Soc.Perkin II, 729, 1976). In all these cases, measurements were made on neutral molecules and values of σ_{para} were derived.

We have used a similar approach to determine σ_{ortho}^+ values from the appropriate benzhydryl cations. By measuring the C4' chemical shift of 4-substituted cations (I) we obtained an excellent correlation with σ_p^+ ($r = 0.990$) and the Dual Substituent Parameter treatment gave $\Delta\delta\text{C4}' = 10.4\sigma_I + 10.7\sigma_R$ (SD 0.6 ppm). Using the shift



of the same (remote) carbon (C4') in 2-substituted cations (II) we were able to determine the following σ_{ortho}^+ values: OMe -0.59, Me -0.10, F 0.19, Cl 0.26, Br 0.29 and CF_3 0.69.

The advantages of determining σ_o^+ in this way are that the measurement is made on the cationic intermediate (i.e. after the transition state) and that the measurement site (C4') is remote from any steric (or proximity) effect of the substituent. The disadvantage is that one is restricted to substituents which do not react with the super-acidic medium in which the cations are generated.

A full account of the work should appear in Aust.J.Chem. at the end of the year.

Bob

R. J. Spear

Yours sincerely,

D. P. Kelly

D. P. Kelly.



April 27, 1977

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

Dear Barry:

RE: Frequency synchronization in the HX-90

The Bruker HX-90 NMR spectrophotometer possesses, as is known, multi-nuclear capability. The frequencies for all nuclei, except those for ^1H and ^{19}F - the so-called X frequencies - are derived from the LO-X section of the machine by quartz oscillators placed in a thermostatted oven. Since these X frequencies are separately generated, they are not synchronized with the masterclock of 5 MHz (LO-P section) from which the ^1H and ^{19}F frequencies are derived. Thus small frequency shifts may occur in the observed spectra when locking on ^1H or ^{19}F and observing an X nucleus. Normally these shifts are less than 1 Hz/24 hours (or a few Hz over a period of one month); they go unnoticed when reference compounds are used for the same X nucleus.

However, since we are interested in the Van der Waals shifts of ^3He in solvent gases, with an expected maximum shift of about one Hz, pure ^3He would be the only choice as a reference. This would be highly impractical as it would require three separate chambers in one NMR tube (i.e. for the sample gas, reference gas and lock compound). Synchronization of the ^3He frequency with the lock frequency eliminates the need for any reference compound, when lock compound and tube geometry are kept the same throughout the experiments.

Frequency synchronization in the HX-90 can be realized in a way similar to that in the WP-60 with only minor modifications. A frequency divider brings a 10 MHz reference frequency from the master clock down to 555.55 Hz, which latter frequency is fed into an X-frequency sampling oscillator which replaces the original quartz oscillator. The output is, as before, a frequency $(90-X)/n$ (where n is 3 or 9), but it is now synchronized with the master clock. The $(90-X)/n$ frequency is subsequently multiplied by n and mixed with a frequency $90 + \Delta f_1$ (Δf_1 being the offset frequency chosen), coming from the LO-P section, to produce the final observation frequency $X + \Delta f_1$. An additional feature is

that the output frequency of the sampling oscillator $(90 - X)/n$ can be raised or lowered in steps of 555.55 Hz within certain limits, thus extending the total offset range Δf_1 available. The latter feature can be used (in some cases) to avoid utilizing the Δf_1 (and Δf_2) offset (and their variations of about ± 0.3 Hz) circuits altogether, which may be important when ultimate frequency stability is required.

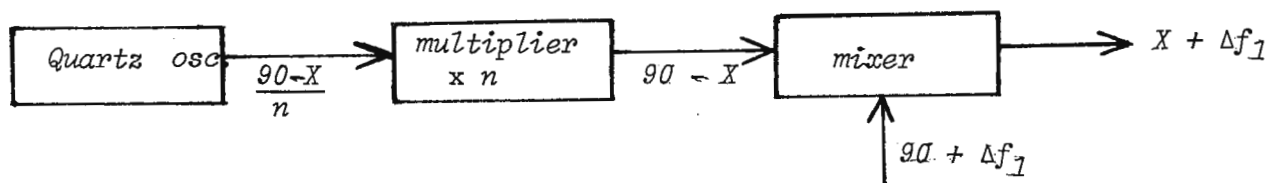
In general this modification will allow HX-90 owners to have full frequency synchronization, whenever the use of a reference compound is either undesirable or not practical. There are many other experiments (such as hetero-nuclear tickling or all long-duration FID accumulations) where this modification would lead to more accurate results.

F.M. Mourits
F.M. Mourits

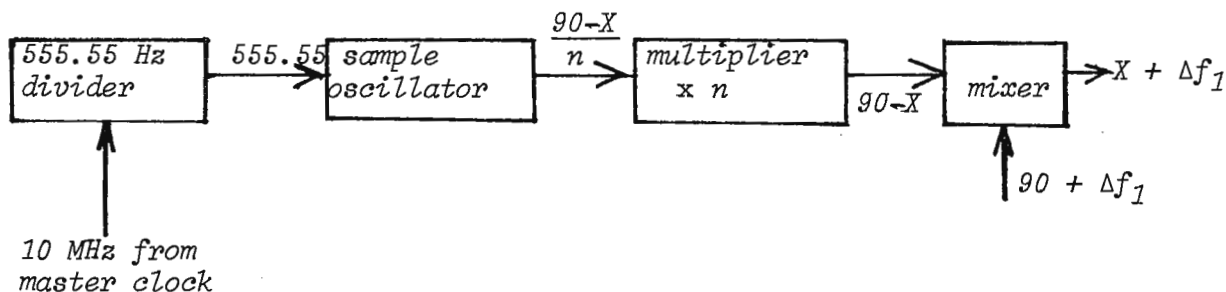
With best regards
F.H.A. Rummen
F.H.A. Rummen

Fig. 1 X-frequency generation before and after modification

BEFORE:



AFTER:





THE OHIO STATE UNIVERSITY

May 2, 1977

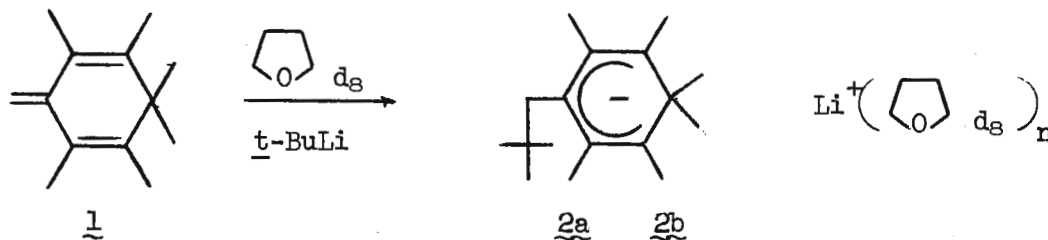
Dr. B. L. Shapiro
 Department of Chemistry
 Texas A and M University
 College Station, Texas 77843

Observation of Two Ion-Pairs
of an Organolithium Compound

Dear Barry:

In response to the dreaded Pink Note:

We have recently been looking at ^{13}C and ^7Li nmr of the cyclohexadienylic lithium compound produced from the hexamethyltriene 1 and t-butyllithium in cyclopentane alone and in the presence of ligands.



The ^{13}C ring shifts qualitatively follow the alternating pattern one would expect from simple MO theory. While the ring shifts vary with different added ligands (t-amines), the most pronounced effects appear in the presence of octa-deuteriofuran, ODF, (our nomenclature). Here, for the first time, there are two resonances for each carbon. Their ratio (lower/upper field) decreases as the temperature is lowered. Furthermore the two sets of shifts vary slightly with temperature, the upfield resonances more than the others, see Table. There is no evidence for line broadening implying some exchange process on the nmr time scale.

We suspect these two sets of resonances represent two kinds of ion-pairs -- one tight and the other loose, the latter (at higher field) being more abundant at lower temperatures. Exchange of lithium between the two sites is slow on the nmr time scale. From intensity ratios we estimate ΔH for



to be $3 \pm .5$ kcal.

The increased sensitivity of the upfield resonances to temperature implies more perturbation of the anion by Li^+ in the tight ion pairs.

Lastly our conclusions are supported by the results from ^7Li nmr. There are two peaks separated by 5.5 ppm. One is 4.00 ppm upfield of external LiCl in methanol, the other 1.44 downfield. We believe the upfield resonance comes from Li^+ in the face of π -loop.

These results were obtained using our Brukerian multi-nuclear pulse spectrometer.

In other work we have found it useful to disentangle ^7Li spectra consisting of several overlapping resonances with different widths by doing T_1 90° - τ - 180° sequences. We can selectively null one resonance at a time thus exposing the others.

There will be a post-doctoral position in my group to do the kind of work described above, starting this summer.

Best wishes.

Sincerely yours,

Gideon

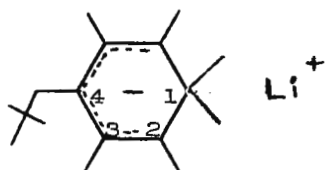
Gideon Fraenkel
Professor of Chemistry

Michael Hallden-Abberton

Michael Hallden-Abberton

GF/kk
cc

Table



i ^{13}C Shifts ppm/TMS
 i' (temperature coefficients)
 $10^{-3} \times \text{ppm}/^\circ$

	i	Δ tight	i'	i	Δ loose	i'
1	38.04	(5.56)		38.31	(6.70)	
2	83.71	(15.18)		83.80	(1.60)	
3	127.71	(8.20)		128.01	(5.3)	
4	92.62	(17.52)		90.40	(2.65)	

(as from 152 Castelnau, London SW13 9ET)

THE OPEN UNIVERSITY

26th April 1977

Dear Professor Shapiro,

An experimental measure of the local diamagnetic term (the Lamb term), obtained from X-ray photoelectron spectroscopy

Recently I have been testing different aspects of the familiar 'local term approximation' of Slichter, Pople, McConnell, and others. This expresses the total shielding $\sigma(A)$ of a nucleus A as

$$\sigma_d^A + \sigma_p^A + \sum \sigma^{AB} = \sigma(A)$$

The superscript A means that the shielding (diamagnetic σ_d , or paramagnetic σ_p) arises from electrons on the atom A only; and $\sum \sigma^{AB}$ represents the net contribution from the rest of the molecule. Chemists find these local terms easier to visualise than the mathematically more rigorous molecular terms of the Ramsey theory. In practice, however, the division of the shielding into the three terms is not achieved with any accuracy, because of difficulties in determining σ_p^A and $\sum \sigma^{AB}$, and further approximations are usually made. The variation in σ_d^A is deemed to be small, and is neglected; and the customary estimation of $\sum \sigma^{AB}$ by the neighbour anisotropy approximation gives values that are small for nuclei other than 'H (and also are unreliable) so these too are neglected. Variations in the observed shift (and in $\sigma(A)$) are therefore taken as variations in σ_p^A ; but unexplained anomalies often arise.

Until the present decade the local diamagnetic term was a purely theoretical concept. Now, however, X-ray photoelectron spectroscopists have shown that 'chemical shifts' in σ_d^A correspond to chemical shifts in the core-electron binding energies E_b that they measure, since both depend on the electrostatic potential at the nucleus due to the surrounding valence electrons.¹⁻³ This was demonstrated for σ_d by Lamb for free atoms, and Ramsey for molecules (I am abbreviating the argument somewhat here). Imagine the valence electrons as a hollow shell of charge Q with a radius r. Then by Gauss's law the

potential is Q/r anywhere within the shell. So a change q in electron density in the valence shell (due to σ or π inductive effects of the ligands) changes both the potential $V(0)$ at the nucleus (on which σ_d^A depends), and the ls-electron ionisation energy, by q/r (with the appropriate signs). We can neglect chemical shifts in $V(0)$ due to the core electrons, since these are not involved in chemical bonding.

This potential model therefore enables us to convert chemical shifts in E_b directly into 'experimental' values of $\Delta\sigma_d^A$. Particularly useful are the gas phase values of E_b measured by Jolly and co-workers (Inorg. Chem. 1974, 13, 2686). I've compared such X-p.e.s. values of $\Delta\sigma_d^A$ with theoretical values calculated by a programme written by Dr. Roger Grinter. This determines σ_d^A for the nuclei C, N, O, and F in a variety of molecules and ions from Pople's equations (J. Chem. Phys. 1962, 37, 53), using a version of the CNDO/S method of Del Bene and Jaffé. σ_d^A values are calculated also by an 'extended Flygare method' which uses the CNDO-calculated atomic charges to interpolate published (Hartree-Fock) values for the free atom and A^+ ions (W.H. Flygare and J. Goodisman. J. Chem. Phys. 1968, 49, 3122; G. Malli and S. Fraga, Theor. Chim. Acta 1966, 5, 275). Comparison with the experimental (X-p.e.s.) values of σ_d^A shows that the extended Flygare method /^(EFM) which amounts to a further parameterisation, significantly improves the CNDO values, which tend to exaggerate chemical shifts in σ_d^A .

For nitrogen the X-p.e.s. comparison shows that the local diamagnetic term spans a range of 10-13 p.p.m., from highly oxidised nitrogen in ONF_3 to reduced nitrogen in CN^- , for example. The difference in σ_d^A between NH_4^+ and NO_3^- , both of which are used as reference standards, is 4.6 p.p.m. (EFM) and 3.2 p.p.m. (X-p.e.s.) - in the gas phase, that is!

A fuller description of the theory and detailed results will appear in the Faraday II Transactions of the Journal of the Chemical Society, and a detailed examination of relaxation effects in the emission of the photoelectron is included. Percipient readers will have noted that the abbreviated description given above assumes the 'frozen orbital' approximation of Koopmans' theorem, that $(E_b - I_s)$ is the negative of the ls-orbital energy. In reality, orbital relaxation greatly speeds the parting electron and lowers the measured binding energy: this effect being irrelevant to σ_d^A , which is a ground state term. Nevertheless, chemical shifts in E_b correspond to chemical shifts in σ_d^A so

long as differential relaxation effects (between different molecules) are small. I've shown that this is indeed the case, by hole-state calculations both for the CNDO and the CNDO-EFM values. I'll give an example of an exception to the overall correlation, so that we can see its significance. X-p.e. spectroscopists have shown that differential relaxation, rather than the change in N-1s orbital energies, determines the trend in E_b within the series of NH_3 and the methylamines. This is because changes in E_b (and in σ_d^A) due to inductive effects are small, and are outweighed by the changes in E_b due to the CH_3 ligand being twice as effective as H in the relaxation process. But all the same, the effects of relaxation, as between NH_3 and Me_3N , correspond to less than 0.3 p.p.m. in σ_d^A . The general conclusion therefore stands, that X-p.e.s. can now give us an experimental measure of σ_d^A .

I hope to write to you again before long on the computations of σ^{AB} and σ_p^A .

Thank you for sending a copy of the ASTM standard E386-76 for High Resolution NMR. TAMU Newsletter should be a good place to discuss the differences in usage as one crosses the Atlantic - perhaps you had this in mind! To represent 'British usage' we can take the Chemical Society's Specialist Periodical Reports on NMR, which lean towards SI and IUPAC recommendations (as discussed in the introductory sections of Volumes 1 et seq.). Thus British chemists are now tending to use B rather than H for magnetic field strength (contrast Note 1 of E386-76).

Yours sincerely,



Joan Mason

References

- 1 H. Basch, Chem. Phys. Letters, 1970, 5, 337.
- 2 M. E. Schwartz, ibid., 1970, 5, 50; 6, 631; 7, 78.
- 3 D. A. Shirley, Adv. Chem. Phys., 1973, 23, 85.

Poul Erik Hansen
DEPARTMENT OF BIOCHEMISTRY



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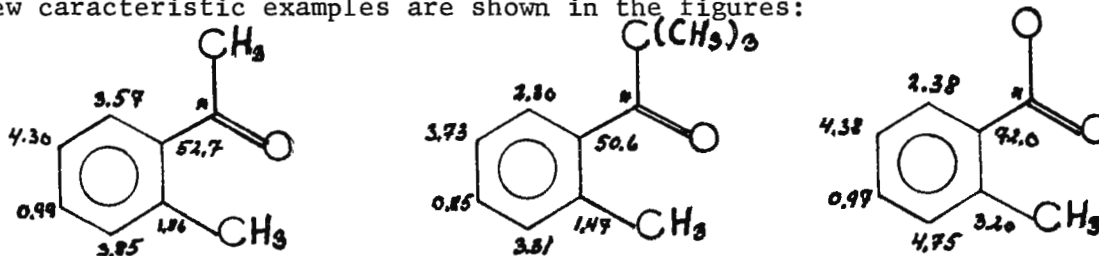
April 29 1977

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

^{13}C - ^{13}C coupling constants in carbonyl compounds. Dependence on orientation.

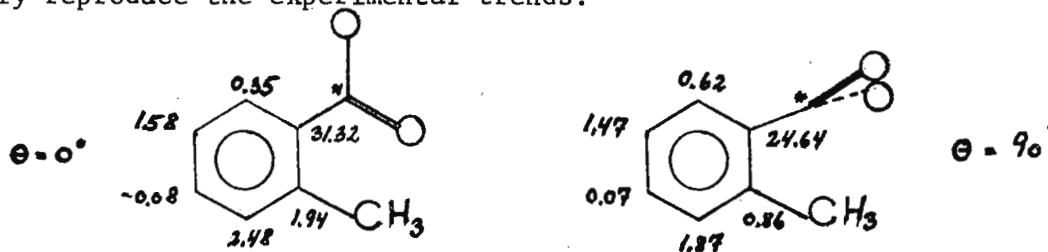
Dear prof. Shapiro:

I am spending a year with Brian Sykes group in Edmonton hence the letterhead. We (prof. Arne Berg and I) have recently investigated long range carbon-carbon coupling constants in a series of aromatic carbonyl compounds (acids, esters, amides, aldehydes and ketones). The compounds investigated comprise nonhindered molecules and molecules in which the carbonyl substituent is subject to ortho and peri interactions. The two and three-bond couplings were found to depend on the orientation of the carbonyl group. A few characteristic examples are shown in the figures:



The following general results have emerged. $^2J(\text{s-c}) < ^2J(\text{s-t})$ for ketones and aldehydes and the reverse for acids and acid derivatives. These findings should clearly be helpful in an estimation of the direction of carbonyl groups. We are presently trying to develop a quantitative theory by studying compounds of well defined geometry. It is our hope that the angle of twist, θ , as well as the rotamer populations can be determined this way. We are also looking into the possibilities of observing the same kind of effects in olefinic and aliphatic acids, ketones etc..

Theoretical calculations (INDO - SOS) on model compounds are found to qualitatively reproduce the experimental trends:



I am in the middle of writing a review on long range carbon-carbon coupling constants. I would be happy to receive reprints or preprints on this subject. Papers on carbon-carbon couplings observed in biosynthetic studies is especially called for.

Sincerely yours

Poul Erik Hansen



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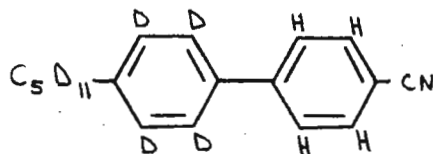
26th April, 1977

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

Dear Barry,

High Power Decoupling with an XL-100 V4412 Probe

Whilst waiting for a new probe to arrive, which I intend modifying to give greater decoupling efficiency, I got impatient to try some $\{^2\text{H}\}$ - ^1H experiments on liquid crystals, and so I had a go with the standard V4412 probe. The sample used is



and the aim was to record a high resolution spectrum of the four protons in the nematic phase. I succeeded by modulating the gyrocode ^2H frequency with a 6 KHz, 5 V audio signal (the ring deuteriums each have a quadrupole splitting of about 12 KHz). The gyrocode gate was used to provide deuterium decoupling only during the acquisition time of 0.2 s, and a delay for cooling to occur of four seconds was used. The gyrocode signal was amplified up to 100 W with an EN1 amplifier and fed to the probe thru a low pass filter and the normal matching box. I got a good spectrum, whose analysis has enabled the asymmetry in the ordering matrix for the ring to be determined, but there was some damage to the system. The variable capacitor in the matching box burnt out, but is easily replaceable, and the silver-ring paddle may also have been damaged. I would be interested to hear of anyone else who has tried for greater decoupling fields with the V4412 probe, particularly ^{13}C - $\{^1\text{H}\}$, which I am also impatient to try on liquid crystal samples.

Best wishes,

Jim Emsley

Varian introduces: the FT-80

A powerful new Fourier transform NMR spectrometer with an experimental array of over 40 nuclei

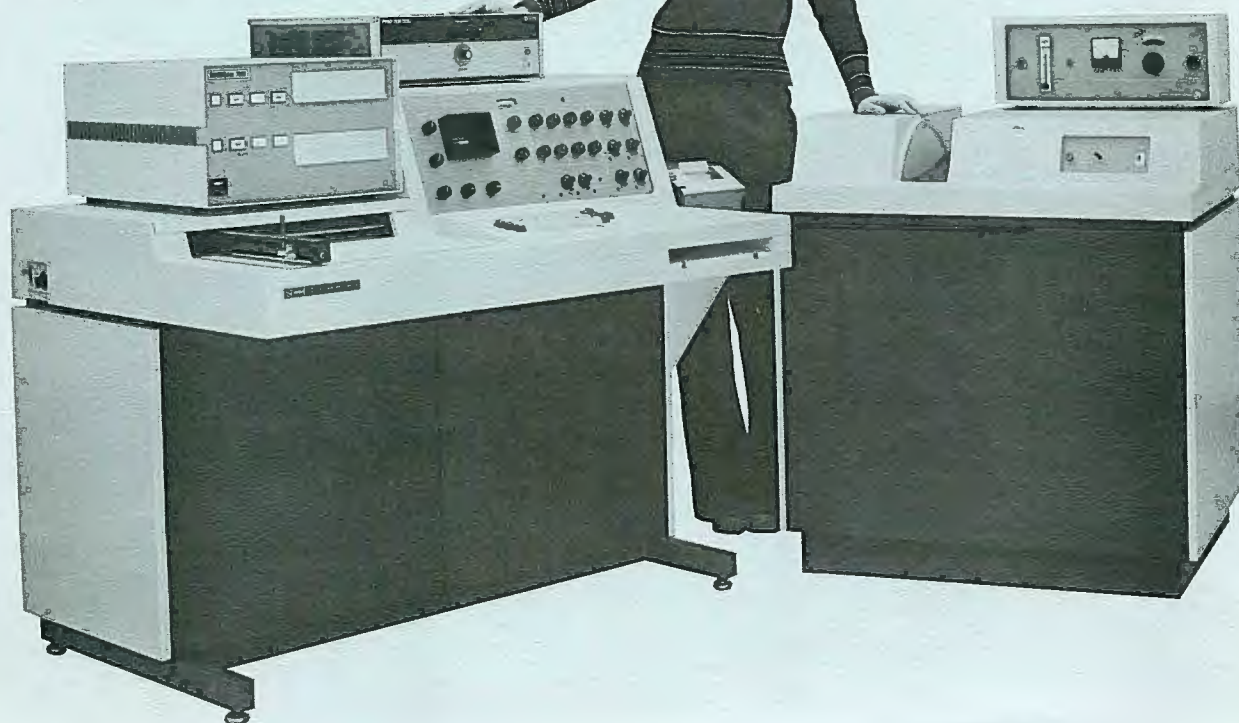
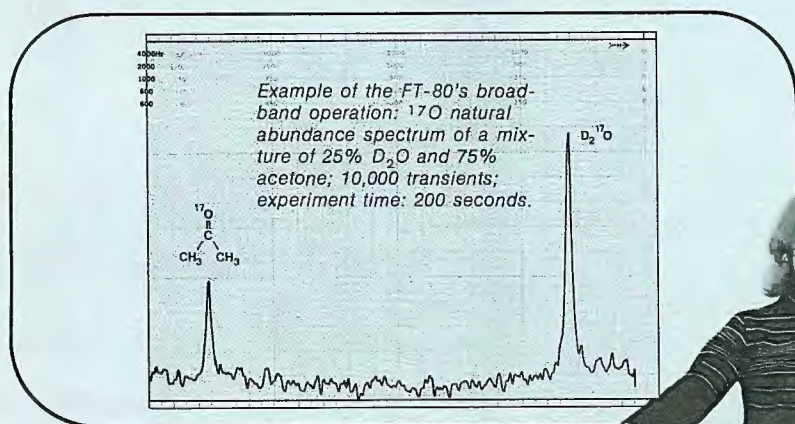
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If you would like more information on the FT-80, write to: Varian Associates, Inc., 611 Hansen Way, Box D-070, Palo Alto, Calif. 94303.

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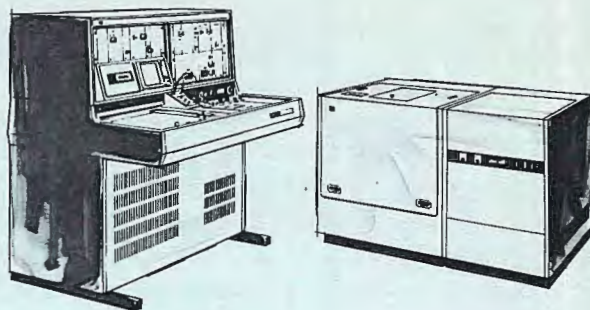
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