Simões, S.J.S.F.; Gil, V.M.S.
M.O. Calculations of Substituent Effects on Geminal Coupling Constants

Martin, J.S.; Green, R.D.
On Anion Complexes and Bihalide Ions

Budde, W.L.
An Internal Lock Signal for Elevated Temperature Investigations

Kuntz, I.D., Jr.
Weak Interactions

Knight, S.A.; Bartlett, C.J.S.
Number of Double Bonds per Molecule Determination Using Phenylsulphenyl Chloride Adducts

Harris, R.K.; Robinson, V.J.
Vicinal (F,F) Coupling Constants

Sivinvee, V.; Kundla, E.; Salum, V.
Nuclear Magnetic Triple Resonance. On Signals at Combined Frequencies

Elguero, J.; Fruchier, A.; Jacquier, R.
Evolution en Solution Aqueuse D'Halogenoamines

Shaw, D.
Wide Sweeps on HA-100

Basalay, R.J.; Martin, J.C.
A Rapid Degenerate Rearrangement Involving an Intramolecular Nucleophilic Displacement

Wind, R.A.; Smidt, J.
Influence of a 1/2 Coaxial Cable on the Signal to Noise Ratio of a Q-Meter

Vignollet, Y.; Maire, J.C.
3-Fluoro-4-nitrophenyltrimethylsilane: 19F Spin Decoupling Experiment

Farrar, T.C.; Johannesen, R.B.; Coyle, T.D.
MAGNENEQ1NB2H6

Bladon, P.; Forrest, G.C.
N.M.R. Study of Consecutive Reversible First-Order Reactions
Mavel, G.
BF₃-Organophosphorus Complexes

Monro, A.M.; Sewell, M.J.
The Conformation of N-Acyl-1,2,3,4-Tetrahydroquinolines

Jardetzky, O.; Putter, I.; Markley, J.
NMR Studies of Selectively Deuterated Proteins

Lauterbur, P.C.
"Isomer Spaces", or "You Can't Get There From Here"

Cavalli, L.
F¹⁹ NMR of CF₂I⁻¹³CF₂I

Deadline Dates:  
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No. 121: 7 October 1968

All Newsletter correspondence, etc., should be addressed to:
Professor Bernard L. Shapiro  
Department of Chemistry  
Texas A&M University  
College Station, Texas 77843
M.O. CALCULATIONS OF SUBSTITUENT EFFECTS ON GEMINAL COUPLING CONSTANTS.

Dear Professor Shapiro,

We have obtained expressions for the effect of a lone-pair on $J_{H_1 H_2}$, $J_{H_1 H_3}$ and $J_{H_2 H_3}$ for the hypothetical fragment

within the framework of the Pople-Santry theory. The most important terms (those corresponding to electron flow) are

$$\Delta J_{H_1 H_2} = 2 \beta \ell t_1 \beta \ell t_2 \left( \beta t_2 - \beta_h, t_2 \right) \beta_h, t_1$$

$$\Delta J_{H_2 H_3} = 2 \beta \ell t_2 \beta \ell t_3 \left( \beta t_2 - \beta_h, t_3 \right) \beta_h, t_1$$

$$\Delta J_{H_1 H_3} = 2 \beta \ell t_1 \beta \ell t_3 \left( \beta t_1 - \beta_h, t_3 \right) \beta_h, t_1$$

The quantities $\Delta J_{H_1 H_3}$ and $\Delta J_{H_2 H_3}$ can be related to the substituent effects on HCC$^{13}$ and HCN$^{15}$ coupling constants.

Yours sincerely

Mr. S.J.S. Formosinho Simões

Dr. Victor M.S. Gil
Dr. Bernard L. Shapiro,
Dept. of Chemistry,
Stanford University.

Dear Dr. Shapiro,

Our studies of anion-molecule complexes in non-H-bonding solvents, announced initially in J. Amer. Chem. Soc. next month; Part II (with R. U. Lemieux and J. Hayami), on pyranoside complexes, will be in Can. J. Chem. in the autumn. A very limited number of preprints is available.

Extension of the work to anion complexes of hydrogen halides (that is, bihalide ions) has provided some intriguing problems. The table below gives the complex shifts on formation of bihalide ions in methylene chloride from HX and Y⁻ (as a tetrabutylammonium salt).

The shift, derived from an iterated Scott-Benesi-Hildebrand analysis, is \( \Delta \sigma_{XHY⁻} - \Delta \sigma_{HX} \). The numbers in brackets are the corresponding chemical shifts of the bihalide ions, in ppm. relative to TMS⁺.

<table>
<thead>
<tr>
<th>MOLECULE, HX</th>
<th>ANION, Y⁻</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Cl⁻</td>
</tr>
<tr>
<td>HCl</td>
<td>-12.5</td>
</tr>
<tr>
<td></td>
<td>(-14.3)</td>
</tr>
<tr>
<td>HBr</td>
<td>-16.1</td>
</tr>
<tr>
<td></td>
<td>(-13.7)</td>
</tr>
<tr>
<td></td>
<td>(-14.)</td>
</tr>
</tbody>
</table>

Association constants are in the range 3 to 50 M⁻¹.

The shifts (and equilibrium constants) are dependent on ion size in a manner consistent with an anion-field dependent interaction. Computation of the linear coefficient in the Buckingham equation for electrostatic shielding,

\[ \Delta \sigma = a \sigma^2 \]

yields values of a (in units of \( 10^{-12} \text{ esu}^{-1} \)) of:

C-H, 3;  Cl-H, 14;  Br-H, 18;  I-H, 27. The correlation

* The scale is, presumably, 'minus-delta'. You may deny us tau, but you'll never get us to use a scale of shielding that runs backwards. Wave numbers are bad enough!
appears to be with bond polarizability, rather than with polarity.

Looking at the matrix of numbers in brackets, you'll note that it's not symmetric. If HX and Y⁻ yielded the same ion as HY and X⁻, you'd expect to see the same shift. Certainly this is not true where iodine is involved.

There are suggestions in the literature [see Nibler and Pimentel, J. Chem. Phys. 47, 710 (1967); Harrel and McDaniel, J. Amer. Chem. Soc. 86, 4497 (1964)] that HBr and Cl⁻ will, in time, produce HCl and Br⁻. We have looked for this in the infrared, and don't see it on a time scale of hours to days. This observation needs further confirmation, and critical tests are in progress.

If interconversion is slow, it suggests that there are distinct species X-H...Y⁻ and X...H-Y⁻, and that their interconversion, via a simple internal proton transfer, is slow. We find this startling. We must admit that our analysis of the equilibrium data from NMR (which shows only a single peak for all H-bearing solutes in solution) is made on the assumption that the complex comes apart the same way it went together.

You can see how this work can have a lot to do with the current debate on the structure of the bihalide ions: distinct XHY⁻ ions would be consistent with the finding of Nibler and Pimentel, that ClHCl is not centrosymmetric; whereas very rapid interconversion or identity of the ions would suggest structures analogous to that of FFIF, where the hydrogen is apparently equivalently bound to both fluorines.

Sincerely,

John S. Martin

Robert D. Green

(Suggested Title: On Anion Complexes and Bihalide Ions.)
Professor Bernard L. Shapiro  
Department of Chemistry  
Stanford University  
Stanford, California 94305

Dear Professor Shapiro:

An Internal Lock Signal for Elevated Temperature Investigations

In recent years there has been a need in our laboratories for a substance which would give a satisfactory lock signal at temperatures above 100° so that all the well known advantages of the internal lock mode of operation could be gained during elevated temperature investigations in sealed evacuated tubes. For about the last year we have been using the compound tris(trimethylsilyl)amine to give a strong, stable lock signal for our Varian HA-100 in the temperature range of 100-200°C. This interesting substance possesses some advantages for this application which may be of interest to the readers of this newsletter:

(a) The compound is prepared easily in one step from inexpensive commercial chemicals.

(b) Its vapor pressure is only about 25 mm. at 100° while HMDS—which is frequently used as a reference for elevated temperature work—exerts a pressure of one atmosphere at 100°.

(c) It has excellent long term thermal stability.

(d) It gives a sharp singlet at δ = 0.229 in diphenyl ether.

(e) The compound is a "solid" at room temperature which, however, exists in a plastic crystalline state. The pure "solid" has a band width at half peak height of about 8 Hz—presumably due to rapid rotational and translational reorientation of the molecules in that state. Therefore, it is convenient to disperse the
compound in a solid or gel at room temperature, establish the lock signal, and then heat the sample to the desired temperature while making the appropriate homogeneity adjustments along the way.

(f) The substance is essentially non-basic but does possess the disadvantage of being susceptible to solvolysis in hydroxylic solvents. In 50% methanol-carbon tetrachloride at 60°, \( k_1 = 1 \times 10^{-5} \) sec\(^{-1}\).

Should any of the readers wish to have more details about using this technique, I will be happy to supply them on request. Best personal regards.

Sincerely,

William L. Budde
Senior Chemist
Dr. B. L. Shapiro  
Department of Chemistry  
Stanford University  
Stanford, California 94305

Dear Barry:

I have a few observations on the use of NMR methods to measure small equilibrium constants.

First, several equations have been proposed for treating the simple case: \( A + B \rightarrow AB \) (B in large excess). These include the Benesi-Hildebrand Eqn. (1,2), a rearranged version proposed by Scott (3) and by Hanna (4), and graphical methods (5). Curiously, these procedures can yield different answers even though they share a common mathematical base and, ref. 3 notwithstanding, a common set of physical assumptions. The difficulty arises because of different weights intuitively assigned to the transformed variables. The general problem is covered in the papers by Wentworth (6). Ideally one wants a data reduction equation which retains linearity between the errors in the original data and in the calculated terms. The Benesi-Hildebrand approach is particularly bad if used in the ordinary way: least-squares-fit to the variables \((\text{observed shift})^{-1}, (\text{concentration})^{-1}\). Such a fit clearly assigns undue weight to the worst points. One should either incorporate the reciprocal weightings in the least-square program or pick another equation. The Scott equation avoids the worst of the reciprocal terms and probably is preferable. In our own work we usually avoid the assumption \( B \gg A \). The closed algebraic solution is available. Instead of calculating the appropriate weighting terms we invert the whole business using the equation and an iterative procedure to find the best fit to the data itself.

Second, I'd like to raise the issue of what concentration units are most convenient for these equilibrium constants. Any experiment which must simultaneously resolve two independent variables (\( K_{eq} \) and limiting shifts for us) can face severe systematic errors unless \( K_{eq} \) is independent of concentration or is a known function of concentration. We're currently pushing moles/liter as the most desirable candidate, primarily on the rationale that only molarity keeps proper track of intermolecular separations as one varies the solvent, although we've collected a modest amount of data from our lab and from the literature which supports the claim that a molarity
equilibrium constant is not strongly concentration dependent. The details will appear in JACS fairly soon.

Third, our experience on the random errors to be anticipated using the dilution experiments indicates that high precision is pretty essential. Errors of ± 1 Hz or more—even in aromatic or hydrogen bonding systems where shifts are large—yield pretty bad K's and limiting shifts (±30% or worse). Enthalpies would be out of the question. Errors of a few tenths of a Hertz can give K's to 5-20%, depending on the system but a van't Hoff ΔH in the range of 0-2 Kcals is going to have a big uncertainty. Good data, presently defined as no point (out of 8-10) more than 0.1 Hz from the best-fit curve, gives a small K (0.1 liter/mole) to 10% and a large K (0.5 l/m) to 1%. ΔH errors are reduced to 100-200 cals/mole if K is known to a few percent.

Best regards,

I. D. Kuntz, Jr.

IDK,Jr:dhl

I. D. Kuntz, Jr.
Assistant Professor of Chemistry

NUMBER OF DOUBLE BONDS PER MOLECULE DETERMINATION USING PHENYL-SULPHENYL CHLORIDE ADDUCTS

In general the integrated intensity of the olefinic hydrogen resonances in an NMR spectrum is no measure of the number of double bonds present in a molecule. Obviously carbon-13 NMR could provide an answer to this problem for the integrated intensity of the olefinic carbon resonances would be proportional to the number of double bonds. However, carbon-13 determinations are precluded in most cases by the general unavailability of carbon-13 spectrometers and in some cases by the large samples (about 500 mg) required by the latter. One method we have used to determine the number of double bonds per molecule by hydrogen NMR is to examine the phenylsulphenyl chloride adduct. This is readily formed by adding phenylsulphenyl chloride to the olefin (both in carbon tetrachloride solutions) at ambient temperature (20 - 25°C). The reaction is usually exothermic, but the temperature of the reaction mixture is easily controlled by water cooling. In most cases the course of the reaction can be roughly followed by the rate at which the colour of the phenylsulphenyl chloride disappears. The NMR spectrum of the adduct will show a band in the aromatic region equivalent in intensity to five hydrogen atoms per double bond in the original sample. Any prominent band or the whole spectrum given by the non-aromatic hydrogen atoms in the molecule may provide a suitable reference intensity. Some results obtained using this method with reference compounds are shown in Table 1.

In carrying out the determination it is preferable to add the phenylsulphenyl chloride in small amounts to the sample until the olefinic hydrogen resonance(s) just disappear. This condition is readily observable in the NMR spectrometer oscilloscope. The method of Mueller and Butler (1) for the preparation of phenylsulphenyl chloride from diphenyl disulphide and sulphuryl chloride is much to be preferred over the classical method using chlorine and thiophenol solutions in carbon tetrachloride. The reactive but rather unstable phenylsulphenyl chloride can in many instances be replaced by the stable 2,4-dinitrophenylsulphenyl chloride. These derivatives are usually crystalline solids, a property which facilitates purification if this step is deemed necessary.
Some words of caution must be given concerning the general use of the method. Very sterically hindered double bonds eg the double bond in lanost-9(10)-ene will not react with phenylsulphenyl chloride. Further phenylsulphenyl chloride and its dinitro derivative can react with some functional groups (eg NH) other than double bonds (2). Notwithstanding these disadvantages we have found it a useful reagent in double bond determinations by hydrogen NMR.

References

(2) N. Kharasch, J Chem Ed, 1956, 33, 585.

TABLE 1

<table>
<thead>
<tr>
<th>Olefin</th>
<th>Double Bonds Found</th>
<th>Double Bonds Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexene</td>
<td>1.02</td>
<td>1.0</td>
</tr>
<tr>
<td>Octene-1</td>
<td>1.10</td>
<td>1.0</td>
</tr>
<tr>
<td>2,2-Dimethyl-hept-3-ene(cis)</td>
<td>0.98</td>
<td>1.0</td>
</tr>
<tr>
<td>Limonene</td>
<td>1.92</td>
<td>2.0</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>0.95</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Dear Barry,

Vicinal (F,F) Coupling Constants

Thanks for the reminder. Your system is so efficient that I no longer bother to count the month since my last subscription. Actually this letter is delayed a little even since the reminder because we've been waiting for some computations to be finished. It now appears that this will take some time yet, so I hasten to send this before you cut off my supply of the Newsletter. However, that means that the results below are still tentative and therefore subject to change without notice.

We have been interested for some time in the problems presented by vicinal (F,F) coupling constants. We are particularly concerned to find the variation of $^3\text{J}_{FF}$ with dihedral angle, because we believe there is commonly a sign variation. We are currently investigating this effect in fluorinated cyclobutanes and cyclobutenes, and have found that cis and trans (F,F) coupling constants are of opposite sign in all five cases studied so far (see the accompanying table). The low value of $^3\text{J}_{FF}$ in perfluorocyclobutane compounds (averaged over the internal rotation) presumably owes much to such variations in sign.

The work on perfluorocyclobutene itself has been accepted for publication in Spectrochimica Acta. In the other cases some of the relative signs may be incorrect. The data for the last compound are the most tentative. However, it is possible in this case to assign the bands due to the CF$_2$ fluorine nuclei by estimating the chemical shifts. This shows that the 9.4 Hz coupling is that between cis fluorines.

We hope this keeps our subscription alive for a bit longer.

Yours sincerely,

Robin Harris

Dr. R.K. Harris


Dr. B.L. Shapiro,
Illinois Institute of Technology,
Chicago, 60616,
U.S.A.

H/T
<table>
<thead>
<tr>
<th>$^2J_{PP}$</th>
<th>$^3J_{PP}(sp^3, sp^3)$</th>
<th>$^3J_{PP}(sp^2, sp^3)$</th>
<th>$^3J_{PP}(sp^2, sp^2)$</th>
<th>$^4J_{PP}$</th>
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<tbody>
<tr>
<td>+198.9</td>
<td>+26.0</td>
<td>-12.3</td>
<td>+6.8</td>
<td>-12.9</td>
</tr>
<tr>
<td>+199.4</td>
<td>+30.4</td>
<td>-12.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>+200</td>
<td>+24.9</td>
<td>-12.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>+200</td>
<td>+5.7</td>
<td>-11.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>+200</td>
<td>±5.4</td>
<td>±3.0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Nuclear Magnetic Triple Resonance. On Signals at Combined Frequencies.

Recently Bystrov\(^1\) has given an experimental verification of the theory of nuclear magnetic triple resonance spectra for weak perturbing \(rf\) field region\(^2\). Making use of beat patterns he also observes the predicted\(^2,3\) signals at combined frequency \(\nu_4 + \nu_3 - \nu_1\). We review at present theoretical conclusions concerning these signals.

Consider the high-resolution triple resonance experiment with \(rf\) fields \(\frac{B_3}{4}, 2H_4 \cos(2\pi \nu_4 t + \varphi_4)\). Let the three frequencies \(\nu_4\) be located near distinct lines of the single resonance spectrum of the compound under investigation. Let the three \(rf\) fields be sufficiently weak in order to perturb only the three lines being simultaneously in resonance. If now the location of the frequencies \(\nu_2\) on the energy level scheme corresponds to Fig. 1 A or B, signals at the combined frequency \(\nu_2 + \nu_3 - \nu_1\) will be induced in receiver coil (in addition to the signals at frequencies \(\nu_3, \nu_2\) and \(\nu_1\)). Note that the location of frequencies in Fig. 1 A, B corresponds to three connected allowed transitions resulting in a new allowed transition. The value of the combined frequency corresponds to the law of conservation of energy. The possible combined frequencies are, therefore, given by \(|\nu_2 + \nu_3 - \nu_1|\) and \(|\nu_1 \pm (\nu_2 - \nu_3)|\).
Making use of a lock-in detector operating with reference signal $\sin[2\pi(v_2 + v_3 - v)]$ one may record the spectral line $cd$ in the spectrum at frequency $v_2 + v_3 - v$ by sweeping frequency $v$. The intensity of this line in the single resonance spectrum is proportional to $|\langle c | \mathcal{I}_1 | d \rangle|^2$, but the intensity of the corresponding line in the combined frequency spectrum will be proportional to $|\langle a | \mathcal{I}_2 | c | \mathcal{I}_3 | b | \mathcal{I}_4 | d \rangle|$. Assuming the observing rf field $H$, to be sufficiently weak to cause nonlinear effects, one obtains maximal signals at combined frequency by equal effective strenghts of of perturbing rf fields: $H^2_2|\langle a | \mathcal{I}_2 | b \rangle| = H_3|\langle b | \mathcal{I}_3 | d \rangle|$, in this case the spectral line will have the shape of a triplet with reversed outer peaks or inner peak.2

The spectrum at a given combined frequency will consist of a limited number of lines selected from the single resonance spectrum in accordance with the above mentioned rule of three connected transitions. We suppose that this will enable to greatly simplify complex spectra.

Although the theory in 2 is restricted to simpler spin systems with nondegenerate transitions and and without equal frequencies of different transitions, the existence of signals at combined frequency by three allowed connected transitions seems not to depend upon this restriction.

A theoretical investigation 3 of a more general case with $H_2$ sufficiently strong to perturb a group of lines has clarified the problem of the signals at combined frequencies in this region. Fig.1 C presents a fragment of
the level system of the transformed double resonance Hamiltonian\textsuperscript{4}. If the frequencies are located as shown in Fig. 1 C a signal at the combined frequency \( \nu_3 + \nu_1 - \nu_2 \) (as referred to laboratory coordinate system) will be induced in the receiver coil. The transition \( \alpha \beta \) in Fig. 1 C may, for example, correspond to one of the resonances in the X part of the double resonance spectrum of an AX system. Then the transition \( \beta \gamma \) will correspond to a line in the A part of the spectrum. This line will occur also in the spectrum at frequency \( \nu_3 + \nu_1 - \nu_2 \). The calculated line shapes are similar to those observed by Anderson in the modulation transfer experiment\textsuperscript{5}. Since the transition \( \beta \gamma \) is not allowed in the region of collapse, the signals at combined frequency will fall off with the collapse of the spin-spin coupling.

V. Sinivee, E. Kundla, V. Salum
Academy of Sciences of the Estonian SSR,
Institute of Cybernetics, Tallinn.
Fig. 1. Frequency location on level scheme giving rise to signals at combined frequencies in a triple resonance experiment: A, B with weak rf fields $H_1, H_2, H_3$, C with a strong rf field $H_2$ and two weak rf fields $H_1, H_3$.

References

1 V.F. Bystrov, J. Molec. Spectry. (to be published)
3 E.Kundla, ibid. (to be published)
Cher Professeur Shapiro,

Il est connu que lors de la réaction du diméthylamino-1 chloro-2 propane Ib avec la phénothiazine, il se forme un mélange de deux isomères IIa et IIb (1).

Pour expliquer la formation de IIb, on admet que la base Ib réagit par l'intermédiaire d'un aziridinium IIb. Cette hypothèse est ancienne et découle du fait que l'on a mis en évidence des sels d'aziridinium au cours de l'hydrolyse d'homologues du gaz moutarde (2,3,4).

De plus, l'évolution des bêta-chloroamines en aziridines est bien connue (5,6) et la RMN s'avère être une méthode de choix pour suivre ces évolutions.

Nous avons donc étudié le comportement de bases susceptibles de conduire non plus à des aziridines mais à des sels d'aziridinium ou à des cycles à azote quaternaire. Nous avons suivi l'évolution au cours du temps des spectres RMN des bases Ia, Ib, Ic et Id dans D2O avec comme référence interne le sel de sodium de l'acide triméthylsilylpropanesulfonique.
Dans le cas de Id on pouvait attendre un composé IIe car des sels d'aziridinium semblables se forment à partir de N-bétachloroéthylpipéridines. L'évolution lente de Id conduit en réalité exclusivement au composé IIId, le signal méthyle à 6,80 τ ne pouvant correspondre qu'à un $\text{N-CH}_3$.

Afin de voir si la cyclisation intramoléculaire dépend du solvant, nous avons pris les spectres RMN de la base Ia (la plus instable) dans le benzène, le trichloroacétionitrile, le nitrobenzène, la pyridine et le diméthylsulfoxide-$d_6$. Toutefois, dans ces solvants, le sel d'aziridinium est insoluble et précipite au fur et à mesure de sa formation. Il n'y a donc pas apparition des signaux correspondants et la baisse de résolution empêche toute étude quantitative de l'évolution. On constate que seule la solution benzénique ne contient pas de précipité au bout d'un jour ; son spectre RMN est celui de la base initiale.

Les études d'évolution d'haloamines tertiaires ayant toujours été faites par des méthodes de dosages potentiométriques, nous tenions à souligner l'extrême intérêt de la RMN dans ce genre de travail que nous poursuivons.

Veuillez croire, Cher Professeur Shapiro, à l'assurance de nos sentiments les meilleurs.

J. ELGUERO

A. FRUCHIER

R. JACQUIER

Le temps indiqué est celui au bout duquel la cyclisation est complète.

\[
\begin{align*}
&\text{Ia} & \text{30 mn} & \text{IIIa} \\
&\text{Ib} & \text{1 h} & \text{IIIb} \\
&\text{Ic} & \text{7 jours} & \text{IIIc} \\
&\text{Id} & \text{3 jours} & \text{IIId} & \text{IIIe}
\end{align*}
\]
Dear Dr. Shapiro,

Jim Feeney has left England for Zurich and I have left the East End for Dalton; hence, may I take over this lab.'s subscription.

Our technique for varying the side-band frequency used to record HR mode spectra may be of interest. This basically involves using the phase detector of the locking unit instead of the one in the integrator/decoupler. The manual oscillator of the V-4354 is disconnected e.g. by the removal of "MAN. OSC. TUNE. NET" card and an external stable audio oscillator giving 1 volt plugged in at MAN. OSC. OUT., J 1506. The spectrometer is then switched as for HA mode with the V-4354 set for frequency sweep, shim switch on and the sweep oscillator off. In this mode you can record an HR spectra on both recorder and the scope with the centre-band suppressed and a choice of side-band frequencies up to about 20 KHz from your external oscillator. This gives nice display field sweep spectra 40 KHz (40 ppm for ²H, 1000 ppm for ³¹P) wide and is useful for other nuclei, liquid crystal and paramagnetic proton spectra.

This idea can be carried one stage further to give calibrated wide sweeps. The pen recorder is coupled to increase/decrease switch of the slow sweep unit via two relays (see circuit diagram); drift corrected for in the normal way and the slow sweep unit adjusted to give a sweep of, say, 1 cm equals 100 Hz at a 250 sec. sweep time. This calibration is achieved using the sweep rate pot and standard audio side-band techniques; once set up it can be used to give shifts to 5% for weeks, without further adjusting.

Enclosed is a wide sweep spectrum; fluorine spectra provide the best examples but being me, the example is a paramagnetic complex i.e. ReCl₄(P Prop₂Ph)₂ (slightly impure)!

Yours sincerely,

Dr. D. Shaw.

Dr. B.L. Shapiro,
Department of Chemistry,
Stanford University,
Stanford, California 94305.

Title: Wide sweeps on HA-100

Your Reference: DS/WJF

Your Reference:

Our Reference:

Telephone: Walton-on-Thames 28766
Cables: Varian Walton
Telex: 261351

![Chemical Structures and NMR Spectrogram](image-url)

- **Structure 1:** P(CH=CH=CH)2 C6H5
- **Structure 2:** P(CH2-CH=CH2)2 C6H5
- **Structure 3:** (P(C6H5)3 and ReCl3(P prop2Ph)3)

**NMR Spectrogram:**
- Peaks labeled as ortho, meta, para, and CH2(α)
A Rapid Degenerate Rearrangement Involving an Intramolecular Nucleophilic Displacement

Sulfonium ion I in a variety of solvents shows peaks in its nmr spectrum for two nonequivalent methyl groups at δ 2.50 and 2.08. The nonequivalence is preserved to 180° C where the compound decomposes. In contrast, II shows a single methyl peak (somewhat broadened with a line width of 8.5 Hz at ambient temperature) at δ 2.68.

A possible structure for II compatible with this would be the symmetrical, internally solvated carbonium ion, IIb. Another possibility would be rapidly equilibrating sulfonium ions IIa and IIc. The latter possibility for the structure was confirmed by the observation at reduced temperatures of peaks for nonequivalent methyl groups, two sharp peaks of equal areas at δ 2.91 and 2.41 at 0°. The coalescence temperature is +17°. The degenerate rearrangement IIa ⇌ IIc most probably represents a nucleophilic displacement on the tertiary carbon atom although we cannot at present rule out the intermediacy of a species represented by IIb. Further work will be directed toward making these results quantitative and looking for evidence bearing further on the mechanism of the rearrangement.
Dear Professor Shapiro,

Influence of a $\frac{\lambda}{2}$ coaxial cable on the signal to noise ratio of a Q-meter.

For studying the mobility of solids we have constructed a nmr-spectrometer of which the LC-circuit is mounted in a cryostat. The detection system is a Q-meter, so the LC-circuit is current-driven by an external oscillator. For the time being the frequency is 30 MHz.

Mainly in order to make calculations easier we use a $\frac{\lambda}{2}$ coaxial cable as the connection between the LC-circuit and the transistorized preamplifier.

Calculations show that the S/N ratio of the system depends on the impedance match between the LC-circuit and the cable.

For the calculation we use as a reference the S/N ratio of a LC-circuit, directly connected to the preamplifier, which is given by:

$$(S/N)_1 = \frac{5x"UQ}{(4\kappa T\Delta f R_p)}^\frac{1}{2}$$

in which formula $R_p$ is the parallel resistance of the LC-circuit, $Q$ its quality and $U$ the voltage over the circuit, the other symbols having their usual meaning. For our experimental set-up $R_p = 4k\Omega$.

Connecting the LC-circuit and the preamplifier with a $\frac{\lambda}{2}$ coaxial cable of which the conductance can be neglected but the attenuation not, leads to a $S/N$ ratio:

$$(S/N)_2 = A(S/N)_1$$

with
\[ A = \frac{1}{(1 + \frac{\alpha \lambda}{2} \frac{R_p}{Z_o}) (1 + \frac{\alpha \lambda}{2} Z_o)^{\frac{1}{2}}} \]

in which formula \( Z_o \) is the characteristic impedance of the coaxial cable and \( \alpha \) its attenuation constant per meter. The formula holds, provided that \( \frac{\alpha \lambda}{2} \ll 1 \).

Furthermore it is assumed that in both cases the input circuit is matched to the amplifier in such a way that the noise figure \( F \) in both cases has the same (minimum) value and that the same voltage \( U \) is present over the LC-circuit.

From the expression for \( A \), which is plotted as a function of \( \frac{R_p}{Z_o} \) for \( \frac{\alpha \lambda}{2} = 4 \cdot 10^{-2} \), it can be seen clearly that the S/N ratio gets worse by the insertion of the coaxial cable. In our case \( Z_o = 135 \) Ohm, so that \( A = 0.68 \), a loss of about 30%.

For \( R_p = Z_o \), \( A \) reaches its maximum. With \( \frac{\alpha \lambda}{2} = 4 \cdot 10^{-2} \) the maximum value is 0.96.

Of course it makes no sense to choose \( R_p = Z_o = 135 \) Ohm, because then \( (S/N)_1 \) lowers.

Instead of this one has to make a tap on the LC-circuit, so that \( R_p' \) which is seen by the preamplifier becomes 135 Ohm. One can prove that in this case the same equation for \( A \) holds as given above, provided that \( R_p \) is replaced by \( R_p' \).

The condition \( R_p = Z_o \) is not very critical, as can be seen from the figure.

Experiments confirmed the calculation.

We will be glad to send details of the calculation to those who are interested.

\begin{center}
\includegraphics[width=\textwidth]{graph.png}
\end{center}

Ir. R. A. Wind,  
Dept. Magnetic Resonance.  

Prof. Dr. Ir. J. Smidt,  
Dept. Magnetic Resonance.
Dear Prof. Shapiro,

The structure of the compound obtained by nitration of m-fluoro-phenylsilane has been determined by $^{19}$F spin decoupling experiment. This derivative can be assumed to have one of the next four formula:

1. $\begin{align*}
  & \text{SiMe}_3 \\
  & \text{B} \\
  & \text{O}_2\text{N} \\
  & \text{F} \\
\end{align*}$

2. $\begin{align*}
  & \text{SiMe}_3 \\
  & \text{B} \\
  & \text{O}_2\text{N} \\
  & \text{M} \\
\end{align*}$

3. $\begin{align*}
  & \text{SiMe}_3 \\
  & \text{B} \\
  & \text{F} \\
  & \text{M} \\
\end{align*}$

4. $\begin{align*}
  & \text{SiMe}_3 \\
  & \text{A} \\
  & \text{NO}_2 \\
  & \text{B} \\
\end{align*}$

The NMR spectrum (fig. 1a) can be analysed as ABMX ($X = F$).

Structure 1 is immediately discarded: the $H_B$ proton would show a single peak broadened by $J_{HH}$ and $J_{HF}$ weak coupling.

The formula 4 is hardly probable due to steric hindrance. Moreover according to SMITH and DIEHL rules the proton NMR spectrum should not display any low field signal. So, we must decide between 2 and 3. On the spectrum (fig. 1a) three large coupling constants are evident, but we have to distinguish between $J_{HH}$ or $J_{HF}$ especially
in the low field region.

After $^{19}\text{F}$ spin decoupling (fig. 1b) any fluorine proton coupling is removed and only one, but one, large ($J_{\text{HH}}^0$) coupling remains.

If we do assume that $J_{\text{FH}}^0 \approx 7$–8 Hz, only in the bands of B is such a coupling apparent. So that the sequence C–C–C– can be discarded and formula 2 is the correct one.

I hope you will accept these elucidations as a real contribution, otherwise according to a procedure "in vogue" I would go on strike!

Thanking in advance.

Sincerely yours.

Y. VIGNOLLET

J. C. NAIRE
Greetings, Barry:

I hope we're not too late to get in our subscription renewal.

We have recently finished the analysis of the high resolution $^{11}$B and $^1$H spectra of $^{11}$B$_2$H$_6$. The $^1$H spectrum is of the AA'A''A'MX'MXX' type and was analyzed using the UEA NMR II program of C. M. Woodman and R. K. Harris*. The dimension statements were enlarged to meet the requirements of the B$_2$H$_6$ molecule.

A total of 32 $^1$H and 32 $^{11}$B spectra were calculated. Although we can't guarantee that the fit is unique, we were unable to find (after trying rather hard) any other combination of parameters which gave as good agreement. The results are: $J_{BB} = + 5$ Hz, $J_{BH_b} = 46.2$ Hz, $J_{BH_t} = + 133$ Hz, $J'_{BH_t} = + 4$ Hz, $|J_{H_4H_5}| = 7.2$ Hz, $J_{H_4H_5}$ (trans or cis) = ± 14 Hz, $J_{H_4H_5}$ (cis or trans) = ± 6 Hz, $J_{H_4H_5}$ (gem) < 3 Hz, and $\delta$ (H$ _t$-H$_b$) = -4.50 ppm.

Best regards,

T. C. Farrar, Head
Magnetism Group

R. B. Johannesen
Inorganic Chemistry Section

T. D. Coyle, Chief
Inorganic Chemistry Section
Inorganic Materials Division, IMR

TITLE: MAGNONEQINB2H6

*Mol. Phys., 10, 437 (1966). (We are most grateful to Dr. Harris for making the program available to us.)
Dr. Bernard Shapiro,  
Department of Chemistry,  
Stanford University,  
Stanford, California 94305.  
U.S.A.

Dear Barry,

**N.M.R. Study of Consecutive Reversible First-Order Reactions**

In the search for further examples of ortho esters of trifluoracetic acid\(^1\) we have examined the monotrifluoracetate of cis-3,4-dihydroxymethylene tetrahydrothiophene (the sulphur analogue of our original example). As expected the solid compound is a single isomer (I) which in solution (in CH\(_3\)CN) reaches equilibrium with the acyclic form (II) and the other cyclic isomer (III). At n.m.r. probe temperature (33.5°) the rate at which this occurs is such that the process can be followed very conveniently by observing the intensities of fluorine resonances of the three forms (I), (II), (III). (\(\delta\) 85.17, 74.95, 83.70 p.p.m. respectively). To obtain the four first-order rate constants we have used and iterative computer program based on the scheme described by Wiberg\(^2\) with algebra taken from Frost and Pearson's book\(^3\). A more detailed study at different temperatures is planned for when we get our new spectrometers.

Yours sincerely,

Peter Bladon

Gordon C. Forrest.

---


\[
\begin{align*}
K_1 &= 0.30 \times 10^{-3} \text{ sec}^{-1} \\
K_2 &= 0.12 \times 10^{-3} \text{ sec}^{-1} \\
K_{-1} &= 0.23 \times 10^{-3} \text{ sec}^{-1} \\
K_{-2} &= 0.65 \times 10^{-3} \text{ sec}^{-1}
\end{align*}
\]

Dear Barry,

We have been investigating - in collaboration with Pr. M. Azzaro (Fac. Sciences, Nice) - a number of CTC complexes boron trifluoride - organophosphorus compound. Due to some outdoor troubles, this research is not yet completed, but we have some noteworthy results on $^1$H, $^{11}$B, $^{19}$F and $^{31}$P resonances (for proton and fluorine, variable temperature investigations have been performed). I restrict myself to a typical adduct BF$_3$ - CH$_3$ P(O)F$_2$ ($\Delta$H formation : -17,07 Kcal/mole):

\begin{align*}
\text{pure BF}_3 \text{ resonances} & : \delta F + 48,4 \text{ p.p.m. (vs. TFA)} \\
\text{adduct BF}_3 \text{ resonances} & : \delta F + 67,6 \text{ p.p.m.} + 2 \text{ p.p.m.}
\end{align*}

For both of these resonances, the "naively expected" high field shift ($\delta$PO $\rightarrow$ BF$_3$) is observed; no BF coupling appear (due to boron quadrupolar relaxation), nor BP coupling as in phosphine complexes R$_3$P$^+$ $\rightarrow$ B$^-$R'$_3$ (see e.g., G. Jugie and J.P. Laurent, Bull. Soc. Chim. France, 1968; p. 2010)\footnote{For these strong complexes, boron resonance shifts by Ca. + 60 p.p.m., and phosphorus resonance by Ca. - 50 p.p.m.}. This may be due to the electronegative oxygen bridge.

\ldots/


Dr. Bernard L. SHAPIRO
Dept. of Chemistry
TEXAS A & M University
College Station, TEXAS 77843
U.S.A.
The especially large change on fluorine chemical shift may be related to the change in boron hybridization: plane $sp^2$ in BF$_3$, nearly tetrahedral $sp^3$ in the adduct.

**pure CH$_3$P(O)F$_2$ resonances**

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<td>F</td>
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<tr>
<td>J P...H</td>
<td>21 Hz</td>
</tr>
<tr>
<td>P...F</td>
<td>1112 Hz</td>
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<tr>
<td>H...F</td>
<td>ca. 6,0 Hz</td>
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**Adduct CH$_3$P(O)F$_2$**

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<td>F</td>
<td>2,26 p.p.m.</td>
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<tr>
<td>P</td>
<td>78 p.p.m.</td>
</tr>
<tr>
<td>J P...H</td>
<td>20,5 Hz</td>
</tr>
<tr>
<td>P...F</td>
<td>1165 Hz</td>
</tr>
<tr>
<td>H...F</td>
<td>ca. 7 Hz</td>
</tr>
</tbody>
</table>

One again, naive expectations on chemical shifts are fulfilled. The low-field trend for proton and phosphorus reflects the polarity reduction $\delta$PO $\rightarrow$ BF$_3$. For fluorine, there is a slight redistribution of charges and probably a change in geometry around phosphorus. The change in PF coupling (certainly of negative sign) agree with these conclusions: one knows (e.g. G.M., Progr. NMR spectr., 1, 251, 1966) that $|J(\text{PF})|$ increases when substituent electronegativity increases, for a given number of F attached to phosphorus. Here, boron "pulling on" oxygen increases its relative electronegativity. The change in FH coupling (probably of negative sign) reflects the same to a lesser extent. Contrarily to the (much stronger) phosphine complexes, no "intermolecular" coupling appear, CH$_3$.....BF$_3$ for example. In the same time, no drastic change is seen when varying temperature up to about 100°C.

With all best regards,

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

Dear Professor Shapiro,

The Conformation of N-Acyl-1,2,3,4-Tetrahydroquinolines

It was reported recently \(^1\) that although N-acetylindoline exists mainly in the endo conformation I, N-acetyl-1,2,3,4-tetrahydroquinoline appears to exist mainly in the exo conformation, II. Our evidence so far in this area agrees only with the indoline case.

\[
\begin{align*}
\text{I} & & \text{II} & & \text{III} \\
\text{X} & & \text{X} & & \text{X} = \text{H, Br, MeO.} \\
\text{CH}_3 & & \text{O} & & \text{CH}_3 \\
\end{align*}
\]

Nagarajan et al. \(^1\) assigned the exo conformation II (X=H) on the basis that the signal for the C\(_2\)-proton could not be distinguished from the other aromatic protons and the signal for the C\(_2\)-protons was found at 0.73 \(\delta \) to lower field than the parent amine. If the hetero ring is assumed to be a mixture of rapidly interconverting half-chairs, then, by consideration of model compounds, \(^2\) deshielding of -0.73 \(\delta \) is within the range which would be expected for both endo and exo conformations. We consider that this evidence does not allow conformations II and III to be distinguished. In support of this, a down-field shift of 0.68 \(\delta \) was reported \(^1\) for the C\(_2\)-protons in the endo conformation I (X=H).

In order to examine the chemical shift of the ortho protons in the tetrahydroquinoline series, we prepared and examined the spectra of the derivatives, I, II (or III) with X=Br and MeO. These spectra enabled us to make the following deductions.

On acetylation of the indolines, the ortho proton moves downfield (~1.6 \(\delta \)) relative to the parent compound. The analogous shift in the tetrahydroquinoline series is approximately half this figure. The fact that only one resonance each was observed for the ortho proton and the acetyl group, and that the deshielding of the ortho proton was significantly less than that of the indoline analogues, suggested that the effect on the ortho proton was probably an average resulting from rapid interconversion.
of conformations II and III. The spectra for the bromo compounds were virtually unchanged at -60°C (the lower limit of our spectrometer), with no sign of signal broadening as would be expected if the two conformers were starting to freeze out. This suggested either that the compounds were almost entirely in the endo conformation, or a relatively low energy barrier existed between the two forms.

Comparison of the UV spectra of the N-acetyl and 6-methoxy-N-pivaloyl tetrahydroquinolines shows the latter to have a greatly reduced absorption intensity. If it is assumed that this effect is due to a considerably greater dihedral angle between the planes of the aromatic ring and the carbonyl group in the pivaloyl compound than in the acetyl derivatives, then it would be expected that if the endo conformation above was populated by the acetyl derivatives, there would be a marked reduction in the deshielding of the ortho proton. The chemical shift found (2.45δ) is similar to that in the acetyl derivatives. This suggests that the acetyl derivatives exist to an appreciable extent in both endo and exo conformations, the increased deshielding which would result from the pivaloyl derivative being in the endo conformation (a reasonable assumption) being reduced by the greater dihedral angle between the plane of the aromatic ring and the carbonyl group.

In summary, we find that the endo conformation I is preferred for the indoline, but in N-acetyl tetrahydroquinolines, conformations II and III are both present to a comparable extent, with a relatively low energy barrier between them. Dipole moment and benzene dilution studies give supporting evidence.

We hope to submit these findings for publication in the near future.

Yours sincerely,

A. M. Monro

M. J. Sewell

Chemical Research Department


3. (a) 4-Methylpiperidine from Varian Associates Spectra Catalogue, Vol. 2, Spectrum 479; acetyl derivative from

4. (a) 2-Methylpiperidine from Varian catalogue 2, spectrum 477; and
(b) N-acetyl derivative from
Dear Barry:

For the first issue of your new TAM NMR letter, we would like to contribute another first which is bound to be of some consequence in the application of NMR spectroscopy to biological problems.

It has been appreciated for some time that NMR is potentially one of the most informative methods that could be applied to the study of protein structure, the structure of binding sites, changes of protein conformation, etc. With an average of 3-5 NMR lines per amino acid and 150 amino acid residues in a small protein, there are 600 or more individual spectral lines in a protein spectrum, whose positions, intensities, and widths reflect the structure of the macromolecule and its behavior under different conditions in great detail.

The main limitation to the usefulness of NMR in protein chemistry has been the fact that the relatively closely spaced amino acid lines overlap and fuse to give rather uninformative spectral envelopes for the protein as a whole. Great hopes have, therefore, been pinned on the 220 Mc spectrometer and indeed some improvement in resolution has been achieved with it, but not nearly enough to make a real difference. In fact, one can show by an easy calculation that even at a 1000 Mc nowhere near the majority of the lines in a protein spectrum would be resolved.

The solution of the problem, therefore, lies in the preparation of selectively deuterated proteins. This has been a major part of our effort in the past two years and we have now prepared an analog of the enzyme staphylococcal nuclease in which all amino acids, except the following are fully deuterated: (1) tryptophan (2) methionine (3) tyrosine, in ring positions 2 and 6 (4) histidine, ring methine 2 (5) aspartic acid, β-methylene and (6) glutamic acid γ-methylene.
The analog has a much simpler high resolution NMR spectrum than the fully protonated enzyme, as shown in Fig. (1) and (2). The binding of calcium ion and the inhibitor 3'5' thymidine diphosphate gives rise to readily observable and readily interpretable changes in the spectrum of the analog. With the preparation of several additional analogs which is underway, we will be able to reach much more detailed conclusions on the conformation of this protein in solution, the structure of its binding sites, and the changes which it undergoes in the process of catalysis, than is possible by any other method.

With best regards,

Yours sincerely,

Oleg Jarretzky

Irving Putter

John Markley
Figure 1
100 Mc NMR spectra of the aromatic region of protonated Nase and the selectively
deuterated Nase. Nase from the Foggi strain contains 4 His (S), 7 Tyr (Y),
1 Trp (T), and 3 Phe residues (8). All spectra were run in a 0.3M NaCl
solution in 99.87% D$_2$O at glass electrode pH meter readings of 8.0 ± .1 at
32°. NMR spectra were obtained with a Varian HA 100 spectrometer at a sweep
rate of 1 cps/sec. The probe temperature was 32°. Spectra were averaged
over the given number of sweeps on a Varian C1024 computer of average transients
(CAT). The external standard used was hexamethyl disiloxane HMS. Peaks of the
inhibitor pdTp are identified by the symbols H$_6$ and H$_1$.
   A. 20% solution of Nase; 60 CAT scans
   B. 6% solution of Nase-D$_1$; 129 CAT scans.
      The bar graph indicates the predicted intensities of the spectral
      lines.
   C. 6% Nase-D$_1$ plus the inhibitor pdTp; pdTp/Nase molar ratio is approxi-
      mately 3; 147 CAT scans.
   C. 6% solution of Nase-D$_1$ plus pdTp/Nase ≈ 3 plus Ca$^{2+}$/Nase ≈ 10; 130
      CAT scans.

Figure 2
A portion of the aliphatic region of the NMR spectrum of Nase and selectively
deuterated Nase. Solutions and experimental conditions are the same as in
Figure 1A-D. Tentative assignments of the S-CH$_3$ peaks of the four methionine
residues of the enzyme are given (M$_1$-M$_4$). The 5-CH$_3$ peak of the inhibitor pdTp
is identified.
   A. Protonated Nase; 31 CAT scans.
   B. Nase-D$_1$; 92 CAT scans.
   C. Nase-D$_1$ + pdTp; 58 CAT scans.
   D. Nase D$_1$ + pdTp + Ca$^{2+}$; 56 CAT scans.
Dear Barry:

"Isomer Spaces", or "You Can't Get There From Here"

Some time ago, while contemplating the non-equivalence of protons in configurationally labile molecules based on trigonal bipyramidal phosphorus, it occurred to me that a systematic geometric method of classifying isomers and their interconversions should be possible, and would be useful in thinking about not only their spectra but all other properties as well. The same thoughts inspired several other people also, and the construction of topological models for chemical systems seems to be becoming a popular competitive sport and pastime. A few preprints of our contribution to the discussion1 are available to those with a sincere and impatient interest in such matters. The rest may get the general drift of things from the following brief account and from a note by Muetterties.2

If we consider, for example, a trigonal bipyramidal molecule with five differently labeled substituents, the labels of the twenty isomers can be assigned in an arbitrary but systematic way as follows:

\[
\begin{align*}
a & \quad (1,2) \quad (3,4,5) \\
b & \quad (1,3) \quad (2,4,5) \\
c & \quad (1,4) \quad (2,3,5) \\
d & \quad (1,5) \quad (2,3,4) \\
e & \quad (2,3) \quad (1,4,5) \\
f & \quad (2,4) \quad (1,3,5) \\
g & \quad (2,5) \quad (1,3,4) \\
h & \quad (3,4) \quad (1,2,5) \\
i & \quad (3,5) \quad (1,2,4) \\
j & \quad (4,5) \quad (1,2,3)
\end{align*}
\]
The convention used is explained by the diagrams below, which also show a "pseudo-rotation" process.

The network of possible unrestricted isomerizations may be represented by the geometric figure projected in Figure 1. Such diagrams may be used to analyze the "pseudorotation" process in molecules in which some constraints are imposed upon such processes. For example, in a spiro compound in which rings join positions 1 and 2 and also 3 and 4, and the latter ring cannot accommodate a 120° angle, only the isomers marked by filled circles and the processes indicated by solid lines in Figure 2 are allowed. Note that racemizations (e.g., c to c′) are not permitted. Topological analyses of this kind seem to have considerable potential usefulness in analysis of complex isomerization processes and of the averaging of resonance signals. Applications to other systems are under study by several groups.

Yours truly,

Paul C. Lauterbur
Associate Professor of Chemistry

FIGURE 1

FIGURE 2
Subject: $^{19}\text{F} \text{NMR of } ^{13}\text{CP}_2\text{I} - ^{13}\text{CP}_2\text{I}$

Dear Prof. Shapiro,

We have recently studied the $^{19}\text{F}$ NMR spectrum of $^{13}\text{CP}_2\text{I} - ^{13}\text{CP}_2\text{I}$ over a range of temperature and we would like to give a preliminary account of it to the readers of the Newsletter. The $^{13}\text{CP}_2\text{I}$ is an example of an AA'BB'X type system, where X is the $^{13}\text{C}$ nucleus. The NMR spectrum at probe temperature (+35°C) of the AA'BB' part, for the molecule in natural abundance, is shown in Fig. 1. In Fig. 2 the expanded low-field band with the corresponding calculated spectrum is reported. Several spectra were obtained at +110°C, -30°C and probe temperature (+35°C). The experimental results of N and L are collected below, together with those already known$^1$ of $^{13}\text{CP}_2\text{Cl} - ^{13}\text{CP}_2\text{Cl}$ and $^{13}\text{CP}_2\text{Br} - ^{13}\text{CP}_2\text{Br}$. It is interesting to note that, whereas the numerical value of L increases substantially when the temperature is lowered, the value of N, even if the change is less marked, seems to vary in the same direction. This means that N and L values of $^{13}\text{CP}_2\text{I} - ^{13}\text{CP}_2\text{I}$ are likely to have opposite signs, contrary to the results of $^{13}\text{CP}_2\text{Cl} - ^{13}\text{CP}_2\text{Cl}$ and $^{13}\text{CP}_2\text{Br} - ^{13}\text{CP}_2\text{Br}$.
Following well-established procedures and using an energy difference, \( \Delta E \), between trans and gauche isomers of 1800 cal/mole, coupling constants in the two possible rotational isomers were calculated.

A detailed account of this work will be sent soon for publication.

Yours sincerely,

Luciano Cavalli

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<th>( \phi )</th>
<th>N</th>
<th>L</th>
<th>( T^o )</th>
<th>( J_t )</th>
<th>( J_g )</th>
<th>( J_t^* )</th>
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1) R.K. Harris, N. Sheppard
   Trans Faraday Soc. 52, 606, 1963

2) G. Serboli, B. Minasso
### Author Index - TAMU NMR Newsletter No. 119

<table>
<thead>
<tr>
<th>Author</th>
<th>Index</th>
<th>Author</th>
<th>Index</th>
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<tr>
<td>Bartlett, C.J.S.</td>
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<td>Harris, R.K.</td>
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<td>Basalay, R.J.</td>
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<td>Jacquier, R.</td>
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<td>Markley, J.</td>
<td>36</td>
<td>Smidt, J.</td>
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<td>Martin, J.C.</td>
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<td>Vignollet, Y.</td>
<td>26</td>
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<td>Green, R.D.</td>
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<td>Wind, R.A.</td>
<td>24</td>
</tr>
</tbody>
</table>

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