

Illinois
Institute of
Technology
N-M-R
Newsletter

No. 112
JANUARY, 1968

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These restrictions apply equally to both the actual Newsletter participant-recipients and to all others who are allowed access to the Newsletter issues. Strict adherence to this policy is considered essential to the successful continuation of the Newsletter as an informal medium of exchange of NMR information.

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Deadline Dates: No. 113: 6 February 1968
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Reminder: For the period August 10, 1967 to August 15, 1968 inclusive, all
Newsletter contributions, enquiries, etc., should be addressed as
follows:

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

-continued on outside back cover

THE UNIVERSITY OF CONNECTICUT

SCHOOL OF LIBERAL ARTS AND SCIENCES

December 7, 1967

Dr. Bernard L. Shapiro
Department of Chemistry
Stanford University
Stanford, Calif. 94305

Dear Barry:

Queries and Integration

1. When NMR Specialties first made available their heteronuclear decoupler for the A-60 they were confident it was only a matter of months before homonuclear decoupling could also be performed. Since then--silence. Has anyone in the audience successfully modified the HD-60A for homonuclear decoupling?

2. Since obtaining our Cat we have encountered some problems regarding signal triggering. Use of internal TMS as a trigger leads to observable side bands which sometimes ~~interferes~~ with the high-field portion of the spectrum. This is particularly acute in our A-60, where we run well above Varian's specs of 1% or less spinning sidebands. Ideally we would like a secondary standard, having most of the attributes of TMS but coming into resonance at very low field or, perhaps, to higher field of TMS. We would welcome suggestions to this problem.

3. Recently the question of integrating simultaneous with spectrum recording has been raised and solutions presented in recent issues. We have been doing this for several years with begged, borrowed (but never stolen) equipment, utilizing a voltage-to-frequency converter coupled to a counter connected to a digital printer. Recently several firms have come out with digital integrators utilizing precisely the same scheme and with such adjuncts as slope and threshold detection, etc. Although advertised for v.p.c. applications they should be near ideal for n.m.r. work. Some of these integrators also have a time base sensing peak maxima. This could be used to advantage in automatically determining peak positions in complex spectral multiplets.

Sincerely,

STORRS, CONNECTICUT 06268

Eugene I. Snyder
Eugene I. Snyder
Assistant Professor of Chemistry

THE LILLY RESEARCH LABORATORIES

ELI LILLY AND COMPANY • INDIANAPOLIS, INDIANA 46206 • TELEPHONE (317) 636-2211

December 8, 1967

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

Dear Dr. Shapiro:

I have very recently joined the staff of the Molecular Structure Determination Section of Eli Lilly and Company, and both Dr. Boaz and myself will in future share the responsibility of maintaining the Lilly subscription to I.I.T.N.N.

Our new Varian HR-100 has just arrived, and I had hoped to send you some results from the machine. However, since our contribution is overdue and since the HR-100 is not expected to be in operation for at least another month, I have decided to forward this note without further delay.

Title: Nature of the Screening Around C=C and C=O Bonds

We have for some time now been engaged in the calculation of nuclear screening changes produced when a C=C or C=O bond is substituted into a molecule¹. Using the McConnell² point dipole approximation as the foundation of our approach, we have attempted to derive a relatively simple but theoretically justified method for the quantitative estimation of nuclear screening changes in a molecule. In the course of this study, we have derived anisotropy values for C-C, C-H, C=C and C=O bonds. These values are shown below (in cm³ molecule⁻¹), and the values reported here are the best ones attained to date (i.e. values which give best agreement between observed and calculated shift values).

$$\begin{array}{ll}
 \Delta\chi_{\text{C-C}} &= + 11.3 \times 10^{-30} & \Delta\chi_{\text{C-H}} &= + 7.5 \times 10^{-30} \\
 \Delta\chi_{\text{C=C}} &= - 12.0 \times 10^{-30} & \Delta\chi_{\text{C=C}} &= -12.1 \times 10^{-30} \\
 \Delta\chi_{\text{C=O}} &= - 39.9 \times 10^{-30} & \Delta\chi_{\text{C=O}} &= -25.9 \times 10^{-30}
 \end{array}$$

* Anisotropy values derived assuming electric and magnetic point dipoles are situated on oxygen atom of carbonyl group.

Dr. Shapiro, December 8, 1967, Page 2

Using the appropriate bond constants listed on the previous page and exercising the necessary caution to avoid violating any of the four "golden rules" (listed below and enclosed in a box for the sake of emphasis*) a considerable degree of quantitative success has been achieved in these calculations.

- Rule I: R the vector distance between the distant group of electrons and the proton under consideration must be equal to or greater than approximately 3Å.
- Rule II: The McConnell equation is not a valid approximation for bonds which do not possess axial symmetry (i.e. C=C and C=O bonds). In these cases the modified McConnell equation¹ must be employed (See Fig. 1).
- Rule III: In calculating the change in screening a given proton experiences upon functionalization of a molecule the screening contribution of all bonds displaced as well as of all bonds introduced upon substitution must be considered in the calculations.
- Rule IV: If gross conformational changes occur as a result of the introduction of a bond or functional group into a molecule, these calculations are no longer valid (i.e. conformational parity must be maintained.).

Calculated shifts for the C-18 and C-19 methyl protons of steroidal androstene and androstanone derivatives, with few exceptions, fall within the ± 3 and ± 4 c/s range of the shift values observed upon introduction of a C=C or C=O bond respectively into the molecule. Similar agreement has been attained for a wide variety of other structural types and a manuscript reporting these results is currently in progress.

I would like to report here the geometrical dimensions of the screening environment around C=C (correction of the value reported earlier in Tetrahedron, 23, p. 2364 (1967)) and C=O bonds recently determined with the aid of the IBM 360 computer here at Lilly. Using equation 1 (Setting $1/3R^3 = 1$) and varying both θ and γ in units of 1° from 0° to 90° , essentially 8100 values (90×90) are calculated for σ . A plot of θ vs γ then reveals the sign of σ (See Fig. 2) for any given combination of the angles θ and γ . The area inside either curves is deshielding whereas the area outside either curve is shielding.

The most obvious point to emerge from this study is that the screening 'cone' or environment around a C=C or C=O bond, derived from equation 1 (See Fig. 1), is considerably different

* Those who have applied this approach with relatively little quantitative and/or qualitative success, should check for any violation of the below-listed rules.

Dr. Shapiro, December 8, 1967, Page 3

from the one presented by Jackman³. The plot of θ vs. γ in Fig. 2, which indicates the shielding and deshielding regions or the magnetic anisotropy around C=C and C=O bonds, clearly implies that, contrary to Jackman's model³, it can no longer be considered a general rule that a proton situated in the plane of a C=C or C=O bond is always deshielded. Indeed, it is quite possible that the reverse can be the case and very recently evidence has been presented in support of this model⁴.

Sincerely yours,

Paul V. Demarco

Paul V. Demarco
Molecular Structure Department

PVD:tc

- 1) J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, L. Saunders, and W. B. Whalley, Chem. Comm. 359 (1966); J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, A. K. G. Nasser, L. Saunders and W. B. Whalley, Chem. Comm. 754 (1966); J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, L. Saunders and W. B. Whalley, Tetrahedron, 23, 2339, 2357, 2375 (1967).
- 2) H. M. McConnell, J. Chem. Phys. 27, 226 (1957).
- 3) L. M. Jackman, Applications of Nuclear Magnetic Resonance in Organic Chemistry, p. 129. Pergamon Press, Oxford (1962).
- 4) G. J. Karabatsos, G. C. Sonnichsen, N. Hsi and D. J. Fenoglio, J. Am. Chem. Soc. 89, 5067 (1967).

$$\sigma = \frac{1}{3R} \left[\Delta\chi_1 (1-3\cos^2\theta) + \Delta\chi_2 (1-3\sin^2\theta.\sin^2\gamma) \right] \quad \text{Eq. 1}$$

Figure 1

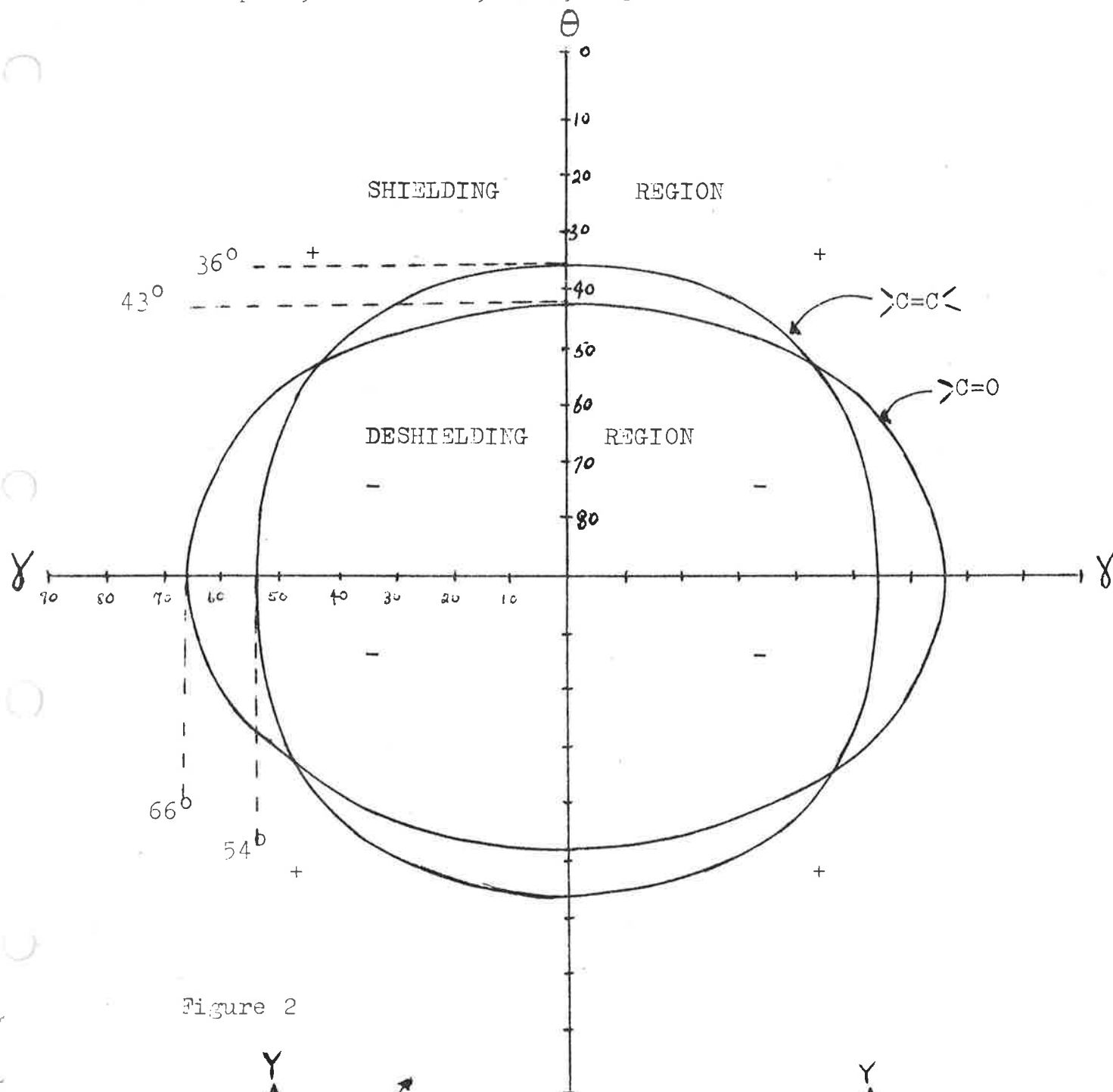


Figure 2

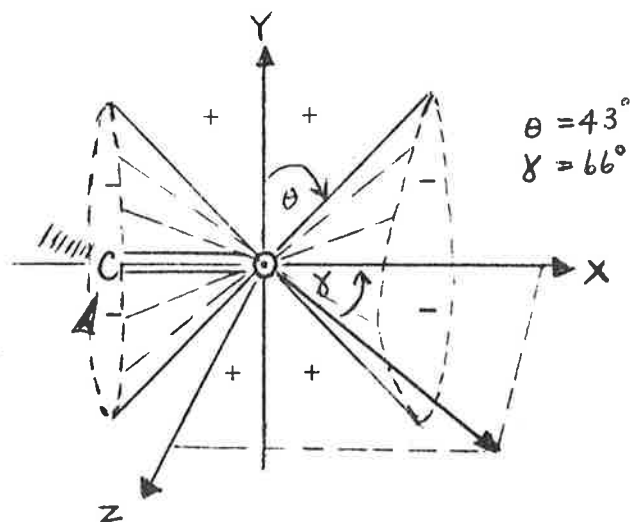
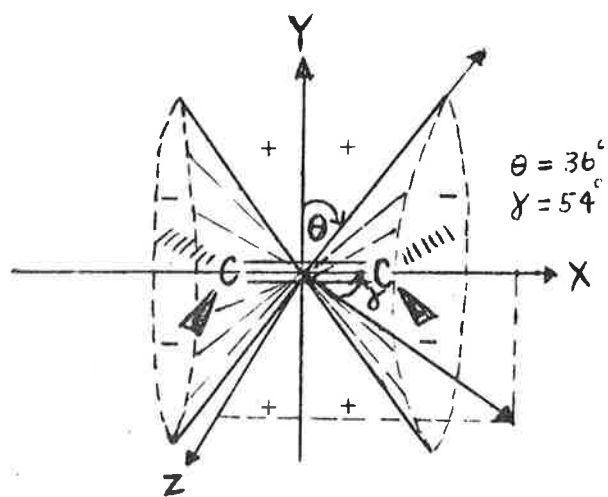


Figure 3

Gulf Research & Development Company

A. Bruce King
 Chief Scientist
 Research & Development

P. O. Drawer 2038
 Pittsburgh, Pa. 15230

ALUMINUM-27 NUCLEAR MAGNETIC RESONANCE OF TRIALKYLALUMINUM COMPLEXES

Dear Dr. Shapiro:

We have made aluminum-27 nuclear magnetic resonance studies on the complexes formed between various trialkylaluminum and nitrogen donor molecules. The line-broadening mechanism is the interaction of the nuclear electric quadrupole moment of the aluminum nucleus with the field gradient about the nucleus. The temperature and viscosity effects have been eliminated by obtaining infinite dilution line widths at constant temperature. Assuming extreme narrowing, the spin lattice relaxation time T_1 equals the spin-spin relaxation time T_2 and it is given by the following equation:

$$\frac{1}{T_2} = \frac{3\pi^2}{10} \cdot \frac{2I+3}{I^2(2I-1)} \cdot \left(1 + \frac{\epsilon^2}{3} \right) \cdot \frac{eQ\partial^2 V}{h \partial Z^2}^2 \cdot \frac{V_m \eta}{kT}$$

ϵ is the asymmetry factor, Q is the electric quadrupole moment, $(\partial^2 V / \partial Z^2)$ is the gradient of the electric field at the nucleus, V_m is the molar volume of the complex and η is the viscosity. It is expected then that the line width will depend on the molar volume of the complex (see attached figure).

The explanation of the deviation of ΔH from the linear dependence on V_m would have to be sought in terms of changes in the size of the axial component of the electric field gradient. Such changes could be effected quite readily by steric factors.

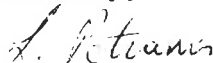


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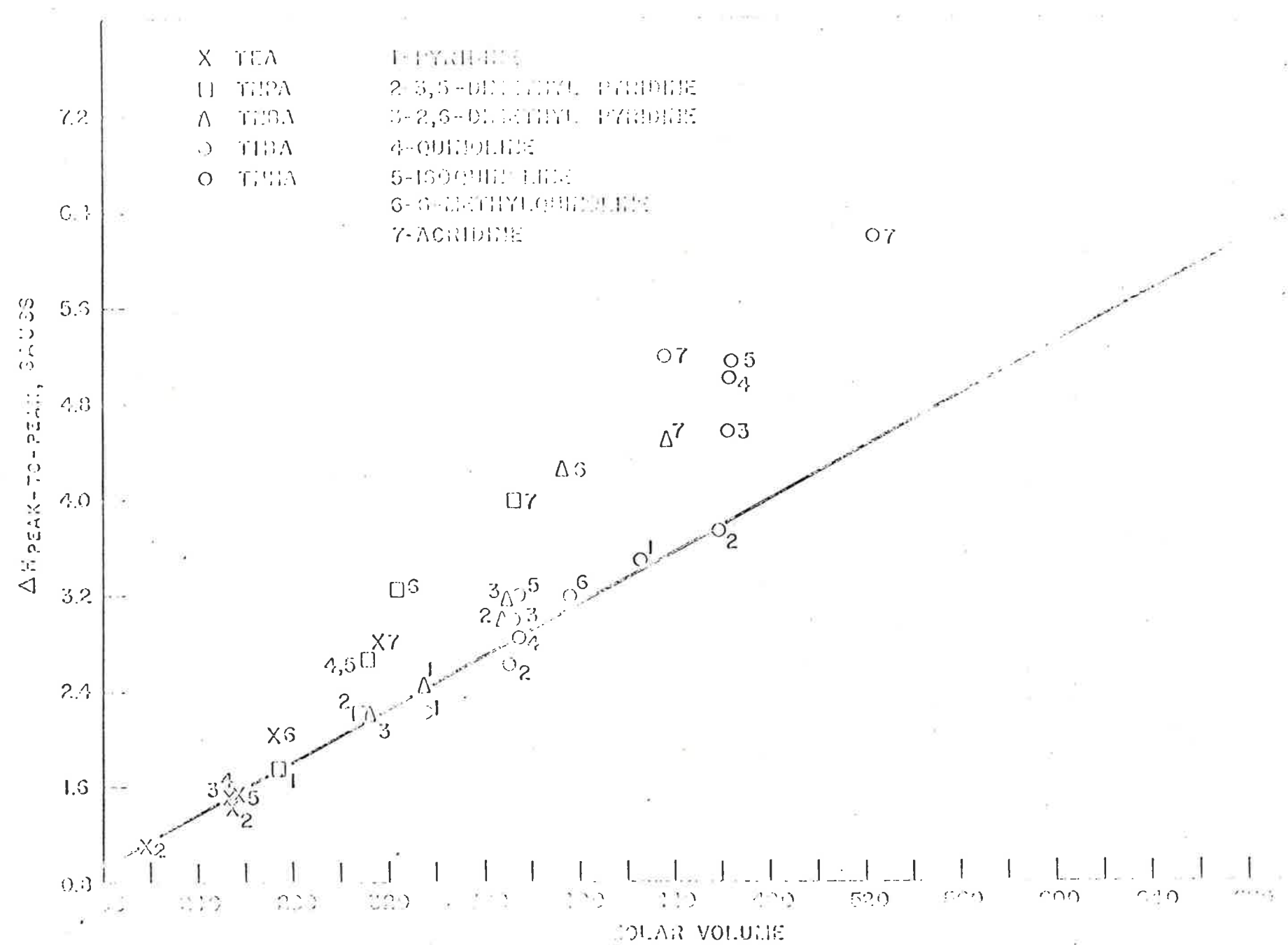
For a given donor, as the aluminum alkyl changes from TEA to TNHA, the complex becomes progressively a prolate spheroid with the result that the electric field symmetry about the aluminum is lower, the axial component of the field gradient is increased, and, therefore, the line broadens. Of course, if the donor also changes from, for example, pyridine to isoquinoline, this effect would be expected to become even more pronounced. The existence also of bulky groups close to the point of the complex formation would cause further broadening of the line.

Steric factors then, in addition to molar volume of the complexed studied, play an important role in determining the line widths. The observed line widths correspond to nuclear quadrupole coupling constants which are reasonable for the aluminum nucleus. A more detailed account of this work will appear shortly in the JOURNAL OF PHYSICAL CHEMISTRY.

Sincerely,



L. Petrakis



KEMISK INSTITUT
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112-9
Dec. 8th 1967
HeL/HJJ/EL

Dr. Bernard L. Shapiro
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Stanford University
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USA

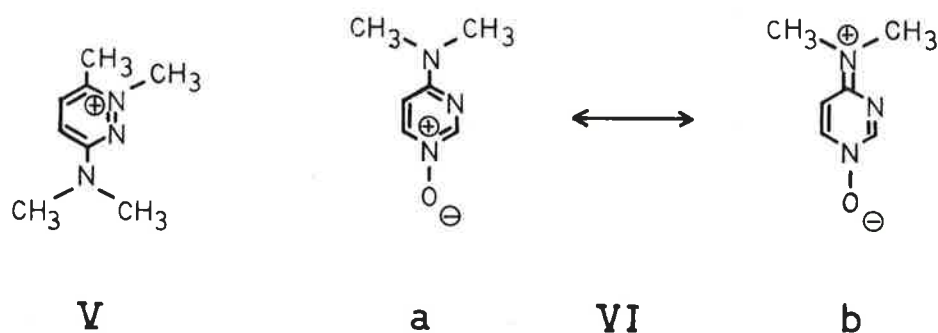
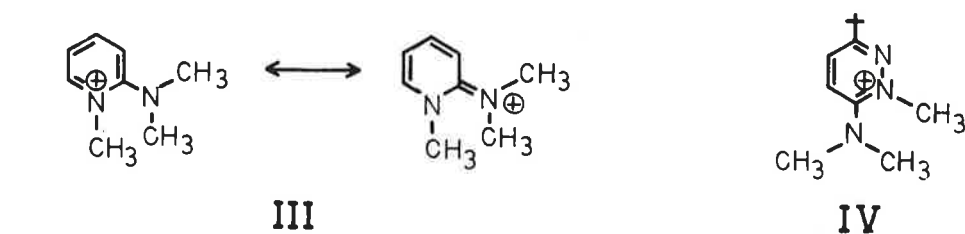
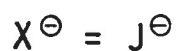
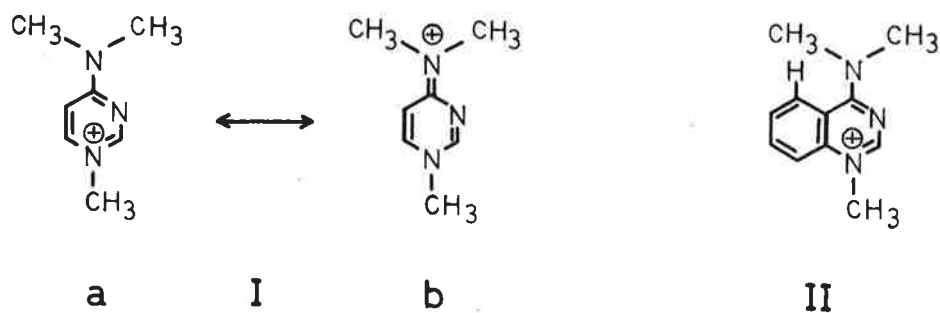
Hindered Internal Rotation in Quaternary N,N-Dimethyl-
aminosubstituted Azaheterocyclic Compounds.

Dear Dr. Shapiro,

We would like to report the results of some recent studies on the temperature dependence of the PMR spectra of ring-quaternized N,N-dimethylaminosubstituted nitrogen heteroaromatic compounds. It was observed that the signal from the dimethylamino protons, in compounds such as I, II, V, and VI, at different temperatures gives rise to two separate peaks due to hindered rotation about the ring-N(CH₃)₂ bond.

In the Table are reported some of the obtained results. The highest barriers are found in compounds as I where the dimethylamino group is "para" to the quaternized nitrogen atom; this would be expected from considering the structures Ia and Ib, which suggest that a charge delocalisation is possible when the methyl groups are in the plane of the aromatic ring. The barriers in the parent compounds were too low to be observed.

-2-



TABLE

Compound	Solvent ^a	T _c (±2°C)	Δv _{AB} ^b c/sec	ΔF _{T_c} [‡] (kcal/mole)
I	D ₂ O	87°	4.3	19.6 ± 0.2
I	DMSO-d ₆	82°	2.5	19.7 ± 0.2
II	(CD ₃) ₂ CO-D ₂ O (4:1)	20°	12.2	15.2 ± 0.2
V	(CD ₃) ₂ CO	-50°	6.5	11.7 ± 0.2
VI	CDCl ₃ -CS ₂ (1:2)	-30°	10.2	12.6 ± 0.2

^a Ca. 10 % (w/v) solutions in all cases.

^b Separation of N-Me signals in c/sec at 60 Mc/sec and at temperatures well below T_c.

-3-

The same considerations would apply to "ortho" substituted compounds such as II and IV. No barrier has been observed in these cases, however, and it is believed that the steric hindrance from the 1-methyl groups prevents the dimethylamino group from attaining coplanarity with the ring. Similarly, the steric interference from H-5 in II may be responsible for the somewhat lower barrier of II compared to that of I.

Compounds having the dimethylamino group "meta" to the quaternized nitrogen atom have low barriers, as expected; the presence of a barrier of the observed size shows that a considerable charge-transfer takes place between the ring and the dimethylamino group.

A lower barrier is found in corresponding N-oxides (VIa,b). A methylation or a coordination of the oxygen atom with an electrophilic reagent would be expected to raise the barrier.

Further studies along these lines are in progress.

Sincerely yours,

Hans J. Jakobsen

Hans J. Jakobsen

Henning Lund
Henning Lund



QUEEN MARY COLLEGE

(UNIVERSITY OF LONDON)

MILE END ROAD · E.1

TELEPHONE · ADVANCE 4811

DEPARTMENT OF CHEMISTRY

14th December, 1967.

Professor B.L. Shapiro.

Dear Barry, Post-doctoral vacancy; P^{31} contact shifts; N^{15}

Sorry you have been put to the expense of subscription reminders.

Personnel news here is that Derek Shaw is forsaking us for Varian at Walton. He will thus add to the concentration of ex-group members south of the Thames, since Duncan Gillies is now at Royal Holloway College. Derek's post-doctoral position is thus open to applicants.

Derek has spent more time on phosphine complexes both paramagnetic and diamagnetic. We now have some P^{31} spectra taken with borrowed Varian accessories and our HA.100: $Re\ N\ Cl_2\ (P\ Me\ Ph)_3$ (diamagnetic) and $Ir\ Cl_3\ (P\ Me_2\ Ph)_3$ also diamagnetic) give two phosphorus resonances in the ratio of 2:1 with separation of 12.4 and 8.85 ppm respectively. The large peak in each case comes from mutually trans phosphorus atoms and has 'wing' lines since the phosphorus atoms are magnetically inequivalent. The trans $P^{31} - P^{31}$ coupling appears to be 320 and 310 ± 5 c/s respectively.* Incidentally we checked the 8.85 ppm shift by decoupling at 9,000 grams and obtained the figure 9.1 ± 0.8 ppm. More exciting perhaps are the results for paramagnetics. For example $Os\ Cl_4\ (P\ Pr_2\ Ph)_2$ gives a contact shifted P^{31} resonance 1205 ± 1 ppm to high field of phosphoric acid. No signals were detected for a number of $Re\ Cl_3\ (PR_2\ Ph)_3$ complexes in the region ± 1500 ppm. We think it highly significant that for the former case $P^{31} - H$ coupling is observed in the proton region whereas in the latter cases 'decoupled' spectra, which we thought arose from fast P^{31} relaxation, are obtained (Chem. Comm. 1965, 82).

Readers may be interested in the proton spectrum of pyridine- N^{15} which Rod Chuck (now migrated to the Rockies via Peter Diehl in Switzerland) obtained over a year ago. We look forward to tickling the N^{15} region when our new probe arrives and the heteronuclear double resonance facility becomes operational on our HA.100.

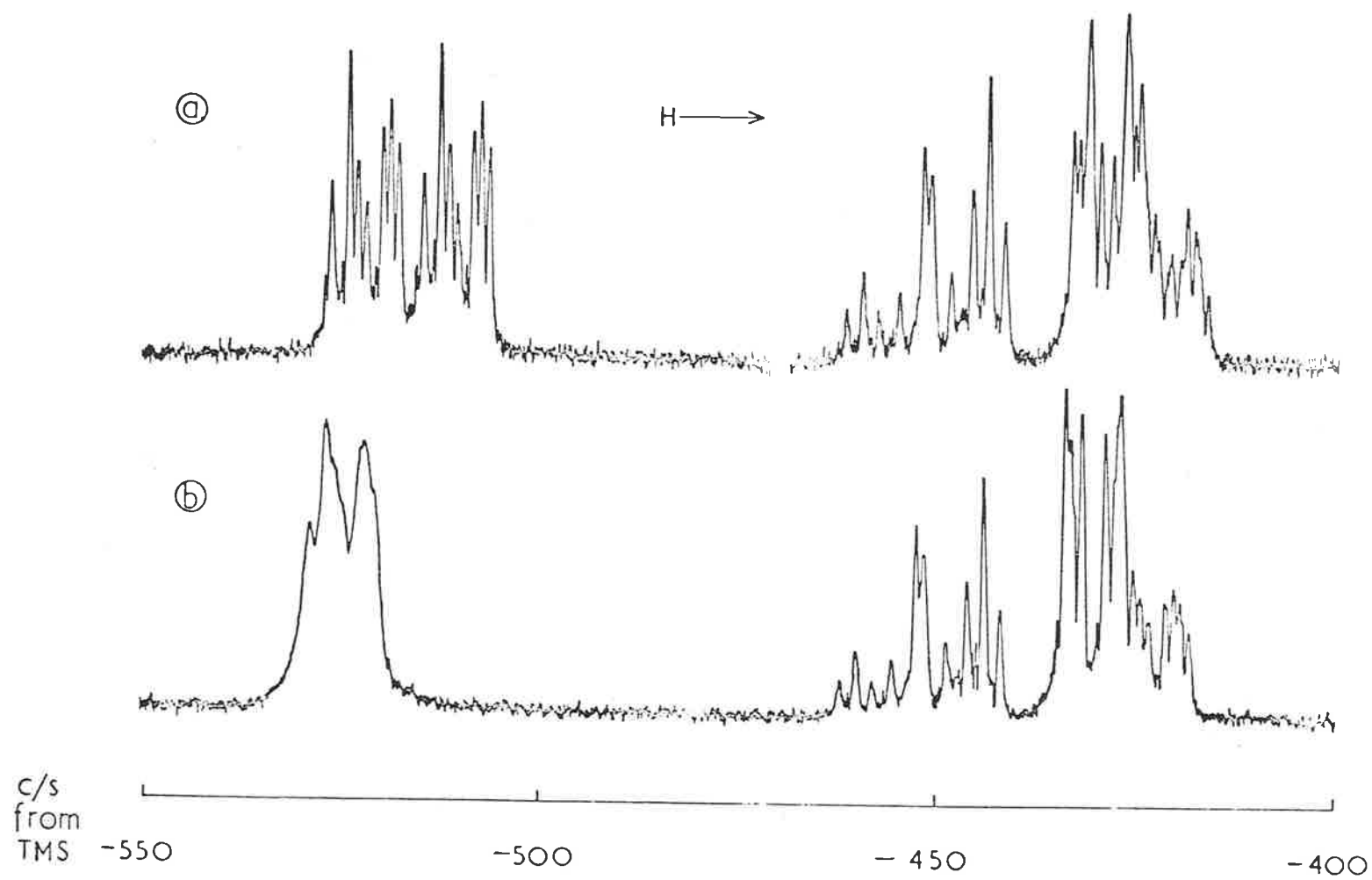
Other N^{15} work will include shift measurements for the substituted anilines- N^{15} which Malcolm Bramwell has been making. Some $N^{15} - H$ couplings (c/s) for acetone solutions of substituted anilines are p- NO_2 , 88.4; p-Br, 83.6; p-I, 84.1; 2,4,6 tri Br, 88.0; 2,4 di Br, 86.0; m- NO_2 , 83. These compare with 81.9 c/s for aniline in acetone.

Best regards,

Ed

E.W. RANDALL.

* Subject to confirmation.



p.m.r. spectra at 60Mc/s of (a) Pyridine-¹⁵N, and (b) Pyridine-¹⁴N.



TEXAS CHRISTIAN UNIVERSITY

Fort Worth, Texas 76129

Department of Chemistry

December 15, 1967

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

More on the Q Relation and a Postdoctoral Position

Dear Barry:

The use of the semiempirical parameter Q , first defined by Hruska, Hutton, and Shaefer, *Can. J. Chem.*, **43**, 2392 (1965), has been extended by the determination of Q values for a number of functional groups. Using the technique recently described by us (*J. Am. Chem. Soc.*, **89** 5018 (1967)) we have arrived at the following additional Q values: NH_2 -0.9; *t*-butyl 2.4; and nitro either 4.0 or 6.5.

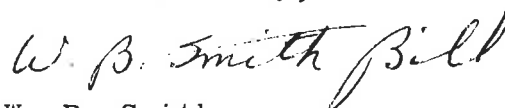
As you will recall, the value for Q^{NO_2} of 4.0 was derived from a series of ortho disubstituted benzenes and served to correlate the chemical shifts of protons ortho to the nitro group with the shifts and Q values for similar protons adjacent to a variety of functional groups. However, the value of 6.5 is required to place the ortho proton in nitrobenzene on the Q - shift plot for the monosubstituted benzenes. This value appears now to be required whenever one has a nitro group flanked by two hydrogens or, indeed, any situation where the nitro group is coplanar with the aromatic ring. Situations which seem to require the 6.5 value may be summarized as follows: monosubstituted benzenes, para and meta disubstituted benzenes, proton 3 in the 2-substituted pyridines, the ortho substituted phenols in carbon tetrachloride, and for proton 3 in the ortho substituted fluoro-benzenes.

The value 4.0 is used for ortho disubstituted benzenes where the ortho substituent is larger than fluorine. Included in the list are the ortho phenols in DMSO. Situations where the resonance interaction is too weak to demand coplanarity of the nitro group also require the 4.0 value. These are found for the cis vinyl proton and H₃ in the 2-substituted pyridinium ions.

We appear to be able to draw reasonable conclusions about the conformation of the nitro group in a variety of situations using the Q - chemical shift plot relation.

Finally, I have a good postdoctoral position available for NMR research starting in September, 1968. If anyone has an interested party, please have them contact me.

Yours sincerely,

A handwritten signature in cursive script that reads "W. B. Smith" followed by a stylized flourish that looks like "Bill".

W. B. Smith
Chairman
Department of Chemistry

WBS:lb



THE UNIVERSITY OF SUSSEX
THE CHEMICAL LABORATORY FALMER BRIGHTON SUSSEX

Professor J. N. MURRELL

Telephone: Brighton 66755

12th December, 1967.

Professor B. L. Shapiro,
Department of Chemistry,
Stanford University,
Stanford,
California 94305, U.S.A.

Dear Professor Shapiro,

A NATO Summer School on N.M.R. at the University
of Coimbra, Portugal

May I take the opportunity of the wide circulation
of your Newsletter to announce a NATO sponsored Summer
School on N.M.R. Spectroscopy which is to be held at the
University of Coimbra, Portugal, for the period 9-20th
September, 1968.

The School will be concerned with the interpretation
and analysis of N.M.R. spectra and the theory of chemical
shifts and coupling constants. Some financial support
may be available for participants.

Further information can be obtained from Dr. V.M.S.
Gil, The Chemical Laboratory, University of Coimbra.

Yours sincerely,

John Murrell

Carnegie-Mellon University

Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania 15213
[412] 621-1100

14 December 1967

Dr. B. L. Shapiro
Department of Chemistry
Stanford University
Stanford, Calif.

Re: Spectral Parameters of Fluorobenzene

Dear Barry:

In the last issue of IITNMR Newsletter 110, 34, Tom Page gave an analysis of fluorobenzene. We have also been working on this (and other) monosubstituted benzenes*, and since our results differ significantly from Tom's, we give them herewith (Table I). Incidentally, I believe that the statements reported by Tom concerning the expected symmetry of the spectrum from a nucleus lying on a plane of symmetry of the molecule, and the effect of a negative coupling constant on that symmetry are incorrect.

In Table I the labelling of the aromatic protons goes from 1 to 5 around the ring, the number 6 being used for the fluorine nucleus. All data are given in cps; the chemical shifts are always referred to TMS at 60.0 Mcps.

The data of entries 1 and 2 were obtained from the analyses of the proton spectra recorded at 60.0 Mcps; those of entries 3 and 4 from the analysis of both the proton and fluorine spectra recorded at 60.0 and 56.4 Mcps respectively. The proton spectra of the latter two entries were recorded with 25 and 50 cps full sweep widths. The data of entry 5 represent the results of the analyses of the proton and fluorine spectra recorded at 100.0 and 94.1 Mcps respectively; the corresponding experimental and calculated spectra are given in Figures 1,2.

In all the analyses the calculated probable errors of each parameter, as given by the LAOCN3 program, were always smaller than 0.01 cps, but those of $J(1,6)$ and $J(3,6)$ were in any case larger than the average value. In the last column of the Table, I have reported the average values of the chemical shifts (entries 3,4,5) and of all the coupling constants (all entries), their standard deviations (in parenthesis) and the corresponding probable errors. The latter, corresponding to 3 (chemical shifts) and 5 (coupling constants) independent determinations furnish a measure of the accuracy of the results whereas those obtained from the LAOCN3 program give, provide the analysis is correct, a measure of the precision of the data. The two sets of errors must not necessarily agree as it is immediately apparent considering the results obtained for the three chemical shifts and for $J(2,3)$, $J(1,6)$, $J(2,6)$, and $J(3,6)$. Roughly speaking the LAOCN3 program takes

B. L. Shapiro

-2-

14, December 1967

into account only the experimental errors with normal distribution whereas the accuracy of the parameters is also affected by all the systematic errors of instrumental and human nature. For reason of space this point will be made clearer and illustrated with a larger number of examples in a forthcoming paper.

The averaging procedure here adopted to determine the accuracy of the data should be restricted to the parameters obtained from repeated analysis of spectra recorded on the same sample (as done for the three chemical shifts); I believe however that the differences of the values of all proton-proton coupling constants are within the experimental errors and that no solvent or concentration effects on these parameters can be deduced from our results. The latter, however, are quite different from those reported by T. Page and the discrepancies between the two sets of data are, on the average 20 times larger than the estimated limit of accuracy.

In the case of the proton-fluorine coupling constants, the averaging procedure leads quite surely to wrong results since there are evidences that these parameters may be solvent, concentration, (and perhaps temperature???) dependent. It must be, however, pointed out that because of the very small difference between the values of the chemical shifts of the ortho and para protons, the $J(1,6)$ and $J(3,6)$ coupling constants are intrinsically the most ill-determined parameters.

This work was performed with the collaboration of R. Kostelnik and C. Sun and I hope that you will consider this contribution fiscally valid in their behalf.

Cordially yours,

S. Castellano

SC:hb

- * Data on fluorobenzene have been reported in the following publications:
S. Castellano and C. Sun, J. Am. Chem. Soc. 88, 4741 (1966);
S. Castellano, R. Kostelnik and C. Sun, Tetrahedron Letters, 46, 4635 (1967).

MELLON INSTITUTE

TABLE I

SPECTRAL PARAMETERS OF FLUOROBENZENE

Entry	1	2	3	4	5	Average	
Solvent	Neat	CCl_4	CCl_3CF_3	CCl_3CF_3	CCl_3CF_3		
Conc. (w/w)		10%	85%	85%	85%		
W(1)	411.880	418.361	413.388	413.418	413.296	413.367	$\pm .043$ (.064)
W(2)	424.333	434.458	426.025	426.063	426.000	426.029	$\pm .021$ (.032)
W(3)	413.764	422.066	415.318	415.375	415.264	415.319	$\pm .037$ (.056)
J(1,2)	8.361	8.363	8.362	8.374	8.341	8.360	$\pm .008$ (.012)
J(1,3)	1.073	1.069	1.053	1.060	1.060	1.063	$\pm .005$ (.008)
J(1,4)	0.429	0.433	0.401	0.422	0.417	0.420	$\pm .008$ (.013)
J(1,5)	2.766	2.738	2.754	2.745	2.749	2.750	$\pm .007$ (.011)
J(2,3)	7.393	7.468	7.428	7.428	7.445	7.432	$\pm .018$ (.027)
J(2,4)	1.808	1.821	1.803	1.802	1.810	1.809	$\pm .005$ (.008)
J(1,6)	9.084	8.914	9.018	9.016	9.114	9.029	$\pm .052$ (.077)
J(2,6)	5.742	5.687	5.686	5.690	5.676	5.696	$\pm .018$ (.026)
J(3,6)	0.236	0.221	0.306	0.299	0.342	0.281	$\pm .034$ (.051)

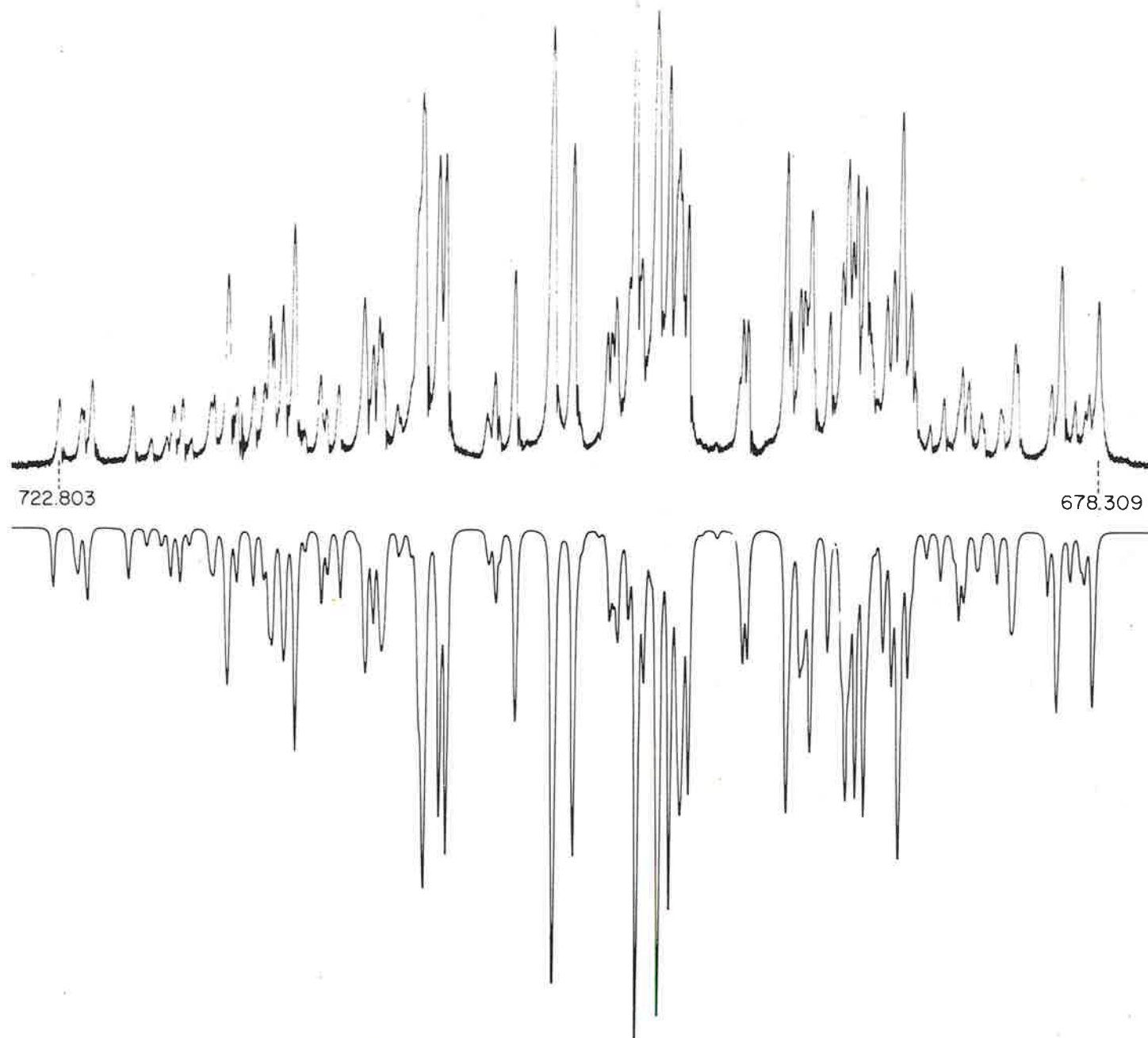


Figure 1. Experimental and calculated proton spectrum of fluorobenzene (100.0 Mc/sec)

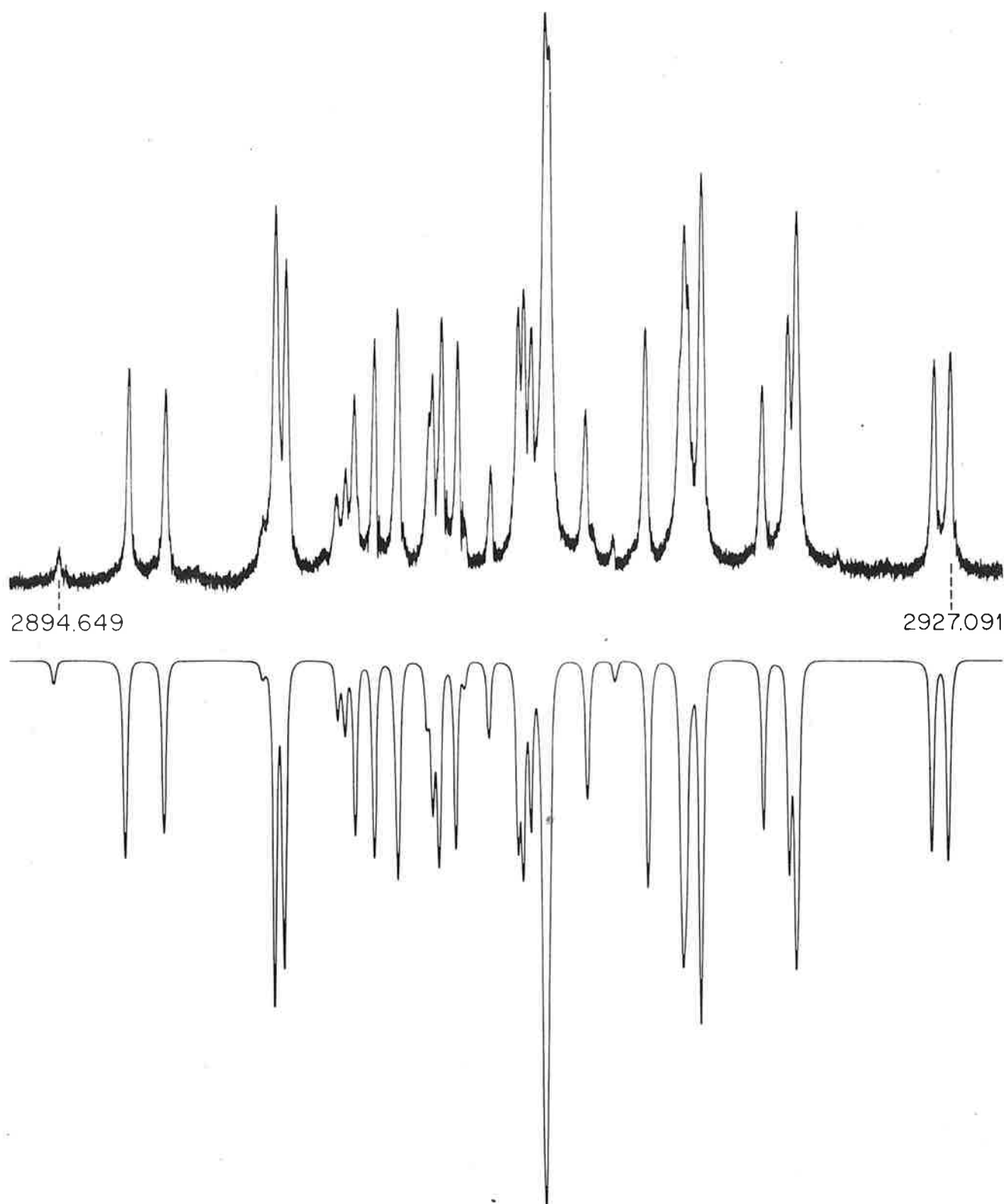


Figure 2. Experimental and calculated fluorine spectrum of fluorobenzene (94.1 Mc/sec)

PRINCETON UNIVERSITY
DEPARTMENT OF CHEMISTRY
PRINCETON, NEW JERSEY 08540

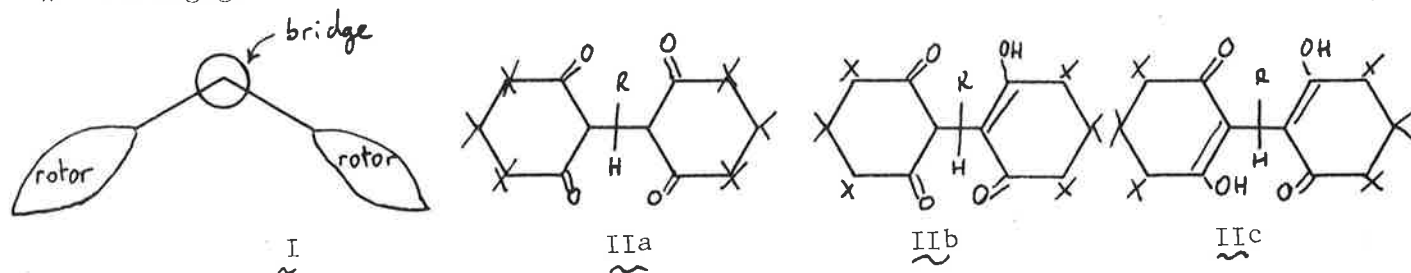
December 6, 1967.

Frick Chemical Laboratory

suggested title : Dynamic structure of Vorländer's compounds.

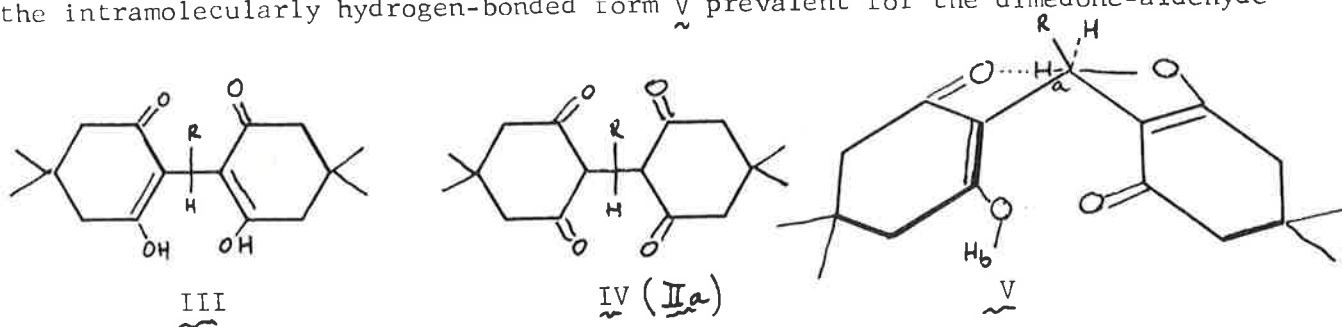
Dear Barry,

We are engaged in a structural and kinetic study of compounds in the general class I :



We have found the Vorländer¹ adducts of aldehydes and β -diketones to be very suitable. Various tautomeric forms, exemplified by the dimedone ($X = CH_2$) or the Meldrum's acid ($X = O$) adducts II, are possible and are easily distinguished by nmr. They correspond to either attractive or repulsive interactions between the two rotating moieties. The dimedone adducts examined so far exist as the dienolic form IIc, whereas the Meldrum's acid compounds exist in the tetraketonic form IIa. In IIc the geminal methyl groups are exchanged by the internal rotations and can thus be used to measure their rates. For instance, in the dimedone-benzaldehyde adduct (IIc, $X = CH_2$, $R = Ph$), $\Delta G^* = 15.8 \pm 0.2$ kcal./mole $\Delta H^* = 11.9 \pm 1.5$ kcal./mole $\Delta S^* = -13 \pm 5$ e.u. (in $CDCl_3$ solution, approximating the real multi-site situation with a 2-site analysis, which the data fortunately allows). These parameters are consistent with the transition state approaching the geometries of the intermediates III or IV.

In the intramolecularly hydrogen-bonded form V prevalent for the dimedone-aldehyde



adducts at low temperatures, the following structural features are important :

1. proximity of the syn substituent labilizes the enolic proton H_b which exchanges considerably faster than its partner. This is consistent with the idea that intramolecular $-OH...O=C<$ hydrogen-bonding is more favorable for H_a than for H_b .
2. in order to minimize non-bonded interactions between the R substituent and the syn groupings such as OH_b , the CHR bridge is tilted towards H_a which suffers a 0.7 ppm downfield shift when R is changed from H to CH_3 , C_2H_5 , iC_3H_7 , or tC_4H_9 . This shift is reciprocated in a downfield shift of the bridge methine proton of comparable magnitude.
3. for the alkyl-substituted compounds, the magnitudes of the observed vicinal coupling constants and their temperature invariance are only consistent with the rotamer having a C-H bond antiparallel with the bridge methine being the only present.

We are now synthesizing a variety of molecules of these and related types, to try to introduce hydrogen-bond acceptors in close proximity to the OH_b proton, for instance. We are collaborating on various aspects with Jim Morrison (University of New Hampshire) and with Sture Forsén (Royal Institute of Technology, Stockholm).

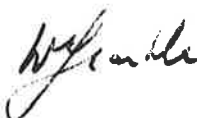
I also have an historical query for the newsletter readers : it is formulated on the accompanying sheet and, I hasten to say, is not subsidized by Le Comité National des Vins de France.

With best regards,

Sincerely,



Pierre Laszlo



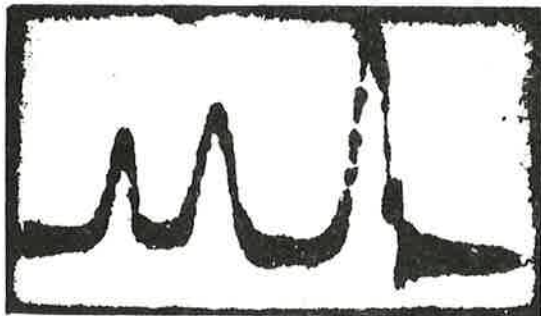
William E. Frankle



Janine Lubochinsky

- (1) D. Vorländer and J. Erig, Liebig's Ann. Chem., 294, 314 (1897).

In 1951, Arnold, Dharmatti, and Packard¹ published the first nmr spectrum of ethanol (why ethanol?), Fig. 1 :



They commented wisely "It seems to us that there may be certain chemical problems besides analysis, such as the study of chemical reactions and equilibria, which can be investigated by this method".

It appears that Arnold, a graduate student of Professor Bloch at Stanford (Bloch received the Nobel prize in 1952), decided not to build up a "Varian Catalog" which had to wait until 1962, but to concentrate upon this interesting ethanol sample.

This led him to notice, again in the company of Packard², and some other alcohol-philos³, the temperature dependence of the OH line. This shift to low-field with a decrease in temperature was readily attributed to association, the "hydrogen-bond shift" had been discovered, and was of course to prove itself to be quite fruitful.

The next chapters of this fairy tale, of this obsession with ethanol, are the understanding of the rules governing first-order spectra⁴, as well as higher-order effects and nmr spectral analysis in general⁴, and double resonance⁵. Arnold⁴ also noticed that the hydroxylic proton would appear as a triplet in purified ethanol, and collapse to a singlet in the presence of H⁺ or OH⁻ impurities :

"Regarding certain chemical problems, the use of high resolution nuclear magnetic resonance techniques may be useful in the study of rate processes, as for example exchange of the hydroxyl protons described above in a range of time intervals which has heretofore been inaccessible".

It remained for Grunwald, Meiboom and coworkers⁶ to examine mixtures of ethanol and water with acid or base catalysts in the range of 10^{-6} to 10^{-5} M, and the nmr study of protolysis reactions started.

(1) J.T. Arnold, S.S. Dharmatti, and M.E. Packard, J. Chem. Phys., 19, 507 (1951).

(2), (3) J.T. Arnold and M.E. Packard, J. Chem. Phys., 19, 1608 (1951), U. Liddel and N.F. Ramsey, *ibid*, 19, 1608 (1951).

(4) J.T. Arnold, Phys. Rev., 102, 136 (1956).

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

(6) E. Grunwald, C.F. Jumper and S. Meiboom, J. Am. Chem. Soc., 84, 4664 (1962).

Z. Luz, D. Gill and S. Meiboom, J. Chem. Phys., 30, 1540 (1959).

CHEMISCHES LABORATORIUM
DER UNIVERSITÄT MÜNCHEN
INSTITUT FÜR ORGANISCHE CHEMIE

8000 MÜNCHEN 2, 8. Dezember 1967
Karlstr. 23 - Tel. 59021

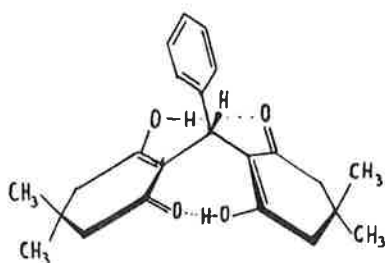
Prof. Dr. Herbert Zimmermann

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

Der Einfluß von Lösungsmitteln auf die konformative
Beweglichkeit eines Sechsringmoleküls.
Die Beschleunigung einer Protonenaustauschreaktion bei
abnehmender Temperatur.

Sehr geehrter Herr Professor Shapiro!

Wir haben das NMR-Spektrum des Addukts von Benzaldehyd an
Dimedon in konzentrierten Lösungen in verschiedenen Lösungs-
mitteln aufgenommen.



"Benzaldimedon"

Das Spektrum ist sehr lösungsmittelabhängig, wobei besonders
die Signale der beiden O-H...O-Wasserstoffbrücken und die der
Methylgruppen Aufschluß über die konformative Beweglichkeit

des Moleküls und seine Wechselwirkungen mit dem Lösungsmittel geben.

Die Koaleszenztemperatur für die Signale der Methylgruppen schwankt zwischen $\leq -30^{\circ}\text{C}$ in Pyridin und über $+32^{\circ}\text{C}$ in Toluol und CS_2 . Die Aktivierungsenergie für das Durchschwingen der $\text{>C(CH}_3)_2$ -Gruppe im Dimedonrest durch die Ringebene wird also weitgehend durch intermolekulare Wechselwirkungen bestimmt. Das ist verständlich, da die betrachtete Schwingung einen großen Raumbedarf aufweist.

Die OH-Signale zeigen, daß in den beiden Wasserstoffbrücken schneller Protonenaustausch stattfindet, jedoch nicht intermolekular oder zwischen den beiden Brücken außer in Pyridin als Lösungsmittel. Pyridin katalysiert den Protonenaustausch, man findet nur ein scharfes Signal bei $-1,7\tau$ für beide Protonen. Eine überraschende Temperaturabhängigkeit zeigt das Spektrum des Benzaldimedons in Chloroform. Während die beiden OH-Signale (τ -Werte: $-1,97$ und $+0,47$) bei $+32^{\circ}\text{C}$ vergleichbare Halbwertsbreiten von $16,5$ bzw. $18,6$ cps haben, verschärft sich das Signal des weniger abgeschirmten Protons beim Abkühlen auf -40° zu einer Halbwertsbreite von 2 cps (τ -Wert: $-2,1$), während das stärker abgeschirmte Proton nur noch schwer zu finden ist: Signalmitte etwa bei $-0,3\tau$, Halbwertsbreite ≈ 72 cps. Offenbar nimmt das Benzaldimedon in Chloroform bei tiefer Temperatur eine Konformation an, in der die Potentialminima der einen Wasserstoffbrücke einander genähert sind und der Protonenaustausch, im wesentlichen durch Tunneleffekt des Protons, erheblich beschleunigt ist. Der Protonenaustausch in der andern Brücke ist ent-

sprechend verlangsamt.

Die erwähnten Effekte treten bei den Addukten aus Acetaldehyd und Formaldehyd an Dimedon nicht auf.

Mit freundlichen Grüßen

H. Zimmermann

Frank Strohbusch

(Herbert Zimmermann)

(Frank Strohbusch)

PS: Wir ziehen um. Unsere neue Adresse ab Dezember 1967 ist:

Institut für Physikalische Chemie der Universität Freiburg
7800 - F r e i b u r g i.Br.
Hebelstrasse 38



DEPARTMENT OF CHEMISTRY
THE UNIVERSITY
SOUTHAMPTON
SO9 5NH

TEL. 0703-56331
TELEX 47661

13th December 1967

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

Dear Dr. Shapiro,

Those of your readers who are interested in the relationship between chemical shifts and π electron densities in aromatic compounds may be interested in the results of some calculations I have been doing. The Karplus and Pople equation, in the form using an average energy ΔE , when applied to carbon-13 chemical shifts gives the correct order of magnitude for the changes produced by substituents, and using a value of 10 eV for ΔE . But when applied to fluorine chemical shifts, the equation gives a result which is wrong on two counts. First, changes in the shielding constant produced by substituents are approximately ten times larger than calculated values, again using $\Delta E=10$ eV. This result is more or less independent of the method used to compute the σ and π electron densities. The same feature appears when the linear relationships between chemical shifts and electron densities are used, and it has been customary to gloss over this discrepancy by calculating a value of ΔE which will reproduce the observed chemical shifts. These experimental ΔE values thus are typically 1 eV or less. However, there appears to be no good reason why ΔE should be so much lower than any of the $\sigma-\pi^*$ excitation energies, moreover, the use of a low value of ΔE to explain large substituent shifts can be ruled out by noting that the magnitude of the paramagnetic contribution to the shielding of the fluorine nucleus in fluorobenzene has been measured to be -284 ± 10 ppm (S.I. Chan and A.S. Dubin, J. Chem. Phys., 46, 1745 (1967)). This value is about 5 times smaller than that calculated by the Karplus and Pople equation using $\Delta E = 10$ eV, and 50 times smaller if ΔE is adjusted to give the correct substituent shifts! I conclude from this that the Karplus and Pople equation when applied to fluorine cannot explain the observed shifts. The most probable explanation for this lies in using an expression for the average value of r^{-3} for a 2p electron

on fluorine which is strictly appropriate only for an isolated fluorine atom, in which the 2p orbital is singly occupied. For a situation in which fluorine has two electrons in a $2p\pi$ orbital the approximate formula is possibly inappropriate since the motion of the two electrons must be strongly correlated. The effect of electron correlation could be to keep the two electrons further from the nucleus and hence reducing the value of $\langle r^{-3} \rangle$ perhaps 5 fold. There may also be an increased dependence of $\langle r^{-3} \rangle$ on electron density.

You will see from the address on this letter that I have moved from Durham to Southampton. Southampton has acquired a large group of magnetic resonators and now has at present four permanent staff members working in this field: Professor Alan Carrington, Drs. Geoffrey Luckhurst and Richard Moss with prime interests in ESR, and myself on NMR. We have also acquired four new spectrometer systems: an HA 100 NMR, two of the large general purpose ESR spectrometers and an E3.

Yours sincerely,

.vvvv

J.W. Emsley.

JWE:js



Eidg. Technische Hochschule
Laboratorium für Organische Chemie
Zürich

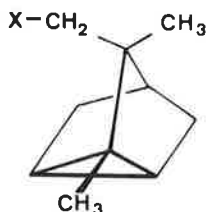
8006 Zürich, 21. Dezember 1967
Universitätstrasse 6
Tel. (051) 32 62 11

Professor B.L. Shapiro
Department of Chemistry
Stanford University
Stanford, California 94305
U S A

Sehr geehrter Herr Professor Shapiro,

Diastereotope Protonen in Π -Tricyclyl-quecksilber-chlorid

Im Rahmen von Untersuchungen über Alkylquecksilber-Komplexe mit chiralen Alkylgruppen wurde in unserem Laboratorium Π -Tricyclyl-quecksilber-chlorid (1) aus dem von Corey (1) beschriebenen Π -Brom-tricyclen (2) aufgebaut.



- 1 X: HgCl
2 X: Br

Im 60 MHz pmr-Spektrum (A) von Π -Brom-tricyclen (2) geben die diastereotopen Methylenprotonen erwartungsgemäss zu einem sauber aufgelösten AB-System bei 3,3 ppm Anlass. In Π -Tricyclyl-quecksilber-chlorid (1) hingegen erscheint das Signal der entsprechenden Protonen im 60 MHz-Spektrum (B) als Singlett bei $\delta_A \cong \delta_B \cong 2,03$ ppm.

Die auf den ersten Blick überraschendere Feststellung bestand jedoch darin, dass die durch Kopplung mit dem Quecksilberisotopen ^{199}Hg (natürliches Vorkommen 16,92%) auftretenden Satelliten der entsprechenden Protonen als gut aufgelöste

Vier-Linien-Systeme in Erscheinung treten. Die Kopplungskonstanten $J_{^1\text{H}-^{199}\text{Hg}}$ entsprechen in ihrer Grössenordnung der bei Methylquecksilberchlorid beobachteten Kopplung von 215 Hz (2,3).

Wir interpretieren dieses ungewöhnliche Spektrum in folgender Weise: Die Signale der diastereotopen Protonen der Molekeln mit kernresonanz-inaktiven Quecksilberisotopen weisen praktisch keinen Unterschied in ihrer chemischen Verschiebung auf. Aus dem 100 MHz-Spektrum (C) geht hervor, dass die chemische Verschiebung nur annähernd gleich, die Differenz jedoch kleiner als 0,04 ppm ist. Unter der Annahme, dass kein Isotopeneffekt vorliegt, kann das Vier-Linien-System der Satelliten nur von einem Unterschied der Kopplung von ^{199}Hg mit diesen Methylenprotonen herrühren. Die Satelliten stellen demnach den AB-Teil eines ABX-Systems dar, wobei

$$\delta_A \approx \delta_B \approx 2,03 \text{ ppm und } J_{AX} = 215,8 \text{ Hz, } J_{BX} = 190,2 \text{ Hz beträgt.}$$

Diese magnetische Inäquivalenz der beiden Protonen in der Quecksilberverbindung (1) deutet unserer Ansicht nach auf einen Unterschied der Kohlenstoff-Valenzwinkel, welche durch das Quecksilberatom und die diastereotopen Protonen eingeschlossen werden. Dabei wird angenommen, dass der Valenzwinkel von Quecksilber 180° beträgt, was in Uebereinstimmung mit bekannten Strukturen von Alkylquecksilber-Verbindungen steht (4).

Mit vorzüglicher Hochachtung

R. Scheffold

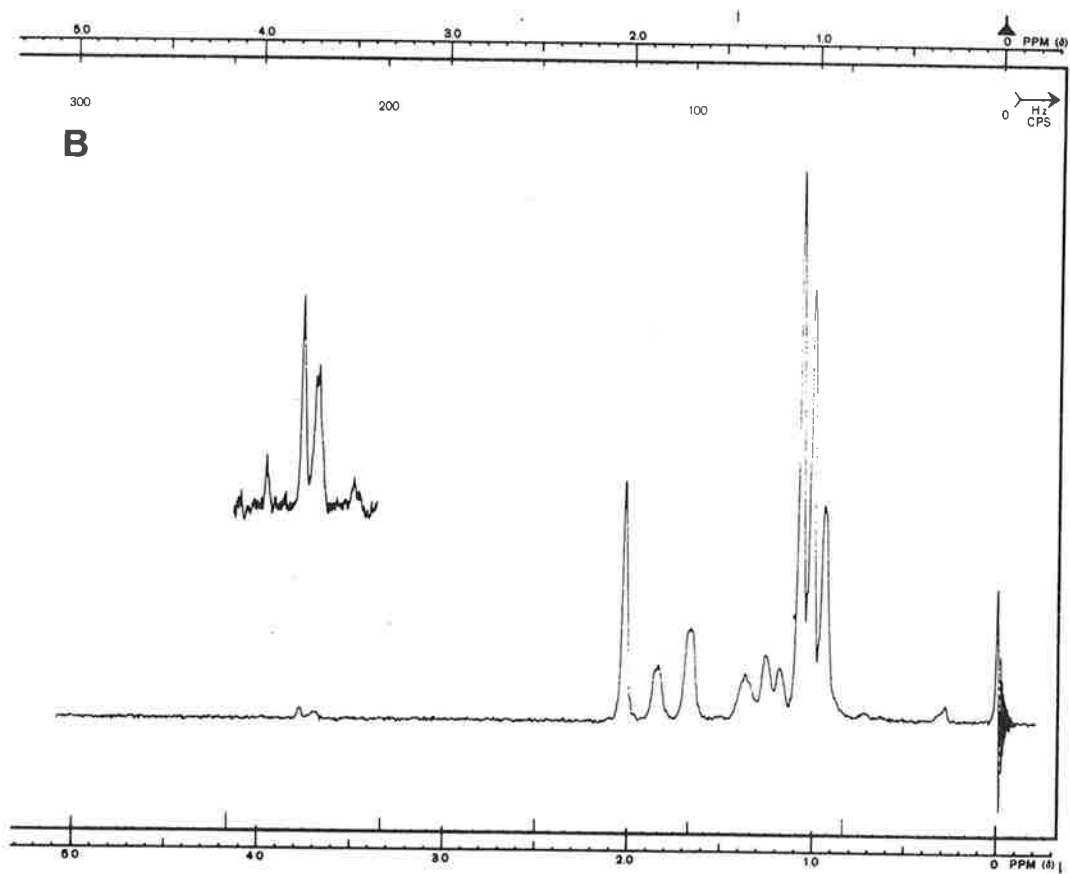
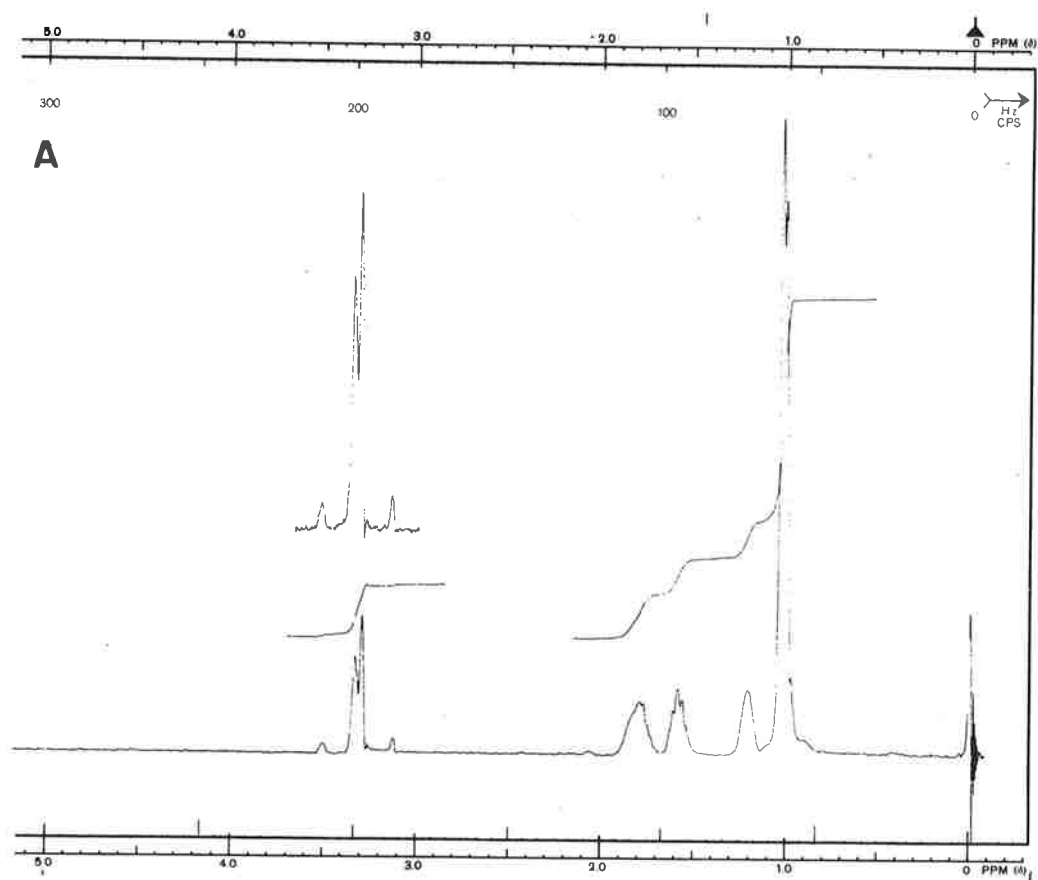
R. Scheffold

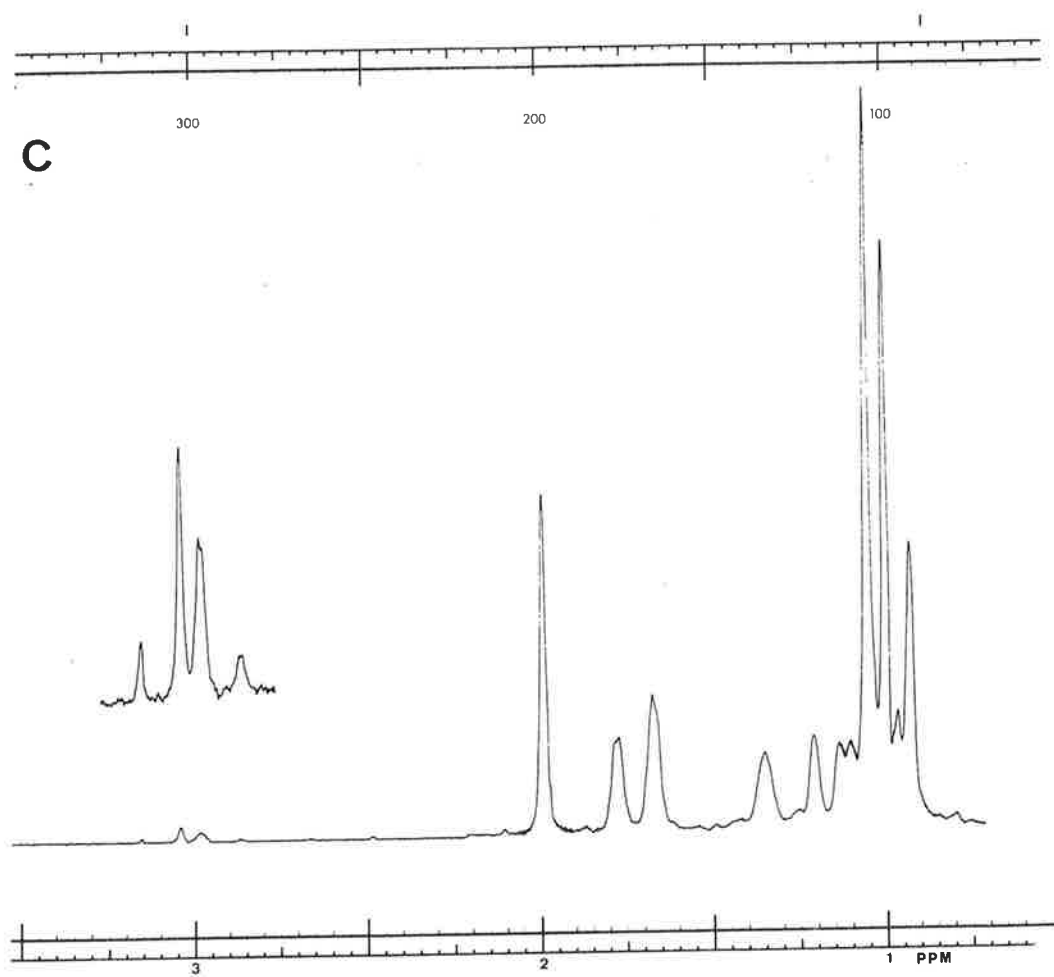
W. Simon

W. Simon

E. Pretsch

E. Pretsch





Literaturstellen

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- (3) R.Scheffold, Helv. 50, 1419 (1967).
- (4) D.Grdenić, Quart.Reviews 19, 303 (1965).

Bruxelles 5, le December 22, 1967.



FACULTE DES SCIENCES
Avenue F.-D. Roosevelt, 50

Service: Organic Chemistry

Dir.: Prof. R.H. MARTIN

(A rappeler dans la réponse)

Applications of internal Nuclear Over-
hauser Effects : 1,2,3,4-Tetramethyl-
phenanthrene.

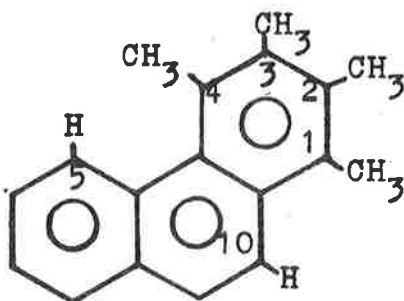
Dr. Bernard L. SHAPIRO,
Department of Chemistry,
Stanford University,
STANFORD, California 94305.

Dear Dr. Shapiro,

Very few applications of internal Nuclear Overhauser Effects (NOE) in organic chemistry have so far been published (1-4).

To our knowledge, no case involving an aromatic proton has yet been disclosed. We wish to report such a case.

In 1,2,3,4-tetramethylphenanthrene,



I

saturation of CH_3 (4) should give a NOE for H (5), whereas saturation of the other CH_3 groups should have no effect on this proton. Saturation of CH_3 (1) could, on the other hand, affect the peri proton H (10).

Results : 60 Mc NMR spectrum of I in CDCl_3 : H (5) multiplet centered at 510 c/s, H (10) doublet centered at 475 c/s, CH_3 (4) singlet at 181 c/s, CH_3 (1) singlet at 156 c/s, CH_3 (2) and CH_3 (3) quasi singlet (6H) at 144 c/s (at 100 Mc this last singlet is partially split in two signals separated by 2 c/s).

For NOE experiments, thoroughly degassed 12.5% CDCl_3 solutions of freshly sublimed 1,2,3,4-tetramethylphenanthrene were observed, at 60 Mc, by a frequency sweep method, using tetramethylsilane as an internal field frequency lock.

Irradiation	Area of the signal in arbitrary units			Enhancement in %
	H(5)	H(10)	H(6)+H(7)+ H(8)+H(9)	
None	21.5 ¹	30.0	100	-
at CH_3 (1)	21.5 ²	33.3	100	11
at CH_3 (2)+ CH_3 (3)	21.9	30.9	100	0
at CH_3 (4)	28.7	30.3	100	33.5

1. Average of 3 different runs on two samples, with H (6) + H (7) + H (8) + H (9) = 100.
2. Value corrected for a small heating effect.

These results fully confirm the assignments made previously, on the basis of chemical shifts only, for the methyl signals.

NOE experiments can therefore yield valuable informations in the field of "overcrowded aromatic hydrocarbons".

Further researches are in progress.

With kind regards,

Yours sincerely,



J.C.NOULS.



R.H.MARTIN.

ACKNOWLEDGMENTS.

Thanks are due to the staff of JEOL CO (Europe) for technical assistance with the double irradiation experiments.

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- 2) M.C.WOODS, I.MIURA, Y.NAKADAIIRA, A.TERAHARA, M.MARUYAMA and K. NAKANISHI, Tetrahedron Letters, 4, 321 (1967).
- 3) J.G.COLSON, P.T.LANSBURY and F.D.SAEVA, J.Amer.Chem.Soc., 89, 4987 (1967).
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STEVENS INSTITUTE OF TECHNOLOGY

HOBOKEN, NEW JERSEY 07030

Department of
Chemistry and Chemical Engineering

December 20, 1967

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

Hydration of $\text{Al}(\text{NO}_3)_3$

Dear Dr. Shapiro:

We have recently completed a study of the hydration of $\text{Al}(\text{NO}_3)_3$ in aqueous media by measuring proton shifts as a function of temperature and concentration. According to the two-state model proposed previously,¹ the shift of the single resonance line is an average shift which can be expressed as:

$$\delta = (hm/55.51)(\delta_S - \delta_N) + \delta_N.$$

As described in our earlier work this equation predicts that a plot of δ versus temperature at different molalities should show all lines converging to δ_S . For $\text{Al}(\text{NO}_3)_3$ this convergence occurs at -6.33 ppm. Rearranging the above equation allows us to calculate the total effective hydration number. For $\text{Al}(\text{NO}_3)_3$ we find $h=14.6$.

This value is unexpectedly large since it is believed that the hydration number of the nitrate ion is zero and that of aluminum is six. The value of six for the aluminum ion has been determined by measuring relative areas under separate signals at low temperatures.² However, this technique may be insensitive to the presence of the secondary layer of water molecules because the exchange of water molecules in this layer is too rapid. Also this method may be insensitive to water molecules bound to the nitrate ions.

Considering the high charge-to-size ratio, it is conceivable that the shifts of protons in the secondary layer can be effected by the aluminum ion. If the secondary layer were formed by hydrogen bonding of two water molecules to each water molecule in the primary layer a total hydration of 18 would result. Replacement of secondary water molecules by nitrate ions would reduce the total hydration number so that an experimental value of 14.6 is quite plausible.

Dr. Bernard L. Shapiro
Stanford University

Page 2

An alternative explanation is also readily apparent. Since the proton shift method is sensitive to both ions, it is possible that the aluminum ion is hydrated to 6 water molecules whereas each nitrate ion is hydrated to 3. If such is the case then the total hydration of aluminum nitrate would be 15, a value in excellent agreement with 14.6. Lowering the temperature would lengthen the residence time of protons in the primary layer of the highly charged aluminum ion but conceivably does not do so for the nitrate ion. Without further evidence, it is difficult to decide which explanation is correct.

References

1. E. R. Malinowski, P. S. Knapp and B. Feuer, J. Chem. Phys., 45, 4274 (1966); 47, 347 (1967).
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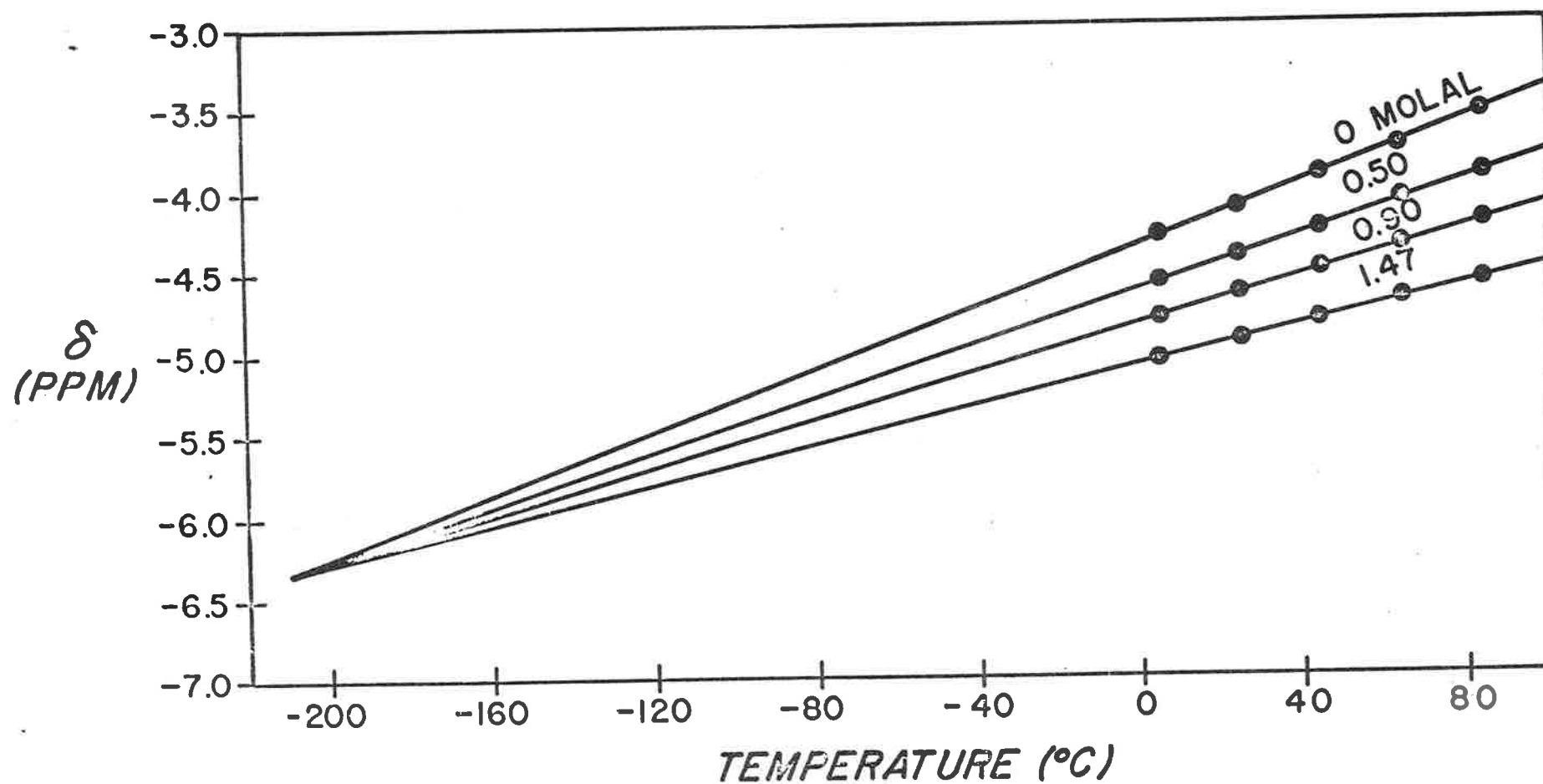
Respectfully yours,

Edmund R. Malinowski

Edmund R. Malinowski

ERM:jef

Paul S. Knapp



CHEMICAL SHIFT (RELATIVE TO ETHANE) OF AQUEOUS $\text{Al}(\text{NO}_3)_3$ SOLUTIONS AS A FUNCTION OF TEMPERATURE AT VARIOUS MOLALITIES

THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

DEPARTMENT OF CHEMISTRY

December 19, 1967

Dr. Barry L. Shapiro
 Department of Chemistry
 Stanford University
 Stanford, California 94305
 U.S.A.

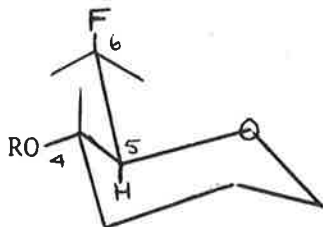
The Favoured Rotamers for Primary-fluoro Carbohydrates

Dear Barry:

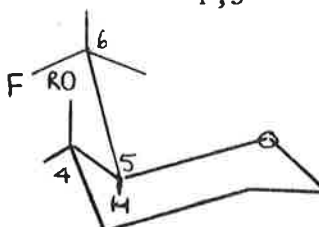
Having only just returned from a 4 month visit to Australia, I feel that I have a slightly better excuse than usual for my tardiness in writing to you.

We are still continuing our studies of specifically fluorinated carbohydrate derivatives and I want to refer for the moment to some of the primary fluorinated derivatives whose shifts I had mentioned previously.

It would appear that the favoured rotamer about the C₅-C₆ bond of these hexopyranose derivatives is critically dependent on the configuration at C₄. Thus D-glucopyranose derivatives (A) show $J_{F,5}$ ca. 29 Hz whilst the



(A)



(B)

D-galactopyranose derivatives (B) give $J_{F,5}$ ca. 15 Hz. A similar conclusion can be drawn from the p.m.r. data for some of these derivatives. Interestingly, the same rotamers appear to be favoured by the "normal" hexopyranose systems, e.g. derivatives bearing an acetoxy substituent at C₆.

I hope to send you shortly a more detailed letter concerning some of our other studies.

With best regards for 1968.

Yours sincerely,

L. Evelyn Laurie

LDH/dj

L. Evelyn (Mrs.) and L. D. Hall



THE UNIVERSITY OF MANITOBA

DEPARTMENT OF CHEMISTRY

WINNIPEG, CANADA

December 15, 1967

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

Dear Barry,

Signs of Long Range H-F Couplings in Fluorotoluenes
 and Benzotrifluorides

IIT NMR 95 27 reported on George Kotowycz' work on the signs of long range H-H couplings in a chlorobromotoluene. Last summer was very happily spent with Steven Danyluk's group at Argonne. Together with David Blears we found that in fluorotoluene derivatives J_{O}^{F,CH_3} and J_{P}^{F,CH_3} are positive while J_m^{F,CH_3} is negative. This sign sequence is opposite to that of the corresponding methyl proton-ring proton couplings. This we interpreted as a consequence of a positive hyperfine coupling constant in the C-F bond, in agreement with the contact shift work of the DuPont group. The detailed results suggest nonnegligible negative π contributions to J_O^{HF} and J_P^{HF} in the ring.

We further found that the signs of J^{H,CF_3} in benzotrifluoride derivatives are the same as those of the corresponding J^{H,CH_3} in toluenes. What has not yet been done is to find the signs of J^{F,CF_3} values.

The detailed discussion of these results will not be available in the literature for some months and therefore I hope that this report is acceptable.

Yours sincerely,


 Ted Schaefer

TS:fl

The University of Wisconsin – Milwaukee

MILWAUKEE, WISCONSIN 53201

DEPARTMENT OF CHEMISTRY

December 21, 1967

AREA CODE – 414
TELEPHONE 228-4411

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

Association of Phenol with Alkyl Halides, Amine, and Phosphine

Dear Barry:

Some time ago we reported association equilibrium constants for the interaction of phenol with diethyl ether, diethyl sulfide, and selenide⁽¹⁾. We found rather good agreement between the constants determined by NMR and IR methods.

Recently we used IR measurements to determine association equilibrium constants for phenol interacting with several alkyl halides in Cl_4 and with tri-n-butyl amine and -phosphine in n-hexane. On trying to apply the NMR technique, we found it possible to determine the product $K\Delta\delta_{\text{ass}}$ (i.e. the equilibrium constant times the association shift) to within a few percent⁽²⁾, but the individual K values (and presumably the $\Delta\delta_{\text{ass}}$ as well) showed considerable scatter, as is evident from the last entries in the Table.

<u>Base</u>	<u>T(°C)</u>	<u>K (liters/mole)</u>	<u>Method</u>
n-Hexyl fluoride	40	.60	IR
n-Butyl chloride	40	.34	IR
n-Butyl bromide	40	.32	IR
n-Butyl iodide	40	.32	IR
Tri-n-butyl amine	40	14.4	IR
Tri-n-butyl phosphine	40	4.8	IR
n-Butyl chloride	40	.15	} NMR, fitting all data NMR, double reciprocal plot ⁽³⁾ of most data
n-Butyl chloride	40	.12	
n-Butyl chloride	6	.31	
n-Butyl chloride	-24.6	.28	

Some reduction of the scatter is of course possible by assuming $\Delta\delta_{\text{ass}}$ to be temperature independent and using an average value, but the remaining uncertainties seem to be distinctly larger than 10% as found by the authors of the double reciprocal plot. We are presently re-evaluating some of our own earlier data and some literature data⁽⁴⁾

Dr. Bernard L. Shapiro
 Page 2.
 December 21, 1967

using the latter method to verify this point.

Also, we have used the correlation between the shift of the OH stretching band on association and the association shift $\Delta\delta_{\text{ass}}$ suggested by Eyman and Drago⁽⁵⁾ and found excellent agreement between the $\Delta\delta_{\text{ass}}$ values so estimated and our experimental averages. More work is being done to extend this correlation.

On the basis of these results, it is fairly certain that the K values determined from NMR measurements are distinctly smaller than those obtained by the IR method. There are some precedents for this result⁽⁶⁾, but we are not close to a good interpretation.

Finally, we have to correct an error in our last contribution to this Newsletter⁽¹⁾. The resolution of our instrument is given incorrectly, and we would like to say simply that the resolution is very good and slightly varying with time.

Sincerely yours,

W. W. Brandt

W. W. Brandt
 Associate Professor

J. Chojnowski
 Research Associate

- (1) ¹¹²⁻⁴³ Newsletter No. 102, p. 6.
- (2) P. H. Emslie, R. Foster, C. A. Fyfe, I. Horman, Tetrahedron 21, 2843 (1965) and Ref (2) of that paper.
- (3) See I. D. Kuntz, Jr. and M. D. Johnston, Jr., JACS 89, 6008 (1967).
- (4) B. B. Howard, C. I. Jumper, M. T. Emerson, J. Mol. Spectr. 10, 117 (1963).
- (5) D. P. Eyman, R. S. Drago, JACS 88, 1617 (1966).
- (6) See Table IV of Ref. (4).



Dartmouth College HANOVER · NEW HAMPSHIRE · 03755

Department of Chemistry · TEL. (603) 646-2501

December 19, 1967

Dr. Bernard L. Shapiro,
Department of Chemistry,
Stanford University,
Stanford, California.

Dear Barry:

At about the time of appearance of the paper of Gillespie and Hartman* reporting the change of sign of the BF_4^- coupling in water-acetonitrile mixtures, Robert Gentzler (Now at the University of Massachusetts) found the same effect in water-dimethylsulfoxide mixtures. By using the tetra-butylammonium salt and dimethyl sulfoxide - solvent B mixtures he was able to establish a set of relative signs for the BF_4^- coupling at .1M in various solvent B's. Assuming (for no particular reason) that the coupling in water is positive, then for most other solvents (DMSO, DMF, dioxane ...) it is negative. For all alcohols except methanol it is zero, or at least very small, and for methanol it is positive. One is tempted to speculate that water and the alcohols are hydrogen bonding to the anion.

The concentration effect on J for NaBF_4 in the solvents giving negative couplings has the same sign as that in water if the signs of the coupling constants are taken into account. That is, whereas increased concentration in water increases the splitting, in DMSO it decreases the splitting.

We are going ahead with mixed solvent studies of BF_4^- solutions, and with concentration effects in non hydrogen bonding solvents - using the Li salt.

I would be very grateful to know what is going on elsewhere. The work mentioned above will be submitted to J. Phys. Chem. in the near future.

Yours truly,

Karl F. Kuhlmann,
Assistant Professor of Chemistry

P.S. Please credit this contribution to the account of P.R. Shafer.

*R. Gillespie and J. Hartman, J. Chem. Phys., 45, 2712 (1966)

/js

Monsanto

C O M P A N Y

INORGANIC CHEMICALS DIVISION

800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
(314) OXford 4-1000

December 29, 1967

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

Dear Barry:

For the I. I. T. NMR Newsletter:

Title: A General Approach to Quantitative Analyses of Multicomponent Mixtures

If a system containing n -components (with mole fractions N_1, N_2, \dots, N_n) gives rise to m NMR peak areas (A_1, A_2, \dots, A_m) which are independent (i. e., no ratio A_i/A_j is invariant to composition change) and $m \geq n$, then quantitative measurement of the relative areas under the m NMR peaks supplies sufficient data for a complete quantitative analysis of the system. If $m > n$, then the system is over-determined and "best" values can be obtained. As a minimum, one must solve n equations in n unknowns chosen from the set of m equations:

$$k \sum_{j=1}^n C_{ij} N_n = A_i \quad i = 1, 2, \dots, m$$


where k is a constant dependent on the units in which the areas are measured, and the coefficients C_{ij} are integers equal to the number of magnetic nuclei per molecule of component j producing a total resonance signal contributing to area A_i . These equations are readily solved by appropriate computer programs (e. g., QUICKTRAN Program LINEQN) once the areas A_i have been experimentally measured and the coefficient matrix C_{ij} for the system established from a knowledge of the molecular structures of the n components and a correct assignment of the NMR areas to specific atoms in these structures. If all the areas are obtained from a single spectrum, then k can be ignored and the calculated relative values of N_n normalized to convert them to mole fractions, i. e.,

$$\sum_{i=1}^n N_n = 1.$$

Data on the same sample from separate spectra obtained from nuclei of different magnetic moment may be used simultaneously provided the areas are appropriately scaled by suitable calibration experiments to establish the ratio of the k 's for the separate spectra. This is very useful when $m < n$ for a single spectrum.

The major advantage of this general approach is that complex calculations for repetitive analyses are reduced to the same routine operation once the matrix C_{ij} for a given system has been established. Although not new, this is a very concise statement of the problem.

Sincerely,



M. M. Crutchfield

ALGEMENE KUNSTZIJD E UNIE N.V. - ARNHEM

TELEGRAMADRES: „ENKA-ARNHEM“ - TELEFOON: (08300) 30603 - TELEX: 45204



CENTRAAL RESEARCHINSTITUUT

Subject: Long-range 4J and 6J Couplings in 2,6-dimethyl-
3,4-dibromophenol

To Dr. Bernard L. Shapiro

Chemistry Department
Stanford UniversityS T A N F O R D (California - 94305)

U.S.A.

Uw kenmerk

Uw brief van

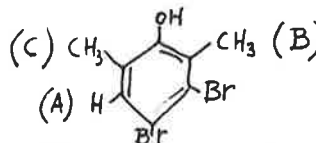
Ons kenmerk
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2256

ARNHEM, Velperweg 76

Datum December 19, 1967

Dear Dr. Shapiro:

2,6-Dimethyl-3,4-dibromophenol is from NMR point of view an interesting molecule because long-range spin-spin-interactions were noticed between all the protons except with that of the hydroxyl group ($\delta = 5.62$ ppm, TMS as internal standard, solvent CS_2). The signal of the meta proton (A) at 7.13 ppm is a septet (fig. 1) with line spacings of 0.68 Hz. The resonances of both methyl groups C and B at $\delta = 2.14$ and 2.33 respectively show each a doublet of quartets (fig. 4). Irradiation on H(A) in a double resonance experiment gave a collapse of the doublets and reveals the $CH_3(A) - CH_3(B)$ coupling over six bonds (fig. 5). One obtains $|J_{BC}| = 0.21$ Hz.



Upon irradiation of $CH_3(B)$, the original septet of the meta-proton (A) changes to a quartet (fig. 3), due to coupling with $CH_3(C)$: $|J_{AC}| = 0.73$ Hz. A somewhat narrower quartet was observed for the meta-proton (A) on irradiation of $CH_3(C)$ (fig. 2). From its spacings $|J_{AB}| = 0.60$ Hz was obtained. These results show clearly that the aromatic proton (A) directly interacts over four and six bonds with the protons C and B respectively and that the interactions are almost of the same size.

The relative sign of the coupling constants J_{AB} and J_{AC} could be determined by either irradiation of the high field or the low field quartet of $CH_3(C)$. In this way the high field and the low field quartets of the $CH_3(B)$ group were respectively decoupled (fig. 6 and 7), indicating that J_{AB} and J_{AC} have the same sign.

The error in the peak position lies within ± 0.01 ppm and the coupling constants are accurate within ± 0.01 Hz.

Please, credit this letter to AKU's contribution.

Yours sincerely,

W.G.B. Huysmans

Central Research Institute of AKU
(Algemene Kunstzijde Unie N.V.)
and affiliated Companies,
Arnhem, The Netherlands.

H. Angad Gaur,
Department of technical Physics
Technische Hogeschool, Delft

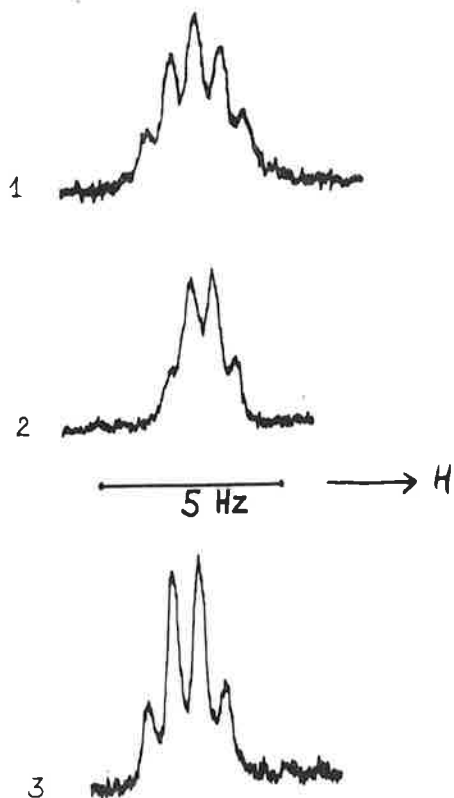


Fig. 1. The spectrum of the H(A) proton.
Fig. 2 and 3. The decoupled spectra of H(A), resulting from irradiation of the $\text{CH}_3(\text{C})$ and $\text{CH}_3(\text{B})$ protons respectively.

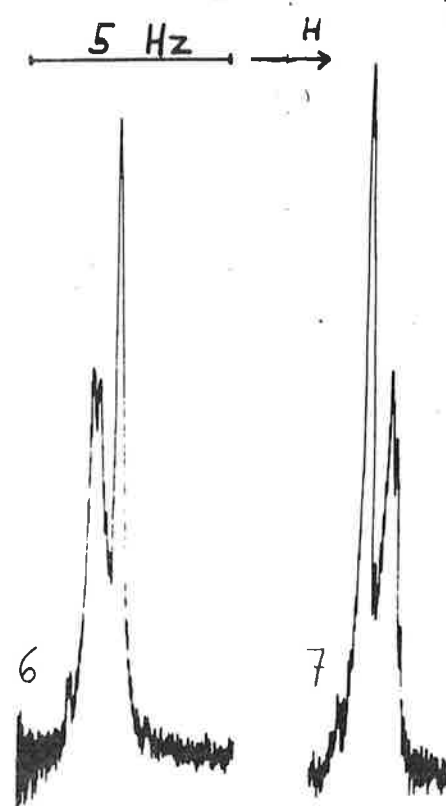


Fig. 6 and 7. The decoupled spectra of the $\text{CH}_3(\text{B})$ protons, resulting from irradiation of the high-field and low-field quartets of the $\text{CH}_3(\text{C})$ protons respectively.

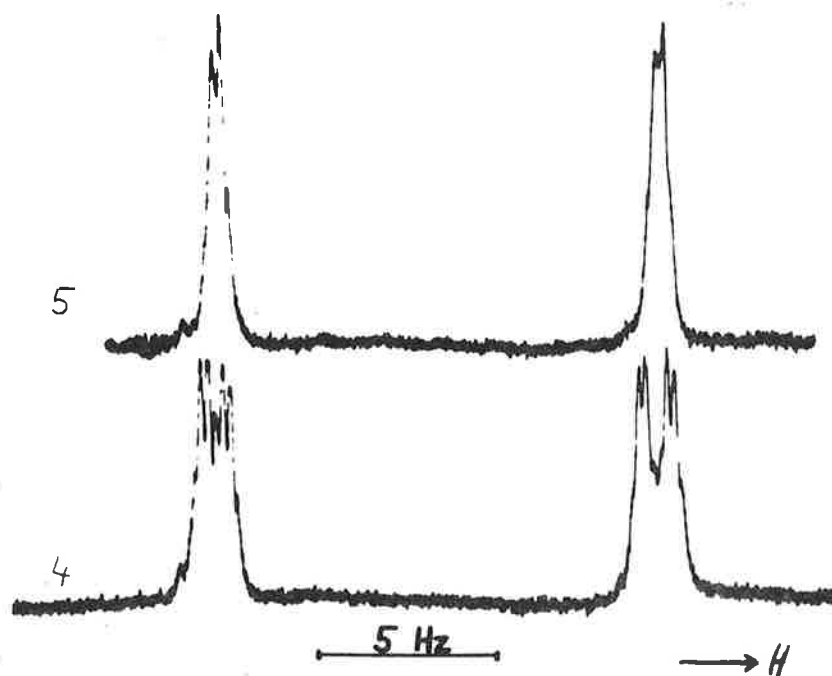


Fig. 4. The spectrum of the $\text{CH}_3(\text{B})$ (low-field) and $\text{CH}_3(\text{C})$ (high-field) protons.

Fig. 5. The decoupled spectrum of the same protons, resulting from irradiation of the H(A).

UNIVERSITY OF BRADFORD

SCHOOL OF CHEMISTRY,

Bradford 7 Telephone OBR4 29567

ENGLAND.

Vice-Chancellor and Principal
E G Edwards PhD FRIC

Please quote ref KDB/DWJ/RL'A/EDB.

29th December, 1967.

Dr. Bernard L. Shapiro,
Department of Chemistry,
Stanford University,
Stanford, California 94305,
U.S.A.

Dear Dr. Shapiro,

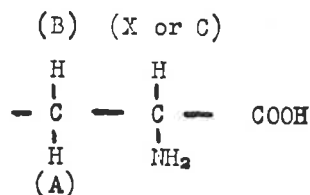
Title: P. M. R. spectra of bis (2-amino-2-carboxyethyl) trisulphide and related amino acids

From the decomposition of cystine in acidic wool hydrolysates, Fletcher and Robson (1) isolated an amino acid to which they gave the formula CyS_3Cy , where $\text{Cy} = \begin{matrix} \text{HOOC} \\ | \\ \text{H}_2\text{N} \end{matrix} > \text{CH} - \text{CH}_2 -$. As a preliminary

to the study of conformation and mobility in wool peptide chains, we have compared the 60 Mc/s P.M.R. spectrum in D_2O solution containing 10% (w/w) CF_3COOD of natural and synthetic samples of bis (2-amino-2-carboxyethyl) trisulphide (supplied by Dr. J.C. Fletcher) with the spectra of some other sulphur-containing amino acids:- cysteine, cystine, cysteic acid, djenkolic acid, cystine-S-monoxide, and lanthionine. The internal reference was the sodium salt of 3-trimethylsilylpropane sulphonic acid.

Cysteine gave an A_3B_2 spectrum and all the other samples gave ABC spectra. For each trisulphide sample, there was a single ABC system. In the spectrum of cystine-S-monoxide, resolution of what appeared to be the AB part of an ABC system, centred at 237c/s downfield from the reference, was sufficiently clear to imply the coincidence of shifts from the chemically different CH_2 groups. A further complex multiplet extended over the range 265 - 285 c/s.

The P.M.R. spectra of the amino acids other than cysteine and cystine-S-monoxide were first analysed as ABX



and the parameters refined as ABC by trial and error on the Bradford University I.C.T. 1909 computer. Final values are summarised in the table.

The Table shows that, within experimental error, the P.M.R. spectra of the 'natural' and synthetic trisulphides are identical, despite differences in infrared spectra reported by Fletcher and Robson (1).

A comparison of the P.M.R. spectra of the trisulphides and cystine-S-monoxide appears to confirm the presence of an unbranched sulphur chain in bis (2-amino-2-carboxyethyl)trisulphide.

Chemical shifts (ν) in c/s downfield from the reference, and coupling constants (J) in c/s, for 60 Mc/s spectra of sulphur-containing amino acids: 10% solutions in D_2O containing 10% CF_3COOD .

Acid.	ν_A	ν_B	ν_C	J_{AB}	J_{AC}	J_{BC}
DL-Lanthionine Cy-S-Cy	195.6	202.0	266.5	-15.0	6.7	4.7
L-Cystine Cy-S-S-Cy	199.8	208.5	270.7	-15.3	8.1	4.2
Cy-S-S-S-Cy, I (from wool hydrolysates)	211.7	219.8	273.7	-15.0	7.9	4.2
Cy-S-S-S-Cy, II synthesised as ref (1)	211.5	219.7	273.3	-15.2	7.9	4.3
Cy-S-S-S-Cy, III synthesised as ref (2).	211.5	219.8	273.4	-15.3	8.0	4.2
Cy-S-S-S-Cy, IV (synthesised by Dr. W.E.Savidge, ref(3))	211.5	219.9	273.6	-15.3	8.0	4.2
L-Cysteic Acid Cy-SO ₃ H	210.1	216.1	271.8	-15.1	8.3	3.3
L-Djenkolic Acid Cy-S-CH ₂ -S-Cy	194.6	202.6	261.1	-15.0	8.3	3.8
L-Cysteine Cy-S-H	189.5		261.5	4.9		
Cystine-S- Monoxide Cy-SO-S-Cy.	Centre at 237		265-285			

Thank you for your Newsletters.

K. D. Bartle
K. D. BARTLE.

Yours sincerely,
D. W. JONES.

R L'Amie
R. L'AMIE.

References.

- (1) J. C. Fletcher and A. Robson, Biochem J. 87, 553 (1963)
- (2) D. Cavalli, C. De Marco, B. Mondovi, and G.B. Mori, Enzymologia 22, 161, (1960).
- (3) W. E. Savidge, J. Eager, J.A. MacLaren, and C.M. Roxburgh. Tetrahedron Letters. 3289 (1964).

Carnegie-Mellon University

Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania 15213
[412] 621-1100

December 29, 1967

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

Dear Barry:

Two papers have appeared in the literature^{1,2} which report nitrogen chemical shifts in substituted nitrobenzenes. Clark and Roberts report the N¹⁵ chemical shifts in para-substituted compounds. Their results (in order of decreasing chemical shift) are -NH₂ ~ OMe > H > CN > NO₂. The more recent work of Witanowski, et al., gives for N¹⁴ shifts (in order of decreasing shift): -NO₂ > H > OCH₃.

Independently of Witanowski, et al., we did a study of N¹⁴ chemical shifts in the same series of compounds. (A preliminary report of our results appeared in the Mellon Institute Quarterly Report, Project 6353, June, 1967).

Our results are the following:

X	-NO ₂	-CN	-CO ₂ He	-OAc	-CHO	-OMe	H	NH ₂
σ (ppm \pm 0.3)	4.6	3.8	2.5	2.4	1.2	0.1	0	-0.9

These values agree, within the stated experimental error, with Witanowski's except for the CHO substituent (Reference 2 reports 4.5 ± 1 ppm). The nitrobenzenes were at ca. 10% concentration in acetone.

Our N¹⁴ spectra were obtained with a Varian V-4210 variable frequency r.f. unit and probe which have been modified to permit frequency sweeping with a GR-1164 frequency synthesizer. The field-frequency ratio is held constant by an external proton lock loop. We expect to report the details of this spectrometer system in the near future.

¹D. T. Clark and J. D. Roberts, J. Amer. Chem. Soc., 88, 795 (1966).

²M. Witanowski, L. Stefaniak, and G. A. Webb, J. Chem. Soc., A, 1065 (1967).

Dr. Bernard L. Shapiro

- 2 -

December 29, 1967

The shifts found by Witanowski and by us are interesting in that the dependence of N^{14} shielding on the electron-withdrawing power of the para-substituent is opposite to that of F^{19} shielding (or ring C^{13} shielding) on the same parameter (cf. Reference 1). The dependence of carbonyl- C^{13} shielding in para-substituted acetophenones is intermediate (i.e., there is practically no change in these C^{13} shieldings as a function of para-substituent). One can advance an argument based on degree of π -bonding of the shielded nucleus to explain these results; we would like to consider the matter further and make some measurements on other series of



(where N^* is a magnetic nucleus) before trying to defend this argument seriously, however.

Best wishes.

Sincerely,

Donald G. Davis

Aksel A. Bothner-By

Suggested Title: " N^{14} Shifts in Nitrobenzenes"

Institut für Elektrowerkstoffe

GEMEINNÜTZIGES FORSCHUNGSGESAMTSTUTUT DER FRAUNHOFER-GESELLSCHAFT

An alle Leser der
IITNMR Newsletters

INSTITUTSDIREKTOR:
PROF. DR. R. MECKE

Neue Ruf-Nr. 3 1391

TELEFON 0761/~~45544~~

78 FREIBURG I. BR.
ECKERSTRASSE 4

Ihre Zeichen

Ihre Nachricht vom

Unser Zeichen

Das Chemische Institut der Universität Tübingen (Prof.Dr.E.Müller)

das Organisch Chemische Institut der Universität Heidelberg (Prof.Dr.H.A.Staab)

und

das Institut für Elektrowerkstoffe Freiburg (Prof.Dr.R.Mecke)

veranstalten in Freiburg am 22. und 23. Februar 1968 ein Symposium über

magnetische Kern- und Elektronenresonanz

und vom 19. - 21. Februar 1968 einen

Einführungskurs in die Kernresonanzspektroskopie

mit einführenden Vorträgen und Auswerteübungen

Anmeldungen und nähere Einzelheiten (Programme, Kursteilnehmergebühr) bitte an
das Sekretariat des

Institut für Elektrowerkstoffe

78 Freiburg/Brsg., Eckerstr. 4

Telefon 31391



31 December 1967

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

Dear Barry:

After a long struggle with myself, I finally reached the conviction that the love of the native country is more important than all the luxury of California, and so we decided to permanently return to Switzerland next March. It might be a good opportunity to express my gratitude to VARIAN for the truly perfect working atmosphere and for the constant stimulation by Wes Anderson, Ray Freeman and many others. May I submit the following contribution as credit for the next few months to obtain the ITNMR Newsletter at my new address:

Laboratorium f. Physikalische Chemie
 Eidg. Technische Hochschule
 Universitätsstrasse 22
 8006 ZURICH, Switzerland

TIME AVERAGING WITH GENERAL PURPOSE COMPUTERS

Together with other more sophisticated applications of general purpose computers in spectroscopy, it seems to become more and more economical to apply them to perform time averaging of weak signals. In this context, the question occurs, what is the connection between the achievable improvement of sensitivity and the word length or dynamic range of the computer memory, and what is the optimum voltage level of the input signal? The same question arises in the use of a special purpose time averaging device.

To permit a maximum number of scans without causing overflow in the computer memory word, it is advisable to select the amplitude of the incoming signal as small as possible. The minimum useful amplitude is determined by the digitizing error which is caused by the quantized response of the analog-to-digital converter at the input to the computer. Thus, the problem boils down to the question, how accurately is it necessary to digitize the spectrometer output to be able to faithfully retrieve the signal?

An ideal A/D converter produces invariably N counts for any signal voltage V between the limits $\Delta V \cdot (N-1/2) < V < \Delta V \cdot (N+1/2)$, where ΔV is the voltage increment which corresponds to one count (see Fig.1). The digitized signal is accurate only within $\pm \Delta V/2$. If the input voltage is deterministic (noise-free), time averaging would not improve the quality of reproduction of the signal. In the presence of an additional random noise component V_n , the situation is different. The number of counts for the input voltage V_s ($V_s + V_n$) is given by a probability distribution $P(N, V_s, V_{rms})$ which depends on the signal voltage V_s as well as on the rms noise voltage V_{rms} (and also on the amplitude distribution of the noise which is assumed to be Gaussian and with zero average). After averaging a sufficient number of scans, one observes the average number of counts $\langle N \rangle$ produced by the signal voltage V_s which is given by

$$\langle N \rangle = \sum_N N \cdot P(N, V_s, V_{rms})$$

In this case, it may be possible to retrieve a signal V_s whose variations are much smaller than the voltage increment ΔV .

The question occurs now what is the deviation between the digitized and averaged signal $\langle N \rangle$ and the original signal $V_s/\Delta V$ and how does it depend on the noise voltage V_{rms} ? This determines the accuracy by which a signal can be retrieved by time averaging. Some curves of the average number of counts $\langle N \rangle$ as a function of the input voltage V_s for different noise levels are indicated in Fig.1. It is seen that the higher the noise voltage V_{rms} is the more linear is the average response of the A/D converter. For $V_{rms} \geq \Delta V$, the maximum possible error of the average response is smaller than $0.0001 \cdot \Delta V$. Signals with an amplitude 1000-times smaller than one count could be retrieved with 10% accuracy. This is probably sufficient for most practical applications.

The A/D converter does not only affect the signal but it also modifies the character of the noise, particularly, it may increase the effective rms noise voltage for two reasons: (1) Any practical A/D converter is to some extent noisy. The inherent noise voltage is typically of the order $0.1 \cdot \Delta V - 0.2 \cdot \Delta V$. The noise voltage of the input signal should be large compared with the inherent noise. (2) The digitizing process changes the amplitude distribution of the noise and increases the rms noise voltage. For an rms noise voltage V_{rms} of $2 \cdot \Delta V$, the increase is 1% only, for $1 \cdot \Delta V$ it is 4% and for $0.5 \cdot \Delta V$ it amounts to 19%. This again puts up a limit for the useful input noise amplitude, $V_{rms} \geq \Delta V$.

The conclusion is: It is possible to satisfactorily retrieve a signal buried in noise by means of time averaging if the noise voltage V_{rms} is greater or at least equal to the voltage increment ΔV corresponding to one count of the A/D converter. The sensitivity will increase with the square root of the number of scans.

This conclusion allows now to answer the initial question about the dynamic range D of the time averaging device. To permit to improve the initial signal-to-noise ratio R_i into a final signal-to-noise ratio R_f , the necessary dynamic range D of the time averaging device must be

$$D \geq 2 \cdot R_f^2 / R_i$$

(R is defined as (maximum signal voltage)/(rms noise voltage)). The factor 2 is included to permit the use of a sign bit. Vice versa, one can say that the maximum sensitivity R_f which can be achieved within a given dynamic range D is

$$R_f = (0.5 \cdot D \cdot R_i)^{1/2}.$$

It depends on the initial sensitivity. This is visualized in Fig.2. It gives the final sensitivity R_f as a function of the initial sensitivity R_i for 1, 100 and 10000 scans. The dynamic range D limits the accessible area in this graph as is indicated. If the maximum number of scans ever to be used is fixed at 10000 (probably a safe number) and if the final S/N ratio is limited to 500 (this is about the dynamic range of a good graphical recorder used to display the result), it is seen that $D = 2^{16}$ just permits to utilize the complete area of practical interest, as indicated by the solid lines. A 12-bit computer cuts off a significant part of this area. For practical applications in NMR, a dynamic range D of 2^{16} is appropriate. In some instances, an additional safety factor may be desirable which could demand double precision representation of the sum signal in computers with a word length of 16 or less bits.

The last question to be answered is whether it is advisable to apply a scaling method instead of a straight addition method. Instead of simply adding trace by trace till the memory is filled up, it is possible to let the first scan already fill the complete dynamic range, add to it the second scan and scale the result such that no overflow occurs. The following scan is scaled by the same factor and added. After each addition a new scaling operation is necessary. On the first sight, it seems that this method might allow unlimited improvement of the sensitivity. But this is not true. As soon as the scaling factor becomes so large that the scaled rms noise voltage which must be added to the memory content becomes smaller than one count, the averaging becomes inefficient and finally no improvement will occur anymore. It is even possible that it will finally deteriorate when the inherent noise of the A/D converter becomes dominant. It can be shown that the mentioned requirements with respect to dynamic range D apply to scaling methods as well.

There is one practical aspect which might favor scaling methods. To efficiently utilize the complete dynamic range in straight addition methods, it is necessary to carefully select the amplitude of the incoming signal. In scaling methods, this is done automatically. On the other hand, if one assumes that the noise voltage is constant in all experiments and that only the signal voltage is varying, this critical adjustment can be made once and for ever. For scaling methods, the programming is considerably more complicated and the necessary additional computing time can be significant.

Sincerely yours,

Richard R. Ernst

Richard R. Ernst

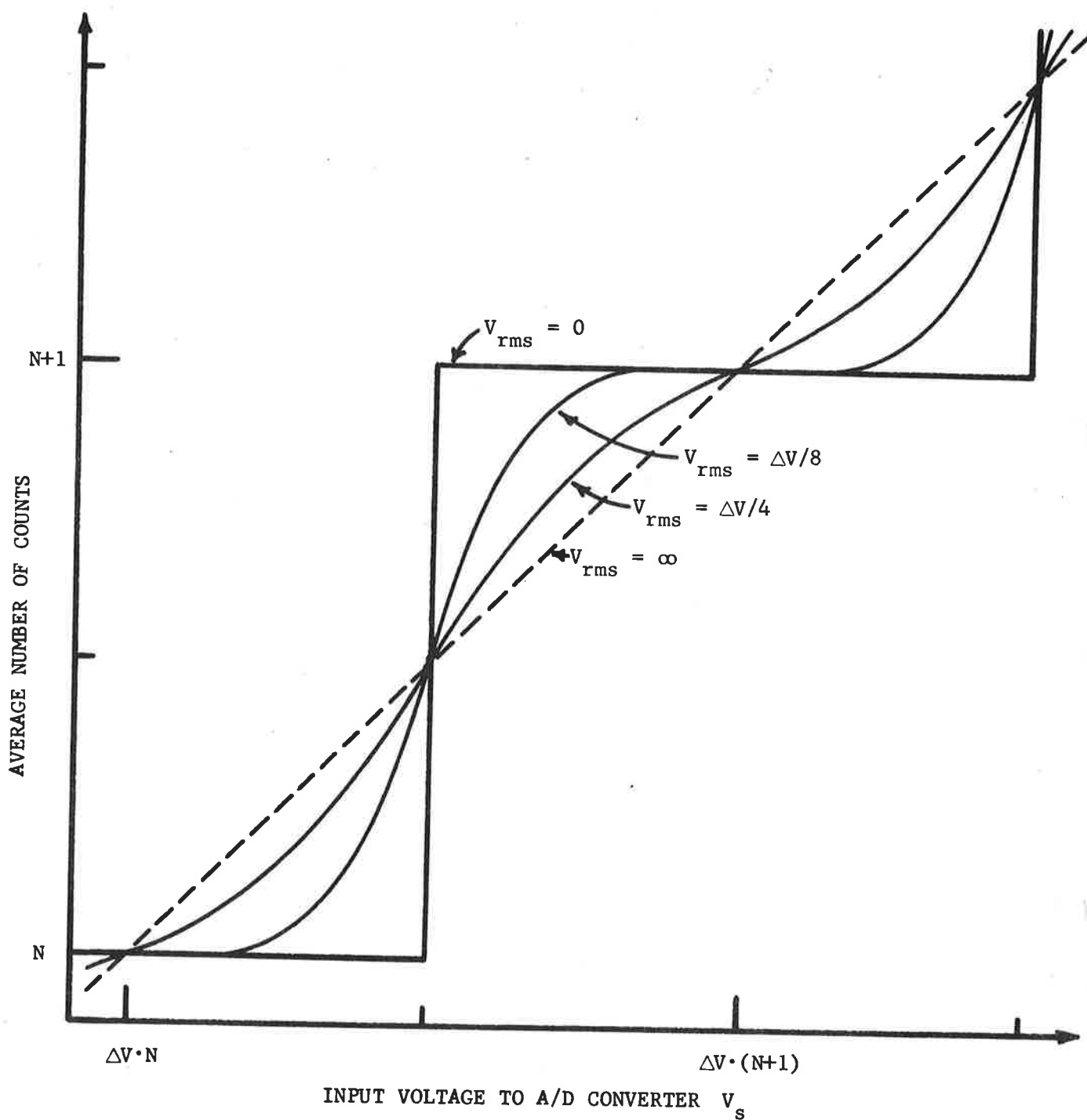


FIG.1: AVERAGE RESPONSE OF AN ANALOG-TO-DIGITAL CONVERTER IN THE PRESENCE OF NOISE WITH THE RMS VOLTAGE V_{rms}

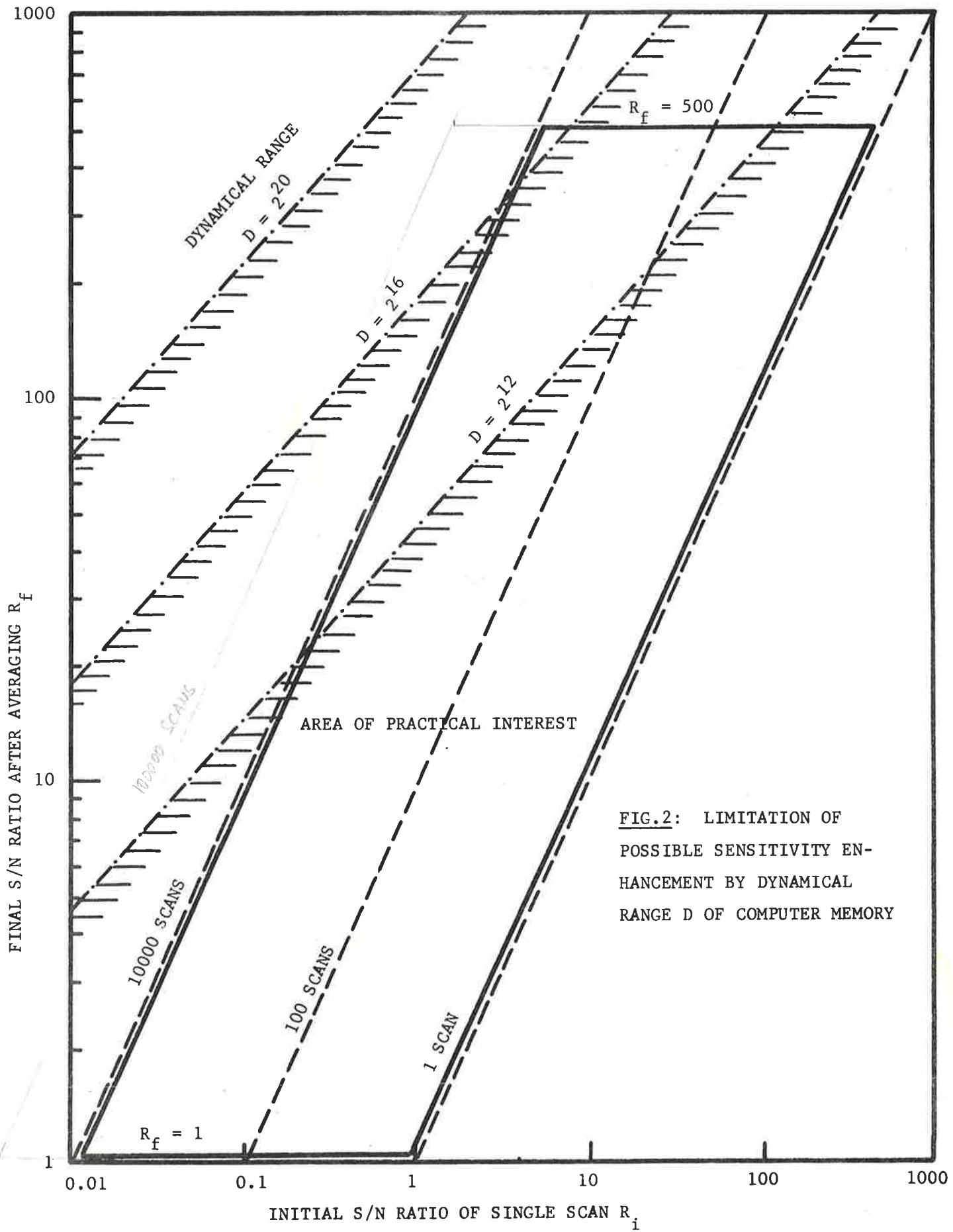


FIG.2: LIMITATION OF POSSIBLE SENSITIVITY ENHANCEMENT BY DYNAMICAL RANGE D OF COMPUTER MEMORY

Koninklijke/Shell - Laboratorium, Amsterdam

BADHUISWEG 3 - AMSTERDAM - N.

TELEFOON (020) - 6 11 11

Dear Dr. Shapiro,

Chemical shifts of aromatic protons in phenyl-substituted anions

We are measuring the NMR spectra of a variety of anions in liquid ammonia¹.

In anions containing a phenyl ring we have observed a simple relation between the chemical shifts of the para and the meta protons relative to benzene:

$$(\delta_{\text{benzene}} - \delta_{\text{meta}}) = 0.47 (\delta_{\text{benzene}} - \delta_{\text{para}}).$$

The relation covers a fairly wide range. With δ in ppm from TMS ($\delta_{\text{benzene}} = 7.42$), δ_{para} ranges from 7.0 to 5.2 and δ_{meta} from 7.2 to 6.35. Deviations are never larger than a few hundredths ppm.

The anions concerned are (side-chain substituted) benzyl, cinnamyl (phenylallyl) and diphenylmethyl anions totalling some 30 spectra. In the region of low values of δ (lot of charge in the ring) one observes, owing to restricted rotation, the two meta protons separately. In these cases the average value of the shifts obeys the relation.

With kind regards,



G.J. Heiszwolf



H. Kloosterziel



E.L. Mackor

1. G.J. Heiszwolf and H. Kloosterziel, Rec. trav. chim. 86, 807 (1967); Dec. 1967.

Amsterdam, 3rd January 1968

Dr. Bernard L. Shapiro
Department of Chemistry
Stanford University
Stanford, California 94305
U S A

Partial bond fixation in a benzo-cyclopropene

Dear Barry,

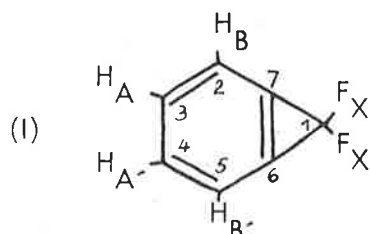
Thank you for the reminder and please excuse the delay of my contribution. Since W.R. Roth is spending his "sabbatical" semester at the University of Wisconsin, I am busy these months teaching Organic Chemistry.

I recently have finished the analysis of the ^1H -spectrum of 1,1-difluoro-benzo-cyclopropene (I), a compound synthesized by Korte, Grimme and Vogel. The results are of interest in connection with the electronic structure of this bicyclic system.

The spectrum of I is of the $\text{AA}'\text{BB}'\text{X}_2$ -type, the fluorine nuclei being magnetically equivalent.

This is born out by the ^{19}F -spectrum, which shows a 1:2:1-triplett with a splitting of 3.4 cps, ca. 80 ppm upfield from external CCl_3F . The same splitting is found in the BB' -part of the proton-spectrum. The molecule therefore is either rigid and planar or rapidly interconverting between two nonplanar conformations, which seems to me a less attractive possibility.

The H,H-coupling constants obtained so far are the result of an approximate analysis, using the unperturbed transitions of the AA' -part in the proton-spectrum (estimated error ± 0.2 cps):



$J_{\text{AA}'}$	= 5.0	$J_{\text{BB}'}$	= 1.1	cps
J_{AB}	= 6.7	J_{AX}	< 0.1	"
$J_{\text{AB}'}$	= 0.9	J_{BX}	= 3.4	"
τ_{A}	= 2.397	τ_{B}	= 2.519	ppm.

An unequivocal assignment of the Larmor-frequencies and the H,F-coupling constants is not possible, but the BB' -protons are assumed to resonate at higher field, since most probably $J_{\text{AX}} < J_{\text{BX}}$.

The vicinal coupling constants found for I are remarkably smaller than those in benzene (7.54 cps (1)), presumably due to HCC-bond angle variations as a consequence of ringstrain. The alternation observed for these constants together with the finding $J_{\text{para}} > J_{\text{meta}}$ indicate partial bond fixation for I (2). The preference of the Kekulé-structure I is in accord with the most probable state of hybridization at C_6 and C_7 : Higher p-character in the orbitals forming the bonds with C_1 and higher s-character in the remaining σ -orbitals, leading to better overlap for the $\text{C}_6 - \text{C}_7$ -bond, but less overlap due to unfavourable bond angles for the $\text{C}_2 - \text{C}_7$ - and $\text{C}_5 - \text{C}_6$ -bonds respectively.

Sincerely yours,

H. Günther

- (1) Read et. al., J. mol. Spectr. 22, 419 (1967).
(2) Günther, Tetrahedron Letters 1967, 2967.

Carnegie-Mellon University

Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania 15213
[412] 621-1100

January 2, 1968

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

Dear Barry:

In the last issue of IITNN (111, 2) Bowers, Chapman and Manatt described a further modification of the Swalen and Reilly program which is needed to use that program for the fitting of nmr spectra in which degeneracy of the energy levels occurs because of the symmetry of the spin-system or the magnetic equivalence of several nuclei. Being unfamiliar with the use of the LAOCOON II or LAOCN3 programs, the authors supposed that perhaps similar modifications of the above programs might also be required for dealing with the same spin systems. The answer to this question, so very tactfully posed, is very simple: NO!

In the LAOCN3 program (as well as in its previous editions) the symmetry of the spin system or the magnetic equivalence of several nuclei is implicitly taken into full account by specifying the sets of spectral parameters which should be equally and synchronously varied during the iterative process. No further information is needed and the program can be used as it stands for any type of spectrum up to a maximum of seven spins. The program has been tested and successfully used in the analysis of about 200 spectra (in our laboratory alone) involving spin-systems with and without symmetry. As an example of its performance, we present in figures 1 and 2 the experimental and calculated 100 MHz proton spectrum of thiepin 1,1-dioxide which belongs to one of the types (AA'BB'CC') mentioned by Bowers, Chapman and Manatt in their communications. The synthesis of the compound and the analysis

Dr. Bernard L. Shapiro

-2-

January 2, 1968

of the spectrum were performed by the first two of us respectively; the corresponding spectral parameters will be published in the near future.

Best regards from all of us.

W. L. Mock

W. L. Mock

M. P. Williamson

M. P. Williamson

S. M. Castellano

S. M. Castellano

A. A. Bothner-By

A. A. Bothner-By

MPW:sa

Figure 1 - Experimental and calculated 100 MHz proton spectra of thiepin 1,1-dioxide (α protons).

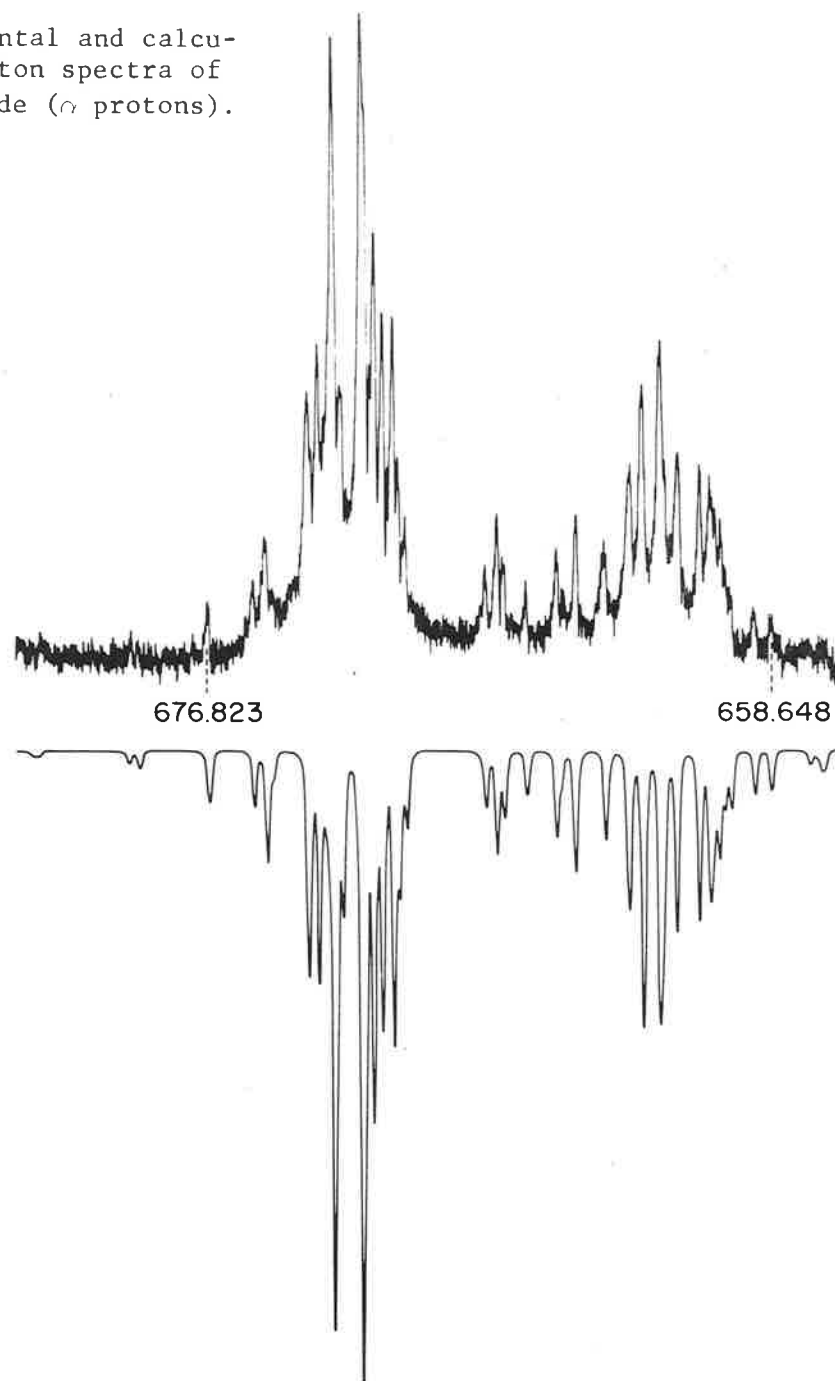
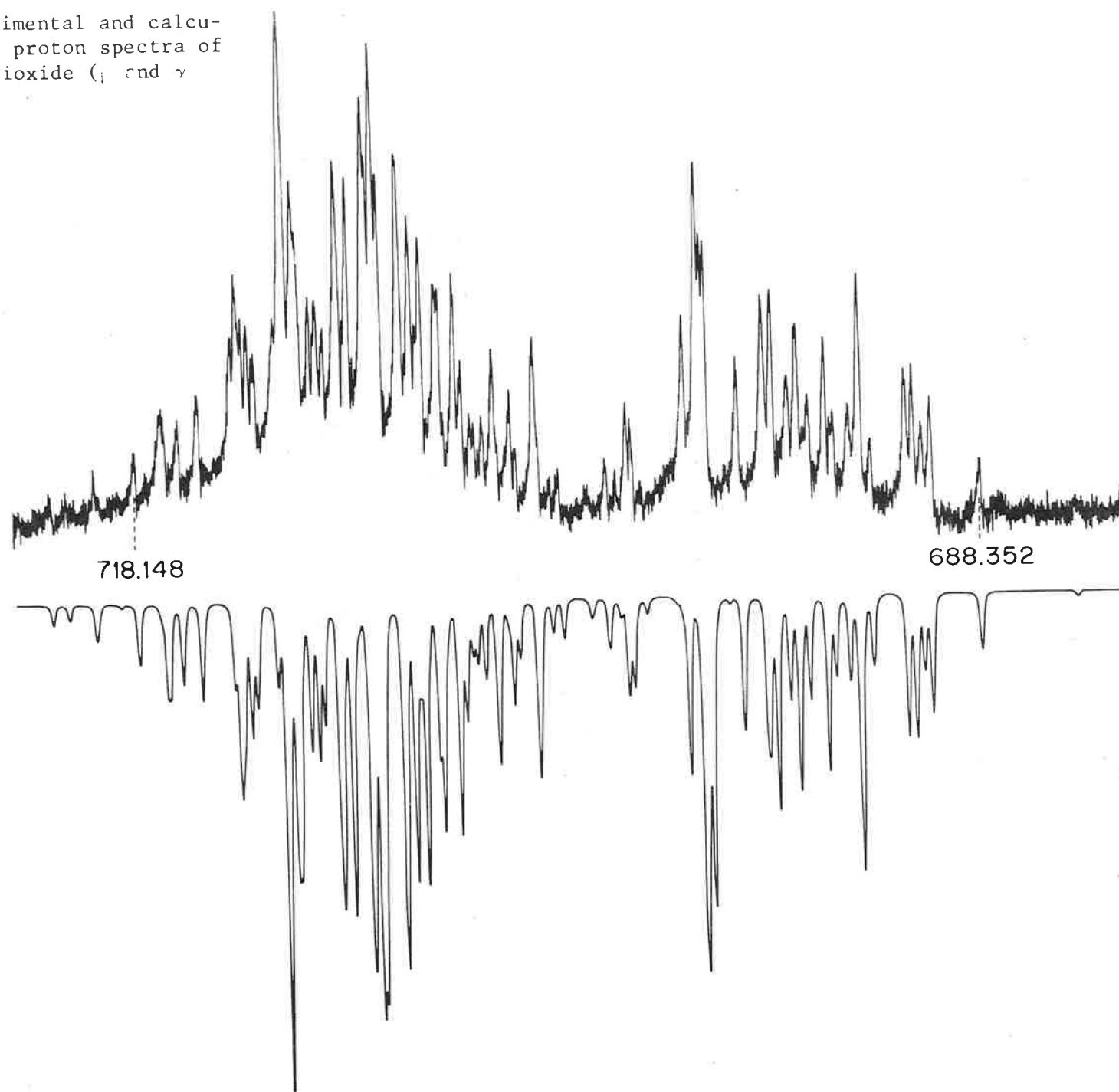


Figure 2 - Experimental and calculated 100 MHz proton spectra of thiepin 1,1-dioxide (β and γ protons)



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MJS/pjw

20th December, 1967.

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

Dear Dr. Shapiro,

The NMR spectra of basic primary alcohols

It is known that many alcohols may be classified by observing their spectra in dimethylsulphoxide (DMSO)¹. In the latter strong hydrogen bonding to the solvent shifts the hydroxyl resonance downfield and reduces the rate of proton exchange so that spin-spin coupling of the hydroxyl proton may be observed.

The absence of the expected spin-spin coupling between the hydroxyl and methylene protons of o-aminobenzyl alcohol in DMSO prompted us to look into the problem further. It is apparent that the amino group of o-aminobenzylalcohol is sufficiently basic to accelerate the hydroxyl proton exchange rate so that no spin-spin coupling is observed.

The NMR spectra² of a number of basic alcohols and of benzyl alcohols in the presence of equimolar quantities of bases of varying pKa have been examined. The results are tabulated:-

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Alcohol	Added base	pKa	Spin-spin coupling
Benzyl alcohol			Yes
o-aminobenzyl alcohol			No
o-nitrobenzyl alcohol			Yes
3-Hydroxymethylpyridine			No
5- β -Hydroxyethyl-4-methylthiazole			No
γ -Dimethylaminopropanol			No
Benzyl alcohol	Aniline	4.62	No
Benzyl alcohol	phthalazine	3.47	Broadening of multiplets, coupling just observable.
Benzyl alcohol	m-Nitroaniline	2.45	Yes
Benzyl alcohol	o-Nitroaniline	-0.28	Yes

When aniline was added to benzyl alcohol in less than a molar equivalent, a gradual broadening of the $-CH_2$ and $-OH$ multiplets was observed.

It can be seen from this limited study that the presence of basic centres in alcohols must be taken into account when interpreting their spectra in DMSO.

We hope this can be considered as our first contribution to the IIT Newsletter.

Yours sincerely,

R. J. Bass

M. J. Sewell

R. J. Bass M. J. Sewell
Chemical Research Department

¹ O. L. Chapman, J.A.C.S., 86, 1256, (1964).

² Spectra were run at normal probe temperatures on a Varian A60 instrument.

BRYN MAWR COLLEGE
BRYN MAWR, PENNSYLVANIA 19010, USA

DEPARTMENT OF CHEMISTRY

TEL: (215) LA 5-1000

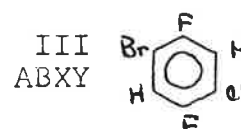
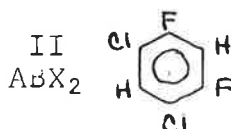
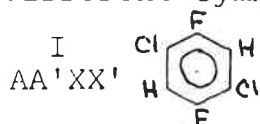
4 January 1968

Prof. B. L. Shapiro
Department of Chemistry
Stanford University
Stanford CA 94305

Title: NMR of some substituted
difluorobenzenes

Dear Barry:

We have completed an analysis of the NMR spectra of the three compounds shown below, each a four-spin system with different symmetry.



The experimental and calculated spectra are exhibited in the accompanying figures. One unusual result is found in the spectra of I. The triplets here are examples of "deceptively simple spectra."¹ We show beneath each experimental spectrum calculations for which $|J_o - J_m| = 0.0$ hz (1B,2B), 3.0 hz (1C,2C), and 4.5 hz (1D,2D). The measured shifts and coupling constants are given in the following table.

Cmpd.	System	¹ H shift	¹⁹ F shift	HF coupling	FF coupling
I	AA'XX'	-400.3	6708.4	ortho meta	avg = 7.3 $ J_o - J_m < 3$
II	ABX ₂	a -440.3 b -416.9	6324.7	ortho meta	8.90 7.55
III	ABXY	a -393.6 b -404.3	x 6272.2 y 6715.3	ortho meta	7.72 6.14 para 14.15

Shifts are relative to internal TMS for ¹H, internal CCl₃F for ¹⁹F; the spectra were recorded at 60 MHz and 56.4 MHz on a Varian A-56/60A. Our work continues with a determination of the absolute signs of the coupling constants using a liquid crystal solvent.

Sincerely yours,

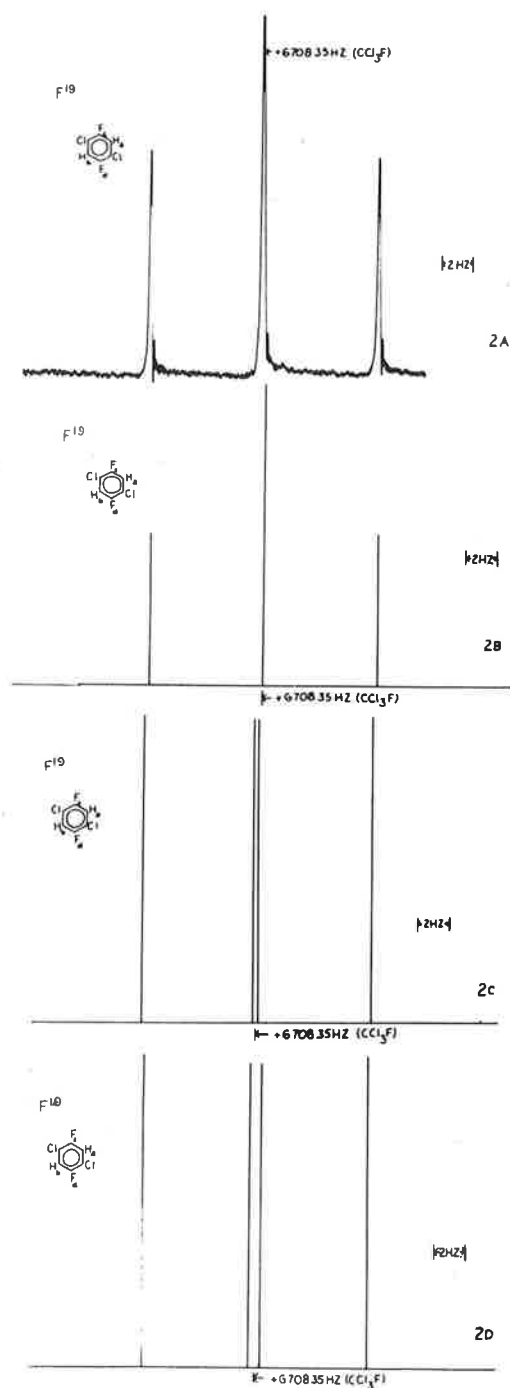
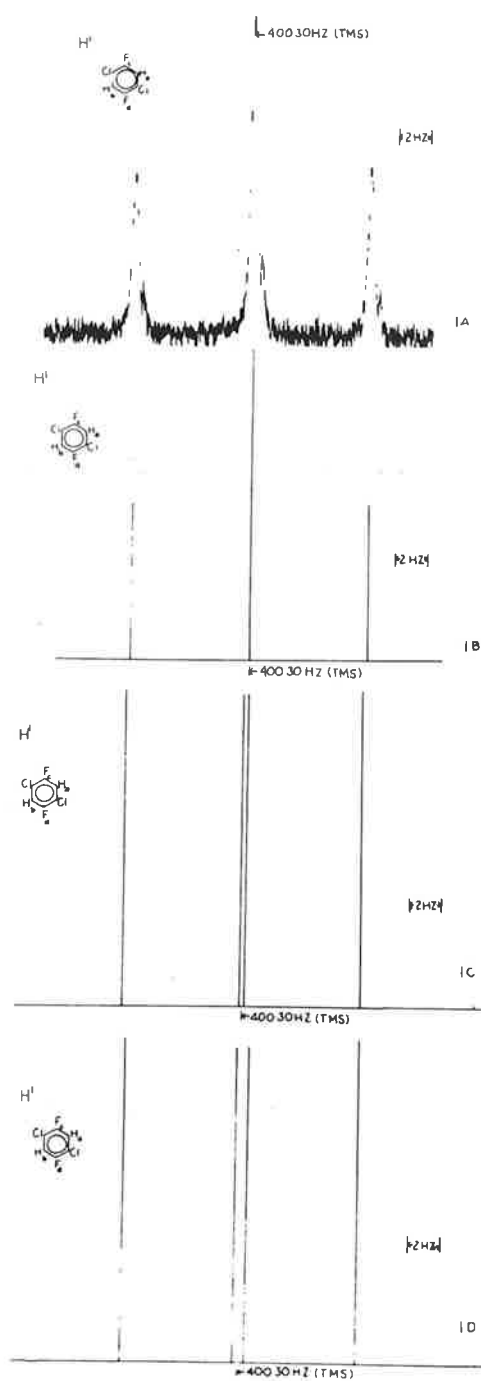
Jay

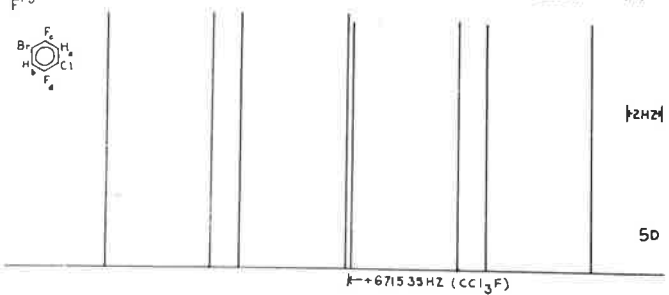
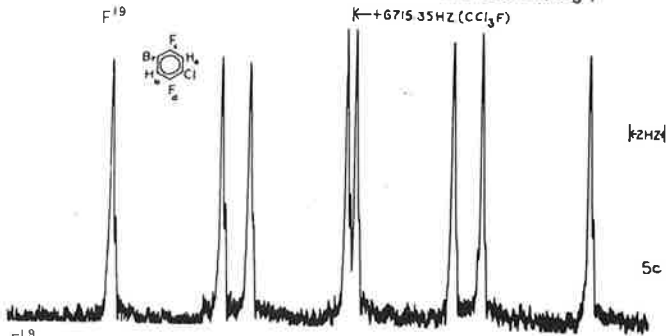
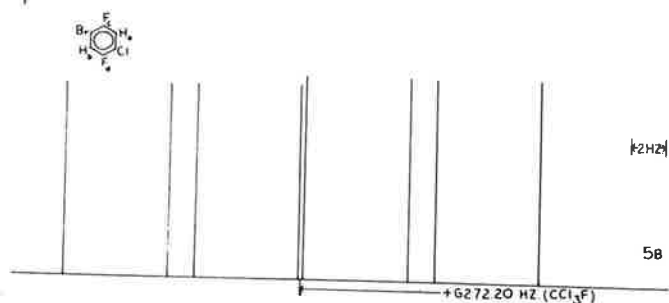
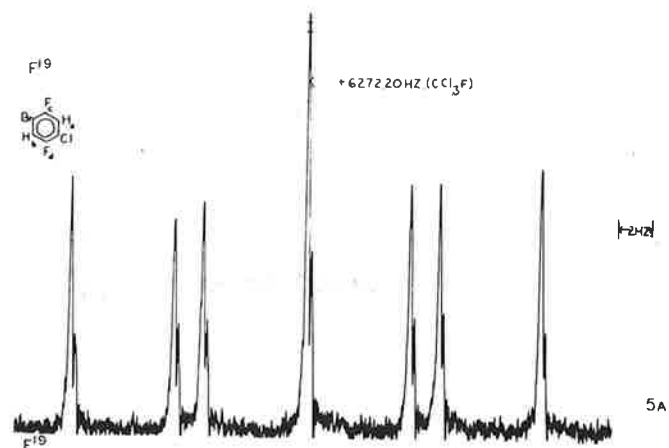
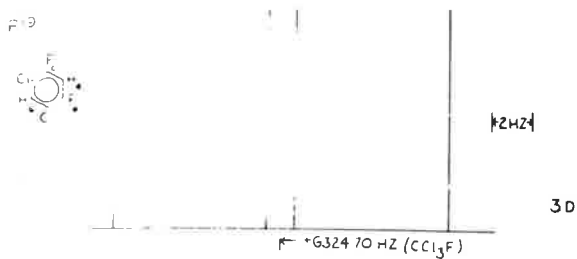
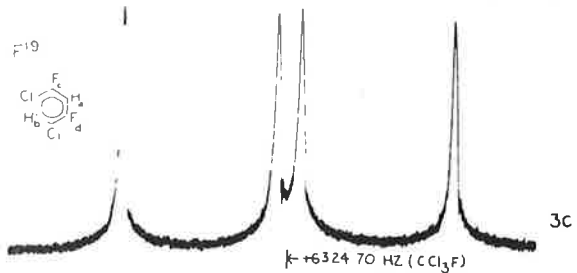
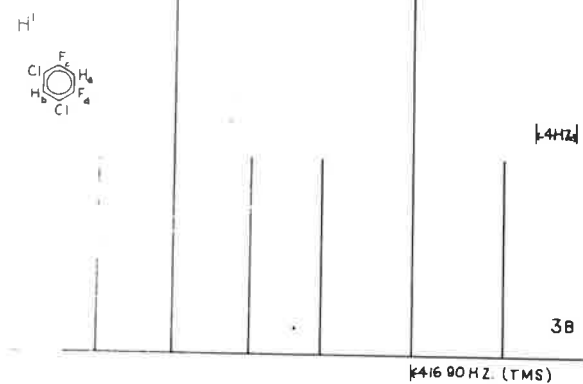
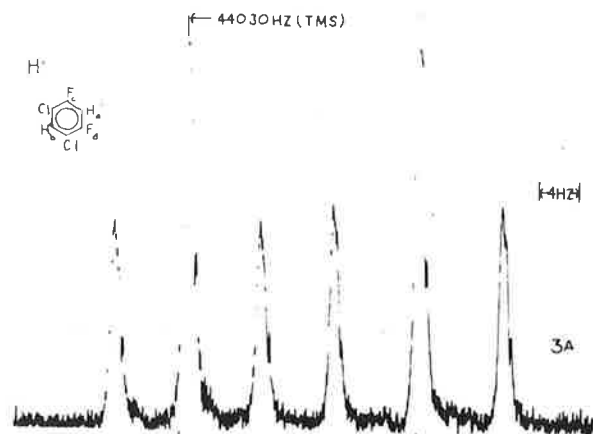
Jay Martin Anderson

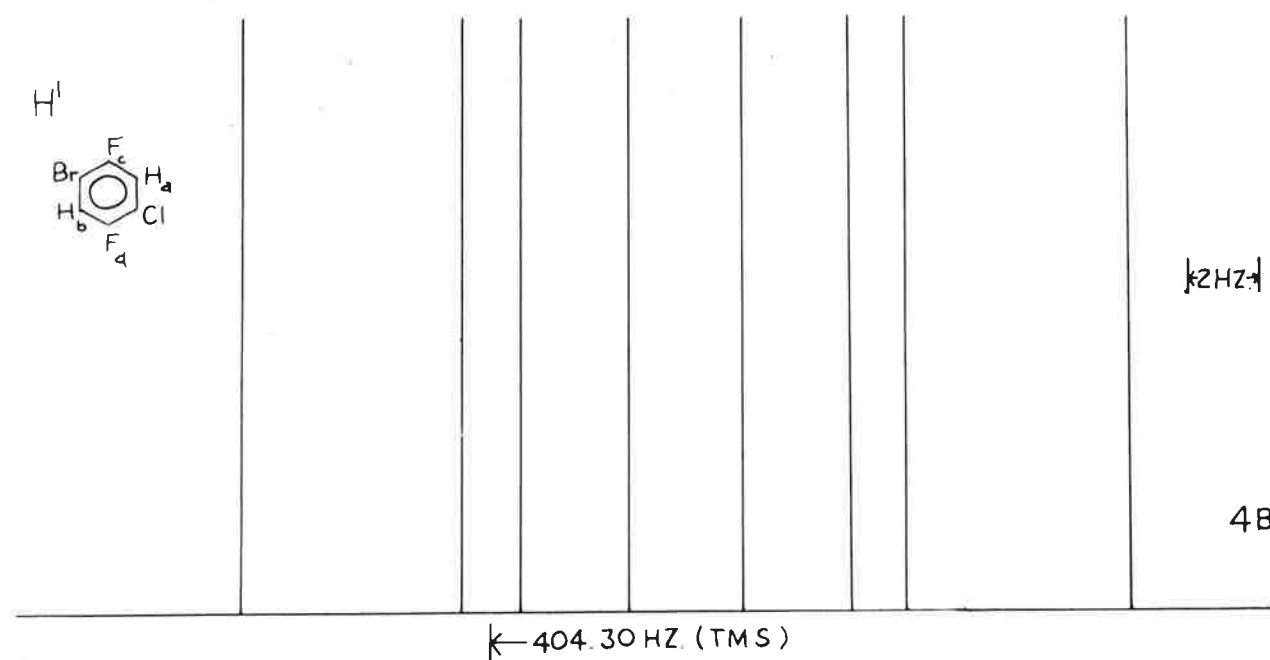
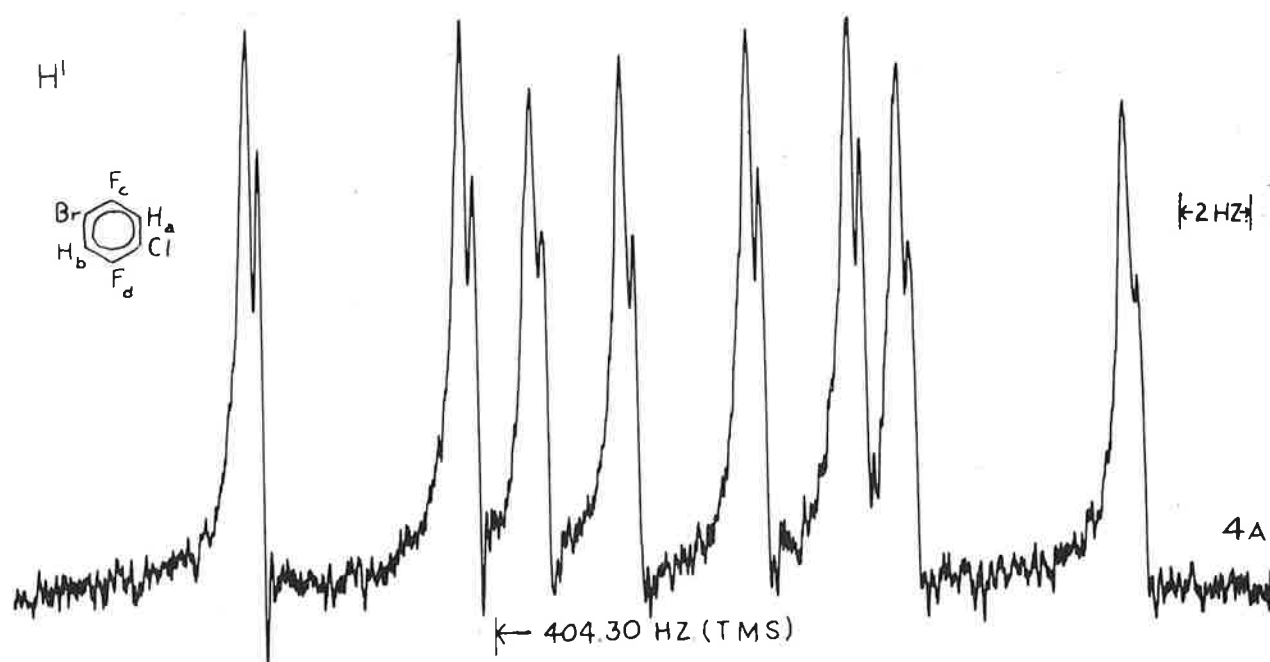
Sara

Sara B. Miller

¹R. J. Abraham and H. J. Bernstein, *Can. J. Chem.* **39**, 221 (1961); the point was suggested to us in communications from Schaefer and Haigh following our iitnmr newsletter 95-31.





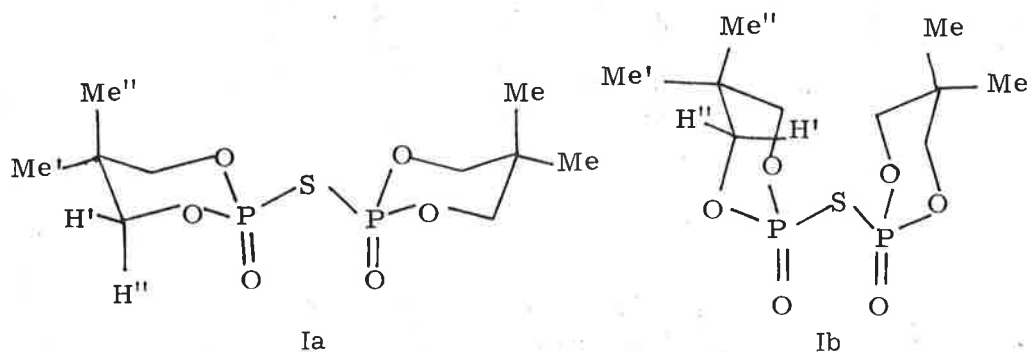


UNIVERSITY OF EAST ANGLIA,
School of Chemical Sciences,
Norwich, England.

4th December, 1967.

Dear Dr. Shapiro,

Use of $^3J_{\text{POCH}}$ in Conformational Analysis



Compounds of type I can exist in three chair forms: Ia with both P=O groups axial, Ib with both P=O groups equatorial, and Ic (not shown) with one axial and one equatorial P=O group. We have been interested in the use of $^3J_{\text{POCH}}$ coupling constants to gain information with respect to the conformations of such compounds, and in view of recent Japanese work¹ we present here a preliminary account of our findings.

The $^3J_{\text{POCH}}$ values obtained from $[(\text{CH}_3\text{CH}_2\text{O}_2\text{P}(\text{X})\text{Y}-)]$ derivatives are probably close to $(\frac{1}{3}J_t + \frac{2}{3}J_g)$ expected for equal proportions of each rotamer¹. Individual values of J_t and J_g were obtained for I, II and III by employing this equation in conjunction with:

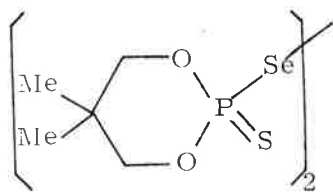
$$J_{\text{POCH}'} = n J_t + (1-n) J_g$$

$$J_{\text{POCH}''} = n J_g + (1-n) J_t$$

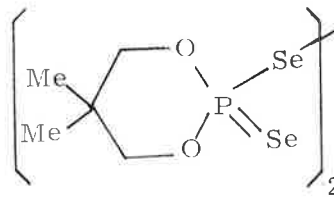
$$\therefore J_{\text{POCH}'} + J_{\text{POCH}''} = J_t + J_g$$

An approximate population (n) of the individual conformers was thus calculated from the observed $J_{\text{POCH}'}$ and $J_{\text{POCH}''}$ values. The individual values of J_t and J_g are similar to those of 28.2 and 1.5 c/s., respectively, calculated by Tsuboi et al.¹ studying (IV), which is held in the conformation shown by the phenyl substituent. J_g and J_t of I indicate that the possible error within the calculations, and percentage populations, is $\pm 10\%$. Commensurate with the decrease of the population of the major conformer in the series I, II, III is the decrease in

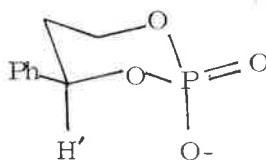
$\Delta\delta(\text{Me}', \text{Me}'')$. We believe that the predominate conformers are in each case those with the group $\text{P}=\text{X}$ axial, but further work is required on this point.



II



III



IV

Compound	(cf. Formulae Ia, Ib)		$J_g + J_t^{(a)}$	$\frac{2}{3}J_g + \frac{1}{3}J_t^{(b)}$	J_g	J_t	%major conformer ^(c) (100n)	$\Delta\delta(\text{Me}', \text{Me}'')^{(d)}$ c/s.
	$J_{\text{POCH}'}$	$J_{\text{POCH}''}$						
I	26.65	1.05	27.7	9.8	1.7	26.0	100 ^(c)	47.3
II	23.35	6.45	29.8	10.4	1.4	28.4	80	30.8
III	15.5	12.1	27.6	10.2	3.0	24.6	60	28.3

(a) $J_{\text{POCH}'} + J_{\text{POCH}''}$

(b) From compounds of the type $(\text{EtO})_2\text{P}(\text{X})\text{Y}$ -

(c) See text

(d) c./s. unit of shift is with respect to a 100 Mc/s. instrument

(a) M. Tsuboi, F. Kuriyagawa, K. Matsus, and Y. Kyogoku, Bull. Chem. Soc. Japan, **40**, 1813 (1967).

SYNTHESIS

* Department of Organic Chemistry, Politechnika, Lodz, Poland.

A. R. Katritzky

J. Michalski

M. R. Nesbit

A. R. Katritzky, J. Michalski* and M. R. Nesbit.

THE UNIVERSITY OF NEW BRUNSWICK
FREDERICTON, N.B.
CANADA



January 4, 1968

PHYSICS DEPARTMENT

Dear Dr. Shapiro:

Subject: F {C¹³} results for
CFC1 = CFC1

Having received the kind blue warning about my impending excommunication (see J.D. Baldeschwieler IITNMR 110-44), I offer the following contribution.

Prof. Saika visited us recently on his way from Tokyo to New York, and we hope that his example will be followed by other world wide n.m. resonators. He brought with him a sample of difluorodichloromethylene, of which about 2/3 was CFC1 = CFC1, of which approximately half was in the trans and half in the cis form, and he suggested that it would be nice to know the signs of the F-F coupling constants relative to the negative direct C¹³ - F coupling constant. The measurement calls for F {C¹³} double resonance, and we built a double tuning adapter for the transmitter coil in the Varian V4331A probe on the basis of the circuit given by S. Manatt and D. Elleman at Session B4 of the 1967 ENC. The following results were obtained:

	<u>CFC1 = CFC1</u>		
	trans	cis	
J (FF) Hz	- 129.7	+ 37.9	} ± 0.5
J (C ¹³ F) Hz	- 291.0	-299.0	
J (C ¹³ CF) Hz	+ 54.5	+ 37.0	
δ (C ¹³ F-C ¹² F) ppm	+ 0.100	+ 0.093	} ± 0.007
δ (C ¹³ CF-C ¹² CF) ppm	+ 0.033	+ 0.038	
δ (trans) - δ (cis) ppm: for F ¹⁹	+ 14.29		± 0.02
for C ¹³	+ 0.3		± 1

δ are the isotope shifts.

The absolute values compare favourably with those listed previously by G.V.D. Tiers and P.C. Lauterbur in J. Chem. Phys. 36, 1110 (1962) except for a 0.24 ppm discrepancy in the F¹⁹ chemical shift difference which may have been caused by a solvent effect.

Sincerely yours,

Reinhold

RK:seb

R. Kaiser, Professor

CARNEGIE-MELLON UNIVERSITY

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