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Newsletter

No.122
NOVEMBER, 1968

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A Monthly collection of informal private letters from Laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication". Reference to the TAMU NMR Newsletter by name in the open literature is strictly forbidden.

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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<p>Deadline Dates: No. 123: 2 December 1968 No. 124: 6 January 1969</p>

All Newsletter correspondence, etc., should be addressed to:

Professor Bernard L. Shapiro
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Texas
A &
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University
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Newsletter

POLICIES AND PRACTICAL CONSIDERATIONS

1. Policy: The TAMU NMR Newsletter (née MELLONMR, then IIT NMR Newsletter) is envisaged as a means for the rapid exchange of information between active workers in the field of nuclear magnetic resonance. As such, it will serve its purpose best if the participants impart whatever they feel will be of interest to their colleagues, and inquire concerning whatever matters interest them. Since the participant is clearly the best judge of what he considers interesting, our first statement of policy is "We print anything". (This is usually followed by the mental reservation "that won't land us in jail".) Virtually no editorial functions are performed, although I feel the time has come when contributions dealing with the likes of how to clean spectrometer cooling coils, etc., should not be considered adequate. The TAMU NMR Newsletter is not, and will not become, a journal. We merely reproduce and disseminate exactly what is sent in. Foreign participants should not feel obliged to render their contributions in English.

2. Subscriptions: We will continue (for the present, v.i.) to send out the TAMU NMR Newsletter without charge, although we would be grateful for the cooperation of all participants as outlined in the section below on "Practical Considerations". We are willing to send your issue by air-mail if you are willing to pay the rather formidable air-mail postage; rates and ground rules on request.

Participation is the prime requisite for receiving the TAMU NMR Newsletter; in order to receive the Newsletter, you must make at least occasional contributions to its contents. We feel that we have to be ruthless in this connection and the following schedule is in effect: Eight months after your last contribution, you will receive a "Reminder letter". If no contribution is then forthcoming ten months after your last contribution, you will receive the "Ultimatum letter", and then the next issue will be your last. If you are dropped from the mailing list, you can be reinstated by sending in a contribution, and you will receive back issues (as available) and forthcoming issues at the rate of nine per contribution. Frequent contributions are encouraged, but no "advance credit" can be obtained for these. In cases of joint authorship, either contributor, but not both, may be credited - please indicate to whose account credit should be given.

PLEASE NOTE: A subject of considerable interest and concern to several present and potential TAMU NMR Newsletter participants - as well as to ourselves - is whether the Newsletter ought to contain material which either appears essentially simultaneously in the formal literature (or is presented at a meeting) or is definitely scheduled to appear very shortly (i.e., within a few weeks) after it would appear in the Newsletter. Our attitude is that a TAMU NMR Newsletter contribution should not duplicate, summarize or abstract material which has been published or which will appear in the formal literature within a small number of weeks of the Newsletter account. On the other hand, let it be firmly emphasized that if the appearance in a journal is several months away - as is frequently the case - a brief account (as an abstract with or without a "Preprint Available" notice, a separate informal account, a selection of material from the manuscript, or what have you) sent in to the TAMU NMR Newsletter fulfills one of the very functions which we feel this Newsletter can provide. We trust that a participant will in each case himself apply the criterion of whether or not his contribution will communicate some subject matter to the Newsletter audience before they could read it elsewhere.

3. Public Quotation: Public quotation of Newsletter contents in print or in a talk is expressly forbidden (except as follows), and reference to the TAMU NMR Newsletter by name in the scientific literature is never permissible. We remind you that in order to quote results or use material from the Newsletter, it is necessary, in each individual case, to obtain the prior permission of the author in question and then to refer to the material quoted as a "Private Communication".

If your copy of the Newsletter is shared with other readers, it is your obligation as the actual recipient of the Newsletter to see that these other readers of your copy are acquainted with and abide by the statements of policy and practical considerations.

4. Practical Considerations: (a) All contributions to the TAMU NMR Newsletter should be sent to the undersigned and will always be included in the next issue if received before the deadline dates, which appear on the cover of each issue.

(b) Contributions should be on the minimum (NOTE!!) number of 8-1/2 x 11" (21 x 27.5 cm) pages, printed on one side only, with at least 3/4" (2 cm) margins on all sides. Black ink, typing, drawings, etc., on white paper are good; grey or blue ink, typing, etc., on anything is ghastly - i.e., high contrast is essential. We are not equipped to deal with large size pieces of paper - e.g. A-60 charts.

(OVER)

Please conserve space by avoiding double spacing (except where necessary), ultra-wide margins, half-filled pages, etc. In general, please plan and construct your contribution so as to fill the minimum number of pages needed. On the other hand, drawings and spectra lose both eye-appeal and utility when they are too small. However, it should rarely, if ever, be necessary for a contribution to exceed four pages in length, including figures.

Since reproductions of various kinds do not themselves reproduce too well, contributors are urged to submit their photographic originals to us (if the size does not exceed 8-1/2 x 11"), and we will be happy to return these if requested. Some law of physics says that photographic reproductions of fuzzy or blurred originals never come out less fuzzy or blurred.

(c) Please provide short titles of all the topics of your contributions, as this will ensure accuracy in preparing the title-page index.

(d) Please do not send in manuscripts, theses, books, etc., and ask us to be your consciences in selecting what should and shouldn't go into the Newsletter.

5. Finances: Although the Newsletter has always been provided free of charge, the size of the mailing list and the work load involved has required us in recent years to obtain partial financial support from outside. So far, adequate financial support has been forthcoming in the form of contributions or "subscriptions" to the Newsletter from companies, schools, research institutions, etc., whose names are listed on the back cover of each month's Newsletter issue, plus other benefactors who wish to remain anonymous. Raising the necessary amount of money by this method is neither an easy nor a congenial task, and we are reluctantly considering a regular subscription fee for future years. It is not pleasant to be forced to go this route, but unless voluntary contributions are forthcoming from a wider segment of our mailing list, some such measure will be necessary. Clearly it will be difficult to maintain the complete openness of the mailing list to all once we impose a mandatory financial barrier, however reasonable. No acceptable alternative means of support have been suggested, but we would be grateful for any ideas. In the meantime, we will be happy to provide the details for voluntary contributions or "subscriptions" to anyone interested.

6. Suggestions: They are always welcome.

B. L. Shapiro
10-30-68.

Address for all contributions and inquiries:

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

Papeete, 22 . x . 68

"FATHER MELLONMR"

You are old Father Mellon, and sorry to say,

You have grown most distressingly formal.

That lighthearted note is fast passing away,

Do you think at your age this is normal ?

In your youth, Father Mellon, you'd accept with a smile

Blank verse, or even a sonnet.

Was it Barry who favored this frivolous style,

Or the Bothner-B in your bonnet ?

Even worse, Father Mellon, you censor our toils,

(Pray, what makes you so awfully crusty ?)

We miss those prescriptions for flushing our coils

And preventing the pens getting rusty.

The fault, Father Mellon, is easy to trace:

That inflexible nine-month rule.

It lowers one's standards, it's quite a disgrace !

(Please accept this subscription renewal).

Suzie

UNIVERSITY OF KENTUCKY

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COLLEGE OF ARTS AND SCIENCES
DEPARTMENT OF CHEMISTRY

September 27, 1968

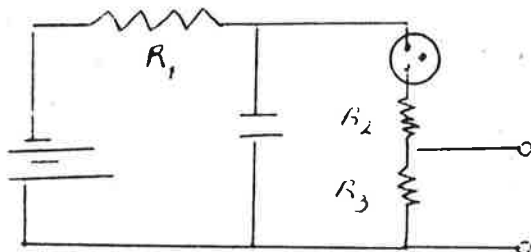
Professor Bernard L. Shapiro
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College Station, Texas 77943

Dear Barry,

As you may have noticed, everyone seems to be talking about digitizing spectra, computer control of spectrometers, etc., these days. However, the number of people who are actually doing it is still rather small. One of the major difficulties seems to be the cost of computers, spectrometer interfaces and the like.

The advantages of having digitized spectra are well known. Given digital spectra and any computer one can readily do signal/noise enhancement, resolution enhancement, line shape analysis and fitting, calibration, integration, base line corrections, and many more desirable things. The problem then is to digitize spectra. The trick is to do it for a minimum investment, preferably with the equipment all ready at hand. We would like to suggest a contest to see who can find the cheapest way to get digital spectra. It just so happens we have an entry for this contest. It is called GABY (Graduate students And a Bell Yet!).

We assume that practically everybody has a CAT of some sort. The CAT is a digitizer. It records a spectrum in some number of channels (1024 in the case of our Varian unit). If you can read each channel individually in some manner you have a digitized spectrum. All this requires is a device which will allow you to advance the CAT one channel at a time and another device which will allow you to read the contents of the channel when you get there.



The first problem can be solved with a neon bulb flasher. The circuit can be found in most elementary electronics books, but we reproduce it here for convenience.

This device will give a pulse whose amplitude depends on the threshold voltage of the neon bulb and the relative values of R_2 and R_3 . How often it pulses depends on the values of R_1 and the capacitor. Generally, R_1 should be 10 to 100 times $R_2 + R_3$. Most people will have the pieces around the lab, but they can be purchased for less than \$2-3. The pulse is fed to the external address advance of the CAT. Every time the light flashes the CAT advances one channel. Since you might not be looking at the light we have attached a bell which rings every time we get a pulse. (Actually, we used a Heath-Kit power supply in place of the battery and a spare recorder which goes swish with every pulse in place of the bell.)

The second problem, reading the value in the channel once you get there, is a bit more complicated. Ideally, we would like the result in decimal, binary, octal, or some such computer compatible form. Again, the CAT presents a backwards solution. It converts the number in the channel into a DC voltage to feed the recorder. All that is required is to read that voltage accurately. In our case we simply plug our digital volt meter into the external recorder jack on our HA-60. It could equally well be done with a meter or with the recorder itself. At this point a graduate student or other suitable slave laborer writes down the number, which is proportional to the number of counts in that channel. When the bell rings again he writes again. (We happen to have a spare key-punch so the student punches the value directly, but this is an unnecessary refinement.)

Using the above procedure we have digitized spectra, fed the results to our Cal Comp Plotter (and our IBM 360/50) and obtained a spectrum which is completely superimposable on the spectrometer readout of the same CAT run. About 30-40 minutes are required to get the 1024 numbers on cards ready to go into the computer.

Obviously, this approach is NOT the best way to get digital spectra. It does have the great advantage of being cheap and permitting you to do computer processing of spectra now. We (particularly the graduate students) hope to be digitizing spectra by more sophisticated means in the near future.

Best wishes,

Stan

Stanford L. Smith
H. E. (Ed) Montgomery
James L. Alderfer

Suggested Title: GABY: A Two Dollar Computer Spectrometer Interface

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October 6, 1968

Professor B. L. Shapiro
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Dear Barry,

I'm sending this Special Delivery in the hope it will arrive on time to save me from being thrown off the mailing list!

Boron-11 and Boron-10 Relaxation Spectra of Boron Hydrides and Determination of Long-Range Boron-Proton Coupling by Means of Proton Spin-Echoes:

Nitrogen-14 to proton scalar coupling constants in acetonitrile¹ and nitromethane² have been determined indirectly by means of a Carr-Purcell Spin-Echo (CPSE) method in which the proton Spin-Echo decay time constant is measured as a function of pulse repetition rate. Both J and the relaxation time of the quadrupolar nucleus, T_Q , can be measured. The analysis of the data is done by means of Eq. 135 of reference 3. I have applied this method to the determination of J ¹¹B-H in trimethoxyboron: $B(OCH_3)_3$. The situation here is complicated by the presence of two boron isotopes, ¹¹B and ¹⁰B, with fractional populations 0.8117 and 0.1883. The proton spin-echoes decay non-exponentially. The echo amplitude is proportional to

$$0.8117\exp(-tR_1) + 0.1883\exp(-tR_2)$$

where the first term comes from protons coupled to ¹¹B and the second from protons coupled to ¹⁰B. R_1 and R_2 are given by Eq. 135 of ref. 3, with the appropriate J and T_Q . In addition, we have $T_Q(^{10}B) = 1.534 T_Q(^{11}B)$ and $J_{11BH}/J_{10BH} = \chi(^{11}B)/\chi(^{10}B)$. Using this information, we have written a computer program to find J and T_Q . The results are (at 26°C):

Frequency of proton resonance experiments on $B(OCH_3)_3$	Boron-11 data		Boron-10 data	
	$J_{BH}(Hz)$	$T_1(msec)$	J_{BH}	$T_1(msec)$
10.748 MHz	2.43	13.6	0.81	21
32.088 MHz	2.37	13.7	0.79	21

As expected, the results are frequency independent, within experimental error. Even though J is small, the change in the CPSE decay time constant (average) when going from very small to very large pulse repetition rates is by more than a factor of 20. The proton relaxation time "in the absence of quadrupolar effect", T_2^0 is about 10 sec for trimethoxyboron at 26°C.

The reader may be curious why such strange frequencies were used for the proton measurements. The pulse apparatus was being used for ¹¹B and ¹⁰B relaxation measurements on boron hydrides, using an HA-100 magnet! We have obtained all sorts of interesting results here. We have used the recently described⁴

Fourier transform method for measuring spin-lattice relaxation times in "complex systems." For example, we have found that the boron relaxation time of the "apex" in pentaborane is much longer than that of the "base" borons. In general, boron relaxation times in boron hydrides are appreciably longer than in BR_3 compounds. The results of temperature dependence studies will soon be available in preprint form. It is clear from these measurements that the broad and featureless lines in the ^{11}B spectrum of pentaborane contain many unresolved lines and are not caused by a large quadrupolar broadening.

We have found a 40% isotope effect on the boron relaxation time when going from B_2H_6 to B_2D_6 , practically invariant with temperature in the range $-40^\circ C$ to $-150^\circ C$. We are using this piece of information in attempting to find better ways of predicting correlation times for quadrupolar relaxation.

Incidentally, the direct determination of the ^{11}B relaxation time in $B(OCH_3)_3$ at $26^\circ C$ gives a value of 15.2 msec, in reasonable agreement with the less accurate value on the previous page, obtained indirectly.

Sincerely,


Adam Allerhand

P.S. All the boron relaxation work was carried out in collaboration with Dr. Jerome Odom and the Boron Chemistry group of Dr. Riley Schaeffer. Mr. Robert Moll also participated in this project.

References

1. N. Boden, J. Deck, E. Gore, and H. S. Gutowsky, J. Chem. Phys. 45, 3875 (1966).
2. A. Allerhand, unpublished.
3. A. Allerhand and E. Thiele, J. Chem. Phys. 45, 902 (1966).
4. R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, J. Chem. Phys. 48, 3831 (1968).

PHYSIQUE EXPÉRIMENTALE MOLÉCULAIRE

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Professeur R. FREYMAN

Paris, le 7 Octobre 1968

Docteur Bernard L. SHAPIRO
Department of Chemistry
Texas A. et M. University

Tautomérie des composés hétérocycliques:
Phényl-3 oxadiazole-1,2,4 et Phényl-3 Δ_3 -oxadiazoline-1,2,4.

Cher Docteur Shapiro,

Dans une précédente lettre (1), nous avons signalé les résultats que nous avons obtenus quant aux signaux des groupements phényle en position -4 des thiazoles et des thiazolines. Nous avons montré que l'examen seul des signaux du phényle permettait de fixer la structure thiazole (phényle : structure à deux multiplets) ou thiazoline (phényle : singulet) de l'hétérocycle.

Nous avons étendu notre étude à l'oxadiazole-1,2,4 substitué en -3 par un phényle et diversement substitué en -5 (aminé, N-alkylaminé, acylé, à la fois N-alkylé et acylé, hydroxylé ou mercapté et leurs dérivés de méthylation).

Nous pouvons dire qu'ici encore le phényle en -3 présente une structure à deux multiplets dans le cas des oxadiazoles-1,2,4 ; mais c'est un singulet dans le cas des Δ_3 -oxadiazolines-1,2,4.

Nous présentons nos résultats sous forme de tableaux indiquant les déplacements chimiques en ppm (T.M.S. en référence interne, concentration molaire de l'ordre de 1 % - 60 M Hz, A60).

.../...

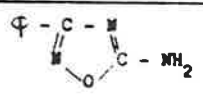
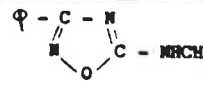
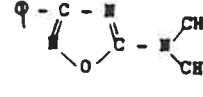
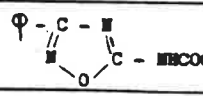
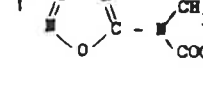
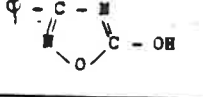
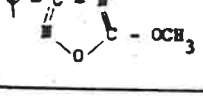
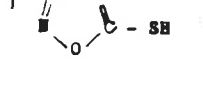
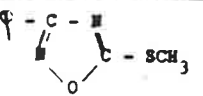
Ainsi, comme dans le cas des thiazoles, l'examen des signaux du groupement phényle en $-\delta$ suffit, à lui seul, pour fixer avec certitude la structure oxadiazole ou oxadiazoline des composés étudiés.

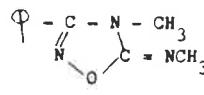
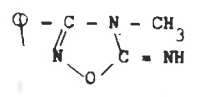
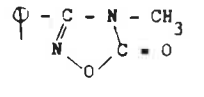
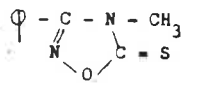
Avec nos sentiments distingués.

Mme M. SÉLIM et M. SÉLIM

M. Selim *M. Selim*

(1) NMR Letters, 1968, n° 113, p. 39.

Oxadiazoles-1,2,4	Groupement phényle en -3			Solvant
	Multiplets : δ en ppm	δ_o (ortho)	δ_m et δ_p (méta et para)	
	8,00 8,05 7,97	7,55 7,55 7,55	0,45 0,50 0,42	CDCl ₃ CH ₃ - CO - CH ₃ DMSO deut.
	8,03 8,04 8,00	7,50 7,51 7,57	0,53 0,53 0,43	CDCl ₃ CH ₃ - CO - CH ₃ DMSO deut.
	8,01 8,06 8,05 7,98	7,44 7,49 7,55 7,53	0,57 0,57 0,50 0,45	CCl ₄ CDCl ₃ CH ₃ - CO - CH ₃ DMSO deut.
	8,09 8,05	7,60 7,62	0,49 0,43	CH ₃ - CO - CH ₃ DMSO deut.
	8,02 8,05 8,08 8,04	7,50 7,53 7,61 7,64	0,52 0,52 0,47 0,40	CCl ₄ CDCl ₃ CH ₃ - CO - CH ₃ DMSO deut.
	7,91 7,90 7,90	7,61 7,62 7,65	0,30 0,28 0,25	CH ₃ - CO - CH ₃ C ₂ H ₅ - OH à 96° DMSO deut.
	8,03 8,07 8,03	7,45 7,50 7,64	0,58 0,57 0,39	CCl ₄ CDCl ₃ DMSO deut.
	7,90 7,98 7,87 7,91	7,66 7,65 7,55 7,66	0,24 0,33 0,32 0,25	CDCl ₃ CH ₃ - CO - CH ₃ C ₂ H ₅ - OH à 96° DMSO deut.
	8,05 8,08 8,07 8,00	7,44 7,49 7,60 7,61	0,61 0,59 0,47 0,39	CCl ₄ CDCl ₃ CH ₃ - CO - CH ₃ DMSO deut.

Δ_3 -oxadiazolines-1,2,4	Groupement phényle en -3	Solvant
	Singulet : δ en ppm	
	7,51 7,56 7,62 7,65	CCl ₄ CDCl ₃ CH ₃ - CO - CH ₃ DMSO deut.
	7,55 7,60 7,65 7,66	CCl ₄ CDCl ₃ CH ₃ - CO - CH ₃ DMSO deut.
	7,58 7,62 7,70 7,71	CCl ₄ CDCl ₃ CH ₃ - CO - CH ₃ DMSO deut.
	7,60 7,65 7,70 7,71	CCl ₄ CDCl ₃ CH ₃ - CO - CH ₃ DMSO deut.

STANFORD UNIVERSITY
STANFORD, CALIFORNIA

DEPARTMENT OF CHEMISTRY

14 October 1968

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

NMR of ^{43}Ca

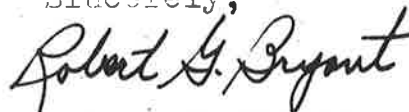
Dear Barry,

I have been studying the nuclear magnetic resonance of various inorganic ions which may be useful for the investigation of biological problems and would like to mention briefly some particularly interesting experiments with ^{43}Ca .

Measurements of the ^{43}Ca relaxation time in acidic solutions indicate that T_2 is close to 1.1 seconds.¹ Since the nuclear spin is 7/2, the nucleus is capable of possessing a significant quadrupole moment. Because T_2 is quite long even compared with smaller alkaline earth ions such as magnesium, either the quadrupole moment is small or the electrical environment of the calcium ion is very symmetric. The addition of adenosine triphosphate decreases the relaxation time markedly and this is most likely due to the chemical exchange² of calcium with the ATP. This exchange rate has been measured² and there is little doubt that the rapid exchange conditions are satisfied thus permitting experiments using the exchange as a chemical amplifier as done for example with the halogen ion probe technique of Stengle and Baldeschwiler.³

Calcium is an absolute requirement for such biological processes as nerve conduction and muscle contraction, but for a variety of reasons it has been difficult to probe the immediate environment of the calcium ions involved in these important systems. Direct observation of the calcium resonance appears to offer a significant tool for probing these interactions.

Sincerely,



Robert G. Bryant

¹Measurements were made on 51.68% enriched ^{43}Ca solutions using the technique developed by Brian D. Sykes for obtaining T_2 from T_1 . B. D. Sykes, submitted.

²Roger Phillips, B.J., Chem. Revs., **66**, 501(1966).

³H. R. Stengle and J. D. Baldeschwiler, Proc. Nat'l Acad. Sci., U.S., **55**, 1020(1966).

P.S. I would like to submit this letter in partial fulfillment of the requirements for a continuing subscription to the newsletter for our group.

THE LILLY RESEARCH LABORATORIES

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October 10, 1968

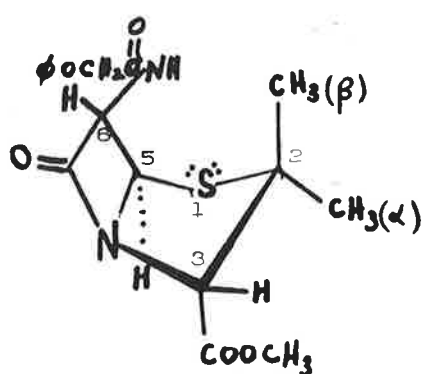
Dr. Bernard L. Shapiro
 Department of Chemistry
 Texas A and M University
 College Station, Texas 77843

Title: Anisotropy study of the
 $S \rightarrow O$ bond in Peni-
 cillin sulfoxides

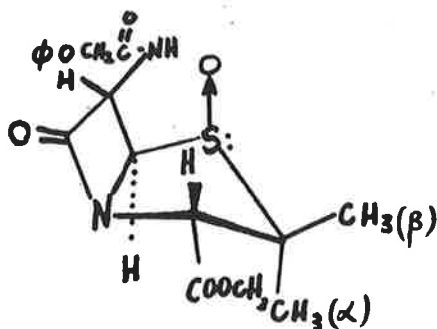
Dear Dr. Shapiro:

My apologies for having to be reminded about our now
 overdue contribution to TAMU NMR Newsletter. Here
 are some results from work which we have recently
 submitted for publication.

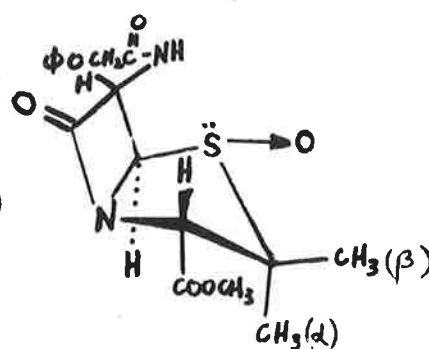
Recently we have had occasion to analyse the NMR
 spectra of phenoxymethyl penicillin (1) and its
 corresponding S - (2) and R - (3) sulfoxides.¹
 From NOE and X-ray studies, the conformations of



1



2



3

1, 2 and 3 were established (as above) and, consequently,
 the spatial position of various protons, relative to
 the $S \rightarrow O$ bonds in 2 and 3, defined.

Dr. Shapiro, October 10, 1968, Page 2

Assuming axial symmetry and acetylenic type anisotropy for the S \rightarrow O bond², we have attempted to calculate (using the McConnell equation) screening changes incurred by different penicillin protons when an S \rightarrow O bond is introduced into 1 (i.e. 1 \rightarrow 2 and 1 \rightarrow 3). The results of these calculations, summarized in the Table, are compared with observed shift values.

Table. McConnell Calculations for Screening Effect of S \rightarrow O Bond^x in R- and S- sulfoxides (2 and 3)

Case	Proton	Q	R(Å)	$\Delta\delta$ Calc.*	$\Delta\delta$ Cbs.
<u>1</u> \rightarrow <u>2</u>	H ₃	20	2.8	[-0.23](-0.47)	-0.23
	H ₅	38	3.0	[+0.21](+0.35)	+0.53
	H ₆	80	3.8	[-0.11](-0.18)	-0.35
	2 α -CH ₃	28	3.7	[+0.17](+0.29)	+0.25
	2 β -CH ₃	80	3.0	[-0.20](-0.33)	-0.15
<u>1</u> \rightarrow <u>3</u>	H ₃	20	3.7	[+0.21](+0.35)	+0.06
	H ₅	78	2.6	[-0.32](-0.54)	+0.80
	H ₆	58	4.0	[-0.02](-0.03)	+0.19
	2 α -CH ₃	87	3.0	[-0.23](-0.39)	-0.08
	2 β -CH ₃	58	3.2	[-0.03](-0.05)	+0.17

^xCalculated and observed shifts are in ppm.

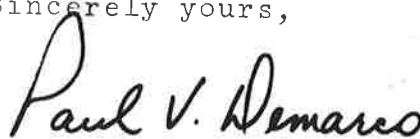
*Values in square and round brackets were calculated using anisotropy values -19.2 and -32.2 x 10⁻³⁰ cm³ molecule⁻¹ respectively (for the acetylenic bond) taken from the literature³.

Although the above results indicate qualitative agreement between observed and calculated shift values for the S-sulfoxide (2), this is not observed to be the case with the R-sulfoxide (3). The magnitude of these observed discrepancies (both qualitative and quantitative) suggests that the screening environment associated with the sulfoxide bond is considerably more complex than previously assumed², especially for protons situated adjacent to such bonds (e.g. compare $\Delta\delta$ Calc. with $\Delta\delta$ Cbs. for H₅ in case 1 \rightarrow 3). In support of this contention Foster, et al. have recently concluded, from studies on a number of 1,4-oxathian S-oxides, that the rationalization of deshielding effects resulting from the S \rightarrow O bond in terms of a syn-axial proximity effect and/or acetylenic anisotropy is an oversimplification. Thus, the above NMR technique for determining sulfoxide stereochemistry should be utilized with extreme caution.

Dr. Shapiro, October 10, 1968, Page 3

A more thorough investigation of S \rightarrow O bond anisotropy and of the origin of the above discrepancies is currently in progress.

Sincerely yours,



Paul V. Demarco
Molecular Structure Department

PVD:pw

- 1) R. D. G. Cooper, P. V. Demarco, J. C. Cheng and N. D. Jones, *J. Am. Chem. Soc.* (1969) (In Press).
- 2) K. W. Buck, et al., *Chem. Comm.*, 759 (1966); A. B. Foster, et al., *ibid.*, 881 (1966); P. B. Sollman, R. Nagarajan, and L. M. Dodson, *Chem. Comm.*, 552 (1967).
- 3) S. Castellans and J. Lorenc, *J. Phys. Chem.*, 69, 3552 (1965); J. A. Pople, *J. Chem. Phys.*, 37, 53 (1962).
- 4) A. B. Foster, et al., *Chem. Comm.*, 1086 (1968).



Eidg. Technische Hochschule
Laboratorium für Organische Chemie
Zürich
Günter Helmchen

122-15

8006 Zürich, October 16, 1968 /jw
Universitätstrasse 6
Tel. (051) 32 62 11

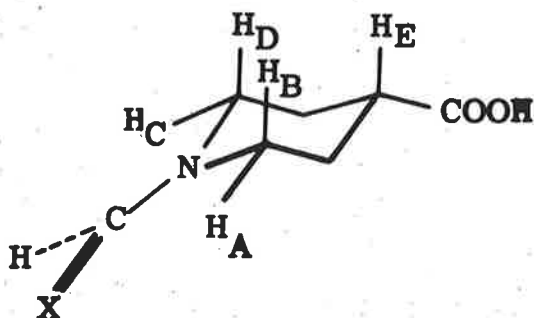
Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77943
USA

Dear Professor Shapiro,

A New Attack on the Problem of Restricted Rotation in Amides and Thioamides

The evaluation of exact activation parameters for the rotation about the CN-bond in amides and thioamides has recently aroused great interest. The method of choice has been the kinetic measurement by n.m.r. spectroscopy. Only Walter et. al.¹⁾ have done conventional kinetics in the case of thioamides, where they succeeded in isolating diastereoisomers. The difficulties and pitfalls of the n.m.r. method are dramatically illustrated by the long list of differing values for the energy barrier in N,N-dimethylformamide (7-27 kcal/mole).

To obtain unambiguous values the following classical approach has been used. One enantiomer each of the amide I and the thioamide II have been



I X = O
II X = S

obtained in crystalline form at low temperature (recrystallization of

the (-)- α -phenylethylamine salts from ethyl acetate, followed by chromatography at -32°C in the case of I, and distribution between ethyl acetate and dilute sulfuric acid at 0°C in the case of II). They racemize in solution at room temperature, the rates fitting excellently first order kinetics. Preliminary data are

for I $[\alpha]_D^{23.5} + 59^{\circ}$ (methanol, $c = 0.68$), $\tau_{1/2} = 1.5$ minutes (23.5°C)

for II $[\alpha]_{546}^{22} + 12^{\circ}$ (methanol, $c = 0.91$), $\tau_{1/2} = 32$ minutes (22°C).

The figures 1 and 2 show the n.m.r. spectra (100 Mc, 30% CDCl_3 , 37°C) of racemic I and II. At higher temperatures coalescence can be observed in both cases. At present we are measuring exactly the kinetics of racemization by polarimetry and hope to determine accurate activation parameters.

With kind regards from Professor V. Prelog.

Sincerely yours,

Joachim Helmchen

1. W. Walter, J. Maerten and E. Rode, Liebigs Ann. Chem. 631, 25 (1966).

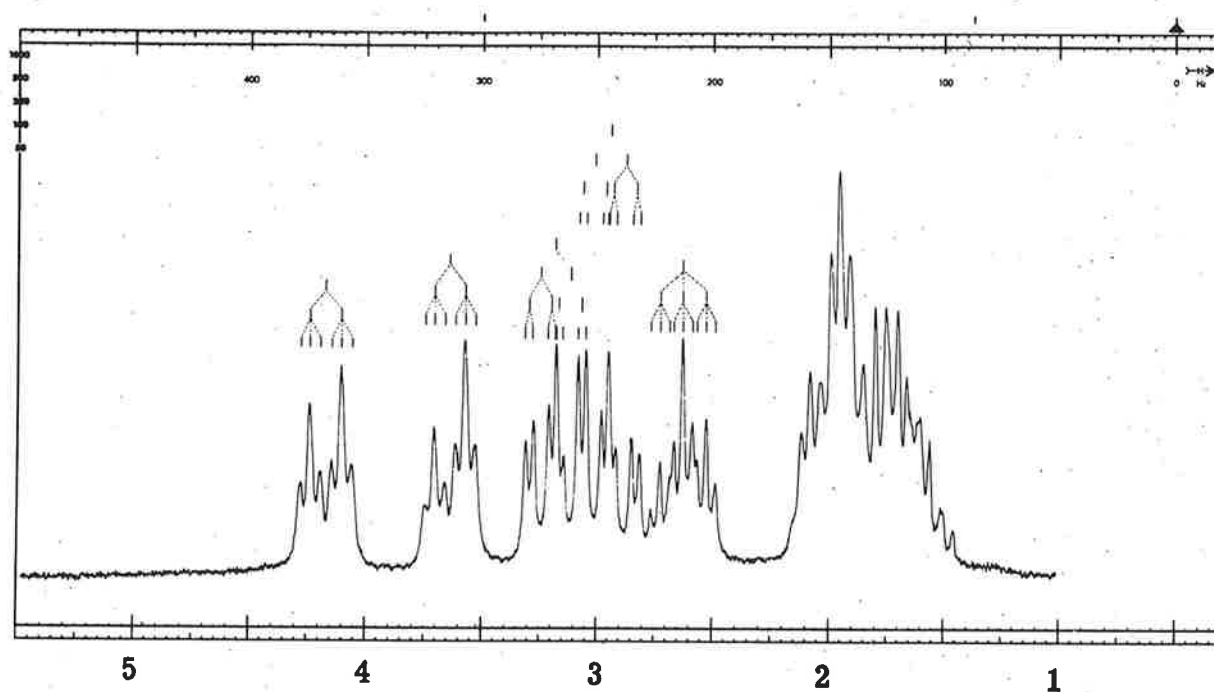


Fig. 1 N-formyl-piperidine-4-carboxylic acid

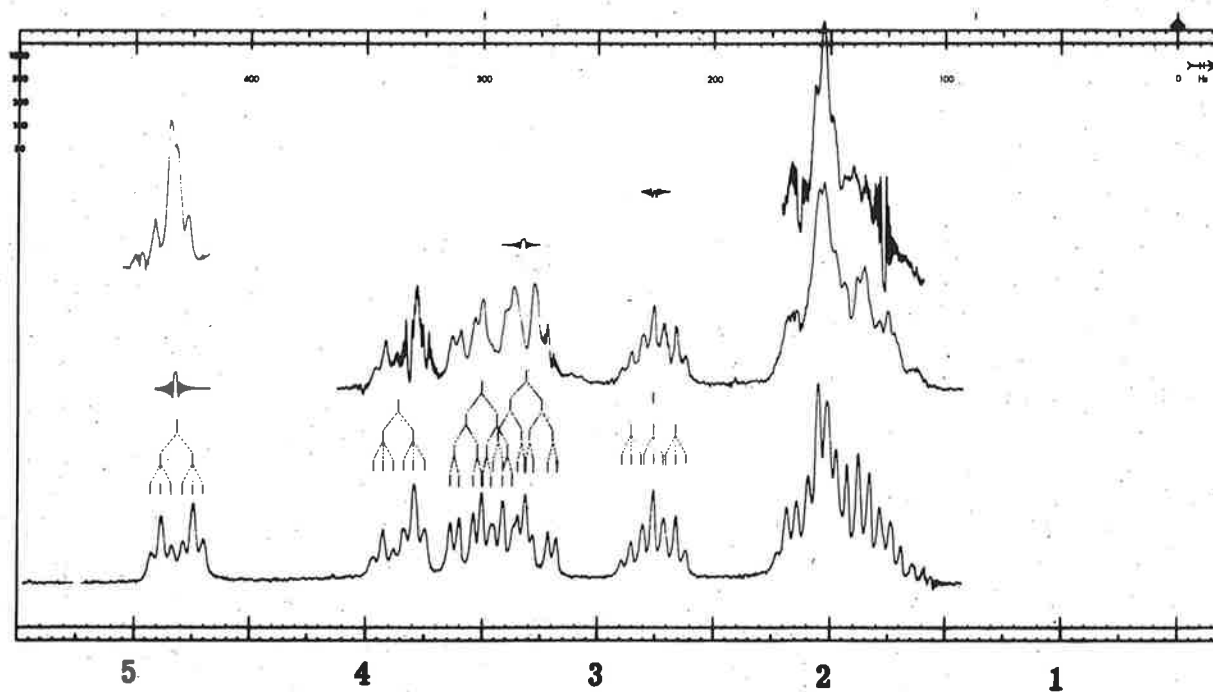


Fig. 2 N-thioformyl-piperidine-4-carboxylic acid

NORTHWESTERN UNIVERSITY

EVANSTON, ILLINOIS 60201

DEPARTMENT OF CHEMISTRY

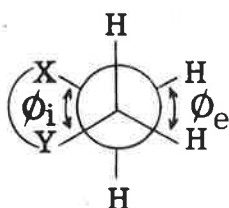
October 17, 1968

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

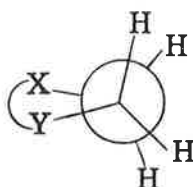
Dear Barry:

Correlation of Solid- and Liquid-State Structures

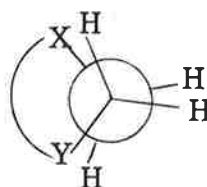
Some time ago,^{1a} we proposed a method for obtaining structural information about saturated six-membered rings in solution. Three cases could be differentiated for molecules with an $X-CH_2-CH_2-Y$ fragment. The ratio of the average J_{trans} to the average J_{cis} is always



Ia



Ib



Ic

1.9-2.3 for "undistorted" segments (Ia), <1.8 for flattened segments (Ib), and >2.5 for puckered segments. If several $-CH_2-CH_2-$ portions are present, the entire ring may be mapped.^{1b} These conclusions follow from the known dependence of the H-C-C-H coupling on dihedral angles. We wanted to compare these solution data with dihedral angles derived from crystal structures. The X-C-C-Y angle (ϕ_i) always decreases as the $H_{eq}-C-C-H_{eq}$ angle (ϕ_e) widens, and vice versa. The X-C-C-Y dihedral angle is available from the literature for undistorted and puckered examples. We recently completed the structure of 4,4-diphenylcyclohexanone in order to have an example of the flattened geometry. We present the data for the three cases in the table. A reliable correlation does exist. As the X-C-C-Y angle widens (greater puckering), the ratio R increases. A smaller R in turn is associated with a flattened chair. If anyone knows of other examples for which both R and ϕ (X-C-C-Y) are known, we would be glad to learn of them.

Sincerely,


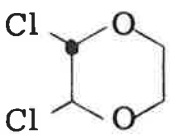
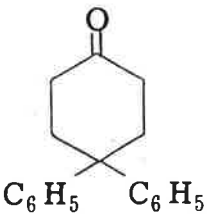
Joseph B. Lambert

Raymond E. Carhart

JBL/kc

Professor Bernard L. Shapiro
 Page Two
 October 17, 1968

TABLE

<u>Molecule</u>	<u>R</u>	<u>$\phi_{X-C-C-Y}$</u>	<u>Type</u>
	3.4 ^{1a}	69° ^{2,3}	Strongly Puckered
	2.0 ⁴	54° ^{5,6}	Relatively Undistorted
	1.6 ⁷	51°	Slightly Flattened

- (1) a. J. B. Lambert, J. Am. Chem. Soc., 89, 1836 (1967).
 b. J. B. Lambert and R. G. Keske, Tetrahedron Lett., 4755 (1967).
- (2) R. E. Marsh, Acta Cryst., 8, 91 (1955).
- (3) H. T. Kalff and C. Romers, Rec. Trav. Chim., 85, 198 (1966).
- (4) D. Jung, Ber., 99, 566 (1966).
- (5) C. Altona and C. Romers, Rec. Trav. Chim., 82, 1018 (1963).
- (6) N. de Wolf, C. Romers, and C. Altona, Acta Cryst., 22, 715 (1967).
- (7) J. B. Lambert, R. E. Carhart, P. W. R. Corfield, and J. H. Enemark, Chem. Commun., 999 (1968).

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

October 18, 1968

RE: RECALIBRATION OF NMR THERMOMETER
TEFLON SPINNING WEIGHT

Dear Dr. Shapiro:

We have redetermined the peak separation of methanol and ethylene glycol. At room temperature, our results agree with the calibration charts supplied by Varian Associates within 1°K, as may be seen from the figures. At 220°K, the Varian chart gives a temperature 4.2°K lower, and at 410°K, it gives 3.4° lower. While the peak separation $|\Delta\nu|$ of glycol fits a straight line perfectly with an error of only 0.3°, the separation of the methanol peaks is not quite linear with temperature. The deviations from linearity are slight however, and a straight line approximation over a range of 60° fits the data within 0.6°, as shown in the figure.

Independently, Neuman (1) has obtained the same result for glycol within 0.8°: $T = 466.5 - 1.691 |\Delta\nu|$.

Our results were obtained with a thermistor probe (2,3) which allows spinning as well as closing of the sample tube. A direct temperature reading is obtained. The probe (2) is very convenient, and some students prefer it for routine use. Since the Varian pressure cap cannot be used, we use a cylindrical spinning weight (4) around the sample tube to prevent lifting.

The teflon spinning weight (4) is very convenient and entirely satisfactory. As a result, our pressure cap is collecting dust.

Sincerely yours,

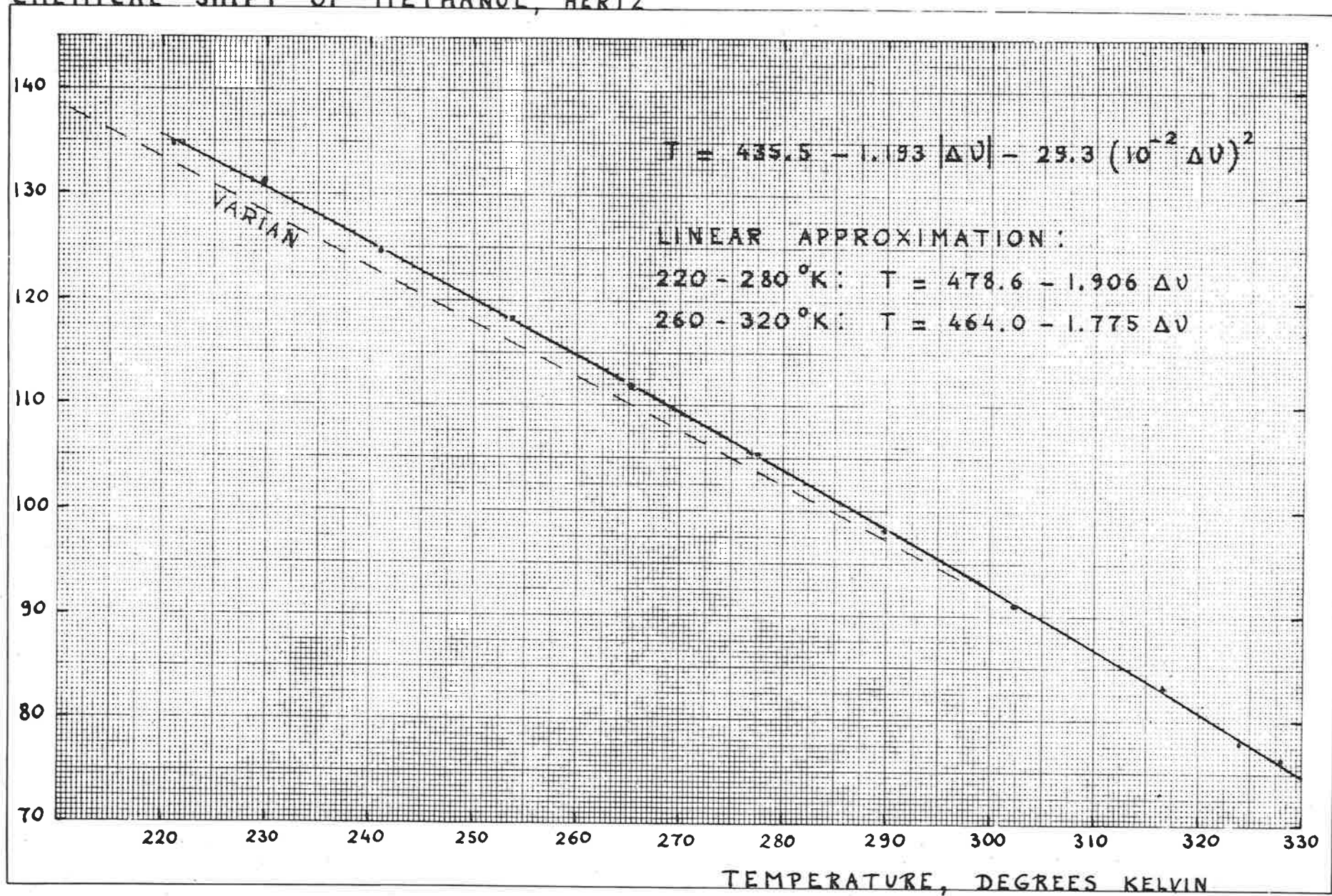
Anthony L Van Geet

Anthony L. Van Geet

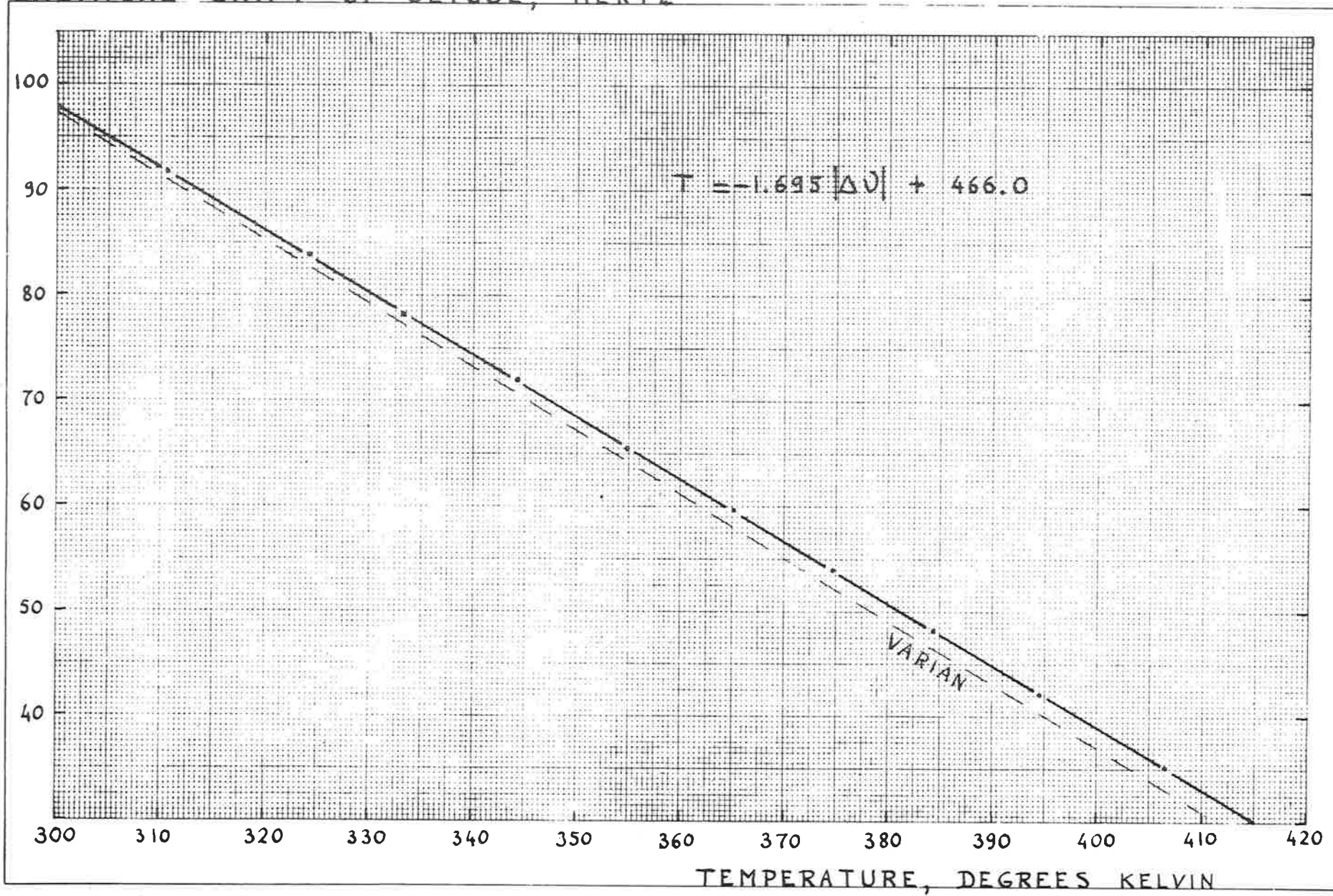
AVG:cd

- (1) R. C. Neuman, Department of Chemistry, University of California, Riverside, California 92502, private communication.
- (2) A. L. Van Geet, Anal. Chem., in press.
- (3) A. L. Van Geet, Rev. Scient. Instr., in press.
- (4) A. L. Van Geet, Anal. Chem., 40, 1914 (1968).

CHEMICAL SHIFT OF METHANOL, HERTZ



CHEMICAL SHIFT OF GLYCOL, HERTZ



D E P A R T M E N T O F C H E M I S T R Y
THE UNIVERSITY OF MICHIGAN • ANN ARBOR, MICHIGAN

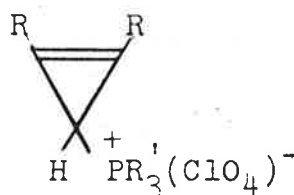
October 14, 1968

Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Title: Unusually High PCH Coupling Constants in
Cyclopropenylphosphonium Salts

Dear Barry:

In order to renew our subscription to IITNMRN we submit data on the PMR spectra of cyclopropenylphosphonium salts. Of particular interest are the PCH coupling constants. To our knowledge they are the first reported measurements of cyclopropene geminal coupling constants and they are abnormally large, exceeding in magnitude J_{PCH} values for phosphorus derivatives of any type.



τ and J for Methine Proton

	<u>Solvent</u>	<u>τ</u>	<u>J_{PCH}</u>
$R = n-C_4H_9$; $R' = \emptyset$	CD_3CN	7.23	52.0Hz
$R = n-C_3H_7$; $R' = \emptyset$	CD_3CN	7.13	51.2
$R = R' = \emptyset$	CD_3CN	6.08	47.1
$R = \emptyset$; $R' = n-C_4H_9$	CD_3CN	7.33	42.8

Based on previously reported studies we tentatively conclude that J_{PCH} is positive in sign. Further details, including effect of anion and solvent on both τ and J_{PCH} , are available in the form of a preprint of a manuscript in preparation.

Sincerely yours,

Dani
Daniel T. Longone

DTL:ap

Carnegie-Mellon University

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

October 18, 1968

Professor Bernard L. Shapiro
TAMU NMR Newsletter
c/o Department of Chemistry
Texas A&M University
College Station, Texas 77843

"Calculations of Directly Bonded Carbon-
Hydrogen Through Bond Coupling Constants"

Dear Barry,

Since our last communication to you we have been continuing our calculations of nuclear spin coupling constants using a finite perturbation method. There will be a paper concerning this method appearing shortly in J.C.P.

Gary Maciel worked with us last spring and summer calculating spin coupling constants for a variety of systems. Tables 1 and 2 display some of these results for JCH (directly bonded) coupling constants in substituted methanes.

As seen in Table 1, the calculated JCH's exhibit the correct trend as electronegative substituents are added directly to the carbon atom concerned. Table 2, on the other hand, shows that when the electronegative atoms are one bond removed from the carbon atom, the resulting trends are in poor agreement with those observed, even being reversed in some cases. However, if an effective nuclear charge correction of the type proposed by Grant and Litchman¹ is applied to the Hydrogen atom, then the tendency is for the trend in Table 2 to reverse itself, i.e. the agreement with the experimental results will be improved. The trends in Table 1 will remain the same (although the values will change).

Good luck to you with your new position.

Sincerely yours,

John

John A. Pople

Jim

James W. McIver, Jr.

Neil

Neil S. Ostlund

Reference:

1. D. M. Grant and W. M. Litchman, J. Am. Chem. Soc. 87, 964 (1965).

Carnegie-Mellon University
Mellon Institute

Professor Shapiro

-2-

October 18, 1968

TABLE 1

Molecule	JCH (Calculated)	JCH (Observed)
HCH_3	122.9	125
HCH_2OH	135.3	141
HCH_2OCH_3	135.5	140
$\text{HCH}(\text{OCH}_3)_2$	151.7	162
HCH_2NH_2	129.9	133
HCH_2F	148.7	149.1
HCH_2F_2	166.8	184.5

TABLE 2

Molecule	JCH (Calculated)	JCH (Observed)
HCH_2CH_3	122.1	124.9
HCH_2CN	122.5	136.1
$\text{HCH}(\text{CN})\text{CH}_3$	119.8	135.5
HCH_2CHO	121.4	127
HCH_2NO_2	129.8	147.7
$\text{HCH}(\text{NO}_2)_2$	143.7	169.4

THE UNIVERSITY OF NORTH CAROLINA
AT
CHAPEL HILL
27514

DEPARTMENT OF CHEMISTRY

October 17, 1968

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

EXCHANGING AB SPIN PAIRS

Dear Barry:

Sometime ago I suggested a method for calculating NMR spectra for strongly coupled spins that are involved in general intermolecular reactions.¹ As an example I wrote out equations for an AB spin system having two different conformations - each being described by a pair of chemical shifts and a spin coupling constant. At that time such an exchange problem was not in the literature, but earlier this year Fujiwara and Reilley reported NMR studies of trans-1,2-cyclohexylenedinitrilo-tetraacetic acid (CYDTA) in which the acetate methylene protons seem to provide just such a system.² They suggested that a broadened quartet in the NMR spectrum resulted from the exchange of methylene protons in the monoprotonated species between two different environments.

I thought that it would be amusing to use the density matrix equations to calculate the line shapes in order to verify the broadening mechanism and to estimate rates of exchange. This involved solving equations of the form

$$I(\omega) = \text{Re}(\underline{1} \cdot \underline{A}^{-1} \cdot \underline{1})$$

where A is a 4 x 4 complex matrix. A GE 235 (CAC) computer was used for this purpose with the results shown in Figure 1. The parameters, which were kindly supplied by Professor Reilley, are:

Conformation I ; $(\omega_{IA}/2\pi) = -21.63\text{Hz}$, $(\omega_{IB}/2\pi) = 21.63$, $(J^I/2\pi) = 15.6\text{Hz}$,
and $(1/\pi T_2^I) = 1.5\text{Hz}$; Conformation II ; $(\omega_{IIA}/2\pi) = -16.16\text{Hz}$,
 $(\omega_{IIB}/2\pi) = -9.84\text{Hz}$, $(J^{II}/2\pi) = 15.6\text{Hz}$, and $(1/\pi T_2^{II}) = 1.5\text{Hz}$.

The calculated spectra satisfactorily reproduce the experimental spectra.

Page #2

October 17, 1968

I hope that this brief report has not been completely unintelligible. Details of the calculation and some discussion of the equations will be published in the Journal of Magnetic Resonance.

Sincerely yours,

Charles

C. S. Johnson, Jr.

CSJ/ef

1. C. S. Johnson, Jr., J. Chem. Phys. 41, 3277 (1964).
2. Y. Fujiwara and C. N. Reilley, Anal. Chem. 40, 890 (1968).

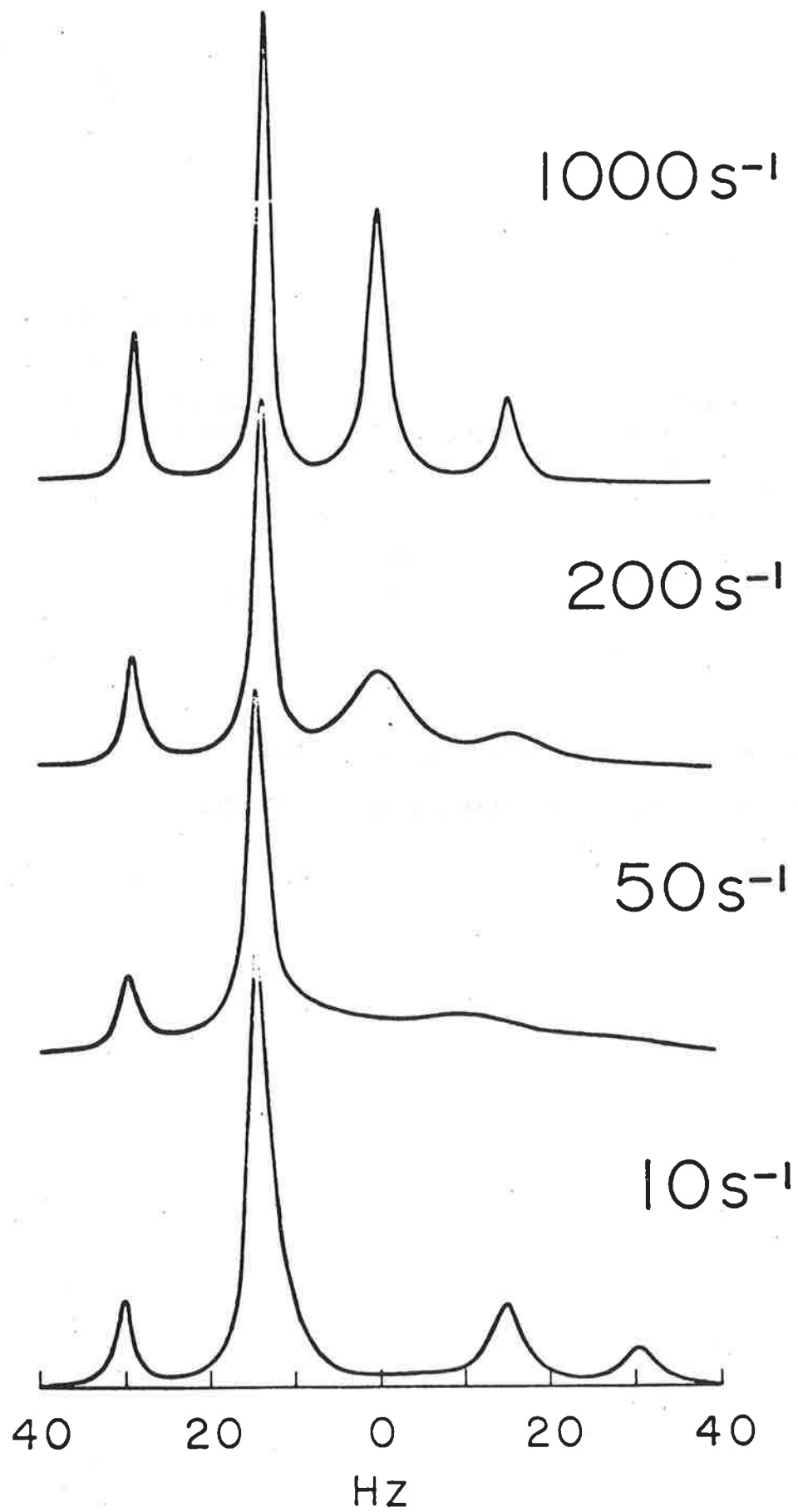


Figure 1.

CYANAMID

AMERICAN CYANAMID COMPANY
 ORGANIC CHEMICALS DIVISION
 BOUND BROOK, NEW JERSEY 08805
 AREA CODE 201 356-2000

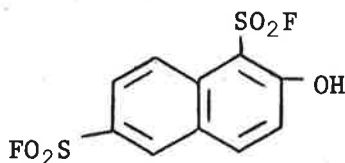
August 22, 1968

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

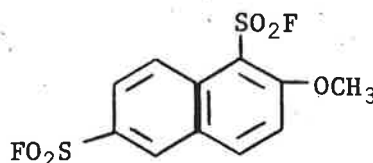
Re: Coupling Constants and Chemical Shifts in 2-Naphthol-1,6-Disulfonyl Fluoride

Dear Doctor Shapiro:

In connection with some NMR studies of derivatives of various 2-naphthol sulfonic acids, the proton spectra of 2-naphthol-1,6-disulfonyl fluoride (I) and its methyl ether (II) were measured at 60 MHz. These spectra showed readily measurable coupling between the fluorine atoms and the ring protons.



I



II

Cyanamid's

Through the courtesy of Dr. J. E. Lancaster of ~~our~~ Central Research Laboratories and Dr. L. Wilson of Varian Associates, PMR spectra in the aromatic region at 100 MHz and FMR spectra at 94.1 MHz of (I) were obtained. The spectra were measured in deuteriochloroform solution with TMS as the internal reference for the PMR spectra and Freon 11 for the FMR spectra. Signal frequencies were measured to the nearest 0.1 Hz. The PMR spectrum is shown in Figure 1; the assignment of signals to various aromatic protons was made with the aid of spin decoupling. This spectrum was analyzed using LACOON III on an IBM 1130 Computer.

Very little has been reported in the literature concerning either the proton shifts or the proton-fluorine coupling in aromatic sulfonyl fluoride compounds. Brownstein (1) observed that aromatic protons ortho to the $-SO_2F$ group are shifted about 0.6 parts per million downfield from benzene protons, and Tiers (2) listed the chemical shifts in para-toluene sulfonyl fluoride. Therefore, the results of the analysis of the aromatic spectrum of (I) may be of interest to your readers.

The parameters obtained from the computer analysis of the PMR spectrum of (I) are:

Dr. Bernard L. Shapiro

-2-

August 22, 1968

τ_3	= 2.563	$J_{3,4}$	= 9.23 c/s
τ_4	= 1.735	$J_{4,5}$	= <0.01 c/s
τ_5	= 1.429	$J_{5,7}$	= 0.56 c/s
τ_7	= 1.443	$J_{5,8}$	= 0.03 c/s
τ_8	= 1.873	$J_{7,8}$	= 9.34 c/s
ϕ_α	= 71.24	$J_{3,F\alpha}$	= 1.30 c/s
ϕ_β	= 66.05	$J_{4,F\alpha}$	= 0.55 c/s
		$J_{5,F\beta}$	= 2.20 c/s
		$J_{7,F\beta}$	= 2.86 c/s
		$J_{8,F\beta}$	= 2.04 c/s

The RMS error for all the calculated frequencies using the above parameters was 0.04 c/s and the standard error of estimate for all parameters was less than 0.01 c/s.

The FMR spectrum of (I) is shown in Figure 2. The downfield signal in the FMR spectrum (quartet at 71.24 ppm downfield from Freon 11) was assigned to the fluorine of the $-\text{SO}_2\text{F}$ group in the 1 position. This group is ortho to the electron donating hydroxyl group. Taft, et al. (3), reported that electron donor substituents para to the $-\text{SO}_2\text{F}$ group in benzenoid compounds lower the resonance of the fluorine atom. An ortho electron donating substituent would be expected to have a similar effect. The upfield multiplet at 66.05 ppm from Freon 11 was assigned to the fluorine of the $-\text{SO}_2\text{F}$ group in the 6 position.

Using the above parameters good agreement is obtained between the calculated and observed PMR spectra of (I) at 60 MHz.

Sincerely yours,

Jessie L. Gove
NMR Laboratory

JLG/cd

References: (1) S. Brownstein, Chem. Rev., 59, 473 (1959).

(2) G.V.D. Tiers, "Nuclear Magnetic Resonance Shielding Values for Hydrogen in Organic Structures," Table II, pp. 2, 3, 17 (1958).

(3) R. W. Taft, F. Prosser, L. Goodman and G. T. Davis, J. Chem. Phys., 38, 380 (1963).

ALGEMENE KUNSTZIJDE UNIE N.V. - ARNHEM

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



CENTRAAL RESEARCHINSTITUUT

Dr. Bernard L. Shapiro
 Texas A & M University
 College of Science
 Department of Chemistry
T E X A S 77843
 U.S.A.

Uw kenmerk

Uw brief van

Ons kenmerk

Toestel

ARNHEM, Velperweg 76

CH 68/160 Huys/ML

Datum October 17, 1968

ONDERWERP: An NMR study of the 4-ethoxydurenol dimer

Dear Dr. Shapiro:

Recently Williams and Kreilick published an NMR study ¹⁾ on the interesting rearrangement and dissociation reaction (Fig.1, processes 1 and 2) of some quinol ethers ($R_1=t-C_4H_9$; $R_2=H$; $R_3=CN$, $COCH_3$, $CO-t-C_4H_9$, CO_2CH_3 , $CO_2C_2H_5$ and $CO_2-c-C_6H_{11}$).

In this connection I would like to report the results which were obtained by studying the NMR spectra of the 4-ethoxydurenol dimer (4-EDD, Fig.2), taken at different temperatures.

Representative 60 MHz spectra of this compound, dissolved in carbon disulphide, are given in Fig. 3a-c and will be discussed separately.

I. The spectrum taken at $-25^{\circ}C$ (Fig. 3b)

This spectrum is easily interpreted and the coding in Fig.2 is used to assign the signals to the particular protons in the molecule. Application of double resonance, and the effect of the rearrangement reaction on the signals, observed at higher temperatures, ensure the right assignment.

II. The spectrum taken at $+39^{\circ}C$ (Fig. 3a)

By gradually increasing the temperature above $-10^{\circ}C$ the rearrangement reaction which interchanges the quinone and aromatic ring protons (cf process 1 in Fig.1) first causes line broadening, then coalescence, and finally line sharpening for each of the following pairs of signals: $CH_3(a)$ and $CH_3(a')$, $CH_3(b)$ and $CH_3(b')$, $CH_2(c)$ and $CH_2(c')$ and $CH_3(d)$ and $CH_3(d')$.

1) D.J. Williams and R. Kreilick, J.Am.Chem.Soc., 89 3408 (1967) and 90 2775 (1968)

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CH 68/160 Huy/ML

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In the spectrum of Fig. 3a only one signal remains for the $\text{CH}_3(\text{a}, \text{a}')$ and $\text{CH}_3(\text{b}, \text{b}')$ groups due to accidental overlap. The linewidths at 48°C of the $\text{CH}_3(\text{a}, \text{a}')$, $\text{CH}_3(\text{b}, \text{b}')$ and $\text{CH}_3(\text{d}, \text{d}')$ signals are only slightly broader ($< 1,5 \text{ Hz}$) than in the absence of exchange broadening at -26°C . The rate of the rearrangement reaction is not yet high enough to result in smaller linewidths. No spectra at higher temperatures could be taken without fast decomposition of 4-EDD. From the coalescence temperatures the free activation energy of the rearrangement reaction was calculated: $\Delta G^\ddagger = 14.9 \pm 0,3 \text{ Kcal/mol}$ at 20°C .

Dissociation of 4-EDD (cf process 2, Fig. 1) into 4-ethoxydurenoxy radicals also took place, as was demonstrated by ESR measurements on concentrated solutions above 5°C . But in the NMR spectra no line broadening, clearly related to this dissociation reaction, was observed.

III. The spectrum taken at -104°C (Fig. 3c)

Gradual lowering of the temperature from -50°C to -110°C results in considerable changes in the spectra which can be explained in terms of one exchange process, operating on several signal groups. Due to a restricted rotation around the carbon-oxygen bond, connecting the two halves of the molecule, the eight methyl groups $\text{CH}_3(\text{a})$, $\text{CH}_3(\text{b})$, $\text{CH}_3(\text{a}')$ and $\text{CH}_3(\text{b}')$ become all magnetically inequivalent, as is shown in the spectrum of Fig. 3c. Purely by accident some methyl groups have the same chemical shift values. Especially the signals of the methyl groups, located nearest to the carbon-oxygen bond, are split most strongly (0.64 ppm for $\text{CH}_3(\text{a}')$ and 0.99 ppm for $\text{CH}_3(\text{b})$ groups). At higher temperatures the increased rotation leads to coalescence of the eight signals into four. From the coalescence temperature the free activation energy was calculated: $\Delta G^\ddagger = 9.2 \pm 0,3 \text{ Kcal/mol}$ at -90°C .

Sincerely yours,

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

W.G.B. Huysmans

W.G.B. Huysmans

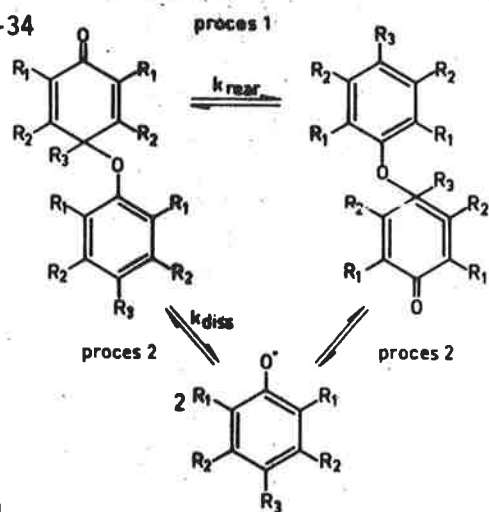


Fig. 1. The rearrangement reaction (Process 1) and the dissociation reaction (Process 2) of quinol ethers and quinone ketals.

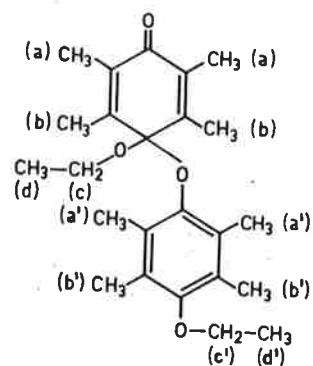
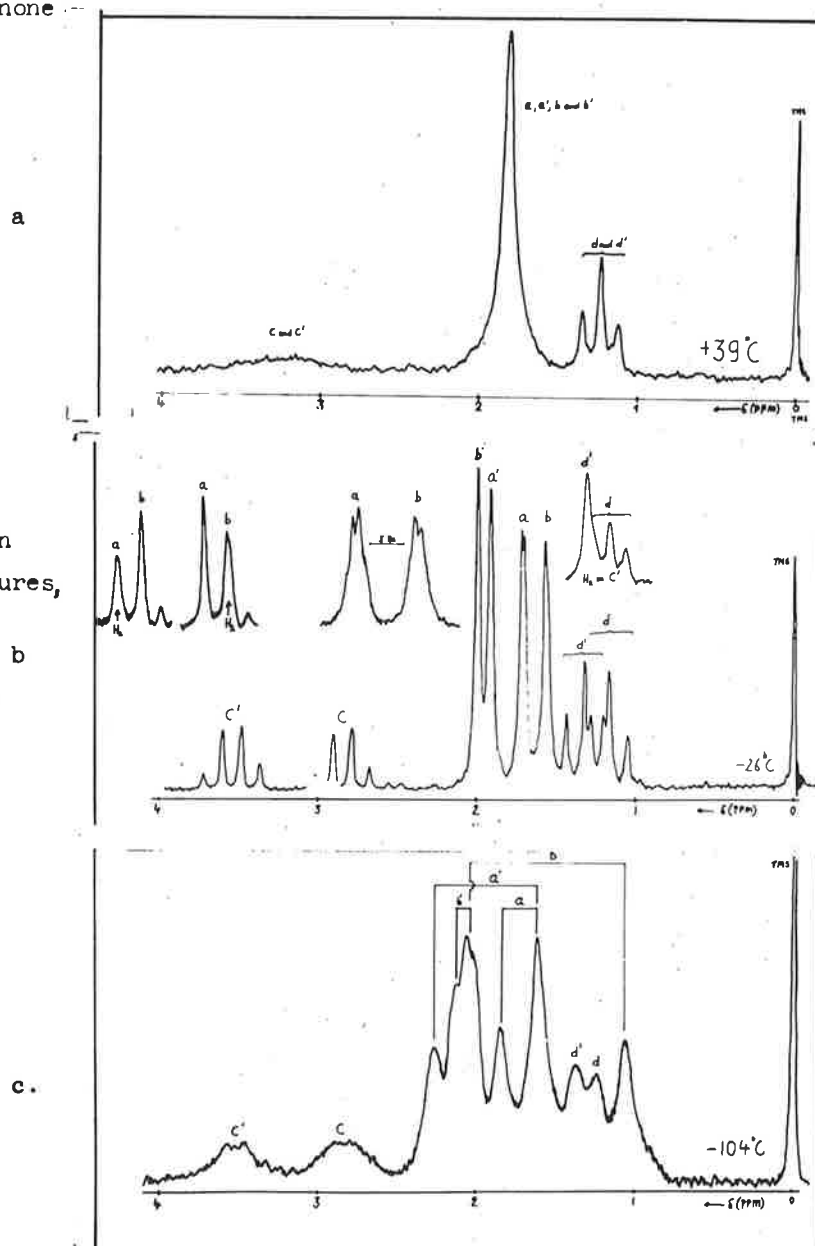


Fig. 2. The structural formula of 4-EDD

Fig. 3. ^{a-c} The NMR spectra, taken of different temperatures, of 4-EDD



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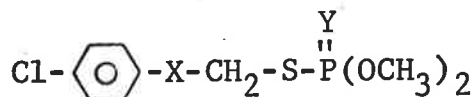
October 21, 1968

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

Re: NMR Parameters for Methyl Trithions
and Methyl Trithion Oxons

Dear Barry:

We have recently completed a study of the NMR spectra of Methyl Trithions, I, and Methyl Trithion oxons, II. The methylene and methyl protons of sulfides (Ia & IIa) and sulfones (Ic & IIc) give doublets due to the phosphorus atom three bonds apart. However, both the methylene and methyl protons of sulfoxides (Ib and IIb) exhibit chemical shift nonequivalence due to the asymmetric sulfur atom.



Ia, X=S, Y=S;

b, X=SO, Y=S;

c, X=SO₂, Y=S;

IIa, X=S, Y=O;

b, X=SO, Y=O;

c, X=SO₂, Y=O;

The spectrum of the methylene and methyl region of IIb is shown in the Figure. The NMR parameters of I and II are listed in the Table.

- 2 -

Please credit this letter to obtain the Texas A & M
University NMR Newsletter starting possibly at issue No. 119.

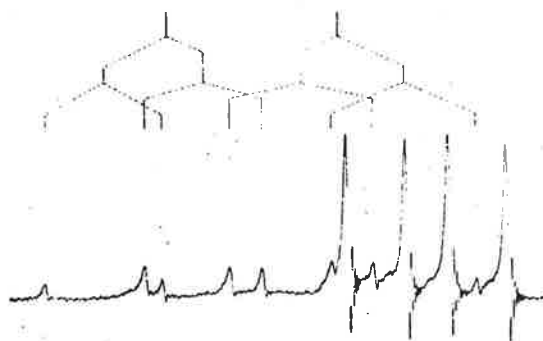
Very truly yours,

Tseng

C. K. Tseng

W. J. Smith

W. J. Smith



CKT:WJS:an
Attachment

TABLE: CHEMICAL SHIFTS AND COUPLING CONSTANTS IN
METHYL TRITHIONS AND METHYL TRITHION OXONS^a

<u>COMPOUND</u>	X	Y	$\delta_{\text{CH}_3}^b$	δ_{CH_2}	J_{POCH}^c	J_{PSCH}	$J_{\text{HH}}^{\text{gem}}$
Ia	S	S	3.38	4.00	15.7	14.2	---
Ib	SO	S	3.41 3.45	3.59 3.90	15.5 15.5	19.8 17.5	13.0
Ic	SO ₂	S	3.33	3.98	15.7	17.3	---
IIa	S	O	3.37	4.07	13.1	12.9	---
IIb	SO	O	3.37 3.50	3.64 4.00	13.2 13.1	18.4 15.2	13.0
IIc	SO ₂	O	3.33	4.02	13.1	15.8	---

(a) Approximately 10% solution in C₆D₆.

(b) Chemical shifts expressed in ppm.

(c) Coupling constants expressed in Hz.

UNIVERSITY OF FLORIDA
GAINESVILLE, 32601

DEPARTMENT OF CHEMISTRY

October 23, 1968

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

Dear Professor Shapiro:

⁶⁹
¹⁶⁹ Tm is a nucleus of the Rare Earth element Thulium with a natural abundance of almost 100%, with the spin 1/2, and its relative sensitivity is of the same order of magnitude as that of ¹⁴N. Although the Larmor-frequency at 10.000 Gauss occurs at 3.49 MHz as compared with the values 3.47 for ³⁷Cl, 3.27 for ³³S, and 3.08 MHz for ¹⁴N, nobody has yet investigated, so far as I know,

the chemical behaviour of Thulium by NMR - spectroscopy.

This seems to be rather surprising since not only the halogene-compounds TmHal₃ and oxides such as TmOCl are more or less stable compounds, but even chelates with β-diketones, as well as other complexes such as (C₅H₅)₃Tm are known¹⁾. As we are investigating electronic structures of aromatic charge-transfer-complexes, of hydrogen-bonded associates, and other types of complexes²⁾, applying double resonance methods such as transient nutation to hetero-compounds³⁾, I think it will be worth-while to use an accessory for ³³S and ³⁷Cl to our Spectrospin KIS-HF 60/90 apparatus also for ⁶⁹Tm-measurements.

Sincerely yours.

EL/jc



References:

- 1) R. D. Fischer and H. Fischer
J. Organomet. Chem. *8 (1967) 155
- 2) E. Lippert
Ber. Bunsenges, 67 (1963) 267
- 3) D. Zéssow and E. Lippert
J. Molecular Structure 2 (1968) 248
(See NMR Newsletter 118 (1968) 51)

Ernst Lippert
Visiting Professor (from Berlin)

THE UNIVERSITY OF WISCONSIN
MADISON 53706

DEPARTMENT OF CHEMISTRY

October 16, 1968

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

Suggested Title: ^{23}Na NMR Study
of Sodium Ion Complexes

Dear Barry:

With some twists in technique and data analysis, ^{23}Na NMR can be used in a manner similar to that of Baldeschwieler & Stengle (PNAS(US) 55, 1020, (1966)) to study sodium ion complexes in aqueous solution. We have studied a number of molecules including some of biochemical interest. As an example we enclose data from HEEDTA [N'-(2-hydroxyethyl)-ethylene-diamine-N'NN-triacetic acid].

The experimental technique involves pulsed NMR (π , τ , $\pi/2$) measurements of ^{23}Na T_1 's at total sodium concentrations as low as 0.01M. using a PAR CW-1 Boxcar Integrator (modified) for signal averaging in a manner similar to that of Hardy & Bloom (Walter N. Hardy, Ph. D. Thesis, Univ. Brit. Col. Phys. Dept., 1964). This works very well and gives T_1 's to an accuracy of about 3% even at the lowest concentrations.

For the presumably rapid equilibrium $\text{Na}^+ + \text{HEEDTA}^{-3} \rightleftharpoons \text{NaHEEDTA}^{-2}$ the average ^{23}Na T_1 is given by

$$(T_1^{-1} - T_{1F}^{-1}) = X_B (T_{1B}^{-1} - T_{1F}^{-1})$$

where X_B is the fraction of Na^+ bound in the complex; T_{1F} and T_{1B} are the relaxation times of the "free" and bound Na^+ respectively. In weak complexes T_{1B} cannot be measured directly; therefore, T_1 data at various concentrations of NaCl and HEEDTA are fit through a two parameter (T_{1B} and K_f) non-linear least squares computer program. Figure 1 shows the pH dependence of the ^{23}Na $T_1^{-1} \equiv R$ for 0.100M. NaCl and 0.095M. HEEDTA; pH is adjusted with HCl and tetramethylammonium hydroxide. The large increase in T_1^{-1} at high pH demonstrates a chelate formation in which basic carboxylate and amino groups are important. At low pH a smaller, less specific, effect is observed. Figure 2 shows the dependence of $R = T_1^{-1}$ of 0.100M NaCl (total $[\text{Na}^+] = 0.100$) as a function of HEEDTA concentration at pH = 11.5. The solid line was calculated using our simple equilibrium model and the mean value of the parameters. For HEEDTA we find $K_f = 8.7 \pm 0.9\text{M}^{-1}$ and $T_{1B}^{-1} = 610 \pm 30\text{sec}^{-1}$ (95% confidence limits).

A preprint is available giving a more detailed description of this work for some compounds.

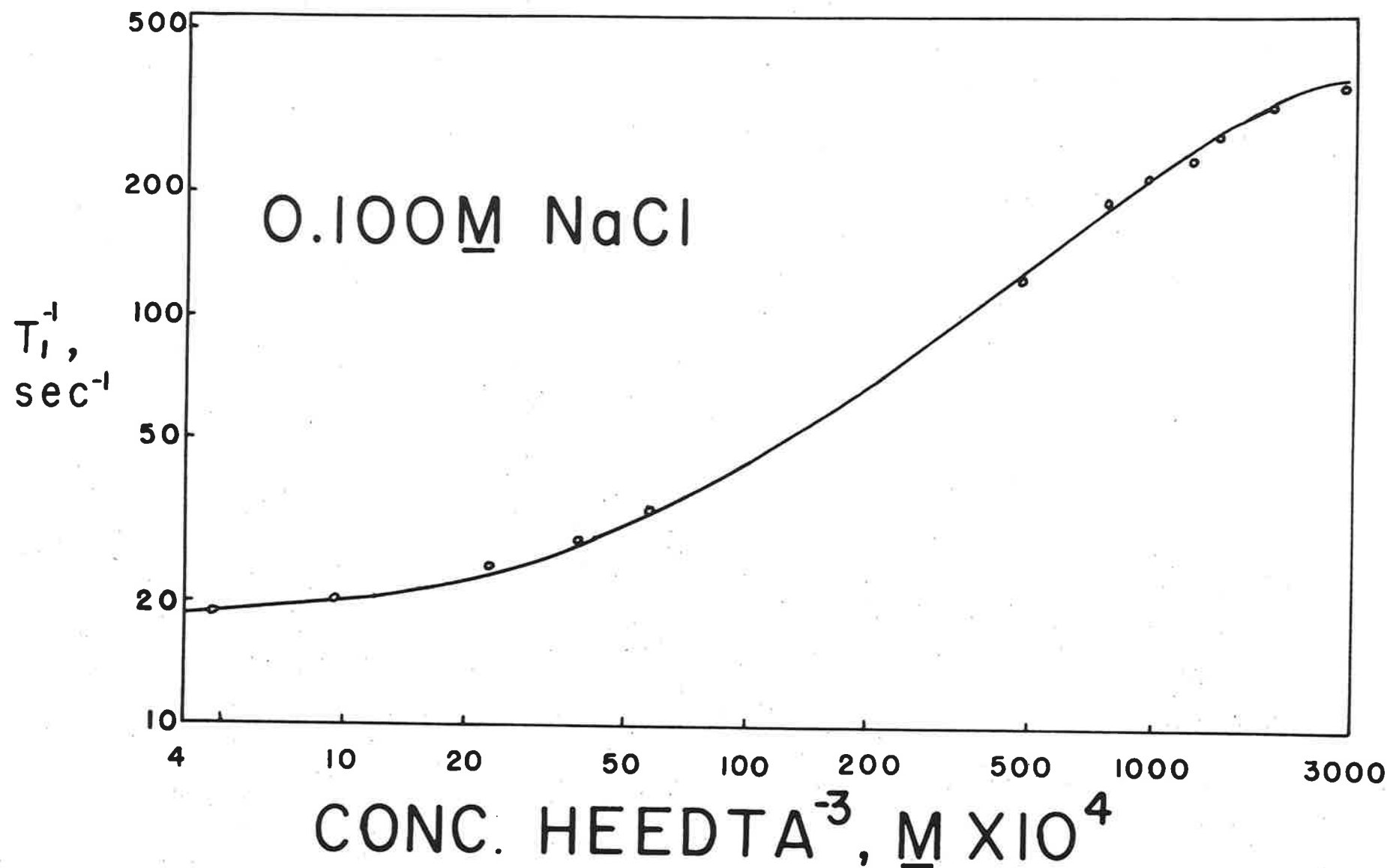
Yours very truly,

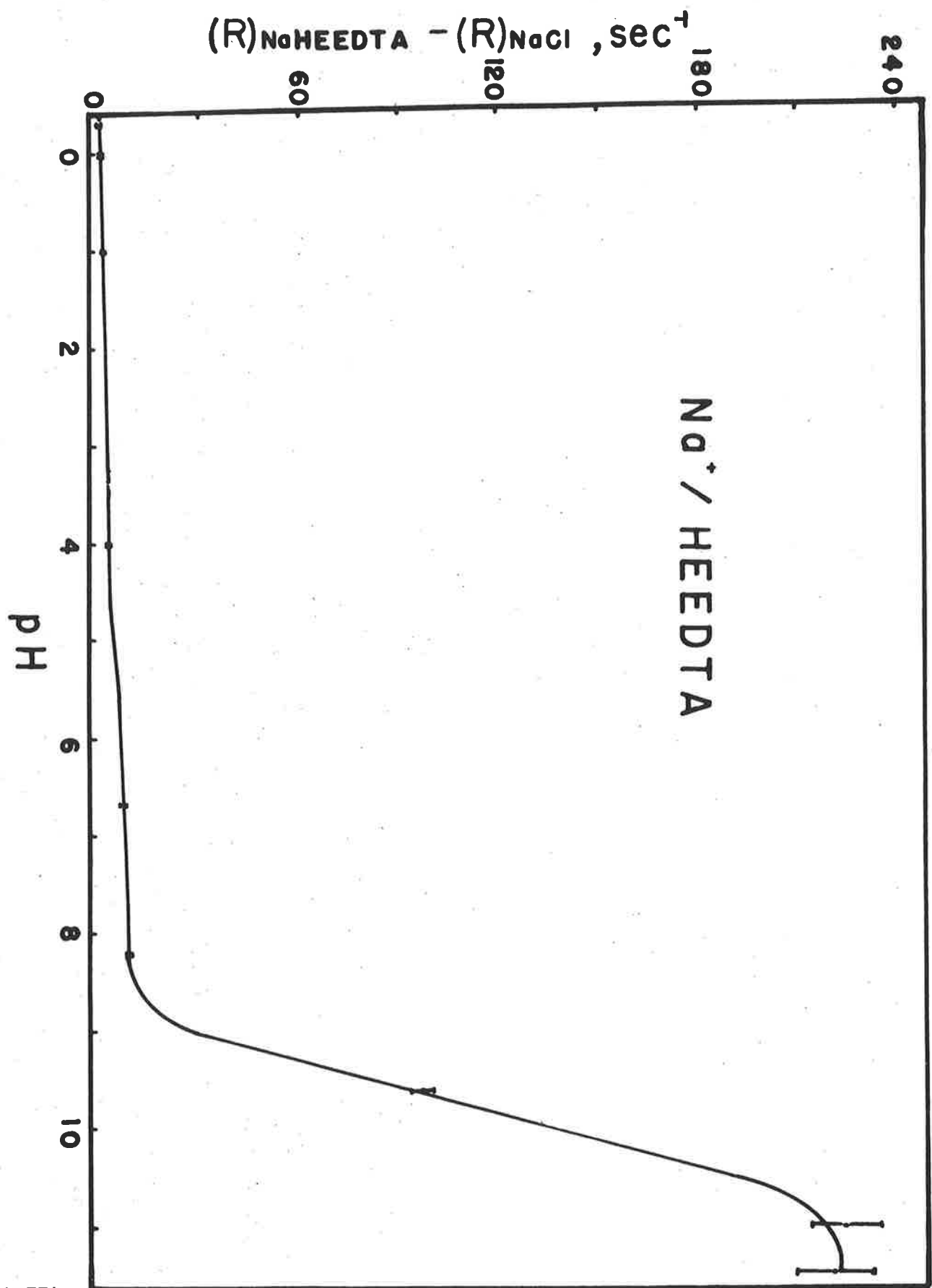
Thomas L. James

Thomas L. James

Joseph H. Noggle

Joseph H. Noggle
Asst. Professor





OTTAWA 1, CANADA



DEPARTMENT OF CHEMISTRY

October 18, 1968.

Professor B. L. Shapiro,
~~Department of Chemistry,~~
~~Illinois Institute of Technology,~~
~~Chicago, Illinois 60616,~~
~~U. S. A.~~ } oops.

Dear Professor Shapiro:

Long Range Shielding Effects

My apologies for causing you to remind me of our subscription. I have recently moved to Strasbourg for a year and consequently things have been rather neglected.

We had a new look at some aspects of anisotropic effects of functional groups. Our investigations are by no means complete, but in the hope of receiving comments from readers here is what we are doing.

We are using long range shielding effects for structure determinations (1) in the steroid and terpene field (2). The angles and distances in the magnetic and electric shielding terms (1) are usually obtained from Dreiding models.

$$\sigma_{\text{magn}} = \sum_{i=1}^3 \chi_i \left\langle \frac{1}{3} R^{-3} (1 - 3 \cos^2 \varphi_i) \right\rangle_{\text{av}} \quad (1)$$

$$\sigma_{\text{el}} = \mu (3 \cos \varphi_i \cos \varphi_k - \cos \varphi_{ik}) / R^3 \quad (2)$$

These models, however, are unrealistic for sterically crowded molecules. Therefore we started to calculate these geometric quantities from atomic coordinates which we get from X-ray data or calculate using appropriate bond lengths and bond angles.

Another problem is the shielding effects of polar functional groups. The usual way to allow for their effects is to add a term $\Delta \sigma_{\text{el}}$ proportional to the el. field gradient at the site of the resonating nucleus (equation 2).

We tried the following approach instead. An el. dipole effects the susceptibilities of all bonds, not only the bond holding the resonating nucleus. For instance the susceptibility χ_x of a bond say along the bond axis should be affected by the

el. field vector perpendicular to that axis i.e. we would have an additional term χ_{el} proportional to $\frac{\mu \sin \theta_2}{R_2^3}$ where

$\theta_2 = \angle \text{dipole } \mu - \text{bond axis}$

$R_2 = \text{distance from dipole center to bond center}$

The total susceptibility about this axis would then be

$$\begin{aligned}\chi_{\text{total}} &= \chi_{\text{magn}} + \chi_{el} \\ &= \chi_{\text{magn}} + \frac{k\mu \sin \theta_2}{R_2^3} \quad k = \text{const.}\end{aligned}$$

and the corresponding shielding term would become

$$\begin{aligned}\sigma &= \sigma_{\text{magn}} + \sigma_{el} \\ &= \frac{(1 - 3\cos^2 \theta_1)}{3R_1^3} \left(\chi_{\text{magn}} + \frac{k\mu \sin \theta_2}{R_2^3} \right)\end{aligned}$$

where $\theta_1 = \angle \text{bond axis} - R_1 \text{ vector}$

$R_1 = \text{distance from bond center to resonating proton}$

In calculations of shift differences the χ_{magn} terms for all unchanged bonds cancel and we are left with a total of $\sum \sigma_{el}$ terms, where n is the number of bonds in the molecule.

We found that the only bonds that contribute significantly to $\sum \sigma_{el}$ are the bonds to the proton in question, the C-C bonds from C-X and the C-H bonds to C-X, where C-X is the polar group. Thus this method seems to compensate for the neglect of inductive effects of polar substituents.

Yours sincerely,

H. Beierbeck

H. Beierbeck,

J. W. ApSimon

J. W. ApSimon,

Associate Professor.

GCP

- References:
1. R. F. Zurcher in "Progress in Nuclear Magnetic Resonance Spectroscopy", ed. J. W. Emsley, J. Feeney, L. H. Sutcliffe, Vol. 2, 1967, p. 205.
 2. J. W. ApSimon, W. A. Craig, P. V. Demarco, D. W. Mathieson, L. Saunders, W. B. Whalley, Tetrahedron 23, 2339 (1967), *ibid.* 23, 2357 (1967).

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October 23, 1968

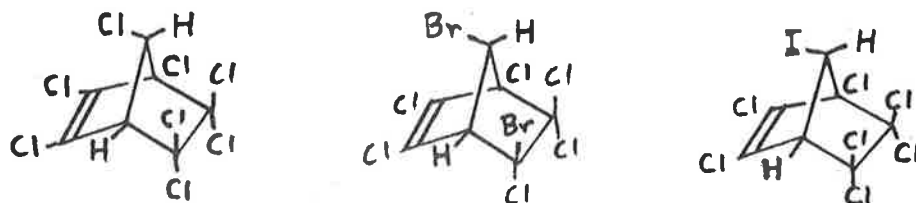
Professor Bernard L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843

Steric Effects and Vicinal Coupling Constants

Dear Dr. Shapiro:

Analysis of the proton magnetic resonance spectra of several series of halocarbons with vicinal hydrogens¹ reveals steric effects due to changes in the size of the halogen atoms in the Cl-Br-I triad.

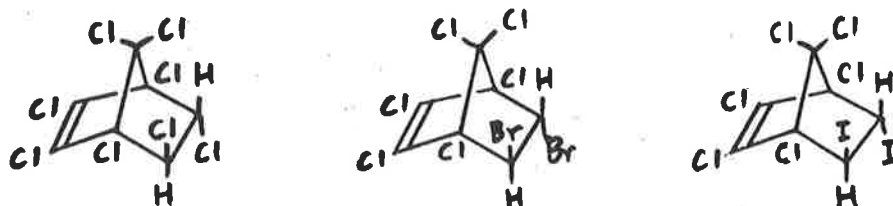
In Figure 1 a Newman-type presentation of the side view (from the bridgehead side) of the general structure representing the following three chlorocarbons is reproduced:



As it is apparent in the adjacent graph, the coupling constant decreases as the size of the halogen (shaded circles) increases. An increase in the steric interaction between the halogen on the bridge and the chlorines of the double bond results in an increase of the approximately 60° dihedral bond angle between the carbon-hydrogen bonds thus effecting, according to the Karplus relationship, a decrease in the coupling values.

In Figure 2 a similar presentation of the following trans compounds is shown:

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October 23, 1968
Page 2



As the size of the variable halogen (shaded circles) increases steric interaction between the anti-7-chlorine (chlorine on the bridge anti to the double bond) and the exo-halogen results in the displacement indicated by the arrows and thus in an increase in the approximately 120° dihedral bond angle between the hydrogens. The result of this change is an increase in the coupling constant and this is illustrated on the adjacent plot. Interaction between the bridge-chlorine and the exo-hydrogen is, expectedly, not as severe as the halogen-halogen repulsion and this is evidenced by the existence of the effect proper. The extent of the interaction is further indicated by the coupling values of compounds in which the anti-bridge chlorine is replaced by hydrogen and in which thus steric repulsion is at a minimum. Thus, the vicinal coupling constant of the trans-dibromo compound (A) is only 2.98 cps, whereas J of the compound with chlorines



on the bridge, (B), was 4.02 cps.

A new aspect of the variation of coupling constant with the size of the halogen is illustrated in Figure 3. As the size of the halogen increases so does the cis coupling between hydrogens. In contrast to the compounds of the previous two categories the cis-adducts of hexachloronorbornadiene and Cl_2 , Br_2 and I_2 are symmetrical and contain the two carbon-hydrogen

Hooker Research Center
October 23, 1968
Page 3

bonds in the same plane. This plane is perpendicular to the plane of symmetry (the latter bisects the double bond and the bridge). The difference between the three adducts is thus not in the dihedral bond angle (which remains zero) but in the in-plane tilt of the carbon-hydrogen bonds with respect to each other: as the size of the halogen (shaded circles) increases the carbon-hydrogen bonds move towards a more parallel alignment with each other and this results in an increase in the proton-proton coupling. The relationship is illustrated by arrows in Figure 3.

Support for this rationalization comes also from the magnitude of the coupling constant of the *exo-cis*-5,6-octachloronorbornene (Figure 4). In addition to the mutual repulsion between the *exo-cis* chlorines there is an extra steric interaction between them and the anti bridge-chlorine. This results in a presumably wider Cl-C-C and thus in a smaller H-C-C bond angle than in the corresponding *endo-cis* compound and thus in an increased coupling interaction (*cis-exo*-5,6-dichloro compound 8.30 cps versus 7.60 cps in the *endo* isomer). Suggestion for the mechanism of coupling will be advanced in the full paper.

Sincerely,



Victor Mark
Research Associate

/ml

(1)(a) Presented at the Chlorocarbon Conference held at the Eastern Research Laboratory of the Dow Chemical Company, Wayland, Massachusetts, May 5-8, 1968; (b) Presented at the 156th Meeting of the American Chemical Society, Atlantic City, September 1968, Division of Organic Chemistry, Paper No. 92.

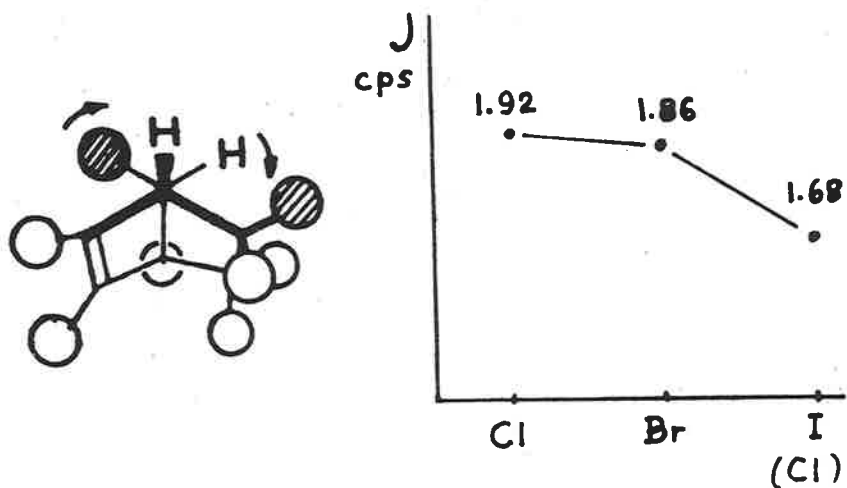


Fig. 1.

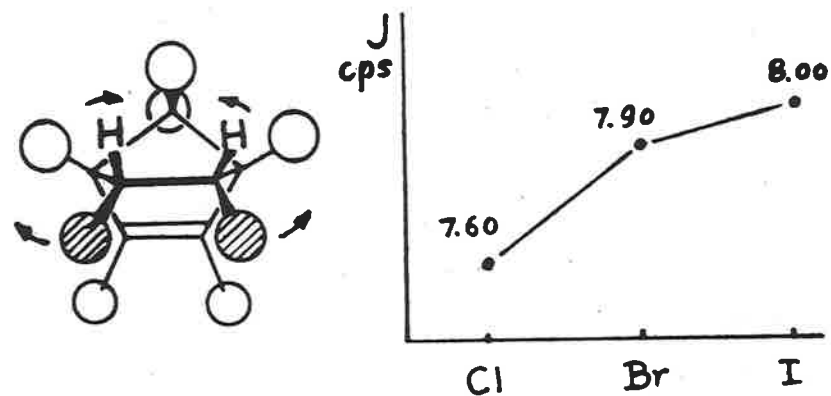


Fig. 3.

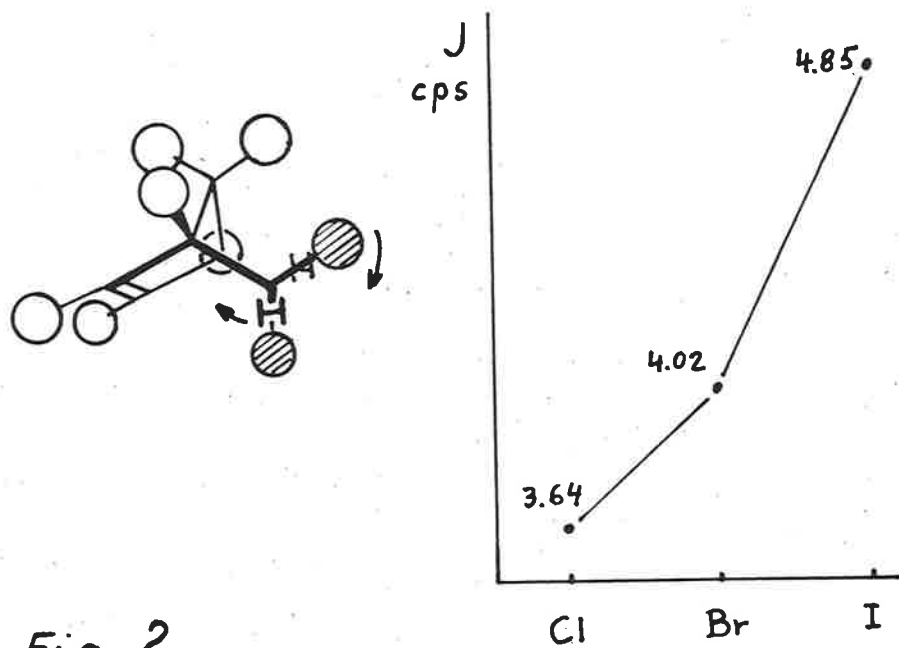
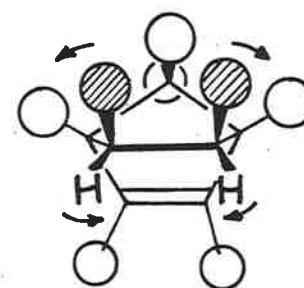


Fig. 2.



Cl_2 8.30 cps

Fig. 4.

UNIVERSITY OF ILLINOIS

THE WILLIAM ALBERT NOYES LABORATORY

October 24, 1968

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

Dear Professor Shapiro:

As a postdoctoral fellow in Dr. Gutowsky's research group for the last 22 months, I have had access to the informative NMR Newsletter. Though I am now leaving I would like to continue receiving it; I hope this contribution will suffice for my initial subscription. I would appreciate my copy being sent to:

Dow Chemical Company
Eastern Research Laboratory
Box 400
Wayland, Massachusetts 01778

Thank you.

 ^{13}C -H Coupling in Trimethylaluminum

During the course of a NMR investigation of the kinetics of bridge-terminal methyl exchange in trimethylaluminum (TMA) we determined the carbon-13 proton coupling constants, J_{13} , for the bridge, J_B , and C-H the terminal, J_T , methyl groups at low temperature where the exchange is effectively stopped. At 35°C the 100 MHz proton NMR of TMA in d_8 -toluene solution exhibited a single line with equally displaced, low intensity ^{13}C satellites due to the naturally abundant ^{13}C nuclei coupling to the methyl protons. This averaged coupling was found to be 113.8 ± 0.3 Hz. Using high spectrometer gain settings at -81°C J_B and J_T were found to be 110.3 ± 0.4 Hz and 116.0 ± 0.4 Hz, respectively. The quoted precision is the standard deviation from the average.

Theoretical considerations indicate that spin-spin coupling between directly bonded nuclei should be mainly dependent on the Fermi contact term. Further theoretical and experimental results have indicated that J_{13} is directly proportional to the S character of the C-H bond.¹ Grant and Litchman² have described an alternate formulation to portray the importance of other factors. Using their approach the following expression can be obtained

$$\frac{J_B}{J_T} = \left(\frac{\Delta_T}{\Delta_B}\right) \left(\frac{N_B}{N_T}\right)^2 \left(\frac{\alpha_B}{\alpha_T}\right)^2 \left(\frac{Z_B}{Z_T}\right)^3 \quad (1)$$

where Δ is the average energy approximation term, N is the appropriate bond normalization constant, α^2 is the fractional S character in the bond and Z is the effective nuclear charge appearing in the radial function of a carbon $2S$ orbital. First assuming all the ratios on the Rhs of Eq. (1)

are equal to unity except $\left(\frac{\alpha_B}{\alpha_T}\right)^2$, this term can be evaluated following

Juan and Gutowsky's substituent approach¹ by using the x-ray results of Vranka and Amma³ and assuming the bridge bond is adequately described as a

methylenated double bond. In this fashion $\left(\frac{\alpha_B}{\alpha_T}\right)^2$ is found to be 0.9524 which

compares favorably with the experimental ratio of 0.9508. The bond polarization effect can be evaluated following Grant and Litchman's approach

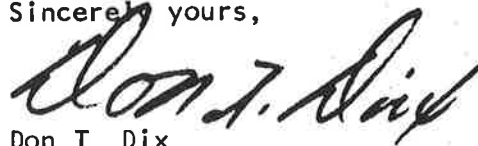
to give $\left(\frac{Z_B}{Z_T}\right)^3 = 1.055$ which if, again, all the other ratios in Eq. (1) are

assumed to be unity indicates that $J_B > J_T$, contrary to that observed.

This order holds regardless of the terminal Al-C bond moment initially assumed.

These qualitative calculations could perhaps be improved by including the normalization ratio; however, this value has been previously argued¹ and more recently shown^{2,4} to be close to one. Intuitively one would expect that formation of the bridge bond would be dependent upon maximum bridge orbital overlap and an electron shift into the electron deficient bridge. Both of these criteria could be satisfied more if a bridge carbon offered an orbital having a higher S character than the terminal one.

Sincerely yours,



Don T. Dix

DTD:naw

¹C. Juan and H. S. Gutowsky, J. Chem. Phys. 37, 2198 (1962).

²D. M. Grant and W. M. Litchman, J. Am. Chem. Soc. 87, 3994 (1965).

³R. G. Vranka and E. L. Amma, ibid. 89, 3121 (1967).

⁴W. M. Litchman and D. M. Grant, ibid. 90, 1400 (1968).

THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

DEPARTMENT OF CHEMISTRY

October 25, 1968.

Professor Barry Shapiro,
Department of Chemistry,
Texas A & M University,
College Station,
Texas 77483,
U.S.A.

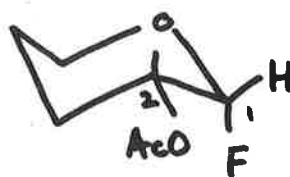
Dear Barry:

Specifically Fluorinated Carbohydrates (Yet Again)

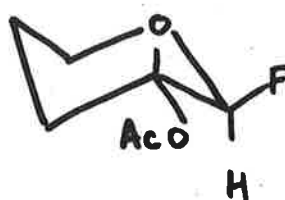
Greetings from the rain-lands.

We have been continuing our studies of specifically fluorinated carbohydrates and have (at long last) managed to write up full accounts of some of our results. Four papers describing our earlier results on pyranosyl fluorides have now been accepted for publication in the Canadian Journal of Chemistry. I have a limited number of preprints available for any persons who wish to write me.

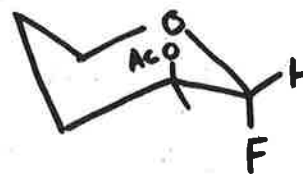
Briefly, we have used a series of fluorinated sugars to establish the stereospecific dependencies of ^{19}F shifts and of vicinal $^{19}\text{F} - ^1\text{H}$ couplings for fluorine attached to a six-membered ring system. The vicinal couplings are much as might be expected, with $J_{\text{trans}} > J_{\text{cis}}$. However, there is a marked difference between the two sets of *gauche* couplings. It is possible to speculate on the source of this difference, which also appears when the C_2 substituent is Cl, Br, or I.



(A)

 $J_{\text{Fa}, \text{H}_{2a}} = 23.8$


(B)

 $J_{\text{Fe}, \text{H}_{2a}} = 12.0$


(C)

 $J_{\text{Fa}, \text{H}_{2e}} = 1.5 \text{ Hz}$
/2.

Prof. Barry Shapiro, Texas.

October 25, 1968.

The contributions to the ^{19}F shifts from the various acetoxy groups are "additive". The geminal ^{19}F - ^1H couplings appear to exhibit a "configurational" dependence analogous to that of geminal ^1H - ^1H couplings. Thus, configurations such as those shown in A, and B give couplings within the range, $J_{1,\text{F}} = +53.1 - 53.5$ Hz while that shown in C gives couplings in the range $+48.6 - 49.5$ Hz.

We have not yet completed our studies of ^4J and ^5J , ^{19}F - ^1H couplings; however, our results to date indicate that $^4\text{J}_{\text{ee}} = +3 \rightarrow 4$ Hz while $^4\text{J}_{\text{ea}} = \text{ca} - 1$ Hz. The signs were determined by double-resonance methods.

I almost beat you to the punch this time because this letter was nearly completed by the time I received your gentle reminder. Eventually I may actually send you a letter ahead of my "quota".

With best regards for your new position.

Yours,



L.D. Hall,
Assistant Professor.

LDH:ef.

Iwan N. Stranski-Institut
 II. Institut für Physikalische Chemie
 der Technischen Universität Berlin

1 Berlin (West) 12, October 22, 1968
 Postanschrift: Hardenbergstr. 34
 Tel.: (0311) 31 07 81, App. 3571
 Institutsingang im Ernst-Reuter-Haus

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

Re.: Determination of $^{13}\text{C} - ^{13}\text{C}$ Coupling Constants by Heteronuclear
 Double Resonance in Natural Abundance

Dear Professor Shapiro,

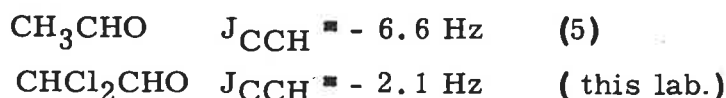
Recently we reported some preliminary results concerning the utilisation of transient nutations (1, 2) in H- $\{ \text{C}-^{13} \}$ double resonance (3). During our studies of the concentration dependence of C-13 chemical shifts this method proved to be well suited for the application of a time averaging device. Using a TMC-CAT we could extend the concentration range down to $2 \cdot 10^{-2}$ molar solutions of $\text{Ph}-\text{C}\equiv\text{CH}$ (resp. $2 \cdot 10^{-4}$ molar in $\text{Ph}-\text{C}\equiv^{13}\text{CH}$) using 5 mm sample tubes and measuring times of 6 - 12 hours. This sensitivity makes it feasible to determine both the magnitude and relative sign of C-C coupling constants in such molecules which are within the known limitations of double resonance methods.

The absolute value of $J_{\text{C}\equiv\text{C}}$ in $\text{Ph}-\text{C}\equiv\text{CH}$ has already been measured using C-13 enriched material (4). With the known parameters we calculated the ABX pattern (neglecting for the moment the influence of the phenyl protons (see (4))) corresponding to 90 MHz. Using the momentum level diagram for both the possibilities $J_{\text{C}-\text{C}} > 0$ and vice versa we chose the most suitable proton frequency for locating the saturating field H_1 . Accumulating for 12 hours we, indeed, observed a Torrey signal, located - within the error limits - at that spectral position which was expected for the progressively connected C-13 line assuming $J_{\text{C}\equiv\text{C}} > 0$.

Other molecules which have been studied so far are

	$ J_{\text{CH}} $	$ J_{\text{CCH}} $	$ J_{\text{CC}} $	[Hz]
$^{13}\text{CH}_3\ ^{13}\text{COOH}$	129.5 ± 0.2	~ 7.1	57.3 ± 0.8	
$^{13}\text{CH}_2\text{Cl}\ ^{13}\text{COOH}$	152.1 ± 0.2	~ 4.0	60.0 ± 0.8	
$^{13}\text{CHCl}_2\ ^{13}\text{COOH}$	181.5 ± 0.2	~ 2.5	69.4 ± 0.8	

The observed spectra (see Fig. 1 for CH_3COOH) revealed the fact that J_{CCH} and J_{CC} are of opposite sign. J_{CCH} has already been established to be negative in similar compounds:



So it seems reasonable to assume in the above mentioned acids $J_{CCH} < 0$ leaving $J_{CC} > 0$.

Several comments are in order:

- 1) If J_{CCH} is unknown and cannot be measured because of the large center proton signal, it is sufficient to offset ν_1 by 0.5 - 2 Hz (see Fig. 1). The non-resonant condition is indicated by the observed Torrey oscillations according to $\Omega^2 = (\gamma H_1)^2 + (\Delta\nu_1)^2$ and brings only a slight deterioration of the signal-to-noise ratio for $\Delta\nu_1 < 1$ Hz if $\gamma H_1 \approx 1$ Hz.
- 2) Leaving the "one night" measuring time unit the sensitivity can still be improved using 10 or 12 mm sample tubes ($\Delta H \approx 0.3-0.5$ Hz should be sufficient).
- 3) The cited error of J_{CC} can be reduced using a C-13-quartz oscillator locked to the proton master crystal. For the moment we use a free-running quartz-controlled C-13-oscillator.

Further details will be published soon.

Yours sincerely,



D. Ziessow E. Lippert

Ref.

- 1) H.C. Torrey, Phys. Rev. 76, 1059 (1949)
- 2) J.A. Feretti, R. Freeman, J. Chem. Phys. 44, 2054 (1965)
- 3) D. Ziessow, E. Lippert, J. Mol. Struct. 2, 248 (1968) and
 IITNMR 118, 52 (1968)
- 4) K. Frei, H.J. Bernstein, J. Chem. Phys. 38, 1216 (1963)
- 5) E. Sackmann, Dissertation, TH Stuttgart 1964

Schematic Single-Resonance Spectra of $^{13}\text{CH}_3\text{COOH}$ (broken line)

$^{13}\text{CH}_3^{13}\text{COOH}$ (solid line)

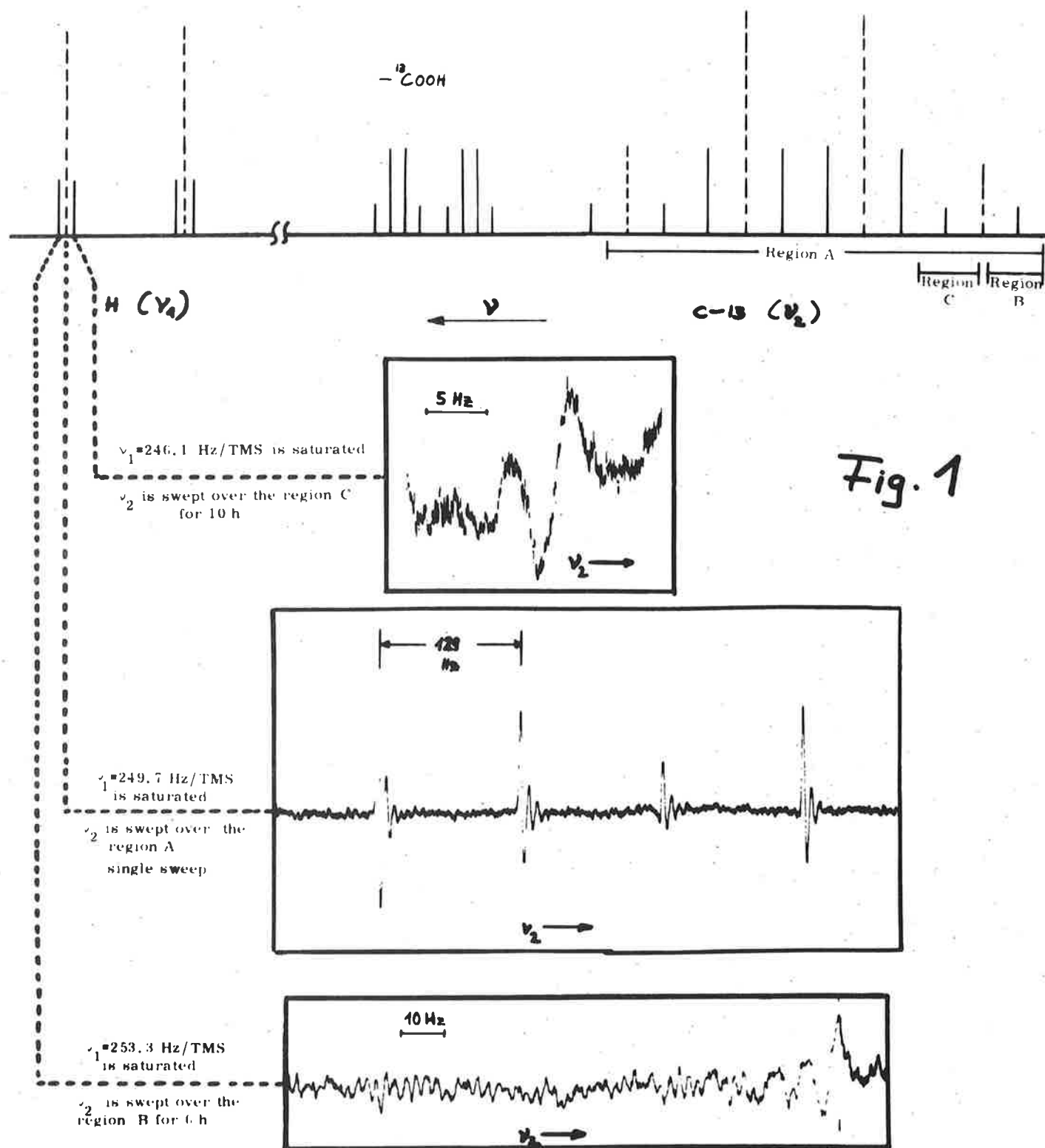


Fig. 1

MCMASTER UNIVERSITY

HAMILTON, ONTARIO, CANADA

DEPARTMENT OF CHEMISTRY

October 23, 1968

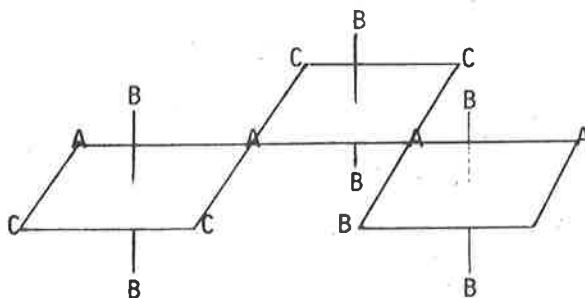
Dr. B. L. Shapiro,
Texas A & M University,
College of Science,
College Station, Texas 77843

Chemical Shifts and Coupling Constants in Liquid SbF_5 ;
Magnetic Non-Equivalence and Chemical Shift Reassignment

Dear Barry,

As part of a continuing investigation of the fluorine spectrum of SbF_5 at 56.4 and 94.1 MHz in various solvents, the 56.4 MHz fluorine spectrum of SbF_5 in Freon-114, CCl_2F_2 , has been obtained and interpreted using Bothner-By's Laocoon III computer program. The fluorine spectrum of neat SbF_5 first obtained by Hoffman, Holder and Jolly (1) at 40 MHz and -10°C , the temperature of best resolution, is shown at the top of the accompanying figure. (At temperatures below -10°C the resolution decreases; at higher temperatures chemical exchange causes collapse to a single line.) The presence of three multiplets, the first having half the intensity of the other two, lead Hoffman, Holder and Jolly to suggest a cis-polymerized structure for SbF_5 . They explained the observed multiplet splittings by a first order coupling scheme with $J_{AB} \approx 70$, $J_{BC} \approx 130$, $J_{AC} < 30$ Hz.

The 56.4 MHz spectrum of a 1.0/0.14 SbF_5 /Freon-114 solution obtained by us at -56°C , the temperature of best resolution, is shown in the middle of the figure. Much better resolution is obtained than is the case for neat SbF_5 , presumably because the solvent reduces the polymer chain length and decreases the viscosity, causing a reduction in the fluorine line width. It is particularly noticeable that the first two peaks of the high field triplet are split (37 and 32 Hz) into doublets, presumably by A-C coupling. We attribute these doublets to unequal A-C coupling, which requires that the previous assignments (1) for B and C be interchanged, i.e., that the assignment of chemical shifts to fluorine nuclei be as shown below.

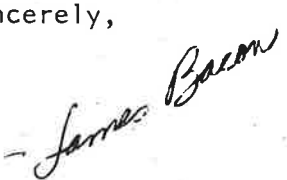


We have calculated six spin theoretical spectra for the SbF_6 unit in the polymer, using Laocoon III. Inspection shows seven different coupling constants in the SbF_6 unit, i.e., J_{AB} , J_{BC} , J_{AC} and J'_{AC} , the cis and trans A-C couplings respectively, and the three geminal coupling constants J_{AA} , J_{BB} , J_{CC} . The observed spectrum depends on all of these except J_{BB} . An off-line plotting system was used to make a line-shape plot of each theoretical spectrum. Comparison of the observed and calculated line shapes for the B resonance was used to fix J_{AB} , J_{BC} and the individual line width (32 Hz). The other four coupling constants were then varied until the C resonance, particularly the doublet splittings, was well reproduced. The theoretical spectrum shown at the bottom of the figure was calculated for $J_{AB} = 85.6$, $J_{BC} = 144.3$, $J_{AC} = 61.5$, $J'_{AC} = -8.5$, $J_{AA} = 25$, $J_{CC} = 85$ Hz. The agreement between observed and calculated multiplet splittings is reasonable - largest deviation 1.8 Hz, standard deviation 1.4 Hz. Estimated errors for the fit are J_{AB} , $J_{BC} \pm 0.2$ Hz; J_{AC} , $J'_{AC} \pm 2$ Hz; J_{AA} , $J_{CC} \pm 5$ Hz.

The coupling constants obtained above are of some interest. The trans coupling, J'_{AC} , is quite small compared to the cis coupling J_{AC} , which is in agreement with the previously published postulate that coupling between the bridging and terminal fluorines in the $\text{Sb}_2\text{F}_{11}^-$ ion is negligibly small (2). The five couplings other than J'_{AC} are all cis couplings and their magnitudes are in the order $J_{BC} > J_{AB} \approx J_{CC} > J_{AC} > J_{AA}$. If we assume that a smaller value of the cis coupling between two fluorine nuclei reflects a deficiency of electrons (rel. to SbF_6^-) in one or both Sb-F bonds, then it appears that any electrons withdrawn by the bridging fluorine from the rest of the molecule come mainly from the fluorines in the C position, i.e., those in the same plane as the bridging fluorines. The bridging fluorines are the most electron deficient fluorines in the molecule, as shown by $J_{AA} < J_{AC} < J_{CC}$.

In summary, the chemical shifts in the SbF_5 polymer can be reassigned on the basis of the symmetry of the SbF_6 polymer unit.

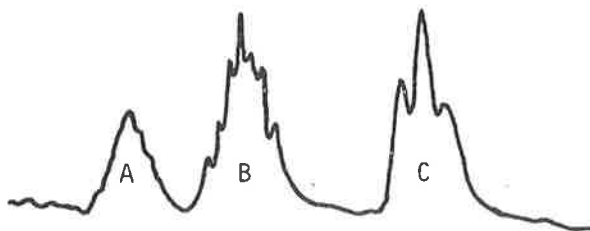
Yours sincerely,


R. J. Gillespie
J. Bacon

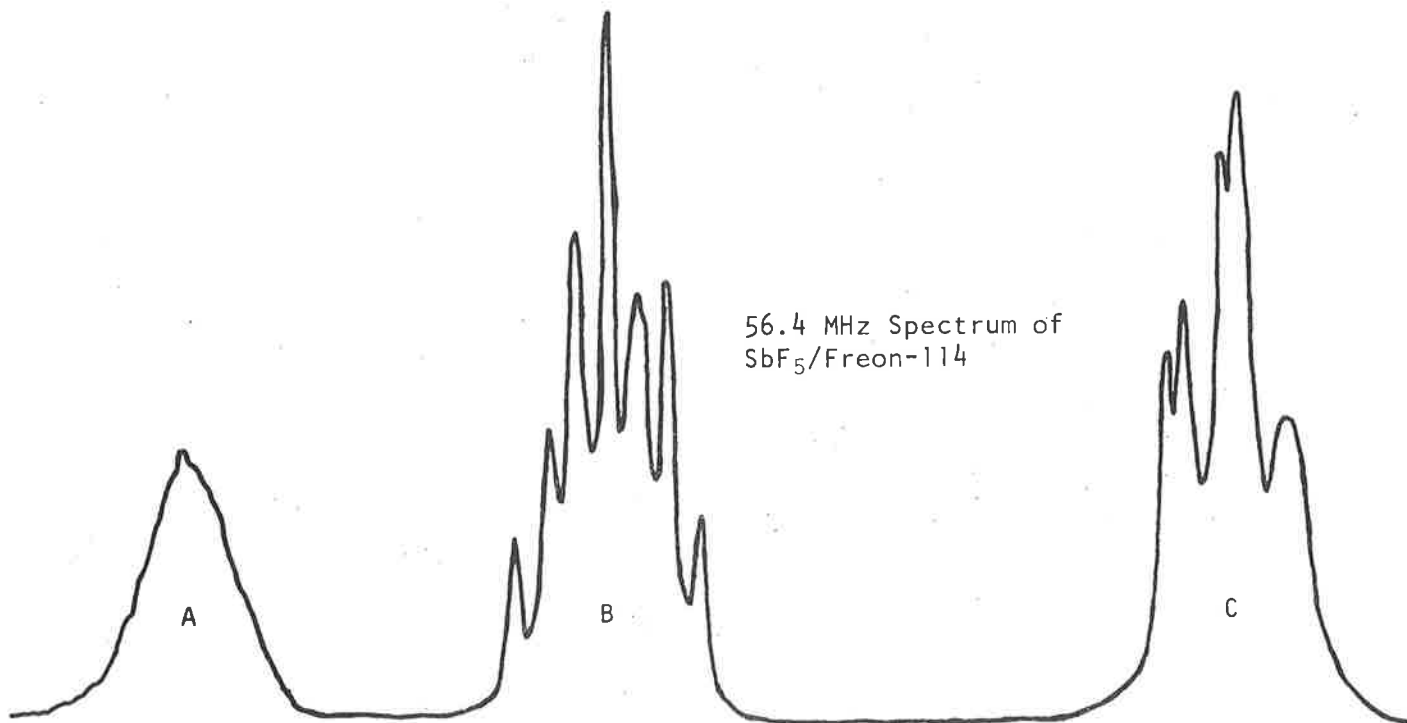
References:

1. C. J. Hoffman, B. E. Holder, and W. L. Jolly. J. Phys. Chem. 62, 364 (1958).
2. R. J. Gillespie and K. C. Moss. J. Chem. Soc. (A), 1170 (1966).

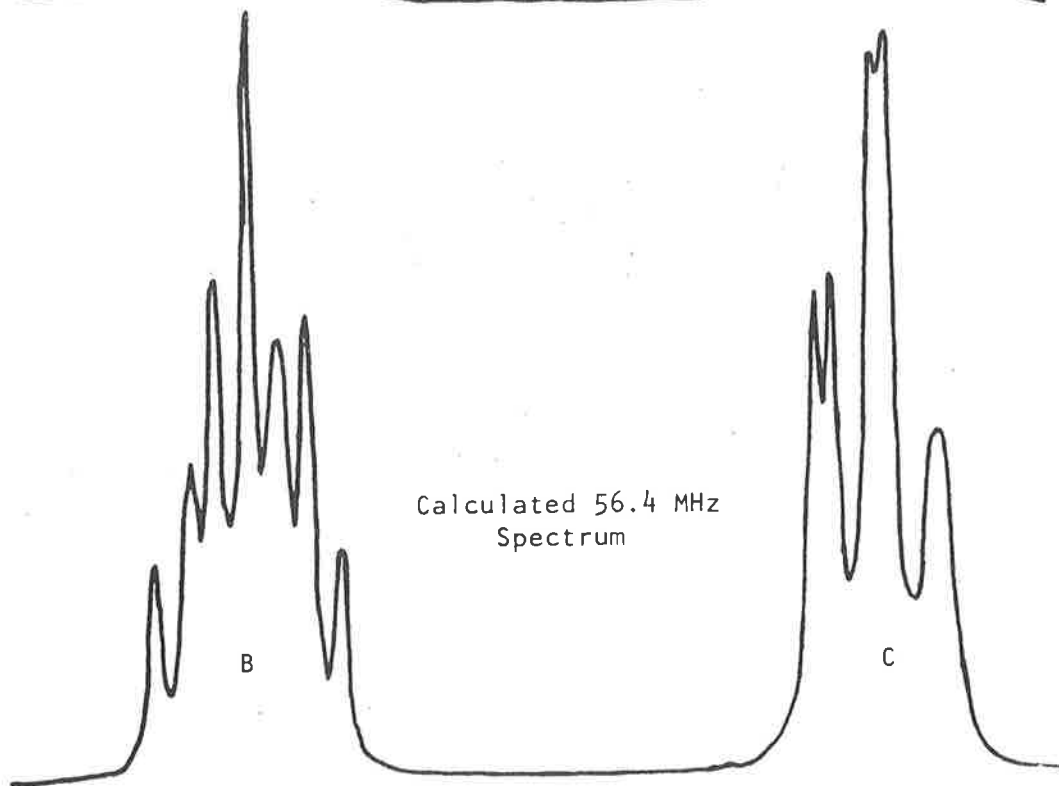
40 MHz SbF_5 Spectrum of
Hoffman, Holder and Jolly



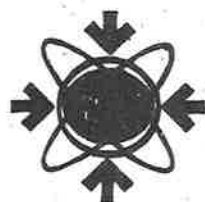
56.4 MHz Spectrum of
 $\text{SbF}_5/\text{Freon-114}$



Calculated 56.4 MHz
Spectrum



INTERNATIONAL SYMPOSIUM ON



&

MAGNETIC RESONANCE

**Monash University
Clayton, Victoria,
Australia**

11 - 14 August, 1969

THE SYMPOSIUM

The Symposium will be held at Monash University in Clayton, Victoria, from Monday 11 August to Thursday 14 August 1969. Chemists are reminded that this is the week preceding the XXII IUPAC Congress which meets in Sydney, New South Wales, 20 — 27 August. The IUPAC Congress incorporates the VII Australian Spectroscopy Conference, and is to be held conjointly with the XII International Coordination Chemistry Conference.

This symposium is sponsored by the Australian Academy of Science.

The scientific programme will consist of papers contributed and papers specially invited. The subjects to be discussed include:

Nuclear magnetic resonance (by high-resolution, wide-line, and spin-echo spectroscopy); electron spin resonance (in solids, liquids and gases); pure quadrupole resonance; ferromagnetic resonance; acoustic magnetic resonance; and cyclotron resonance.

It is hoped to emphasize the more physical aspects of these phenomena.

The language of the symposium is English.

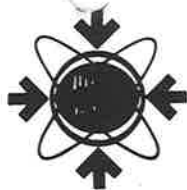
E. R. ANDREW	J. ITOH
R. G. BARNES	L. M. JACKMAN
R. BERSOHN	C. KIKUCHI
R. BLINC	W. LOW
P. J. BRAY	H. M. McCONNELL
A. CARRINGTON	R. ORBACH
T. P. DAS	J. G. POWLES
S. FONER	A. SAUPE
R. FREEMAN	N. SHEPPARD
S. FUJIWARA	C. P. SLICHTER
D. M. GRANT	J. H. van der WAALS
H. S. GUTOWSKY	J. S. WAUGH

The attached application form should be completed by each intending member of the symposium and should be returned as soon as possible.

A registration fee of \$A40, or \$A20 in the case of a graduate student, will be payable in due course. This will include the price of a symposium dinner on Wednesday 13 August. For an additional \$A2, the book of abstracts will be air-mailed in advance. Further information will appear in the second circular of May 1969.

Application forms and all general correspondence should be addressed:

*The Executive Secretary
Australian Academy of Science
Gordon Street
Canberra City, A.C.T.
Australia 2601.*



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J. R. Pilbrow (Secretary)
*Physics Department
Monash University
Clayton, Victoria
Australia 3168*

CONTRIBUTED PAPERS

Prospective members who wish to present a research paper should state this on the application form and, if possible, include their chosen title or topic. If not, they are asked to submit

the title by 31 December 1968 through the Executive Secretary. Contributors will be advised as to their acceptance by 1 March 1969. They should then send in an abstract before 30 April 1969. The abstracts will be printed and made available at the symposium, and on special order they will be air-mailed in advance.

About twenty minutes of a session will be allowed for each contribution, including a time for discussion.

The venue city is Melbourne (population, 2½ millions), well served by airlines from Sydney (70 minutes away) and other capitals. Monash University, in the suburb of Clayton thirteen miles from the centre of Melbourne, was opened in 1961 and now enrolls some 8600 students.

Full accommodation is available on campus in the university's comfortable new halls of residence. The bedrooms are all single; bathrooms and other facilities are provided on each floor.

Children can be accommodated. The daily tariff will be about \$A7.50 each, including three meals.

There are half a dozen modern motels situated a short drive from the university. Motel suites, which typically consist of a bedroom for three and a private bathroom,

are let at a daily rate. Current tariffs range from \$A7 to \$A10 for single accommodation with breakfast, and \$A3 to \$A4 for each additional person.

Intending participants should indicate on the application form the accommodation they are likely to need.

TRAVEL

The organising committee has appointed QANTAS, Australia's Round-the-World Airline, as official international carrier for the Conference. All enquiries concerning travel may be made at your nearest QANTAS office or QANTAS appointed agency.

There are frequent air services linking Melbourne with Sydney, which is Australia's main overseas air terminal and the venue for the IUPAC Congress.

IUPAC Congress Information

Details of the 1969 IUPAC Congress and International Coordination Chemistry Conference may be obtained by way of the registration form enclosed, or else directly from the following address:

Chairman of the Organising
Committee
XXII IUPAC Congress
Box 2249 U, G.P.O.
Melbourne, Victoria
Australia 3001.

**INTERNATIONAL SYMPOSIUM ON ELECTRON
AND NUCLEAR MAGNETIC RESONANCE**
Monash University, Clayton, Victoria

11 — 14 August 1969

APPLICATION FORM

If you are interested in attending this Symposium or wish to receive the second circular in May 1969, complete this form and return it promptly to:

*The Executive Secretary,
Australian Academy of Science,
Gordon Street,
Canberra City, A.C.T.
Australia 2601.*

NAME (block letters) ^{Title} _____

Surname _____

Given Names _____

PROFESSIONAL ADDRESS _____

My main scientific interest in the Symposium is

P.T.O.

My attending the Symposium is -

very likely ☐ — likely ☐ — unlikely ☐.

I wish to contribute a research paper ☐ —

Tentative TITLE or TOPIC _____

I do not wish to contribute a paper ☐.

I shall be able to arrange my own accommodation ☐.

I shall probably want accommodation to be arranged ☐ —

and I prefer — a Hall of Residence ☐

— a nearby motel ☐.

I wish to receive information concerning the XXII IUPAC Congress and the XII International Coordination Chemistry Conference, to be held conjointly in Sydney, 20 — 27 August 1969 ☐.

Date _____

Signature _____

Printed in Australia
May 1968

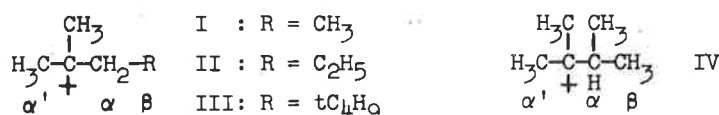
Koninklijke/Shell - Laboratorium, Amsterdam

BADHUISWEG 3 AMSTERDAM - N.
TELEFOON (020) - 6 11 11

Dear Dr. Shapiro,

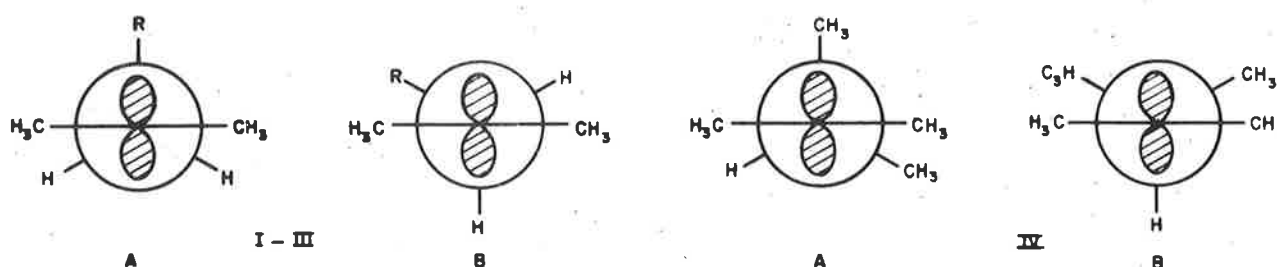
Long-range coupling constants in carbonium ions

The long-range coupling constant $J_{\alpha,\alpha'}$ in alkylcarbonium ions varies markedly with the structure of the cation



In t-pentyl ion (I) and 2-methylpentyl ion (II), $J_{\alpha,\alpha'} = 4.5$ Hz and gives rise to well-resolved triplets of the methyl groups. In 2,2,4-trimethylpentyl ion (III), however, it is much smaller (probably ~ 2 Hz), resulting in only broadened methyl and methylene signals. In 2,3-dimethylbutyl ion (IV) the value of $J_{\alpha,\alpha'}$, calculated from the splitting (4.5 Hz) of the hybrid methyl peak, which equals $\frac{1}{2}(J_{\alpha,\alpha'} + J_{\alpha,\beta})$, is 3.7 Hz, assuming $J_{\alpha,\beta}$ to have the same value as in I (5.3 Hz).

We believe this variation of $J_{\alpha,\alpha'}$ to be associated with the preferred conformations of the respective cations.



In III, conformation A, in which the dihedral angle φ between the $\alpha\text{C-H}$ bonds and the direction of the empty p_z orbital is 60° , is largely preferred to B. In I and II, also conformations B, in which φ is 0° for one of the α -protons, will give a substantial contribution, which to a smaller extent will also be the case with ion IV. This suggests that the value of $J_{\alpha,\alpha'}$ decreases with increasing value φ . A similar effect has been observed earlier (Colpa, MacLean and Mackor, Tetrahedron 19(1965) Suppl. 2, 65) in the case of methylbenzenium ions. The coupling between the aliphatic proton at the site of protonation and the para-methyl group has a value of 2.1 Hz in hexamethylbenzenium ion, in which the angle between the C-H bond and the axis of the ion is larger than in the other benzenium ions owing to repulsion between the methyl groups, as compared with values of 3.5 - 4 Hz in the other methylbenzenium ions.

This contribution should be accredited to Dr. E.L. Mackor.

With kind regards,

D.M. Brouwer

Amsterdam, 1st November 1968

EXPERIMENTAL NMR CONFERENCES

November 1, 1968

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

Dear Barry:

The 10th Experimental NMR Conference will be held Thursday, February 27, through Saturday, March 1, 1969, at the Mellon Institute, Pittsburgh, Pa. The conference is devoted to new developments in advanced instrumentation and experimental techniques. It is not intended as a forum for the presentation of results obtained by standard NMR methods.

Sessions will consist largely of invited papers, but a limited number of contributed papers may be accepted. Anyone desiring to present a paper should submit to the conference chairman or the appropriate session chairman the title and a short preliminary abstract. Session chairmen will assign the length of invited and contributed papers.

The following sessions are currently being planned by the indicated session chairmen:

Pulse techniques in high resolution NMR

R. Freeman
Analytical Instrument Division
Varian Associates
Palo Alto, California 94303

Superconducting solenoids

F. A. L. Anet
Department of Chemistry
UCLA
Los Angeles, California 90024

Computers in the analysis of high resolution spectra

E. Lustig
Food and Drug Administration
200 C Street, SW
Washington, D.C. 20204

Dynamic nuclear polarization

J. M. Anderson
Department of Chemistry
University of Illinois
Urbana, Illinois 61801

Developments in ^{13}C NMR

D. M. Grant
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

Anisotropies in chemical shifts and coupling constants from solid state NMR	T. C. Farrar National Bureau of Standards Washington, D.C. 20234
High resolution techniques: spin decoupling, temperature control, etc.	R. E. Lundin Western Regional Laboratory, USDA Albany, California 94710
On-line computers in NMR	T. J. Flautt Procter and Gamble Box 39175 Cincinnati, Ohio 45239
New developments in the study of oriented molecules	B. P. Dailey Department of Chemistry Columbia University New York, N.Y. 10027
Sources of error in the measurement of exchange rates	C. S. Johnson, Jr. Department of Chemistry University of North Carolina Chapel Hill, N.C. 27514

Topics other than those listed above will be included, with both invited and contributed papers. For example, talks are expected in such areas as New NMR techniques applied to biological problems, Studies of less receptive nuclei, and High resolution studies of relaxation times. The conference chairman will assign the lengths of such papers.

Additional information plus an application to attend may be obtained from the Secretary:

Dr. Jay Martin Anderson
Department of Chemistry
University of Illinois
Urbana, Illinois 61801

Those wishing to attend are requested to reply before December 13.

Sincerely,



E. D. Becker, Chairman, 10th ENC
National Institutes of Health
Bethesda, Maryland 20014
(Phone 301-496-2194)

Committee:

J. M. Anderson
A. A. Bothner-By
T. J. Flautt
P. R. Shafer
B. L. Shapiro
K. L. Williamson

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