Texas A & M University N-M-R Newsletter

No. 127
APRIL, 1969

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OVER

Deadline Dates: No. 128: 5 May 1969
No. 129: 2 June 1969

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

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

SHELL DEVELOPMENT COMPANY
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EMERYVILLE, CALIFORNIA 94608

March 10, 1969

AIR MAIL

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

Dear Barry:

^{13}C NMR AT DISNEYLAND

I think your readers would like to know about the 1969 Pacific Conference on Chemistry and Spectroscopy to be held October 6-10, 1969, at the Disneyland Hotel in Anaheim, California. This is to be a National meeting of the Society of Applied Spectroscopy jointly with the Western Regional Meeting of the American Chemical Society. A full-day session on ^{13}C NMR is scheduled for Tuesday, October 7. The tentative lineup of speakers on ^{13}C includes John Roberts of Cal Tech, Roy Johnson of Varian, J. B. Stothers of the University of Western Ontario, Gary Maciel of U.C. at Davis, David Grant of the University of Utah, Bob Kurland of S.U.N.Y. at Buffalo, Frank Bovey of Bell Telephone, Paul Lauterbur of S.U.N.Y. at Stony Brook, H. Sternlicht of U.C. at Berkeley, and H. L. Retcofsky or R. A. Friedel of the U.S. Bureau of Mines.

In addition, we expect to receive a few submitted papers on miscellaneous NMR and NQR, to be presented in another session.

Disneyland proper is normally closed Monday and Tuesday this time of the year. Plan to attend the NMR sessions and go to Disneyland some other day. Bring the wife and leave the kids at home so that you will have more fun!

At the Pittsburgh ENC you mentioned getting the ^{13}C NMR people together for a discussion at the Disneyland meeting. To arrange this, you should contact the SAS program chairman:

W. F. Ulrich
Beckman Instruments, Inc.
Scientific Instruments Division
2500 Harbor Blvd.
Fullerton, California 92634

Sincerely yours,

JOHN L. JUNGNICKEL

JLJ:fmp
cc: W. F. Ulrich

127-2

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Department of Chemistry

7 March 1969

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

Dear Barry:

Because of the many high-temperature experiments now being performed on internal-lock instruments, the need for a high-boiling nonabsorbing solvent and a high-boiling lock is particularly pressing.

We wish to suggest t-butylbenzene (or t-butylbenzene-d_5), a high-boiling solvent whose only appreciable absorption is its lock signal. It may be prepared in a matter of hours from benzene (or benzene-d_6) and t-butyl chloride (cf. Vogel, p. 513) in good yield. It is nonviscous at room temperature and has an enormous liquid range (m.p. -58°C; b.p. +169°C). The t-butyl protons absorb 1.28 ppm downfield from TMS in CCl_4.

Although the region extending one ppm up and downfield from the t-butyl absorption in the neat liquid is obscured, t-butylbenzene-d_5 should prove quite useful in the study of, e.g., fluxional molecules, where one is primarily concerned with olefinic and allylic absorptions.

The price of commercially available benzene-d_6 (~$2/g.) will not make synthesis of t-butylbenzene-d_5 prohibitively expensive (compare this with toluene-d_8 which, at $17/g., is widely used as a low-temperature solvent). Excluding labor, a reasonable cost estimate for the production of t-butylbenzene-d_5 is ~ $6/g.

Sincerely,

Henry Maltz D. J. Sardella

short title: A Useful High-Temperature Solvent/Lock

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March 9, 1969

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

Positions Available

Dear Barry,

At present we are planning the extension of our magnetic resonance laboratory in instrumentation, space, students, post-doctoral and staff positions.

The interested candicates may contact the undersigned for further details.

Sincerely yours,

Daniel Fiat

Daniel Fiat

DF/gk

CABLE ADDRESS: WEIZINST (Israel) מען למברקים: PHONE: 951721 טלפון:

PRINCETON UNIVERSITY
DEPARTMENT OF CHEMISTRY
PRINCETON, NEW JERSEY 08540

Frick Chemical Laboratory

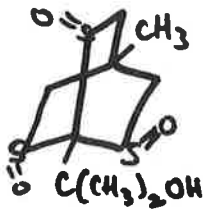
March 12, 1969

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

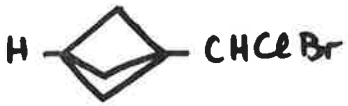
Dear Barry:

Demonstration of Intrinsic Diastereotopism

Just a brief comment on the very elegant demonstration of "intrinsic diastereotopism" (we're the guilty party for this coinage, too[1]), reported by Gerhard Binsch in TAMU-NMR Newsletter, 124, 40 (1969). Since his compound I bears an amusing family resemblance to hypothetical compound II which we discussed in this very connection a couple of years ago[2] (as a sort of Gedanken experiment), it might not be unprofitable to ask: What symmetry properties are required in such molecules for the demonstration of intrinsic diastereotopism?

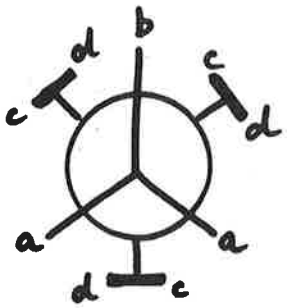


I



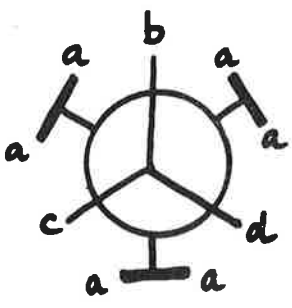
II

An analysis of the essential features held in common by I and II reveals the answer (refer to projection formulas of I and II, i.e., I' and II' respectively).



I'

a = CH_3



II'

a = H

1. The molecule must contain two moieties, one a rigid bicyclic structure ("B") with 3-fold axial symmetry, the other a group ("CR_3") of lower symmetry which is attached to the bridgehead atom in such a manner that the single bond lies along the C_3 axis of B. It follows that free rotation around the B-CR_3 bond occurs with 3-fold degeneracy (as in CH_3Cabc or in CH_3Ca_2b, for example).

2. Either one of the two moieties, B or CR_3 (but not both), is chiral by itself, i.e., when unattached to the other moiety. Obviously, after bond formation B-CR_3 must then be chiral.

3. Either one of the two moieties, B or CR_3, contains two sensor nuclei a which are enantiotopic so long as B and CR_3 are not bonded to each other. Since chiral systems cannot contain enantiotopic nuclei[2], the present condition is linked to that in the preceding item (2), and it follows that the chiral moiety cannot contain the sensor nuclei a.

The rest is obvious: enantiotopic nuclei in B or CR_3 (whichever is the achiral moiety) placed in a chiral environment (that of the molecule B-CR_3) cease being enantiotopic and become diastereotopic (and ipso facto anisochronous). The degeneracy of the rotation around the B-CR_3 does the rest, for it insures the non-occurrence of conformational isomerism. That's all.

Sincerely yours,

Kurt Mislow

(1) R. A. Lewis, O. Korpiun, and K. Mislow, J.Am.Chem.Soc., 90, 4847 (1968), ftnote 26b.

(2) K. Mislow and M. Raban, in "Topics in Stereochemistry", Vol. 1, N. L. Allinger and E. L. Eliel, Ed., John Wiley and Sons, Inc., New York, N. Y., 1967, Chapter 1; cf. especially pp. 32-34.

C I B A RESEARCH CENTRE

Bombay 63, India

March 7, 1969

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

"NMR Spectra of 3,4-dihydroisoquinolines"

Dear Professor Shapiro:

I do not know how often organic chemists find that expected signals for protons in NMR spectra are missing. We want to report one such mysterious 'case of the missing proton'.

We recently ran for Professor B.R. Pai, Presidency College, Madras 5, the NMR spectrum of norhydrastinine (3,4-dihydro-6,7-methylenedioxy isoquinoline) in $CDCl_3$ on a Varian A-60 spectrometer and were puzzled at the result (Fig.1). Even at high amplitudes, below 7.5 ppm (from TMS internal standard) where we would have expected the C-2 proton, we could not get a visible signal and integration revealed less than 20% of one proton. In the 2-4 ppm region, two approximate triplets were expected but not seen. The visible broad peak due to the benzylic CH_2 between 2.2 and 3.0 ppm integrated for 2 protons; between 3 and 5 ppm no peak was seen, but integration showed the presence of about 1 proton. This phenomenon was reproducible in $CDCl_3$ on different occasions and with different samples of norhydrastinine. A few other 3,4-dihydroisoquinolines from Professor Pai gave similar spectra in $CDCl_3$. The NMR spectrum of norhydrastinine in CCl_4 (Fig.2) and of its methiodide in D_2O were unexceptionable. We speculate that in $CDCl_3$, the C-1 and C-3 protons may be unusually strongly coupled to the nitrogen quadrupole, giving rise to the observed spectrum. Our CCl_4 must have been sufficiently acidic to protonate the nitrogen and remove quadrupole coupling. The extreme case is of course the methiodide.

Extreme broadening due to quadrupole coupling of protons attached directly to nitrogen is well-known; but possibly not for proton on

carbon bound to nitrogen. To our knowledge we have an unique case and would like to invite comments from your readers.

With regards,

Yours sincerely

K Nagarajan

Dr. K. Nagarajan

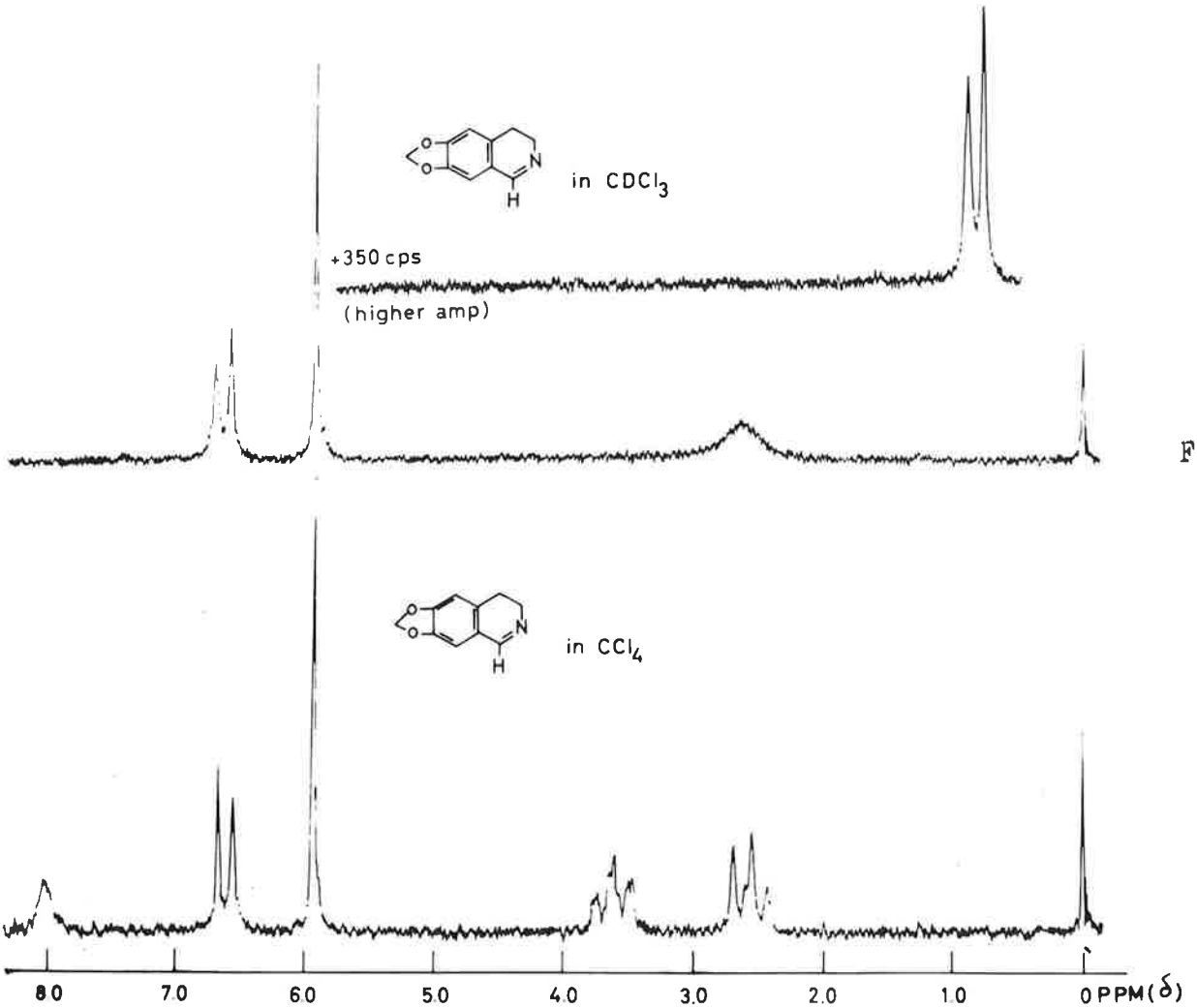


FIG. 1

FIG

27-8

VISION OF APPLIED CHEMISTRY
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CONSEIL NATIONAL DE RECHERCHES DU CANADA

OTTAWA 7.

March 11, 1969

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

Title: Relaxation and Cis-Trans Isomerism in Amides

Dear Barry,

We would like to report our results on the longitudinal relaxation times T_1 of methyl groups of some amides in benzene and deuterobenzene solutions.

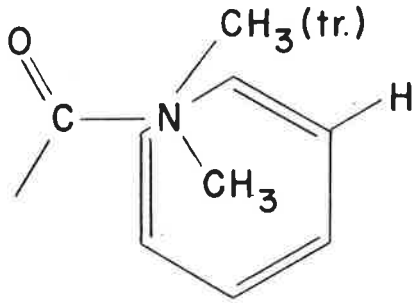
The T_1 times shown in the Table were obtained by a saturation-recovery method, proposed by Van Geet [1]. By investigation of the Overhauser effects in the spectra of dimethylformamide in some solutions it was shown that it is safe enough to treat the recovery as one exponential curve.

The difference of the relaxation rates $1/T_1$ in benzene and deuterobenzene solutions with the same concentration

$$\Delta = (1/T_1)_{C_6H_6} - (1/T_1)_{C_6D_6}$$

is larger for a trans-methyl group than for a cis-methyl (see Table). The only reason for a difference is the change in the intermolecular interaction arising from substitution of protons by deuterium in the solvent molecules. The observed specific changes are in agreement with the structure of a collision complex between amide and benzene molecules [2,3]. In this complex the benzene molecule is coplanar

. . /2



with the amide and the axis of symmetry of the benzene ring is closer to the position of the cis-methyl group. This means that the protons of benzene are closer to the trans-methyl protons and therefore the mutual dipole-dipole interactions for these protons are stronger than for cis-methyl protons. Moreover, the cis-methyl is screened by the benzene molecule of the complex from the bulk benzene. Thus, the trans-methyl relaxation rate has to be more sensitive to the substitution of the benzene protons by deuterium.

It seems probable that such an approach could be useful for assignment of cis-trans isomerism about the amide bond in N-methyl substituted amides and peptides. It might be an absolute method, because it does not require both isomers to be available.

Please credit this contribution for receiving the NMR Newsletters at the address:

Dr. V. Bystrov,
Ul. Vavilova, 32,
Institute for Chemistry of Natural Products,
Academy of Sciences of the U.S.S.R.,
Moscow V-312, U.S.S.R.

and thank you very much for your reminder.

Sincerely yours,

S. Brownstein V. Bystrov

Dr. S. Brownstein Dr. V. Bystrov

SB/VB/dn

References:

[1] A.L. Van Geet and D.N. Hume, Anal. Chem., 37, 983 (1965); A.L. Van Geet, Anal. Chem., 40, 304 (1968).

[2] J.V. Hatton, R.E. Richards, Molec. Phys., 5, 139 (1962).

[3] P. Laszlo, in Progress in NMR Spectroscopy, J.W. Emsley, J. Feeney and L.H. Sutcliffe, Eds., vol. 3 (Pergamon Press, Inc., Oxford, 1967), ch. 6.

Table. The Longitudinal Relaxation Times (sec.) and the Difference Δ(sec.$^{-1}$) for Amides in 5% v/v Solutions in Benzene and Deuterobenzene

Compound	trans-NCH_3			cis-NCH_3		
	T_1		Δ	T_1		Δ
	C_6H_6	C_6D_6		C_6H_6	C_6D_6	
Dimethylformamide	13.3	18.3	0.020	10.6	11.9	0.010
N-Butyl-N-Methylformamide[a)]	7.8	9.3	0.020	6.6	6.9	0.007
N-Methyl-2-Pyrrolidone	8.4[b)]	10.2[b)]	0.021	-	-	-
N-Methyl-2-Piperidone	8.4[b)]	10.7[b)]	0.027	-	-	-
1,4-Dimethyl-2,5-Piperazinedione[c)]	6.3	7.3	0.022	4.3[d)]	4.5[d)]	0.010[d)]

a) The equilibrium mixture of the cis- and trans-isomers.

b) The measurements were done with irradiation of the C-CH_2C multiplet to decouple the N-CH_2 triplet to remove partial coincidence of it with the N-CH_3 signal.

c) 2% w/v solution.

d) For N-CH_2-CO protons.

University of East Anglia

From the Dean
Professor A. R. Katritzky

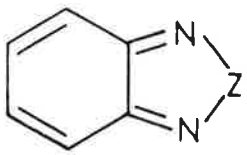
School of Chemical Sciences
University Plain
Norwich NOR 88C
Telephone Norwich 56161

13th March, 1969

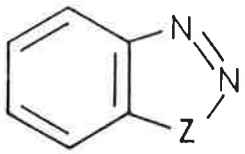
Dear Dr. Shapiro,

Bond Fixation from J-values

We are preparing for publication the results of an investigation of compounds of types I and II. The coupling constants for these compounds (10% w/v solutions), shown in Table, allow deductions regarding the CC-bond orders in the benzene ring which are of interest in considering their chemical reactivity. When this work was essentially completed Brown and Bladon (Spectrochim. Acta 1968, 24A, 1869) published a study of some derivatives of type I including Ia and Ic. Our results confirm and extend some of their conclusions.



I a : Z = S
b : Z = NMe
c : Z = O



II a : Z = S
b : Z = NMe

Table

		4,5	5,6	6,7	4,6	4,7	5,7
Benzofurazan	CCl_4	9.11	6.43	9.11	0.84	1.12	0.84
	$CDCl_3$	9.12	6.44	9.12	0.88	1.14	0.88
2-Methylbenzo-triazole	CCl_4	8.67	6.77	8.67	1.05	1.06	1.05
	$CDCl_3$	8.70	6.71	8.70	0.96	0.98	0.96
Piazthiole	CCl_4	9.05	6.51	9.05	0.88	0.76	0.88
	$CDCl_3$	8.80	6.56	8.80	1.02	0.92	1.02
1-Methylbenzo-triazole	CCl_4	8.39	6.91	8.59	0.96	1.00	1.18
	$CDCl_3$	8.40	6.98	8.55	1.06	0.91	1.13
Benzo-(1,2-d)-(1,2,3)-thiadiazole*	CCl_4	8.44	7.25	8.08	1.19	0.73	1.03
	$CDCl_3$	8.35	7.05	7.88	1.04	0.78	1.00

* From W.H. Poesche, J.Chem.Soc (B), 1966, 568.

Yours sincerely

A.J. Boulton P. Halls A.R. Katritzky

27-12
DEPARTMENT OF PHYSICS

THE UNIVERSITY OF NEW BRUNSWICK
FREDERICTON, N.B.

March 18, 1969

Prof. B. Shapiro
Department of Chemistry
Texas A and M University
College Station
Texas 77843

Double Resonance Information on
Dewar - Hexafluorobenzene Couplings

Dear Barry:

The analysis of the spectrum of hexafluorobicyclohexadiene (Dewar form of hexafluorobenzene) has recently been discussed in the Newsletter (124 - 2 and 125 - 38). Eight sets of coupling constants were found to fit the observed spectrum, and these sets were related by certain exchanges and relative sign reversals. In an effort to reduce the ambiguity we have performed some double resonance measurements. The following description refers to the figures in 124 - 5 and 6 in which the designations $\mathcal{B}_1$ and $\mathcal{B}_2$ should be interchanged. When the line at +2.6 Hz in the A spectrum (inner component of AB quartet of $\mathcal{B}_2$ subspectrum) was weakly irradiated, the lines at +1.2 Hz and at +30.6 Hz in the $\mathcal{B}_2$ part of the X spectrum were observed to decrease considerably in peak height while the line at -27.5 Hz in the same X subspectrum showed a small (15 %) increase. Lines at +27.5 Hz, -1.2 Hz and -30.6 Hz in the same X subspectrum showed little, if any, intensity change. Additional measurements in the X spectrum with the line at -2.6 Hz in the $\mathcal{B}_2$ subspectrum or that at +5.6 Hz in the $\mathcal{A}_2$ subspectrum of the A fluorines irradiated gave similar results.

Our interpretation of these intensity changes as intramolecular generalized Overhauser effects shows that the sum $(J_{AX} + J_{AX'})$ must have the same sign as the greater of the two quantities $\{(-J_{AA'} + J_{AA''} - J_{XX'})$ and $(J_{AA'} - J_{AA''} - J_{XX'})\}$ and the opposite sign of the smaller of these two quantities. Of the 8 parameter sets listed in 124 - 3, the following four satisfy these conditions:

.....2

Prof. B. Shapiro
March 18, 1969

no.	$J_{AA'}$	$J_{AA''}$	$J_{AA'''}$	J_{AX}	$J_{AX'}$	$J_{XX'}$
1	14.08	-3.02	0.06	10.02	-7.09	-9.40
2	14.08	-3.02	0.06	-7.09	10.02	-9.40
3	-3.02	14.08	0.06	10.02	-7.09	-9.40
4	-3.02	14.08	0.06	-7.09	10.02	-9.40

I do not know of any method that would discriminate between these four sets by means of measurements on the spectrum. Even if more were known about relaxation transitions between different symmetry species the decision would not be simple. A comparison with similar coupling situations in other molecules favours sets 3 and 4 over 1 and 2, and it gives set 4 a slightly higher probability than set 3 although caution seems necessary because Dr. R.K. Harris has found the couplings corresponding to J_{AX} and $J_{AX'}$ in hexafluorocyclobutene both to be positive (+6.8 and +16.4 Hz).

Yours sincerely,

Reinhold

R. Kaiser, Professor

RK:seb

27-14

CHIMIE ORGANIQUE PHYSIQUE

FACULTÉ DES SCIENCES
UNIVERSITÉ DE NANTES

38, Bd Michelet, - 44 - NANTES
B. P. 1044
Tél. (40) 74-50-70

Nantes, le 31.1.69

Professeur Bernard SHAPIRO
Department of Chemistry
Texas A.M. University
College of Sciences

TEXAS 77 843

Deuterium content of organic molecules by NMR

Cher Professeur SHAPIRO,

Au cours de recherches sur la deutériation de composés organiques (1) nous avons été amenés à étudier systématiquement les différents procédés de dosage de deutérium par R.M.N.

Pour la détermination du taux de deutériation moyen, nous avons envisagé deux types de méthodes :

1 - Méthodes par substitution de tubes échantillons :

a) Utilisation d'un seul tube A :

La substance deutériée X_D est introduite dans un tube A et les signaux des protons résiduels sont intégrés. Sans modifier les réglages du spectrographe, on vide le tube A et on introduit la substance protonée X_H homologue de X_D. Les signaux des protons résiduels sont alors intégrés et le taux de deutériation se déduit aisément de ces mesures d'intensités.

b) Utilisation de deux tubes A et B :

La substance deutériée X_D est introduite dans le tube A et la substance homologue protonée X_H dans le tube B. On compare les intensités des signaux des protons correspondants de X_H et de X_D et on en déduit le taux de deutériation.

2 - Méthodes utilisant un étalon interne

a) Etalon intramoléculaire

On compare l'intensité des signaux relatifs aux protons résiduels du site deutérié à celle des signaux d'autres protons de la même molécule.

b) Etalon intermoléculaire

On introduit une masse connue de substance étalon dans un tube contenant une masse connue de la substance deutériée X_D.
Le taux de deutériation se calcule alors aisément.

° ° °
° °
°

.../...

Nous avons évalué la précision de ces différentes méthodes en déterminant l'erreur moyenne $\bar{E}$ et l'écart-type σ_E de cette erreur.

Substitution de tube	$\bar{E} - \sigma_E$		$\bar{E} + \sigma_E$
1 tube	3,3 %	à	5,9 %
2 tubes	3,8 %	à	7,3 %
Etalon interne			
intramoléculaire	1,4 %	à	2,4 %
intermoléculaire	1,5 %	à	2,5 %

Nous avons comparé nos résultats à des déterminations de taux de deutériation réalisées par spectrométrie de masse.

	RMN étalon intermoléculaire	Spectrométrie de masse
Toluène	62,5 %	60,5 %
Hexaméthyl phosphotriamide	30,2 %	28,5 %

Dans les cas considérés, la concordance est très satisfaisante. La R.M.N. est plus intéressante que la spectrométrie de masse pou la détermination du taux moyen de deutériation ; en effet pour des précisions analogues, la R.M.N. est plus rapide et nécessite un appareilla moins coûteux.

Le détail de ce travail sera publié ultérieurement (2).

G.J. MARTIN M.T. QUEMENEUR M.L. MARTIN

(1) H. NORMANT, Th. CUVIGNY, G.J. MARTIN - Bull. Soc. Chim. France 1969

(2) G.J. MARTIN, M.T. QUEMENEUR, M.L. MARTIN - Organic Magnetic Resonanc

Glaxo Research Limited

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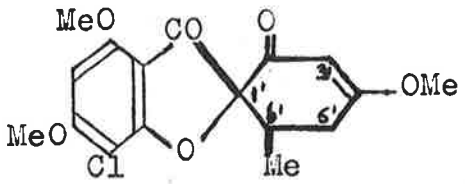
22nd January, 1969.

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

Dear Professor Shapiro,

Isogriseofulvin

We have recently investigated the 100 MHz proton spectrum of isogriseofulvin (I), a compound that we previously examined at 60 MHz. The original, lower frequency, deuterochloroform spectrum displayed long-range coupling between the 3'-olefinic proton at τ4.45 and one of the 5'-methylene protons, but this coupling could not be reliably assigned because of the complexity of the 5'- and 6'-proton pattern between τ6.5 and 7.9. At 100 MHz, however, a 0.3M solution of isogriseofulvin in pyridine gave a spectrum amenable to first-order analysis yielding the results given below. Sign relationships between some of the coupling constants were determined by selective decoupling experiments.



(I)

$J_{5'\alpha-5'\beta}$	= -16.4 Hz	$J_{3'-5'\beta}$	= 1.4 Hz
$J_{5'\alpha-6'\alpha}$	= + 5.0 Hz	$J_{6'\alpha-CH_3}$	= 6.3 Hz
$J_{5'\beta-6'\alpha}$	= +11.5 Hz		

Since the 6'-methyl group is known to have the β-configuration, the allylic coupling is established as being to the 5'β-proton. Dreiding models suggest a half-chair conformation for the cyclohex-3'-en-2'-one ring of isogriseofulvin, in which the dihedral angles (ϕ) between the 5'α- and 5'β-carbon-hydrogen bonds and the

Contd./

plane of the 3'-double bond approximate to 30° and 90°, respectively; these angles are of the order to be expected for the observed allylic coupling to the 5'β-, but not to the 5'∝-proton, and provide further qualitative support for the theoretically predicted dependence[2] of the coupling constant upon $\sin^2\phi$.

Yours sincerely,

J.E. Page R.A. Fletton G.F.H. Green

References

1. Green, G.F.H., Page, J.E. and Staniforth, S.E., J. Chem. Soc., 1963, 144.

2. Karplus, M., J. Chem. Phys., 1960, 33, 1842.

Institute of Chemical
Kinetics and Combustion
Academy of Sciences
90, Novosibirsk
U.S.S.R.

February 24, 1969

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

The ^{14}N and ^{13}C NMR contact shifts of some paramagnetic Ni(II) complexes in solution.

Dear Professor Shapiro:

During my visit to Varian AG research laboratory I investigated the ^{14}N and ^{13}C NMR spectra of some Ni(II) paramagnetic complexes as well as corresponding diamagnetic ligands. The ^{14}N contact shifts in solutions of Ni(II) acetylacetonate (Table 1) have been measured under the condition of fast exchange between bulk and coordinated molecules.

The shifts $\frac{\Delta H}{H}$ given in the Table 1 are the observed shifts recalculated to 2 : 1 ligand to Ni(II) ratio and to room temperature (298°K). The results presented in Table 2, have been obtained for individual complexes in water solution. In calculating the isotropic coupling constants A and the spin densities ρ the magnetic moment of Ni(II) was supposed to have a pure spin value and the hybridization of ^{13}C and ^{14}N spin-con-

taining orbitals to be sp^3 (except pyridine).

It followes from the results obtained that the d_{z^2} (or $d_{x^2-y^2}$) unpaired electron of Ni(II) is delocalized essentially to nitrogen atoms. Spin densities on the NH_2 hydrogens and α-carbons are negative and therefore originate mainly from spin polarization of the NH and NC bonds. Positive spin densities on CH_2 hydrogens and β-carbons are probably due to superconjugation.

The details of this investigation will be published in Zhur.Struct.Khim. I am very grateful to Dr.J.Feeney and to Dr.U.Scheidegger for invitation to spend a month in Varian laboratory as a summer visitor and to Dr.L.Andersson for his assistance and advice.

Sincerely yours

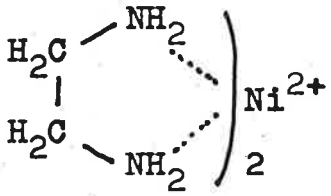
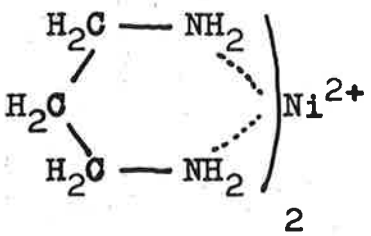
Molin Yu.Molin

Table 1. The results of ^{14}N NMR investigation in solution of Ni(II) acetylacetonate.

N	solvent	$(-\frac{\Delta H}{H})\times 10^6$	A, Mc	$\rho \times 10^3$
1	**aniline**, $C_6H_5NH_2$ *	10150 ± 500	10,4	54
2	diethyl amine, $(C_2H_5)_2NH$	11170 ± 300	11,4	59
3	dipropyl amine, $(C_3H_7)_2NH$	11160 ± 600	11,4	59
4	t-butyl amine, $(CH_3)_3\,CNH_2$	11330 ± 500	11,6	60
5	piperidine, $C_5H_{10}NH$	13260 ± 500	13,5	70
6	pyridine, C_5H_5N	15400 ± 300	15,7	61

*) ~ 1 : 1 mixture with $CHCl_3$

Table 2. Contact shifts and spin density distribution in $Ni(NH_2CH_2CH_2NH_2)_2(NO_3)_2$ and $Ni(NH_2CH_2CH_2CH_2NH_2)Cl_2$ (~ 1,5 M solutions in water).

complex	nucleus	$(-\frac{\Delta H}{H})\times 10^6$	A, Mc	$\rho \times 10^3$
	$I_{H(NH_2)}$	−163 ± 4	−2,30	−3,2
	$^1H(CH_2)$	85 ± 4	1,20	+1,7
	^{14}N	13050 ± 400	13,3	+69
	^{13}C	−313 ± 20	−1,11	−2,9
	$^1H(NH_2)$	−169 ± 4	−2,39	−3,4
	$^1H(\alpha\text{-}CH_2)$	155 ± 4	2,19	+3,1
	^{14}N	15400 ± 400	15,7	+82
	$^{13}C(\alpha)$	−222 ± 20	−0,79	−2,0
	$^{13}C(\beta)$	63 ± 20	0,22	+0,6

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March 12, 1969

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

EXPERIENCE WITH THREE-SPIN ANALYSES

We have been experimenting with the computer programs LAOCN[1] and EXAN[2] using the IBM 360/30 computer and an EAI-3500 Dataplotter. We find that some ABX systems are difficult to treat by either program.

To compare the results by the two programs a standard spectrum was calculated using the LAOCN program. The spectrum was an eclipsed narrow-coupled case, Figure 1. The lines of this spectrum were analyzed by LAOCN and by EXAN and the results were compared. The LAOCN iterative program gave three other solutions which were exact fits to this spectrum, Figures 2-4. In addition there were four more solutions with the sign of J_{AB} reversed. (Reversal of all signs furnished eight more solutions but aside from renumbering of the lines there was no difference in line frequencies or intensities). The parameters are collected in Tables I and II.

The standard spectrum, (Figure 1) was next analyzed by EXAN. For the first analysis the line-frequency table (eq. 2a of ref. 2) was constructed labeling the lines of the standard spectrum as if it were indeed an eclipsed narrow-coupled case. For a second EXAN analysis the line assignments in the standard spectrum were switched around to start the analysis of this spectrum as a partly-eclipsed narrow-coupled case. This rearranged two of the columns in the line-frequency table as expected. The results are collected in Tables I and II, respectively.

Both EXAN analyses yielded the eight possible solutions that were expected. The results were compared to the LAOCN solutions. When spectra were recalculated by LAOCN from the computed EXAN parameters (to complete the cycle) the original line frequencies were not obtained. The discrepancy in line frequencies was obtained by the iterating LAOCN program and the root mean square errors are recorded in the tables.

It was apparent that the results varied slightly for the two different ways of starting EXAN, especially in the narrow-coupled cases. It was also noticed that the greatest discrepancy between LAOCN and EXAN occurred when the root was near the -2.0 limit. This required division by a number which was nearly zero and probably introduced truncating errors in the EXAN calculations.

We find that degenerate ABX spectra, in which the A and B nuclei share a common energy level, are difficult to treat by either program. Results obtained on these degenerate systems will be discussed in my next contribution to these letters.

For the present, EXAN results from tangent cases or roots near the ±2.0 limits should be considered carefully and used with caution.

Sincerely,

George Slomp
Physical and Analytical
Chemistry Research

mjc

enclosures

REFERENCES

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2. S. Castellano and J. S. Waugh, *J. Chem. Phys.*, *34*, 295 (1961).

Figure 1. Eclipsed Narrow-Coupled ABX

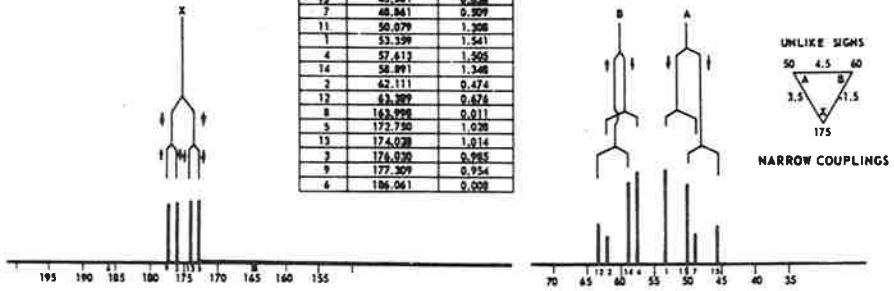


Figure 2. Partly-Eclipsed Narrow-Coupled ABX

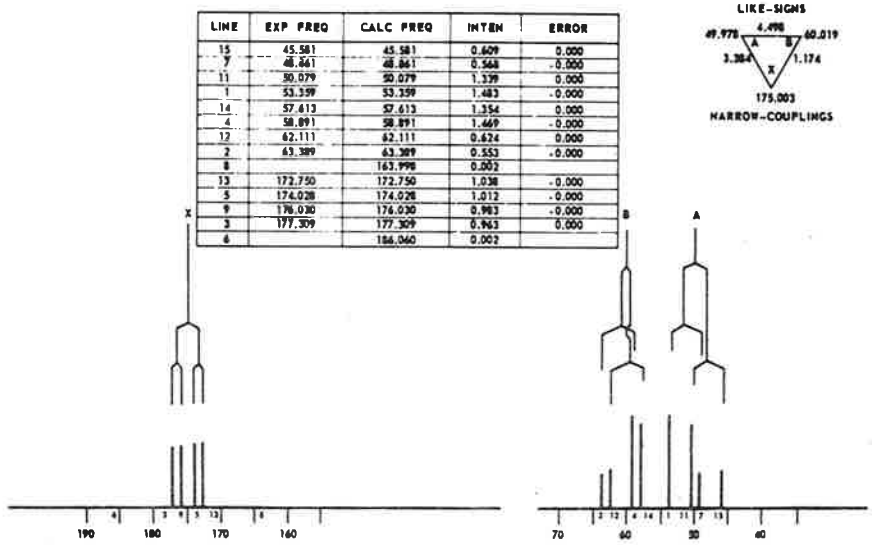


Figure 3. Eclipsed Wide-Coupled ABX

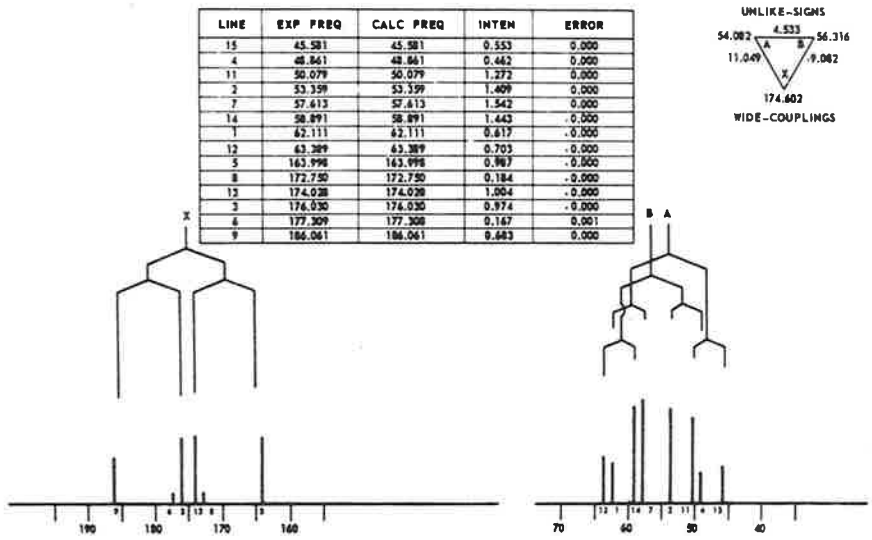


Figure 4. Partly-Eclipsed Wide-Coupled ABX

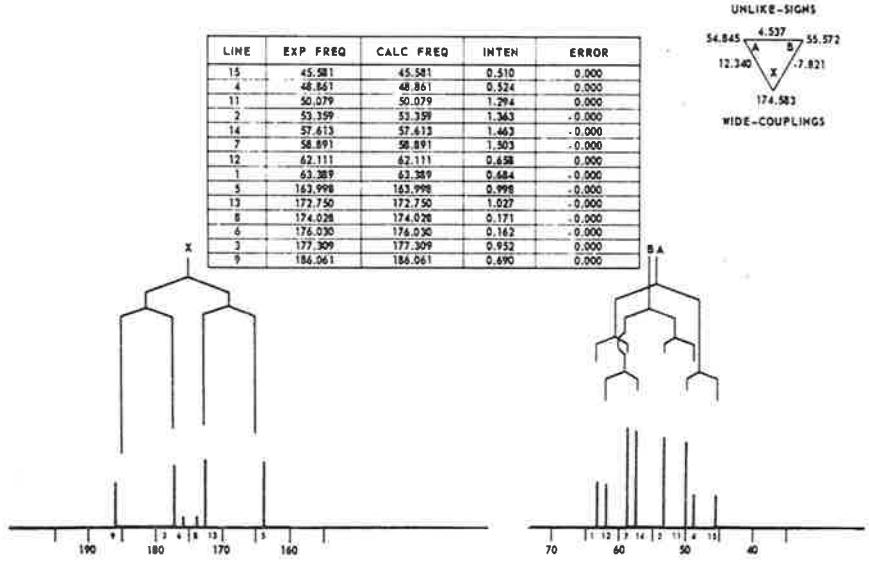


TABLE I

Analysis of ABX Spectrum by LAOCN and EXAN.
EXAN Entered as an Eclipsed Narrow-Coupled Case.

Solution	Case	Root	ν_A	ν_B	ν_X	J_{AB}	J_{AX}	J_{BX}	Error
LAC-1	Eclipsed Narrow-Coupled	-	50.000	60.000	175.000	4.500	3.500	-1.500	Standard
LAC-1a	" "	-	50.003	59.998	175.000	4.500	-3.500	1.519	0.000
E1-2	" "	-1.9966	49.976	60.026	174.998	4.500	3.489	-1.489	0.024
E10-2	" "	-1.9953	50.000	60.001	174.999	4.500	-3.521	1.517	0.003
LAC-2	Partly-Eclipsed Narrow-Coupled	-	49.978	60.019	175.003	4.498	3.384	1.174	0.000
LAC-2a	" "	-	49.977	60.020	175.004	-4.499	3.369	1.190	0.000
E2-2	" "	-1.9994	49.761	60.255	174.984	-4.498	-3.344	-1.215	0.221
E6-2	" "	-1.9989	49.903	60.100	174.997	-4.498	3.344	1.215	0.075
LAC-3	Eclipsed Wide-Coupled	-	54.082	56.316	174.602	4.533	11.049	-9.082	0.000
LAC-3a	" "	-	53.878	56.512	174.610	4.527	-10.982	8.951	0.000
E1-1	" "	-1.9374	54.083	56.316	174.601	4.533	11.052	-9.085	0.002
E10-1	" "	-1.9374	53.878	56.512	174.610	4.527	-10.982	8.952	0.000
LAC-4	Partly-Eclipsed Wide-Coupled	-	54.845	55.572	174.583	4.537	12.340	-7.821	0.000
LAC-4a	" "	-	54.662	55.753	174.586	-4.522	12.335	-7.753	0.000
E2-1	" "	-1.9368	54.847	55.570	174.583	-4.538	-12.344	7.825	0.002
E6-1	" "	-1.9366	54.662	55.752	174.586	-4.522	12.338	-7.755	0.001

TABLE II

Analysis of ABX Spectrum by LAOCN and EXAN.
EXAN Entered as a Partly-Eclipsed Narrow-Coupled Case.

Solution	Case	Root	ν_A	ν_B	ν_X	J_{AB}	J_{AX}	J_{BX}	Error
LAC-1	Eclipsed Narrow-Coupled	-	50.000	60.000	175.000	4.500	3.500	-1.500	Standard
LAC-1a	" "	-	50.003	59.998	175.000	4.500	-3.500	1.519	0.000
E2-2	" "	-1.9966	49.954	60.050	174.996	-4.500	-3.478	1.478	0.047
E6-2	" "	-1.9954	49.978	60.025	174.998	-4.500	3.506	-1.503	0.026
LAC-2	Partly-Eclipsed Narrow-Coupled	-	49.978	60.019	175.003	4.498	3.384	1.174	0.000
LAC-2a	" "	-	49.977	60.020	175.004	-4.499	3.369	1.190	0.000
E1-2	" "	-1.9994	49.881	60.125	174.995	4.498	3.366	1.193	0.099
E10-2	" "	-1.9988	49.965	60.033	175.002	4.498	-3.365	-1.194	0.012
LAC-3	Eclipsed Wide-Coupled	-	54.082	56.316	174.602	4.533	11.049	-9.082	0.000
LAC-3a	" "	-	53.878	56.512	174.610	4.527	-10.982	8.951	0.000
E2-1	" "	-1.9373	54.083	56.316	174.601	-4.533	-11.054	9.087	0.002
E6-1	" "	-1.9373	53.879	56.512	174.609	-4.527	10.986	-8.955	0.002
LAC-4	Partly-Eclipsed Wide-Coupled	-	54.845	55.572	174.583	4.537	12.340	-7.821	0.000
LAC-4a	" "	-	54.662	55.753	174.586	-4.522	12.335	-7.753	0.000
E1-1	" "	-1.9369	54.847	55.571	174.583	4.538	12.342	-7.823	0.002
E10-1	" "	-1.9366	54.662	55.753	174.586	4.522	-12.335	7.752	0.001

27-26

MERCK INSTITUTE
FOR
THERAPEUTIC RESEARCH
RAHWAY, NEW JERSEY 07065

Department of Biophysics

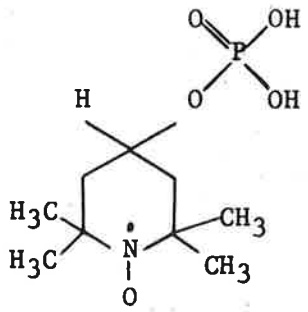
March 14, 1969

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

Dear Doctor Shapiro:

The use of stable free radicals, or spin labels, as probes to investigate the structure of proteins was pioneered by McConnell[1] and has become widely used in the last few years. In most of these studies, the spin label has been covalently attached to the protein and its relative rotational freedom has been determined from its EPR spectrum (though Sternlicht and Wheeler[2] have observed non-specific broadening of the NMR spectrum of lysozyme on covalent attachment of a spin-label).

We have now studied the effects of a spin-labelled inhibitor on the high-resolution NMR spectrum of ribonuclease. The inhibitor, 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-oxyl-monophosphate (TEMPOP) was synthesized for us by Dr. John Hannah of the Synthetic Chemistry Department.



TEMPOP

The effects of low concentrations of this compound on the four histidine C2-H peaks in the NMR spectrum of ribonuclease are shown in the figure. 0.1mM TEMPOP has no effect, but higher concentrations produced broadening of the C2-H peaks of histidine-12 and (to a lesser extent) histidine-119. The peaks of histidines-48 and -105 were unaffected. The main aromatic region of the NMR spectrum of the enzyme was also unaffected by TEMPOP at concentrations up to 5 mM.

It is clear that the unpaired electron of the spin-labelled inhibitor is relatively close to histidine-12, somewhat further from histidine-119 and distant from histidine-48 and -105 and the phenylalanine and tyrosine residues. This is entirely consistent with the results of studies of the enzyme by chemical modification[3], X-ray diffraction[4,5] and NMR[6,7]. The use of spin-labelled inhibitors in conjunction with NMR seems, therefore, to be a useful tool for the determination of the amino-acid residues in the immediate vicinity of an inhibitor binding site.

Would you please use this contribution to start a subscription for G.C.K.R.? Address after June 1st, 1969: Medical Research Council, Molecular Pharmacology Research Unit, Old Press Site, Mill Lane, Cambridge, England.

Yours sincerely,

Gordon C. K. Roberts

Oleg Jardetzky

Title: Effect of Spin-labelled inhibitor on enzyme NMR spectrum.

References

1. See Hamilton, C. L. and McConnell, H. M., in "Structural Chemistry and Molecular Biology," Rich, A. and Davidson, N. (eds). San Francisco, W. H. Freeman, p. 115 (1968).

2. Sternlicht, H. and Wheeler, E., in "Magnetic Resonance in Biological Systems," Ehrenberg, A., Malmstrom, B. G. and Vanngard, T. (eds). New York, Pergamon Press. p. 325 (1967).

3. Crestfield, A. M., Stein, W. H. and Moore, S., J. Biol. Chem., 238, 2413 (1963).

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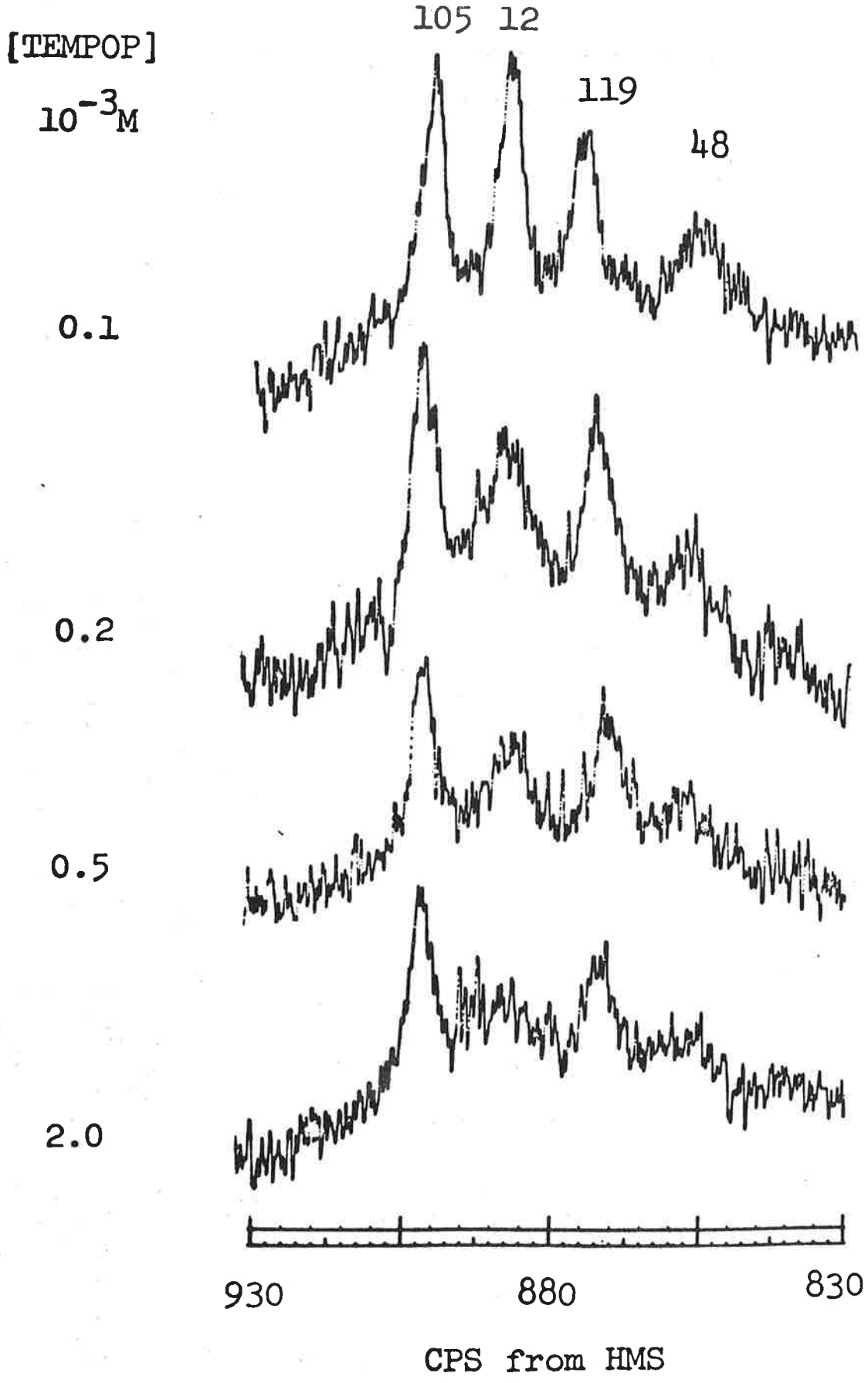
5. Wyckoff, H. and Richards, F. M., personal communication.

6. Meadows, D. H. and Jardetzky, O., Proc. Nat. Acad. Sci., 61, 406 (1968).

7. Meadows, D. H., Roberts, G. C. K. and Jardetzky, O., in press (1969).

Figure

Imidazole C2-H region of the NMR spectrum of 0.0065M ribonuclease (0.2M NaCl, pH (meter reading) 5.5, 99.8% D_2O) in the presence of increasing concentrations of TEMPOP. Spectra were obtained at 100 MHz with a Varian HA-100 spectrometer at a probe temperature of 32°. The external standard (lock signal) was hexamethyldisiloxane (HMS). Each spectrum was time-averaged over 40-50 sweeps using a C1024 CAT.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10^{-3}M
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930
880
830
CPS from HMS

STEVENS INSTITUTE OF TECHNOLOGY

HOBOKEN, NEW JERSEY 07030

Department of
Chemistry and Chemical Engineering

March 17, 1969

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

ASYMMETRIC SPINNING SIDEBANDS FROM COAXIAL CELLS

Dear Dr. Shapiro:

Asymmetric spinning sidebands can be made to appear in the NMR spectrum of material contained in the annular region of a coaxial cell. These sidebands are caused by applying linear gradients in the magnetic field.

For example, when a coaxial cell containing acetonitrile in the central tube and chloroform in the annular region is rotated at moderate velocity in a homogeneous field a symmetric pattern of sidebands appears. These bands are spaced at multiples of twice the spinning frequency (see top spectrum). However, when a linear gradient is placed along the Z-axis (the direction of the applied field) intermediate sidebands appear to the right of the main chloroform signal (see middle spectrum). When the gradient is directed along the X-axis (perpendicular to the applied field) the opposite effect results; i.e. intermediate sidebands appear on the left (see bottom spectrum). The linear gradients are produced by simply adjusting the X and Z-gradient dials of a Varian A60A Spectrometer.

This phenomena is theoretically predictable. Molecules in the annular region of such a cell system experience an oscillatory field H_ℓ which can be expressed as

$$H_\ell = \langle H_a \rangle + \Delta H_a \cos 2(\omega_s t + \phi) + H_g \cos (\omega_s t + \phi_1)$$

where $\langle H_a \rangle$ is the average field, ΔH_a is the field gradient produced by the coaxial cell system, H_g is the amplitude of the applied linear gradient, ω_s is the velocity of rotation, t is time, and ϕ and ϕ_1 are the phase angles which relate the modulating fields of the coaxial cell and linear gradients to the R.F. field. Putting this expression through the field modulation theory of Williams and Gutowsky [J. Chem. Phys. 25, 1288 (1956)] equations predicting the observed phenomena are easily obtained. Details of this work will appear in the Journal of Magnetic Resonance.

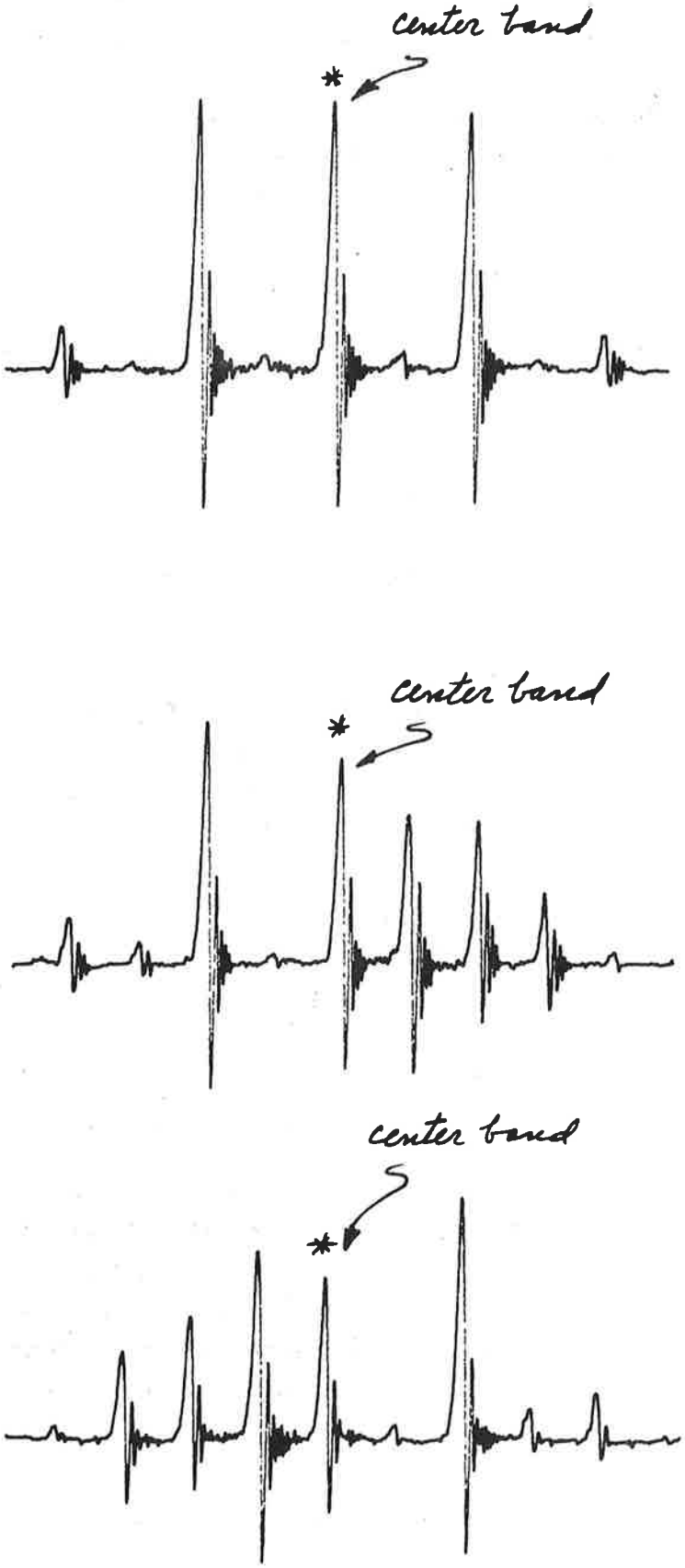
Spinning sidebands produced from a coaxial system offer an excellent method for studying the homogeneity of the field since the presence of intermediate sidebands is indicative of the degree of inhomogeneity.

Sincerely,

Edmund R. Malinowski

Edmund R. Malinowski
Associate Professor of Chemistry

ERM:sml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Prof.B.L.Shapiro
Department of Chemistry
Texas A & M University
College Station
Texas 77843
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Title: Non-equivalence of methylene groups in acetals

Dear Dr.Shapiro:

Although the subject of non-equivalent methylene groups has been treated extensively I would like again to mention a case which we came across in the NMR-spectra of a variety of aliphatic acetals. ABX_2 and ABX_3 type patterns are observed in all spectra of symmetrical acetals of the type

$$R_1 - CH(O - CH_2 - R_2)(O - CH_2 - R'_2)$$

with $R_1 = - CH_3, - C_2H_5, - nC_5H_{11}$

$R_2 = R'_2 = - CH_3, - C_2H_5, - nC_4H_9, - iC_4H_9, - nC_5H_{11}$

as well as in a number of unsymmetrical acetals. Geminal and vicinal coupling constants as well as $\nu_o \delta$-values between H_A and H_B in the methylene-groups are practically independent of solvent and temperature in the range from 30° to 180°C, e.g. in the case of caproaldehyde-diethylacetal. The following geminal and vicinal coupling constants and $\nu_o \delta_{AB}$ values at 100 MHz were observed ($CDCl_3$-solutions)

Vorstand: Kurt Hansen, Vorsitzender; Wilhelm Brenschede, Detlef Delfs, Hanns Gierlichs, Herbert Grünewald, Hans Holtschmidt, Hermann Holzrichter, Wilhelm Meyerheim, Walter Salzer, Friedrich Silcher, Herbert Weber, Walt Wilhelm, Heinz Wollthan

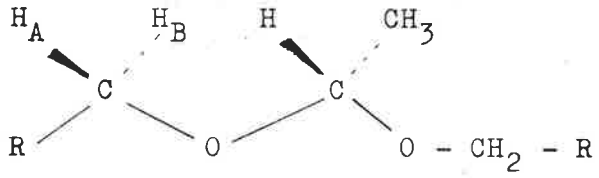
Vorsitzender des Aufsichtsrats: Otto Bayer
Sitz der Gesellschaft: Leverkusen

Art.-Nr. 9864 135 - 11915/8

and could be verified by spin-decoupling:

	J_{AB}	$J_{AX} = J_{BX}$	$\nu_o \, \delta_{AB}$ [Hz]
Acetaldehyde-diethylacetal	(-) 9,4	7,0	15,0
Acetaldehyde-di-n-pentylacetal	(-) 9,0	6,3	16,6
Propionaldehyde-diethylacetal	(-) 9,5	6,8	14,2
Caproaldehyde-diethylacetal	(-) 9,5	6,7	13,8

Although an asymmetric center is lacking in these compounds the effective asymmetry of the grouping



H, CH_3, OCH_2R

is sufficient to cause a doubling of the signals.

A literature search showed that Martin and Martin [1] mention the case of diethylacetal in their recent review; however we thought some of your readers may nevertheless find the observation of interest. Would you, please, credit this contribution to the account of Dr.D.Wendisch.

Sincerely yours

V. Kaiser

---

[1] M.L.Martin and G.J.Martin, Bull.Soc.chim.France, 1966, 2117.

MONASH UNIVERSITY

P.O. BOX 92,
CLAYTON. VICTORIA. AUSTRALIA, 3168

TELEGRAMS:
MONASHUNI. MELBOURNE

DEPARTMENT OF CHEMISTRY

TELEPHONE:
544 0611

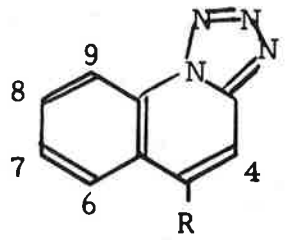
19 March, 1969

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

Suggested Title: "Long-range couplings in tetrazolo[a] quinoline and related molecules"
OR "Strenua nos exercet inertia"

Dear Barry:

We have of late, in our usual Micawberish fashion, been using our HA 100 to look at tetrazolo[a] quinoline (I) and the 5-Methyl derivative (II) in case anything interesting turned up. It did, in the form of a multitude of long-range couplings linking the protons of the two six-membered rings.



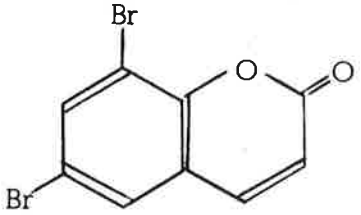
(I) R=H
(II) R=Me

(I) was investigated first, and the expected "zig-zag" cross-ring coupling J_{59} (0.6 - 0.7 Hz) and the peri J_{56} (0.3 Hz) were immediately evident. However, the appearance of the lines assignable to proton 6 suggested that coupling with H_4 was also of an appreciable magnitude, although this could not be proved at this stage. The two "triplets" of H_7 and H_8 occurred adjacently at the high-field end of the spectrum, with the

lines of H_8 considerably broader than those of H_7. It was found that irradiation of H_4 sharpened up the lines of H_8 markedly. Hence a coupling J_{48} (through seven bonds) of about 0.3 Hz seemed indicated.

The 5-Methyl compound (II) was then called in to improve these couplings beyond doubt. With irradiation of the methyl protons, the couplings J_{46} and J_{48} revealed themselves beautifully (instrumental resolution being about 0.25 Hz with the couplings 0.30 - 0.35 Hz). Concurrent irradiation of H_4 cleanly removed both couplings.

Round about the same time this work was being done, the paper by Jarvis and Moritz[1] on long-range coupling in substituted coumarins appeared. Analogous couplings, with similar magnitudes were reported for these molecules, e.g. 6, 8 dibromocoumarin, (III) which have a basically very similar structure to (I).



(III)

Further work on these long-range couplings in (I) and related molecules, including determinations of some relative signs, is in progress.

1 M.W. Jarvis and A.G. Moritz, Aust. J. Chem., 21, 2445 (1968)

Best wishes,

Mike

M.L. Heffernan

Geoff

G. M. Irvine.

UNIVERSITY OF CALIFORNIA, LOS ANGELES

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SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY
LOS ANGELES, CALIFORNIA 90024

March 25, 1969

Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77834

Dear Professor Shapiro:

It is my sincere desire that this contribution would serve to initiate my subscription to the TAMU NMR Newsletter. Failing in that, I assure you that in wadded form it will serve amply to clean the outside of spectrometer cooling coils.

Calculating and Plotting Simple NMR Spectra Using a Table-top Computer

The advent of table-top computers (Olivetti-Underwood, Hewlett-Packard, Hwang) has brought some of the advantages of large high speed computers within the range of the most modest budget. Although the Olivetti-Underwood Programma 101 has the most limited capability of these, even it is able to perform some tasks occasionally useful to the NMR spectroscopist. An unusual application is the plotting of simple NMR spectra on the paper tape output, discussed here. An example in the form of a program to calculate and plot theoretical two-spin spectra is given on the following page, using a pseudo-digital-to-analog conversion to produce the plot. Relative intensities may be plotted to within ±2.5% with no restriction on relative peak position accuracy. Use of this technique on table-top computers of greater storage capacity should make possible the calculating and plotting of more complex theoretical static spectra, and even spectra of simple exchanging systems.

The calculation of the two-spin spectrum from $\Delta\nu$ and J, together with presentation of values for the plotting routine, is contained on half of one magnetic card, the plotting routine on the other. Peaks separated by an amount less than the grid of the frequency axis are printed as one peak with a correct relative intensity.

The portability, speedy processing, and simple operation of the table-top computer, together with its turn-around time equal to execution time, enable this application to be an especially useful instructional tool.

Sincerely,

Wm. D. Larson

Wm. D. Larson

101 olivetti underwood programma 101 olivetti underwood programma 101 olivetti underwood programma 101 olivetti underwood programma 10

CALCULATION INSTRUCTIONS

AV	B/↓
S	B-
B/↑	D/-
S	C/V
B↑	C↓
/◇	A/↑
S	D/↑
D/↑	÷
/◇	C↕
/◇	B/V
B/↓	C↓
A×	A/↑
B/↕	R/S
B↓	D↑
A×	×
B/+	-
AV	A↕
B/↕	C/↕
A*	B/↓
A◇	B-
B+	D/÷
A◇	/↕
A*	-
B/+	B/↕
A◇	B↓
B+	D/÷
A◇	/↕
/◇	-
B↓	B↕
B/÷	/◇
C/↕	/◇
B/↓	A/↑
A÷	D/↓
C/-	↓
A◇	V
C↕	
B/↓	
A÷	
C/+	
A◇	
A◇	
C/↕	
C↓	
A◇	
C/÷	
C↕	

PLOTTING INSTRUCTIONS

AV	E↓
/◇	A◇
A◇	A/↑
A◇	D/↓
A◇	↓
A◇	A◇
D↓	A◇
E↕	A◇
AY	A◇
C/↓	S
C/Y	A/W
E↓	↓
A◇	A◇
B↓	W
C↕	A/Y
AW	C↓
C↓	B/↕
C/W	C↕
AZ	W
B/↓	B/V
/Y	D↓
C↓	A◇
B↕	Z
C↕	
W	
B/Y	
A/↑	
D/↓	
-	
C/↕	
A/↑	
R/S	
D↓	
E↓	
÷	
E↕	
Y	
B/W	
A/↑	
D/↓	
-	
C↕	
C↓	
/W	
B↓	
C/V	

With "Record Program" OFF:
11111111111111111111 D↑

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

26th March, 1969.

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

Dear Professor Shapiro,

Digiac Computer on the HA 100 - Switching 'scope signals.

In September we received a Digiac Computer from Digico Ltd., Letchworth, England for Time-Averaging on our HA 100. As this is the first Digiac to be used with an HA 100; I thought you might be interested in our experiences.

The Digiac is similar to the JEOL Computer but cheaper. As interfacing to the HA 100 is relatively simple, we have done this ourselves. We have also written our own accumulation program as the existing programs using trigger peaks etc., are unnecessarily complicated for the HA 100 in HA mode. We have been very pleased indeed with the results so far but we have not done any very long runs yet (see below). The system is easy to use and reasonably foolproof. The start of the accumulation is triggered by a magnet mounted on the pen carriage actuating a reed switch attached to a rail along the upper edge of the recorder. The length of the scan is set at the start of the accumulation and the computer controls the motion of the pen carriage via a modified Time Average switch and relay (K 901). To simplify the switching of the recorder inputs and outputs, the Recorder switch (S 1104) of V 4391 has been replaced by a 3-way, 4 pole switch to give positions 'Normal', 'Accumulate' and 'Read Out' with checking of these settings by the computer.

The computer works on a negative analogue voltage. This was converted to a positive voltage for the HA 100 by biasing which results in the baseline being the maximum value. This is not the disadvantage it seemed at first as on 'normalising' the maximum value for read-out, the spectrum is always drawn about the same size - the effect of accumulation is to reduce the height of the noise. Of course, the read-out spectrum can be expanded if desired. The program also allows non-destructive integration (with reset) and punched tape output. A disadvantage is the lack of a 'scope to monitor progress but the procedure of stopping the accumulation and reading-out on the recorder does not seem too laborious.

The computer includes control lines (i.e. relays controlled by the computer) and sense lines of which only a few have been used up in

the basic accumulation process. We have just used two more control lines to solve (we hope) our difficulty of loss of homogeneity on long runs. The field is liable to deteriorate after a while and the Auto-Shim has a nasty habit of 'unlocking'. The result is that good accumulations are spoilt by addition of low resolution or even unlocked spectra. To prevent this, before each scan the analogue input is switched by a control line from the normal 'spectrum' output to a simple crystal diode rectifier circuit connected to the vertical (Y) axis of the oscilloscope (Cf TAMU NMR Newsletter 120-50). If the lock signal has dropped below a value preset in the program, the accumulation is stopped; otherwise the analogue input is switched back to the spectrum and another scan added. This facility may be switched out if not required.

I will be very pleased to send details of these modifications and the programs to anyone who is interested.

Like many HA 100 owners, we have interfered with the switching to the 'scope Y axis. We have intercepted the lead from J 1105, V 4391 to the scope to allow observation on the 'scope and a frequency counter of either of two external audio oscillators, the HR sideband modulation or the internal Manual Oscillator modulation as alternatives to the normal function defined by switches S 1306 of V 4354A and S 1101 of V 4391. One use is to measure the sideband frequencies whilst drawing out HR spectra. Since our 'decoupling' modulation is applied via a 100:1 transformer, we can monitor the frequency even at low ν_2 power (i.e. 'tickling') without amplification of the signal to the counter. The latter has been very useful recently in the determination of J_{PP} in cis $(PMe_3)_2PtX_2$, (X = Cl, Br and I). The first 'outer' lines of these $X_9AA'X'_9$ spectra (R.K. Harris, Canad.J.Chem. 1964, 42, 2275) are obscurred by the ^{195}Pt satellites of the rest of the spectrum but 'tickling' of their position causes splitting and collapse of the clearly visible first 'inner' lines allowing direct evaluation of J_{PP}. I get values 18·9, 16·2 and 14·0 ±0·2 Hz respectively. Incidentally, our recently acquired Levell TG 66A Decade Oscillator is ideal for this work as well as providing external manual oscillator frequencies for 'wide lock'.

Yours sincerely,

R J Goodfellow

R.J. Goodfellow.

Organisch-Chemisches Institut
der
Technischen Universität Berlin
Direktor: Prof. Dr. F. Bohlmann

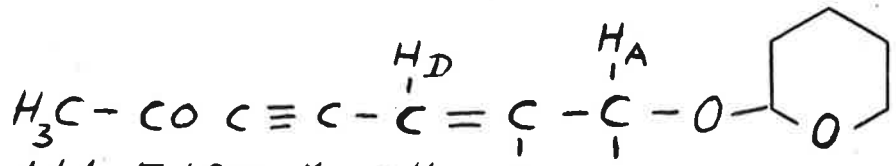
1 Berlin 12, den März 21, 1969
Straße des 17. Juni Nr. 115 (Chemiegeb.)
Fernruf: ~~52 51 81, App. 252~~ 314 2252

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

Unusual large chemical shift differences of methylene protons-influence of methylgroups on allylic coupling.

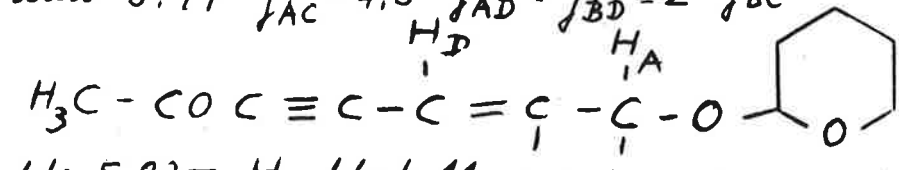
Dear Dr. Shapiro

We just have some date which might be of interest for some of your readers. The NMR-spectrum (HA 100, CCl_4) of 1 is surprisingly clear in the methylene region resulting from an unusual large chemical shift difference of H_A and H_B. The same feature can be seen in the spectrum of 2, but beside this there is a large difference in the allylic coupling constants of 1 and 2. The same results we got with many similary compounds.



1

H_A ddd 5.69 τ J_{AB} = 16 H_B ddd 5.99 J_{AC} = 4.3 J_{AD} = J_{BD} = 2 J_{BC} = 4.8



2

H_A ddq 5.82 τ H_B ddq 6.11 J_{AB} = 16 J_{AC} = J_{AD} = 0.8 J_{BC} = J_{BD} = 0.7

Yours sincerely

F. Bohlmann

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
CONSUMER PROTECTION AND ENVIRONMENTAL HEALTH SERVICE
WASHINGTON, D.C. 20204

FOOD AND DRUG ADMINISTRATION

March 20, 1969

Handling of mg Samples

We have been handling milligram samples in a capillary with a technique that was developed mainly with GLC collection in mind; however, this technique can also be applied when the sample capillary is filled by a syringe or capillary action. The technique compares favorably with similar ones reported (1-4), and combines the following advantages:

1. There is greater flexibility as to the amount of sample collected by GLC.

2. No transfer of the sample from the GLC collection tube to the NMR tube is necessary.

3. Filling and positioning of the collection tube in the probe is less cumbersome than with other microcells.

4. All components are commercially available at low cost and can be assembled quickly.

The assembly is shown in Figure 1 and differs from the one reported by Flath et al. (1), in that, once the sample holder has been adapted, the capillary tube containing the collected (or added) sample can easily be inserted from the top. (Some of the newer holders do not need to be adapted).

GLC Collection Equipment and Assembly. Stainless steel tubing, 1/4 inch x 1 inch and 1/8 inch x 1-1/2 inches; Swagelok reducer, 1/4 inch to 1/8 inch, stainless steel; Swagelok 1/4 inch nut with ferrules, stainless steel; rod and holder from NMR microcell assembly (1) (Kontes Glass Co., Vineland, N. J.); precision NMR tubes, polished. Collection tubes as follows: Drummond "Microcaps," disposable, 100 µl capillary pipettes and long-stemmed, 7-3/8 inch disposable pipettes (NMR Specialties, New Kensington, Pa.) Cut the stainless steel tubing with a standard tube cutter and ream the constrictions left at the ends of the tubing to a diameter which will just accommodate the capillary tube. This will permit efficient collection of the sample.

Assemble the apparatus and connect to the exit port of a gas chromatograph, as shown in Figure 2.

Collection of High Boiling Fractions. Insert the capillary as shown in Figure 2 just before the effluent arrives at the exhaust port. It may

be necessary to conduct a test run to determine the proper position of the capillary that will permit condensation of the sample in the middle portion of the capillary.

Collection of Low Boiling Fractions. Insert the capillary part-way in the assembly, and cool the middle portion of the capillary tube, e.g., with a piece of dry ice, just prior to sample elution in order to condense the sample in the desired region.

Collection Samples in Excess of 5 mg. Replace the capillary tube with a long-stemmed pipette, and follow the same procedures outlined above for the collection of low and high boiling fractions.

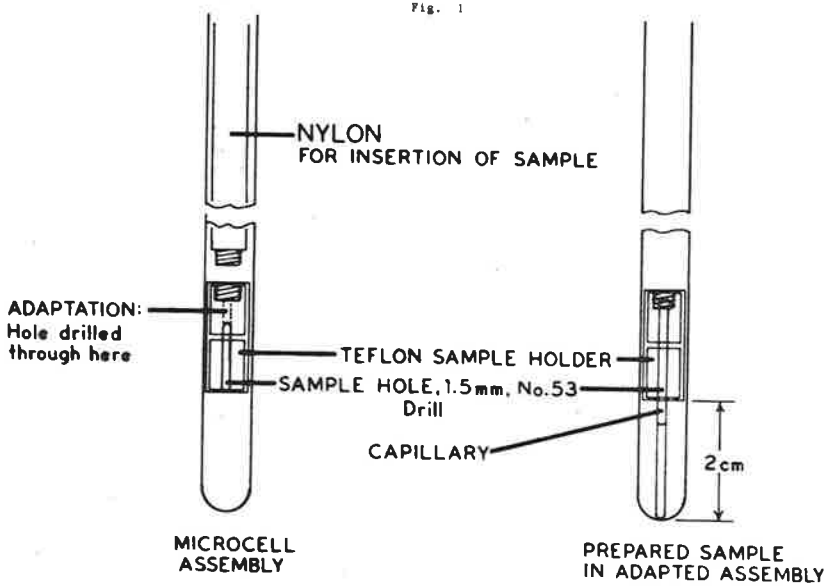
NMR Analysis. Upon collection of the desired fraction, remove the capillary and seal the cold end uniformly. By means of a microliter syringe, introduce 10-20 µl of a solvent spiked with TMS, midway down into the capillary tube, while slowly withdrawing the syringe. Tap the capillary so that the solvent washes the sample down into the tube. A solution height between 1 and 3 cm is required to obtain suitable NMR spectra. Seal off the remaining portion of the tube so that the final length is 5-6 cm, taking care not to degrade the contents of the capillary tube in the process. Drill the Teflon holder all the way through with a #53 bit and insert the capillary (from the top if the upper seal is of a larger diameter than the capillary tube). Screw the nylon rod part-way into the holder and insert the assembly into a NMR tube. Adjust as shown in Figure 1, making sure that the bottom of the capillary tube touches the bottom of the NMR tube. This centers the tube for spinning.

The present method provides an inexpensive and adaptable technique for recording NMR spectra of milligram quantities without time averaging and of smaller amounts with time averaging. Positioning of the assembly is easier than with bulbs (1), because of the increased length and the wobble problem of the free floating capillary (2, 4) is virtually nonexistent because the tube is held at the top and bottom. More rf power and higher gain settings are required to record spectra because of the small filling factor. See Figure 3A, B, and C for a comparison of spectra.

1. R. A. Flath, N. Henderson, R. E. Lundin, and R. Teranishi, Appl. Spectry. 21, 183 (1967)
2. C. S. Slaymaker, ibid., 21, 42 (1967)
3. B. Milazzo, L. Petrakis, and P. M. Brown, ibid., 22, 574 (1968)
4. L. R. Provost and R. V. Jardine, J. Chem. Ed., 45, 675 (1968)

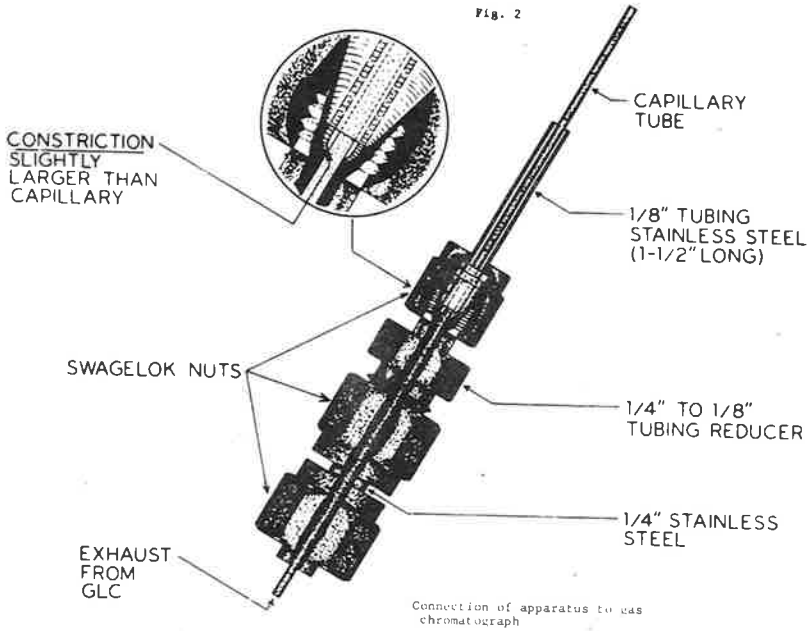
D. Mastbrook
D. Mastbrook
E. Ragelis
E. Ragelis

Fig. 1



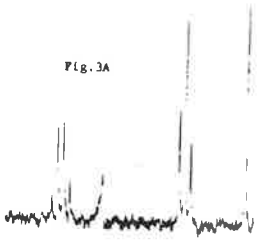
Microcell assembly for NMR analysis of milligram samples.

Fig. 2



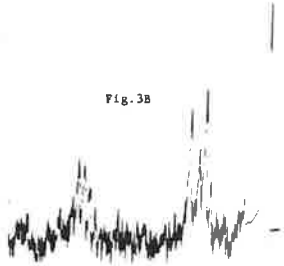
Connection of apparatus to gas chromatograph

Fig. 3A



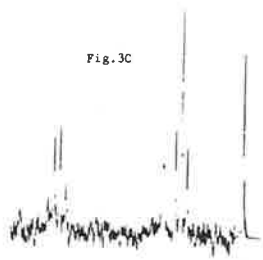
Capillary tube containing 1 ul of ethanol in $CDCl_3$ and TMS (present work)

Fig. 3B



Microcell (1) containing 1 ul of ethanol in $CDCl_3$ and TMS. This is the best spectrum obtained from a lot of five bulbs (Kontes Glass Co.)

Fig. 3C



Semimicrotube (NMR Specialties) containing 1 ul of ethanol in $CDCl_3$ and TMS

These spectra were recorded on a Varian A-60 spectrometer

127-44

INSTITUTE OF CHEMICAL PROCESS FUNDAMENTALS
CZECHOSLOVAK ACADEMY OF SCIENCE
PRAHA-SUCHDOL 2

March 21st, 1969
390/Schr

Professor B. L. S h a p i r o
Department of Chemistry
Texas A & M University
College Station,
T e x a s 77843

re: Additivity of Chemical Shifts and U.V. Spectra of Ethylenes

Dear Professor Shapiro:

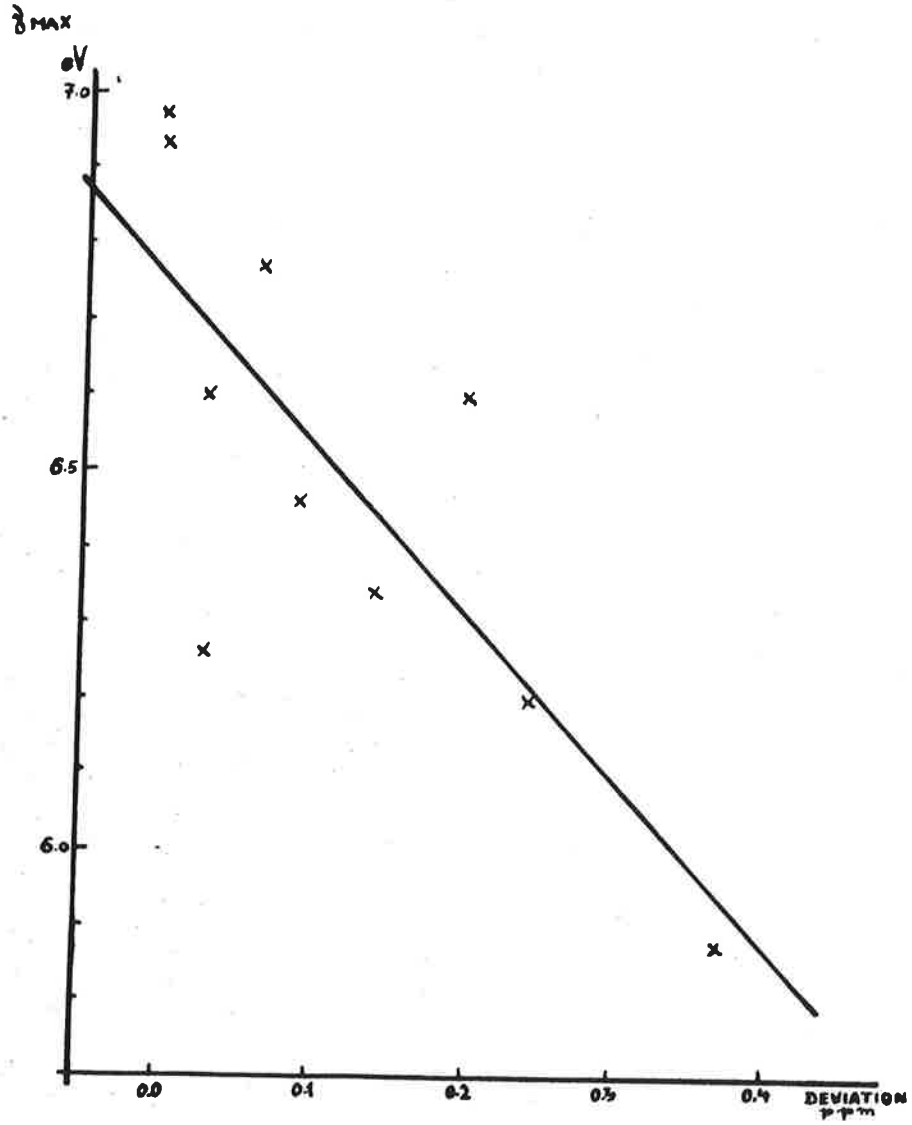
In their work Vladimiroff and Malinowski /J.Chem.Phys. 46, 1830 (1967)/ have shown that "from ultraviolet spectra it is relatively easy to decide when deviations from additivity will not occur, but it is not easy to decide when deviations will occur". It might interest the readers to learn that a correlation exists between the deviations and the U.V. absorption maxima of some ethylenes.

The chemical shifts of ethylenic protons in trimethylsilyl substituted ethylenes were shown to be direct additive (the pairwise additivity could not be tested) /Coll.Czech.Chem.Commun. 31, 1411 (1966) and ibid 33, 4419 (1968)/. The same holds for ethylenes substituted by tert.butyl or tert.butyl and trimethylsilyl groups. The N.M.R. and U.V. spectra of these compounds were published recently by Bock and Seidl /J.Organometal. Chem. 13, 87 (1968)/. From the attached drawing it is clear that a correlation exists between the deviations from additivity and the position of the U.V. absorption maxima for these series of compounds. Perhaps other curve

than a line would fit the points better. The line drawn in the figure corresponds to the correlation coefficient r = 0.793 which, in turn, indicates that the correlation is significant even at 1 % significance level.

Sincerely yours,

Jan Schraml



27-46

CHEMISCHE LABORATORIA
DER RIJKS-UNIVERSITEIT
Afd.: Prof. Dr. L.J.Oosterhoff
Wassenaarseweg
Leiden
Telefoon 4 83 33
P.O. Box 75

LEIDEN, March 24th 19 69

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

Dear Professor Shapiro,

Thank you for your reminder. Please credit this contribution to the subscribtion of Mr. Sekuur,

Some time ago we modified the computer programs NMRIT and NMREN (version of R.C. Ferguson, D.W. Marquardt and R.M. Stanley). for the IBM 360/50 computer. In agreement with earlier reports a drastic reorganisation of common blocks was needed. Moreover we made a plotroutine for the CalComp plotter.

However, the more elegant approach of LAOCOON forced us to occupy us also with this program. December 1966 we received a listing of the program LAME. (LAOCOON with the Magnetic Equivalence; C.S. Haigh. TAMU NMR 121,54). We found that the only difficulty of this program for using it on the IBM 360/50 (FORTRAN G level) was, that it is not allowed to use subscribted parameters in a DO-loop. (f.i. a statement like DO 21 JJM = 1,IMROW (JJ) had to be replaced by

```
L = IMROW (JJ)
DO 21 JJM = 1,L)
```

To make it possible to compute and plot the spectra in the same run. we added a subroutine SPECT, based upon the analogue option in NMRIT.

Moreover we increased the accuracy of the Jacobi subroutine MATRIX. We thought it was useful to diagonalize in double precision. While rebuilding the subroutine to double precision, we saved a good deal of the additional required memory locations by introducing storage mode 1 for the Hamiltonian matrix (the upper triangle of the symmetric matrix is stored in a linear array). If necessary it should be possible to accumulate the eigenvectors in single precision (in our version the eigenvectors are accumulated in double precision).

Listings of our versions of LAME and NMRIT / NMREN are available upon request.

Yours sincerely,

(J.A. den Hollander)

(Drs. R. Kaptein)

Short title: Calculating NMR-spinsystems with IBM 360/50

FACULTY OF ARTS AND SCIENCES
UNIVERSITY OF PITTSBURGH
PITTSBURGH, PENNSYLVANIA 15213

DEPARTMENT OF CHEMISTRY

25 March, 1969

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

Dear Barry:

P-C-C-C-H and P-C-O-H Couplings; A Request for Computer/Spectrometer Interface Information

Your bilious pink communication arrived during a period of non-convergence, so our contribution must deal with yet another chapter in the continuing story of phosphorus-proton couplings.

We have recently examined the spectra of a number of disubstituted ethyl [XCH_2-CHY-P(O)$(OR)_2$, I] and propyl [XCH_2-CHY-CH_2-P(O)$(OR)_2$, II] phosphonates (X, Y = OH, OR, NHR, OCOR). Certain of the features of these spectra were anticipated, e.g. temperature independent ß-proton non-equivalence in I, but two features merit mention. In the spectra of II (X = Y = OH; X = OMe, Y = OCOR), coupling of phosphorus with the γ-protons was observed (J = 1.1-1.2 Hz). Previously reported four-bond P-H couplings have involved pi-bond or heteroatom transmission; coupling through three intervening sp^3 hybridized carbons appears to be unique. Secondly, a P-C-O-H coupling (J = 10.0 Hz) was observed for I, X = OEt, Y = OH. The observation of this coupling is presumably the result of the formation of a strong intramolecular hydrogen bond involving the phosphoryl group. The coupling is not, however, general for α-hydroxyalkylphosphonates. A manuscript describing the studies of I and II is available for interested parties.

In July, I am moving to the University of Toledo and will acquire new instrumentation. The most immediate problem which we face is the compatibility of a JNM-4H-100 and a DEC PDP-8/I-C system; our initial need is for spectrum accumulation. We should be eternally grateful to any reader who has dealt with this interfacing problem and would share his wisdom.

Best regards,

Clay

C. E. Griffin

127-48

DEPARTMENT OF THE AIR FORCE
AIR FORCE MATERIALS LABORATORY (AFSC)
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

REPLY TO ATTN OF: AFML/MAYH/52280

24 MAR 1969

SUBJECT: Degassing NMR Samples of Low Volatility

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

Dear Professor Shapiro:

De-aerating NMR liquid samples can be an extremely tedious and time-consuming task if freeze-pump-thaw cycling of the liquid is carried out in the standard 4 mm ID sample tube. Complete removal of the dissolved air is hindered by the unfavorably small surface area/volume ratio. Ideally, the liquid sample should be degassed elsewhere in the vacuum system where it can be manipulated and eventually returned to the NMR tube by distillation (e.g. IITNMR 100-8).

This isn't always possible, however. If the liquid has too low a vapor pressure to permit liquid nitrogen pumping then another means of transfer within the vacuum system must be used to return the degassed liquid to the NMR sample tube.

Described below is a quick and easy method of degassing liquid samples with low volatility. A few ground glass ball and socket joints and a minimal glass blowing ability are all that is needed.

The NMR tube is butt-sealed to the modified ground glass joint, A. After adding the previously measured sample to the cup, B, the joint is then attached to the vacuum manifold through the adapter, C. The sample is frozen by immersing the cup in a suitable coolant, such as liquid nitrogen, and the entire system is evacuated. Now the liquid can be efficiently degassed by freeze-pump-thaw cycling since it exposes a much greater surface area.

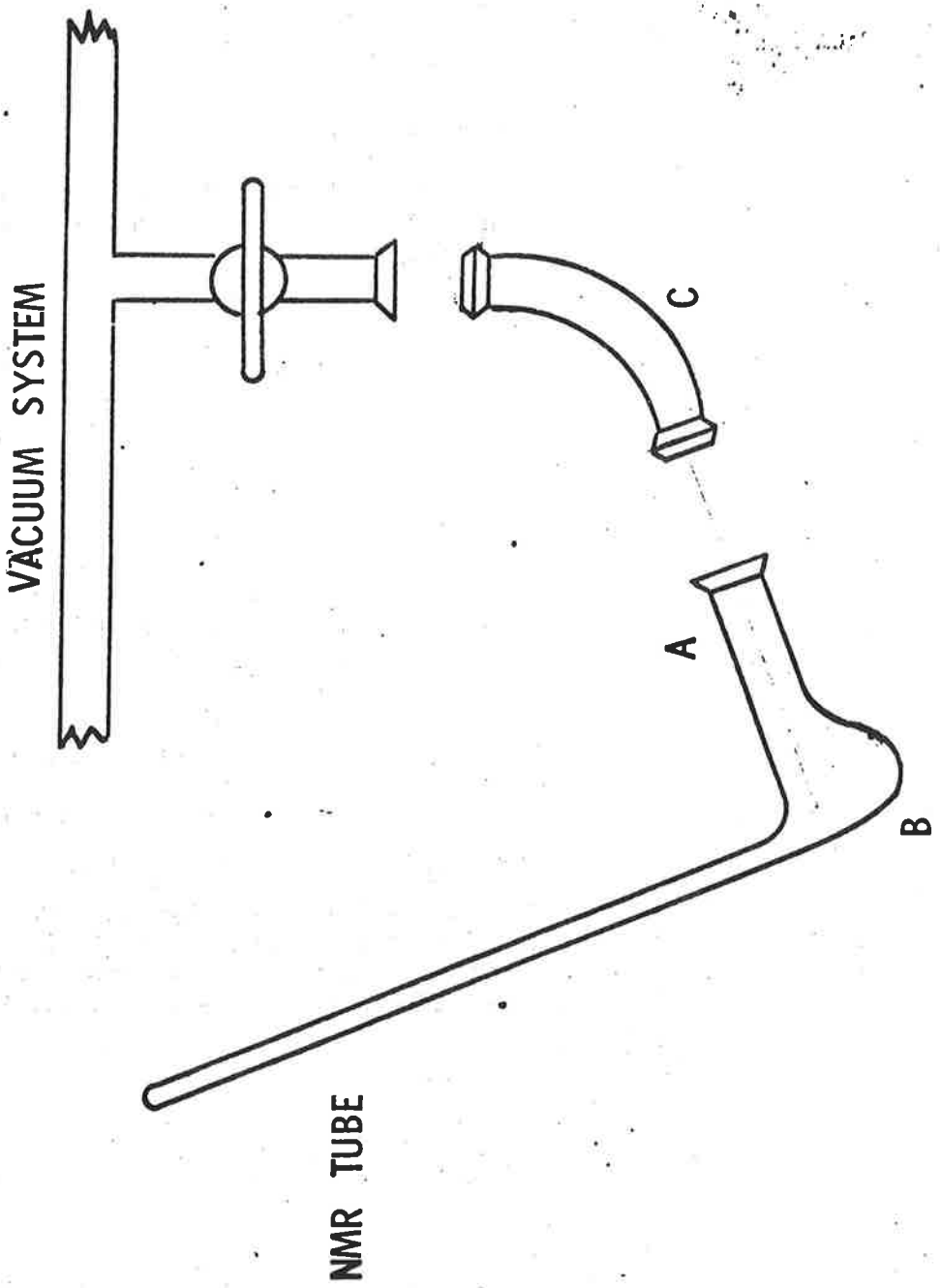
After degassing, A is rotated 180^{o} while holding C in place. With the NMR tube pointing down, the sample is transferred to the tube by gravity. There the liquid is frozen one more time for flame-sealing. During the sealing-off operation, the valve to the vacuum system should remain open and the pressure continuously

monitored. Any leak which should develop at the seal-off point will then be readily noticed.

Sincerely,

Roger E. Rondeau

ROGER E. RONDEAU
Exploratory Studies Branch
Materials Physics Division



Southern Illinois
University

CARBONDALE, ILLINOIS 62901

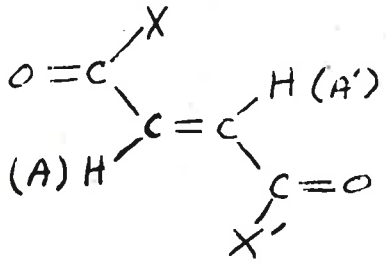
Department of Chemistry

March 27, 1969

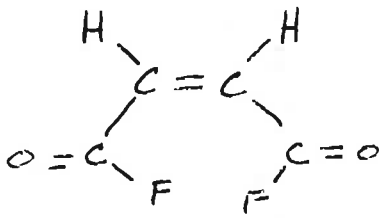
Dr. B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Dear Barry (or should I say, Howdy Aggie!):

We have been studying the vibrational and NMR spectra of several fumaryl halides (I) and maleoyl fluoride (II) in order to learn something about the stability of the possible conformers.



I



II

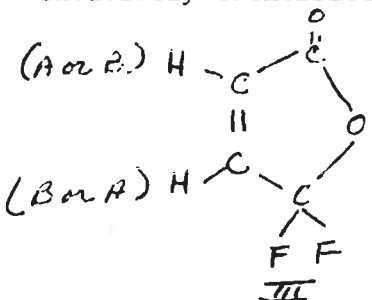
The temperature studies are incomplete but your readers may be interested in the NMR parameters. When X is F in (I) an 8 line AA'XX' NMR spectrum is obtained which can be fit with the parameters.

J_{AA} = 15.67 Hz; J_{AX} = 6.77 Hz; $J_{AX'}$ = -0.23 Hz; $J_{XX'}$ = 0.27

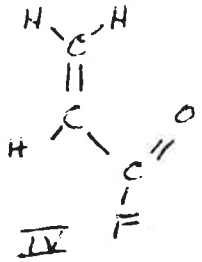
The parameters are solvent and temperature dependent and are similar to those for acrylyl fluoride[1] (CH_2CHCFO). The negative sign attributed to $J_{AX'}$ has not been unambiguously established. It was originally assigned a value of zero and not allowed to vary during the caluclations (using LAOCN3). The RMS error in this instance was 0.053 and the largest error in any line was 0.101 Hz. Allowing $J_{AX'}$ to vary reduces the RMS error to 0.019 and the largest line error to 0.026 Hz.

The equilibrium configuration in (II) is probably non-planar with either O---O, O---F or F---F in proximity to one another. Only $J_{AX} + J_{AX'} = -6.3$ Hz can be deduced from the four line room temperature spectrum. We are hoping more information can be obtained at lower temperatures or from the analysis of the ^{13}C-F and ^{13}C-H satellite spectra.

There is only one report of the preparation of (II)[2]. Under the conditions employed we believe these authors prepared fumaryl and not maleoyl fluoride. We have identified both using lower reaction temperatures. We also have tentatively identified compound (III) as one of the products.



III



IV

The parameters for (III) are as follows:

$\delta_A - \delta_B = 0.92$ ppm; $J_{AB} = 5.9$ Hz; $J_{AF} = 0.7$ Hz; $J_{BF} = 0.9$ Hz

The small vicinal HF coupling is consistent considering the small dihedral angle[3]. It is also in the range of that predicted for a postulated cis conformation of IV (~ -3.0 Hz)[1].

Sincerely,

Tom Vasileff

Tom Vasileff

David Koster

1. D. F. Koster, J. Amer. Chem. Soc., 88, 5067 (1966).
2. W. R. Hasek, W. C. Smith and V. A. Engelhardt, J. Amer. Chem. Soc., 82, 543 (19
3. K. L. Williamson, et. al., J. Amer. Chem. Soc., 90, 6717 (1968).

Suggested Title: NMR Spectra of Fumaryl and Maleoyl Fluoride.

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CORVALLIS, OREGON 97331

March 25, 1969

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

Title: "NMR Studies on Bisphenols; A model for Protein, Phenol interaction"

Dear Barry:

Hexachlorophene and other chlorinated bisphenols strongly bind to certain proteins (Arch. Biochem. Biophys. 56, 476, 1955) but the sites of attachment and the mechanism of binding for interaction are not known. Other phenols are known to interact with proteins at the free amino groups as well as at other sites to form relatively stable complexes (Biochemistry 4, 1936, 1965; Biochemistry 5, 2602, 1966). Such phenol-protein binding, therefore, may play an important role in determining the biological activity of phenolic compounds (J. Biol. Chem. 241, 169, 1966).

We have recently investigated the interaction between bisphenols (bithionol and hexachlorophene) and the amides N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA) and N-methylacetamide (NMA). Complexing of the chlorinated bisphenols with these simple amides provides a model system in which to study the molecular basis of the action of the bisphenols with polypeptides or proteins. Additional studies also have been carried out on the association of the chlorinated bisphenols with dimethylsulfoxide (DMSO) and acetone.

Proton magnetic resonance spectra of bithionol and hexachlorophene in carbon tetrachloride solution containing DMF, acetone and DMSO have now been recorded. The chlorinated bisphenols strongly interact with the carbonyl-containing solvents as shown by downfield shifts in the resonance peak for the aromatic, methylene and phenolic protons of bithionol and hexachlorophene in the presence of different solvents. A marked low field shift of the phenolic proton in the presence of the

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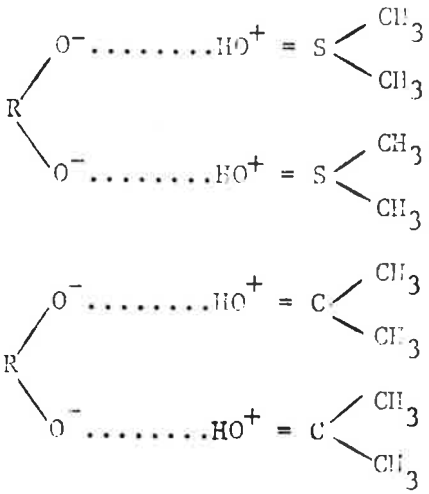
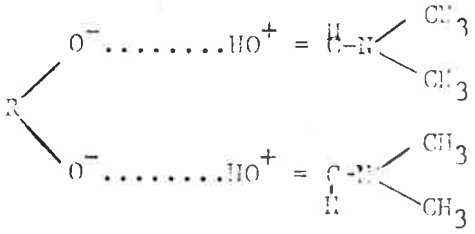
carbonyl type solvents indicates that strong hydrogen bond formation occurs between the phenolic group of the bisphenols and the oxygen atom in DMF, acetone and DMSO (Can. J. Chem. 41, 148, 1963). The chemical shift of the various proton resonances peaks showed a strong solvent and bisphenol concentration dependence with a maximum displacement of the phenolic protons occurring at an approximately 2 to 1 molar ratio of solvent to bisphenol. The structure of the associated ion pair complex (Biochemistry 6, 150, 1967) then could be represented as





The phenolic proton displacement remained essentially unchanged by further increases in the concentration of acetone. As the concentrations of DMSO and DMF was increased, however, to yield molar ratios of solvent and bisphenol greater than 2 to 1, the downfield shift of the phenolic proton resonance was reduced. These latter results can be explained on the basis of a complete dissociation of the hydrogen bonded ion pair complex to form the following type of protoanted solvent species (Can. J. Chem. 39, 1711, 1961)

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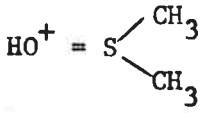

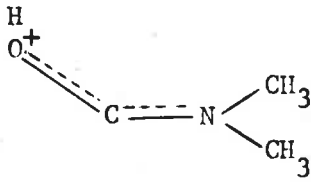

The high dielectric constant of DMSO and DMF supports the formation of a cationic solvent species. Solvent-solute hydrogen bonding then is deminished resulting in a reduced chemical shift of the phenolic protons. Acetone, which has a much lower dielectric constant than DMSO and DMF, gives no evidence for formation of similar protonated cations. Other intramolecular hydrogen bond species are undoubtedly also present in the bisphenol-carbonyl solvent mixtures. The exchange of phenolic protons between all of the various species present is so rapid that only a single average resonance peak is observed. The chlorinated bisphenols are, thus, apparently able to protonate carbonyl solvents such as DMF and DMSO in a manner analogous to that observed with trifluoroacetic acid (J. Am. Chem. Soc. 86, 4774, 1964), a compound known to produce helix-random coil transformations in polypeptides. The interaction between simple amide solvents and bithionol or hexachlorophene is being studied as a model of the more complex interactions which occur between chlorinated bisphenols and proteins.

Sincerely yours,

Riz Haque

R. Haque

D R Buhler

D. R. Buhler

:sb

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