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Newsletter

No. 149
FEBRUARY, 1971

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Deadline Dates: No. 150: 1 March 1971 No. 151: 5 April 1971

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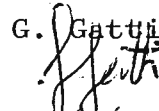
Prof. B.L. Shapiro
 TAMU NMR Newsletter
 Department of Chemistry
 Texas A&M University
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Dear Prof. Shapiro,
 Thank you for your reminder.

CONFORMATION OF POLYETHYLENE IN SOLUTION

In connection with studies on conformation of macromolecules we have recently examined at 165°C the PMR spectrum of a copolymer obtained from $\text{CD}_2=\text{CD}_2$ (in large excess) and $^{13}\text{CH}_2=\text{CH}_2$. We have observed under deuterium decoupling the ^{13}C satellites of the CH_2-CH_2 fragment. The pattern is that of a typical AA'BB' subspectrum with $J_A \neq J_B$. From the values of the vicinal coupling constants $J=6.5$ Hz and $J'=8.5$ Hz we have calculated an energy difference $E_{\text{gauche}} - E_{\text{trans}} = 0.7 \pm 0.1$ Kcal/mole following a method recently described*.

Sincerely Yours,

G. Gatti


* R.J. Abraham, G. Gatti J. Chem. Soc. B 962 (1969)

Doz. Dr. H. Dürr

Institut für organische Chemie

der Universität des Saarlandes

Doz. Dr. W. Tochtermann

Institut f. org. Chemie

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Telefon: 302-2209..

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Dr. B. L. Shapiro

Dept. of Chemistry

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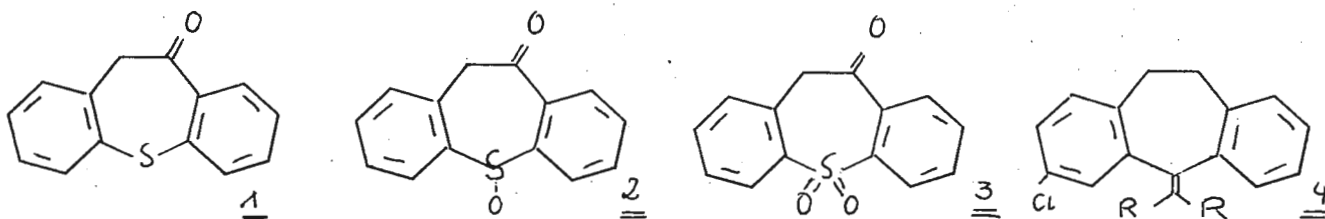
College Station/Texas 77843

U S A

Sehr geehrter Dr. Shapiro:

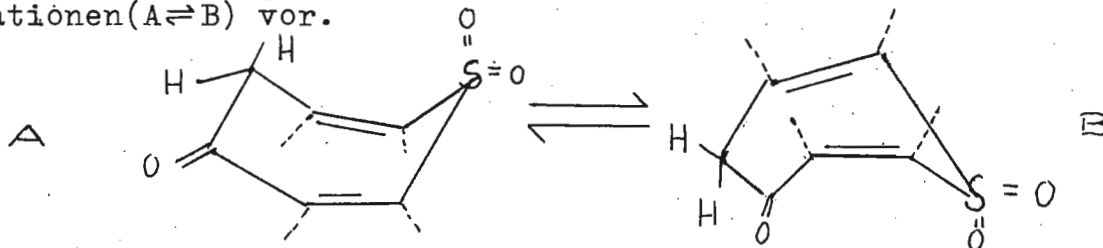
Energie-Barriere in einem 7-Ring-Heterocyclus

Vor einiger Zeit¹⁾ beschrieben wir die NMR-spektroskopische Untersuchung der Ringinversion des Thiepinons(1) und Sulfinylepinons(2).



In dieser Zuschrift soll die NMR-spektroskopische Studie der Ringinversion des Sulfonylepinons(3) behandelt werden.

Bekanntlich liegen 10,11-Dihydro-dibenzol[b,f]thiepine¹⁾ wie auch die homologen Azepine²⁾ in Boot- bzw. verdrillten Bootkonformationen (A \rightleftharpoons B) vor.



Beim schnellen Umklappen des Hetero-7-Ringes sollten die beiden geminalen Methylen-Protonen in 11-Stellung ein Singulett ergeben. Bei genügend tiefer Temperatur sollte die Geschwindigkeit der Ringinversion so verlangsamt werden, daß axiales und äquatoriales Proton getrennt beobachtbar sein sollten. Man würde ein AB-Spektrum erwarten. Dies ist tatsächlich bei den Thiepin-Derivaten 1¹⁾ und 2²⁾ der Fall. Auch das Sulfonylepinon 3 zeigt nun oberhalb -44° (in CDCl_3

(/CS₂= 1:2) ein Singulett. Bei -44°C beginnt das Signal aufzuspalten und man erhält bei -62°C ein AB-Spektrum mit den folgenden Parametern:

<u>3</u>	$\tilde{\tau}$	$\frac{\tilde{\tau}_A}{\tilde{\tau}_B}$	J _{AB}	$\Delta\nu_{AB}$	T _c	k _c	ΔG_c^\ddagger
	[ppm]	[ppm]	[Hz]	[Hz]	[°K]	[sec ⁻¹]	[kcal/Mol]
CDCl ₃ :CS ₂ =1:2	5.20	4.50 5.88	17.5	83	229	218.5	10.70

Diese Werte wurden mit den bekannten Gleichungen erhalten, wobei

$$k_c = \frac{\tilde{\pi}}{\sqrt{2}} \sqrt{\Delta\nu^2 + 6 J_{AB}^2} \quad (\text{sec}^{-1}) \quad \text{und} \quad (1)$$

$$\Delta G_c^\ddagger = RT_c \ln \frac{k_b \cdot T_c \sqrt{2}}{h \pi \sqrt{\Delta\nu^2 + 6 J_{AB}^2}} \quad (\text{kcal/Mol}) \quad (2)$$

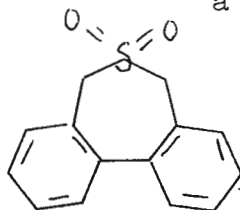
ist.

Um nun die thermodynamischen Größen von E_a, ΔS^\ddagger und ΔG^\ddagger zu erhalten, wurde eine Auswertung nach der "Freiburger"-Methode⁴⁾ vorgenommen. Diese Methode ist nach neueren Untersuchungen³⁾ einer "line shape-analysis" weitgehend ebenbürtig. Für den AB-Fall erlaubt diese Methode eine exakte Auswertung oberhalb von T_c (=Koaleszenztemperatur); unterhalb T_c kompliziert die Spin-Spin-Kopplung eine genaue Analyse beträchtlich. Die Anwendung der "Freiburger"-Methode ergab sich für das Dibenzo[b.f.] sulfonyl-epin-10(11H)-on (3) folgende Parameter:

T	k	
[°K]	[sec ⁻¹]	
256	20.75 · 10 ⁻²	E _a = 10.4 _g ± 0.3 kcal/Mol
246	9.25 · 10 ⁻²	
236.5	3.19 · 10 ⁻²	$\Delta G_{-40}^\ddagger = 10.88 \pm 0.02$ kcal/Mol
229	2.18 · 10 ⁻²	$\Delta H_{-40}^\ddagger = 11.6 \pm 0.02$ kcal/Mol
		$\Delta S_{-40}^\ddagger = -3.4 \pm 1.2$ e.u.

Der E_a-Wert von 10.4 kcal/Mol ist wesentlich kleiner als der in dem ähnlich gebauten Dibenzo[a.d.]cycloheptadien(4) (E_a = 20.8 kcal/Mol).

Das verwandte S.S-Dioxid des 5.7-Dihydro-dibenzo[c.e.]thiepins(5) weist eine E_a = 18.2 kcal/Mol auf⁶⁾. Das bedeutet u.E., daß die



51

Carbonylgruppe nicht wesentlich zur Versteifung des Hetero-7-Ringes beiträgt, sondern daß die Energiebarriere vorwiegend von dem Dibenzo-cycloheptadien-Teil bestimmt wird. Die SO₂-Gruppierung erschwert die Ringinversion des Sulfonyl-epinons 3 im Vergleich zum

Thiepin 1 in bekannter Weise³⁾.

Mit freundlichen Grüßen

Ihre



(H. Dürr)



(H. Kober)



(W. Tochtermann)

Literatur

- 1) H. Dürr, Z.f.Naturforsch. 22b, 786 (1967).
- 2) K. Ackermann, J. Chapuis, D.E. Horning, G. Lacasse, J.M. Muchowski, Can.J.Chem. 47, 4327 (1969).
- 3) W. Tochtermann, Fortschr.chem.Forsch. 15, 378 (1970), s. dort weitere Literatur.
- 4) H.G. Schmid, H. Friebolin, S. Kabuß und R. Mecke, Spectrochim. Acta 22, 623 (1966).
- 5) A. Ebnöther, E. Jucker und A. Stoll, Helv.Chim.Acta 48, 1237 (1965).
- 6) J.O. Sutherland and M.V. Ramsay, Tetrahedron (London) 21, 3401 (1965).

Princeton University DEPARTMENT OF CHEMISTRY
PRINCETON, NEW JERSEY 08540

January 6, 1971

Dr. B. L. Shapiro
Department of Chemistry
Texas A and M University
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SAMPLE TUBES FOR FROZEN SOLUTIONS

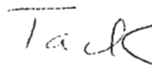
Dear Barry,

For those uncounted millions of your readers who are eager to begin their studies of frozen aqueous solutions but have been inhibited by our references to cracking sample tubes and (on rare occasions) fractured inserts (1), I have happy news.

The solution to these troubles presented itself at lunch recently at the local delicatessen. I'm pleased to report that the 6" polypropylene drinking straws made by Union Carbide (appropriately named "Glad" straws) are, as it were, expressly designed for our purposes. They are thin walled (.006"), uncrackable and fit neatly into the Wilmad 505 tubes. They are also extremely inexpensive - the commercial price being about a dollar per 1,000.

We have used 5 minute epoxy to seal the end. Such a seal will take many freeze-thaw cycles but may develop leaks after much use. Heat sealing is possible but more tedious.

Best wishes,



I. D. Kuntz
Department of Chemistry

IDK:ME

- (1) *Science* 163, 1329 (1969)
and papers in press in JACS

EMORY UNIVERSITY
ATLANTA, GEORGIA 30322

January 11, 1971

DEPARTMENT OF CHEMISTRY

Via Air Mail

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

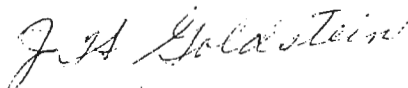
Post Doctoral Position Open

Dear Barry:

We have a post-doctoral opening in NMR spectroscopy and will be happy to receive inquiries from anyone interested.

The effective date for this ipening is flexible and can be either Summer or Fall, 1971. Correspondence should be addressed directly to the undersigned.

Sincerely,



J. H. Goldstein
Professor of Chemistry

JHG:lt

CHEMISCHE LABORATORIA
DER RIJKS-UNIVERSITEIT

Afd.: Drs. R. Kaptein
Wassenaarseweg
Leiden
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LEIDEN, January 11, 1971

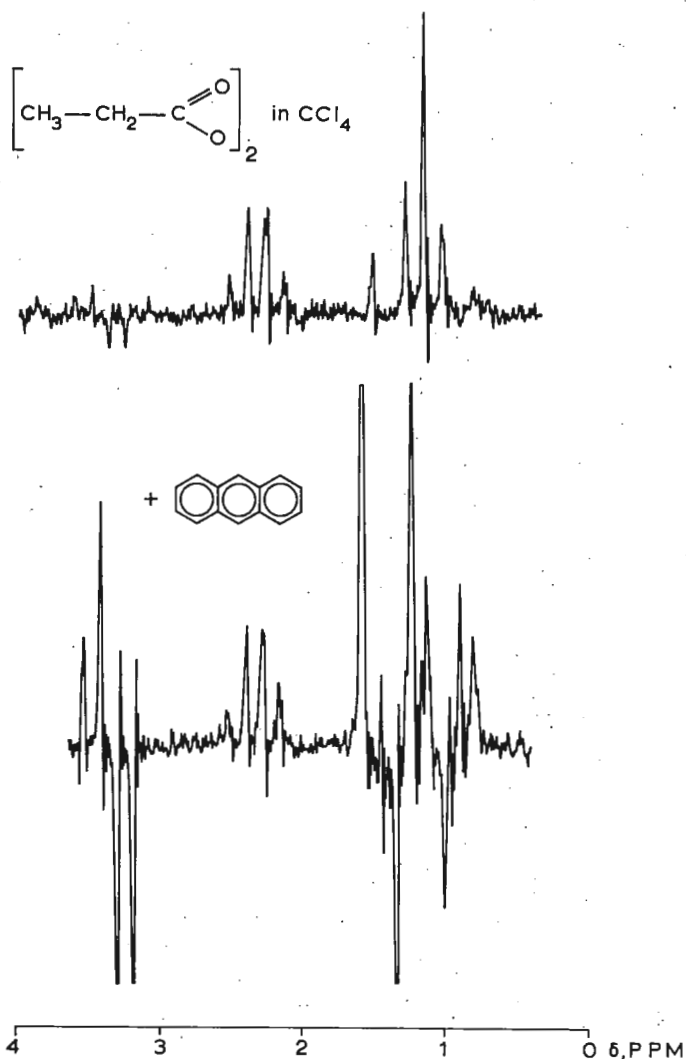
Prof. Bernard L. Shapiro,
Dept. of Chemistry
Texas A & M University
College Station, Texas 77843
U.S.A.

Chemically Induced Dynamic Nuclear Polarization,
A Photoreaction and two simple rules

Dear Dr. Shapiro,

In the course of our work on CIDNP, we have studied the photosensitized decomposition of some acyl peroxides with NMR¹. Comparing results with the thermal decomposition² it was found that direct photolysis proceeds via an excited singlet state and that in the presence of ketones, such as acetophenone, benzophenone, acetone and cyclohexanone, all signals reversed sign, emission (E) becoming enhanced absorption (A) and vice versa, which according to radical pair theory^{3,4} indicates sensitization by triplet state ketones. This is not a world shaking finding but it shows how eminently suitable CIDNP is for this kind of studies.

A somewhat more remarkable result was that in the presence of anthracene an enhancement occurred by a factor 9 compared with direct photolysis, indicating sensitization by excited singlet state anthracene. Because of the short life-time (10^{-9} sec) of singlet state anthracene this must be a very effective process.



In the figure the 60 Mc spectra (modified DA-60) are shown of the photolysis of 0.13 M propionyl peroxide in CCl_4 and this enhancement can be seen for the products ethylchloride (δ 3.52 and 1.42 ppm) and butane, δ (CH_3) 0.90 ppm.

Figure 60 Mc NMR spectrum obtained during irradiation of 0.13 M Propionyl peroxide in CCl_4 (top) and in the presence of 0.07 M anthracene (bottom)

Rules for CIDNP.

For those who occasionally look at CIDNP spectra and want quick answers without wading through the theory, we give two simple rules, by which all qualitative predictions of radical pair theory can be made for the case that reactions are run at high fields (larger than a few thousand Gauss). We look at the spectrum of nucleus i , that belonged to radical a of the pair a b . This spectrum is described by the sign of two quantities

Γ_{ne} and Γ_{me} :

For net polarization : $\Gamma_{ne} = \mu \epsilon \Delta g A_i \begin{cases} + : A \\ - : E \end{cases}$

For multiplet effects : $\Gamma_{me} = \mu \epsilon A_i A_j J_{ij} \sigma_{ij} \begin{cases} + : E/A \\ - : A/E \end{cases}$

where $\Delta g = g_a - g_b$ (g-factors of radical a and b), A_i and A_j are hyperfine coupling constants, J_{ij} is the nuclear spin coupling constant in the product and μ , ϵ and σ_{ij} have the following signs:

$$\mu \begin{cases} + & \text{for triplet precursor or pair formation} \\ & \text{by free radical encounters} \\ - & \text{for singlet precursor.} \end{cases}$$

$$\epsilon \begin{cases} + & \text{recombination product} \\ - & \text{"escape" product (e.g. transfer reaction product)} \end{cases}$$

$$\sigma_{ij} \begin{cases} + & \text{nuclei i and j were present in the same radical} \\ - & \text{i and j belonged to different radicals.} \end{cases}$$

As an example we will apply the second rule to the spectra presented in the figure the pair consists here of two ethyl radicals, $A(\text{CH}_2) = -22\text{G}$, $A(\text{CH}_3) = +27\text{G}$, formed from a singlet precursor ($\mu = -$). The product ethyl chloride has $J_{ij} > 0$ and is a transfer product ($\epsilon = -$); of course $\sigma_{ij} = +$, so we have $\Gamma_{me} = - \cdot - \cdot + \cdot + = -$, hence A/E and this is observed, confirming the singlet nature of the sensitization. For butane only ϵ changes sign, the other labels remaining the same so we have E/A.

We have found these rules very useful for quick determinations of precursor multiplicities, signs of coupling constants etc.

Please credit this contribution to the account of Mr. T.J. Sekuur.

Yours sincerely,

Robert Kaptein

Robert Kaptein

Jan A. den Hollander

Jan A. den Hollander

1. R. Kaptein J.A. den Hollander, D.Antheunis and L.J.Oosterhoff, to be published
2. R. Kaptein, Chem. Phys. Letters, 2, 261 (1968)
3. a) B.L.Closs, J. Am. Chem. Soc. 91, 4552 (1969)
b) G.L.Closs and A.D. Trifuna, ibid 92, 2183, 2186 (1970)
4. R. Kaptein and L.J. Oosterhoff, Chem. Phys. Letters, 4, 195, 214 (1969)

Doz. Dr. H. Kessler
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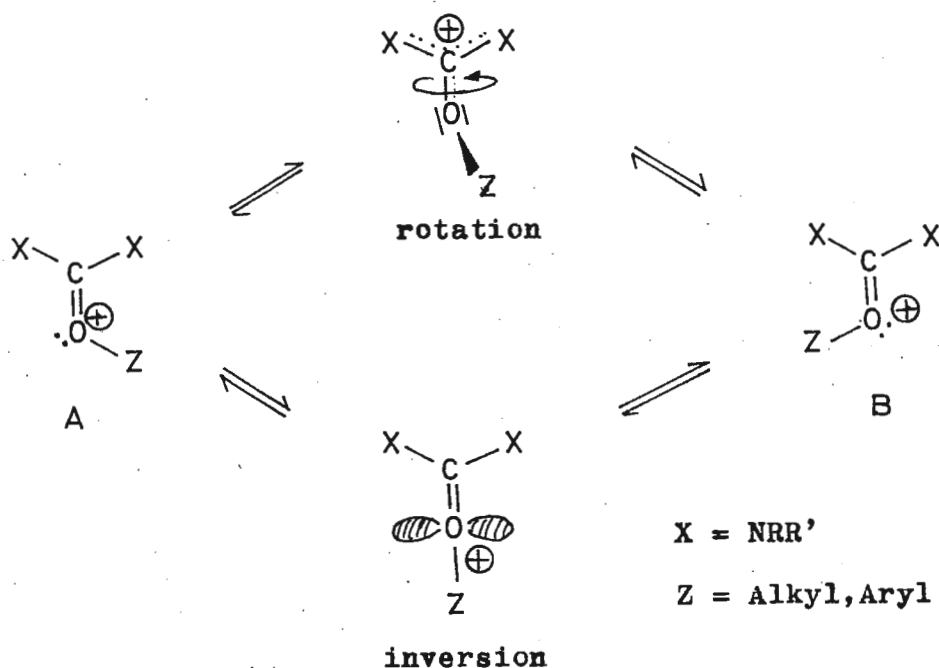
74 Tübingen, den 11.1.1971
 Wilhelmstraße 33

Professor B.L. Shapiro
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 Texas A and M University
College Station, Texas 77843
 USA

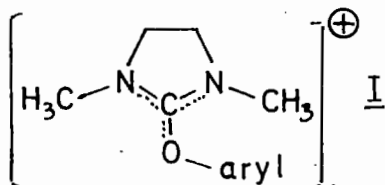
Planar Inversion of Oxygen


Dear Professor Shapiro,

One year ago we had sent you a letter in which we had been able to prove the rotational mechanism of syn-anti-topomerization¹⁾ on C-S-double bond in thiuronium salts²⁾. We are now sure that in oxygen analoga (uronium salts) the mechanism is the inversion on oxygen.



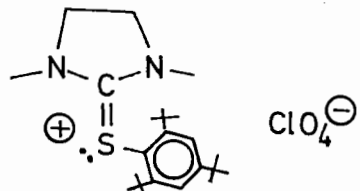
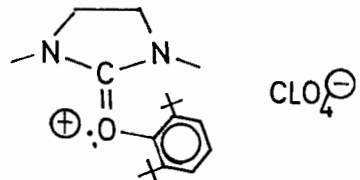
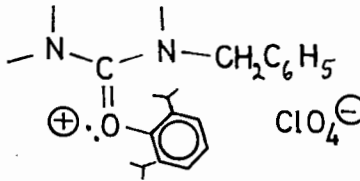
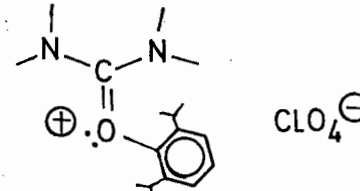
In Tetramethylarylyluronium salts $[X=N(CH_3)_2]$ the N-methyl-signals in NMR split into a doublet on cooling at about -40 to -60° . This is caused by hindered C-N-rotation about the partial CN-double bond (supported by a slightly negative Hammett- ρ -value and other substituent effects). The spectra of the cyclic compounds I show no



temperature dependence of the N-CH₃-groups, even if aryl is  (2a table). The syn-anti-topomerization in uronium-salts is fast with respect

to the NMR-time scale.

Table

Compound	ΔG^\ddagger [kcal/mole]	
	syn-anti-topomerization ¹⁾	enantiotopomerization ¹⁾
<u>1</u> 	18.5	-
<u>2</u> 	< 10	-
<u>3</u> 	< 10	> 24.6
<u>4</u> 	< 10	< 15

The comparison of this result with the relatively high barrier in 1 shows that not rotation about C-O-double bond is the mechanism in 2 because the shorter CO bond distance should increase the rotational barrier. The inversion is strongly supported by studying the magnetic nonequivalence of the i-propyl-groups in 3. This is the same stereochemical relationship as we have recently pointed out in guanidines in which nitrogen inversion is the mechanism³⁾.

To our knowledge these results give the first prove of inversion on planar oxygen⁴⁾.

Sincerely yours,



H.O.Kalinowski



H.Kessler

1) For the nomenclature see:

G.Binsch, E.L. Eliel und H.Kessler, TAMU-Letter 145, 26 (1970).

2) H.Kessler und D.Leibfritz, TAMU-Letter 136, 40 (1970);

H.Kessler und H.O.Kalinowski, Angew.Chem. 82, 666 (1970); I.E. 9, 641 (1970).

3) H.Kessler und D.Leibfritz, Tetrahedron Letters (London) 1970 1423; Chem.Ber. in press.

4) see: H.Kessler, Angew.Chem. 82, 237, (1970); I.E. 9, 219 (1970) and references cited therein.

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8001 Zürich January 12, 1971
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Leitung: Prof. Dr. H. Labhart

Professor B.L. Shapiro
Department of Chemistry
Texas A+M University
College Station, Texas 77 843
U.S.A.

Modification of a VARIAN HA 100 Probe for CIDNP during photolysis
at $\lambda \geq 200$ nm.

Dear Dr. Shapiro:

While studying CIDNP during photolysis of peroxides in solution we felt the need for a NMR probe operating at 100 Mc/sec and allowing the observation of the effects during in-situ irradiation of the samples with UV light of wavelength $\lambda \geq 200$ nm, since most peroxides decompose at wavelengths below 300 nm. Therefore we applied the technique described by Closs (1) (for a 60 Mc/sec instrument and for irradiations with $\lambda \geq 300$ nm) to modify a V 4332 room temperature probe of our VARIAN HA 100 D spectrometer. The coarse tuning paddles and part of the case were removed from the backside of the probe and a rectangular opening was cut into the glass tube carrying the Faraday shielding and the transmitter coil. The two glass tubes of the insert were replaced by quartz tubes (Heralux quality). The sensitivity of the instrument was not changed by these manipulations.

During our experiments we irradiate from the backside of the magnet with an AH 6 1-kw high pressure mercury lamp the light of which is focussed with a suprasil lense onto the receiving region of the sample. Quartz sample tubes are used.

As an example for the signal-to-noise ratios of CIDNP spectra obtained, the phenyl region of NMR spectra during and after photolysis of a saturated solution of 4-4'-dichloro-dibenzoylperoxide in a $\text{CCl}_4/\text{CH}_3\text{J}$ mixture is shown in the figure. A 4-fold improvement of

the photosignals over those found for irradiations with $\lambda = 300$ nm was achieved. The first spectrum taken during irradiation shows the A_2B_2 -spectrum of the peroxide at $\delta = 8.04$, $\delta = 7.96$, $\delta = 7.51$ and $\delta = 7.43$ and additional emission (E) and enhanced absorption (A) lines of the products $Cl \text{ } \phi \text{ } Cl$ [$\delta = 7.25$ (E)], $J \text{ } \phi \text{ } Cl$ [$\delta = 7.63$ (E), $\delta = 7.54$ (E), $\delta = 7.11$ (E), $\delta = 7.01$ (A)] and $Cl \text{ } \phi \text{ } - \underset{\text{O}}{\underset{\text{O}}{\text{C}}} - O - \phi \text{ } Cl$ [$\delta = 7.18$ (A), $\delta = 7.09$ (A)].

The second spectrum taken after 2 minutes irradiation shows weak normal signals of the products $Cl \text{ } \phi \text{ } Cl$ and $J \text{ } \phi \text{ } Cl$.

BPO decomposes from an excited singlet state. The radical pair $Cl \text{ } \phi \cdot \cdot O - \underset{\text{O}}{\underset{\text{O}}{\text{C}}} \phi \text{ } Cl$ which is formed by loss of CO_2 may recombine

giving the positively polarised ester or may release phenyl radicals which react with the solvent and give the mainly negatively polarized substituted benzenes (2,3,4,5).

1. G.L.Closs and L.E.Closs, J.Am.Chem.Soc. 91 (1969) 4549
2. H.Fischer, Z.f.Naturforsch., in press
3. M.Lehnig and H.Fischer, Z.f.Naturforsch., in press
4. R.Kapteijn, J.A. den Hollander, D.Antheunis and L.J.Oosterhoff, Chem.Comm. 1970, 1687
5. B.Blank and H.Fischer, to be published

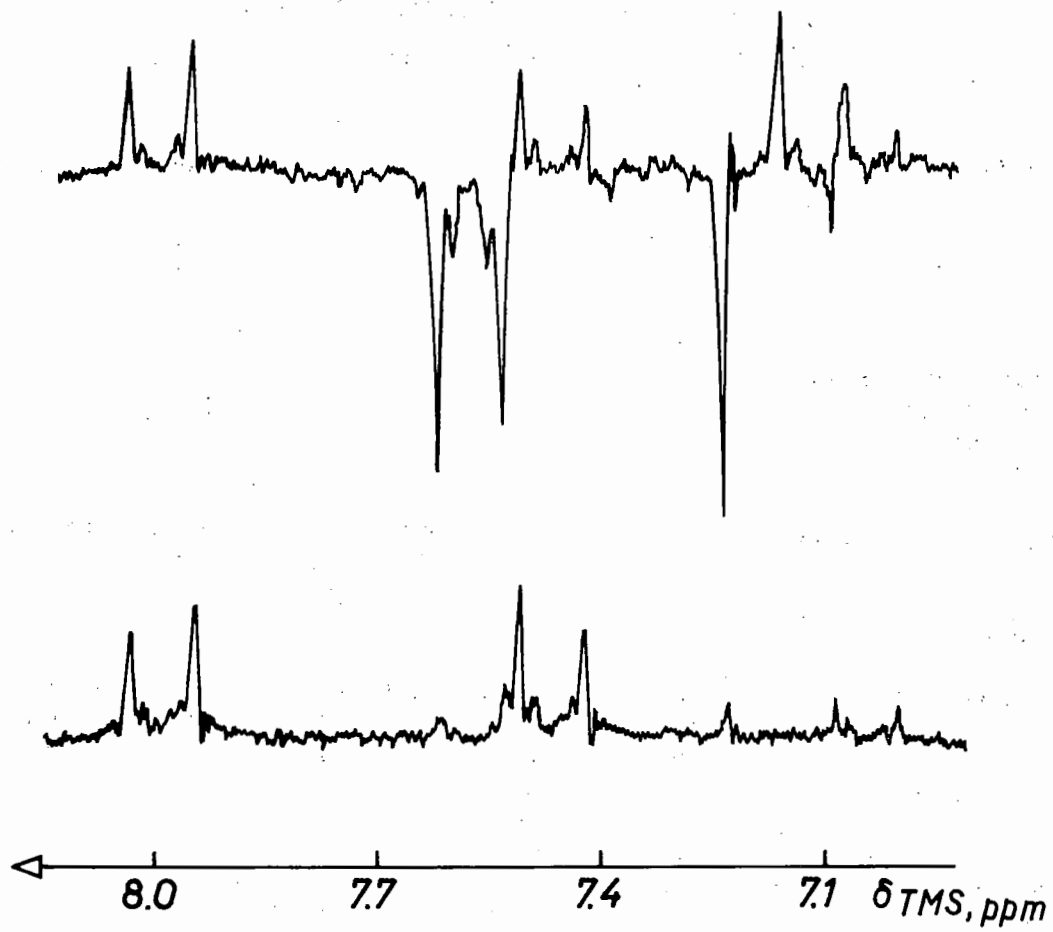
Yours sincerely,

H. Fischer

Hanns Fischer

Manfred Lehnig

Manfred Lehnig





UNIVERSITY OF SOUTH CAROLINA
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Department of Chemistry

January 13, 1971

Professor Barry Shapiro
1101 Merry Oaks
College Station,
Texas 77840

TITLE: An INDO Perturbation Theory of Magnetic Shielding Constants: Carbon 13 C
Chemical Shifts

Dear Barry:

I would like to initiate my subscription to the TAMU NMR Newsletter with this letter describing some of my Ph.D. thesis research. This work was done under the supervision of Professor Gary E. Maciel, then at U. C. Davis, and in collaboration with Dr. James W. McIver, Jr., at SUNY at Buffalo.

We have applied the finite perturbation theory of Pople, McIver and Ostlund¹ to the calculation of ^{13}C shielding constants at the INDO MO level of approximation. We used the INDO method because of its computational practicability and in view of the recent successes that this method has had in the calculation of spin-spin coupling constants.²⁻⁴ Furthermore, the INDO method is attractive as a method of calculating magnetic shielding constants since the result would then be a relatively complete and unified approximate treatment of magnetic resonance parameters.

The theory as employed here uses gauge invariant atomic orbitals (GIAO) as the basis set. Applying the finite perturbation scheme directly with the inclusion of the GIAO and the standard INDO parameters the theory was incapable of reproducing any of the experimental trends. From our experiences with the spin coupling calculations we felt this failure was due, in part, to the inadequacies of the basic CNDO/INDO parameters. Hence, we limited our subsequent calculations to hydrocarbons and treated the β^0 and $\frac{1}{2}(I + A)$'s for C and H as parameters. An altered set of parameters is: Hydrogen; $\beta_{\text{H}}^0 = -12$, $\frac{1}{2}(I + A) = 7.176$, carbon; $\beta_{\text{C}}^0 = -17.$, $\frac{1}{2}(I + A) = 17.051$ and $\frac{1}{2}(I + A) = 8.572$. Theoretical values for the exchange integrals S_{F}^2 and G^1 were used here, however, it was later found that these integrals have little effect on the overall results. A summary of the results using the altered set of parameters is shown in Table I.

Professor Shapiro

Page 2

January 13, 1971

The results in Table I show that with the altered set of parameters the INDO framework provides a scheme capable of accounting for most of the patterns of the experimental chemical shifts for hydrocarbons. Two papers describing this work have been submitted to JACS for publication.

Combining this theoretical technique and our XL-100-15 here at USC we are currently extending this parameter scheme to the remainder of the first row elements.

Sincerely yours,



Paul D. Ellis






Assistant Professor of Chemistry

PDE/bc

References:

- 1) J. A. Pople, J. W. McIver, Jr., N. S. Ostlund, J. Chem. Phys., 49, 2960 (1968)
- 2) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, J. A. Pople, J. Amer. Chem. Soc., 92, 1, 11, 4151, 4497, 4506 (1970).
- 3) P. D. Ellis and G. E. Maciel, ibid, 92, 5829 (1970).
- 4) P. D. Ellis and G. E. Maciel, Molec. Phys., 20, 0000 (1971).

Table I. Calculated ^{13}C Chemical Shifts Using the "New" INDO Parameters.

Compound	σ_d^A	σ_P^A	σ_T^A	δ^A	Experimental δ^A
1. CH_4	61.26	-55.20	6.06	120.62	130.8
2. <u>Cyclo</u> - C_3H_6	58.90	-65.21	-6.31	108.25	130.7
3. C_2H_6	59.78	-56.72	3.06	117.62	122.8
4. $^*\text{CH}_3\text{CH}_2\text{CH}_3$	60.05	-60.47	-0.42	114.14	113.1
5. $\text{CH}_3^*\text{CH}_2\text{CH}_3$	58.35	-55.04	3.31	117.87	112.6
6. $^*\text{CH}_3$ - 	60.33	-60.74	-0.41	114.15	107.2
7. $^*\text{CH}_3\text{CH}=\text{CH}_2$	60.12	-60.07	0.06	114.50	107.0
8. <u>Cyclo</u> - C_6H_{12}	58.78	-62.41	-3.62	110.94	100.9
9. $\text{CH}_3\text{C}\equiv\text{CH}$	59.95	-58.53	1.42	115.98	-
10. $\text{CH}_3\text{C}^+(\text{CH}_3)_2$	60.80	-82.47	-21.67	92.89	81.3
11. $\text{HC}^+(\text{CH}_3)_2$	60.63	-88.71	-28.09	86.47	67.8
12. $\text{CH}_3\text{C}\equiv\text{CH}$	59.88	-132.44	-72.56	42.00	58.7
13. C_2H_2	98.87	-133.36	-74.49	40.07	54.8
14. $^*\text{CH}_2=\text{C}=\text{CH}_2$	60.44	-143.08	-82.64	31.92	54.0
15. $\text{CH}_3\text{C}\equiv\text{CH}$	57.11	-143.43	-86.32	28.24	43.0
16. $\text{CH}_3\text{CH}=\text{CH}_2$	59.96	-166.01	-106.05	8.51	12.0
17. C_2H_4	59.30	-168.29	-108.98	5.58	5.4
18. CH_3 -  *	58.49	-172.71	-114.21	0.25	3.34
19. CH_3 - 	58.79	-173.47	-114.68	-0.12	0.50
20. C_6H_6	58.31	-172.87	-114.56	0.0	0.0
21. CH_3 - 	58.14	-174.47	-116.32	-1.76	-0.29
22. $\text{CH}_3^*\text{CH}=\text{CH}_2$	57.67	-177.83	-120.16	-5.60	-7.1
23. CH_3 - 	56.74	-180.39	-123.66	-9.10	-8.8
24. $\text{CH}_3\text{C}^+(\text{CH}_3)_2$	53.68	-261.26	-207.58	-93.02	-70.4
25. $\text{HC}^+(\text{CH}_3)_2$	54.72	-283.34	-228.61	-114.05	-60.0
26. $\text{CH}_2=\text{C}=\text{CH}_2$	56.26	-232.82	-176.56	-62.07	-84.0

COLLEGE OF ARTS AND SCIENCES
DEPARTMENT OF CHEMISTRY

January 19, 1971

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

Proton NMR Spectra of Paramagnetic Amine Adducts of Ni(II) Complexes

Dear Barry,

We have been examining the NMR line broadening and NMR shifts brought by paramagnetic complexes, especially the amine adducts of nickel(II) 0,0'-dialkyl-dithiophosphates, $Ni(S_2P(OR)_2)_2$. The $Ni(S_2P(OR)_2)_2$ complexes are particularly useful for such studies since they are soluble in a wide variety of organic solvents. The alkyl group can be readily varied to improve solubility characteristics. Purple, planar, diamagnetic $Ni(S_2P(OR)_2)_2$ compounds form brown, paramagnetic (S=1), 5-co-ordinate adducts with secondary aliphatic and sterically hindered aromatic amines and green, paramagnetic (S=1) trans-octahedral adducts with primary amines. The NMR spectra of solutions of $Ni(S_2P(OR)_2)_2$ complexes in amines under rapid exchange conditions, i.e., room temperature in most instances, exhibit contact shifts and paramagnetic broadening consistent with the presence of paramagnetic adducts. Since the formation constants of the amine adducts are small^{1,2}, we wish to stress the importance of working in neat amine solutions whenever possible. This maximizes the concentration of the preferred adduct and permits the ready detection of the amine proton resonance which is very broadened. The large upfield contact of amine protons are diagnostic of amine-nickel interaction and in many instances this allows quick identification of the amine peaks for the free amines.

Those readers interested in examining paramagnetic effects on the NMR spectra of amines or other molecules with donor functional groups in nonaqueous solvents may find nickel(II) dithiophosphates most useful. The complexes are readily prepared³. The isopropyl derivative is available from Alfa Inorganics. Also, the g-values of nickel(II) compounds are relatively isotropic⁴ and dipolar contributions to the observed paramagnetic shifts can be ignored most of the time. Details of our work will be available⁵ in the not-too-distant future.

The TAMU Newsletter is circulated here by Dr. S. L. Smith and I hope you will credit him with this contribution.

Sincerely yours,



John R. Wasson

References

1. R. L. Carlin and D. B. Losee, Inorg. Chem., **9**, 2087 (1970).
2. M. Nanjo and T. Yamasaki, J. Inorg. Nucl. Chem., **32**, 2411 (1970).
3. G. M. Woltermann and J. R. Wasson, Inorg. Nucl. Chem. Letters, **6**, 475 (1970).
4. R. J. Kurland and B. R. McGarvey, J. Magn. Res., **2**, 286 (1970).
5. J. R. Angus, G. M. Woltermann, W. R. Vincent and J. R. Wasson, J. Inorg. Nucl. Chem., **33**, (1971) in press; J. R. Angus, M. S. Thesis, University of Kentucky, August, 1971.

THE UNIVERSITY OF TOLEDO / TOLEDO, OHIO 43606 / [419] 531-5711

*College of Arts and Sciences
Department of Chemistry*

15 January 1971

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

JEOLCO 4H-100/PDP-8/I CAT Interfacing

Dear Professor Shapiro:

With relatively simple programming and a minimum of cost, we have interfaced our 100 MHz JEOLCO (4H-100) spectrometer to a PDP-8/I computer in order to perform CAT experiments. Novel features which build on the recent description of a similar project with a Varian spectrometer are incorporation of a 1024 point storage and display routine and the method of computer control utilized in the JEOLCO nmr instrument.

Basic needs in addition to the spectrometer and computer (equipped with an AX-08-XR lab peripheral) are a relay driver and an amplifier to convert the 0-10mv nmr signal to -1 to +1 volt. Once begun (sweep width selection and program initiation), the whole experiment can be controlled from the nmr console by a series of buttons to signal changes in status to the computer through the AX-08 contingency input.

A potential (0 or 13 volts) applied by the computer to an nmr relay determines whether the spectrometer scans upfield or downfield. The downfield scan is non-recording and goes to the end of the recorder thus establishing the same starting point for each upfield recording sweep. The sweep width is easily varied by changing the sweep time controlled by the RC clock switch on the face of the computer.

Each scan records and stores 1024 points each of which is the average of seven readings (boxcar averaging). Since the AX-08 digital to analog output can only display a grid 512 points on a side, an apparent limitation is placed on oscilloscope or X-Y-recorder display of data to a string of 512 points. This was easily overcome by displaying the spectra in two halves on the top and bottom of the oscilloscope (or recorder) screen. The data display (including scanning and determining the scanning rate) is performed by the computer on the spectrometer oscilloscope or an X-Y-recorder.

The program presently employed uses less than one quarter of the 8K memory locations available to us leaving the option of more points per scan or more extensive boxcar averaging.

Since jacks and switches for tapping off the nmr signal, controlling the sweep and applying an external signal to the oscilloscope were already built into the spectrometer, the interfacing was considerably easier than might have been anticipated. Complete details of the system can be supplied on request.

With best regards,

James E. Gano

H. Bradford Thompson

:mr

1. J. W. Cooper, TAMUNN, (144), 4 (1970).

Please credit this contribution to Clay Griffin's subscription.



Eidg. Technische Hochschule
Laboratorium für Organische Chemie
Zürich

W. Giger
c/o Professor Dr. W. Simon

8006 Zürich, January 20, 1971 fo
Universitätstrasse 6
Tel. (051) 32 62 11

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

^{14}N NMR Spectrum of $^+\text{ND}_4$

Dear Professor Shapiro,

Nitrogen-14 magnetic resonance suffers very much from the line broadening due to electric quadrupole relaxation. Detection of coupling between the ^{14}N nucleus and some other nuclei is only possible if there is a highly symmetrical field gradient around the nitrogen nucleus.

As an example of "High-Resolution ^{14}N NMR" we have observed the spectrum of the tetradeuteroammonium cation by direct measurement. This compound gives quite an unusual spin system by connecting one nucleus with a spin quantum number of 1 with four equivalent nuclei likewise with spin 1. According to the rules of first order spectra the ^{14}N signal is split into nine lines with the intensity ratio 1:4:10:16:19:16:10:4:1 ($J_{^{14}\text{N-D}} = 8.3 \pm 0.1$ Hz).

The ^{14}N spectrum was recorded in one scan with our Bruker-Spectrospin HFX-90 spectrometer equipped with a ^{14}N frequency operating at 6.49 MHz. The sample, a saturated solution of tetradeutero-ammoniumchloride in deuterated water (about 7 M at room temperature), was contained in a 10 mm o.d. tube. Some drops of deuterated trifluoroacetic acid were added to prevent fast exchange of the deuterium nuclei. No internal lock was used. The line width ($\Delta\nu_{1/2} = 2$ Hz) is about the same we measured for the normal ammonium ion.

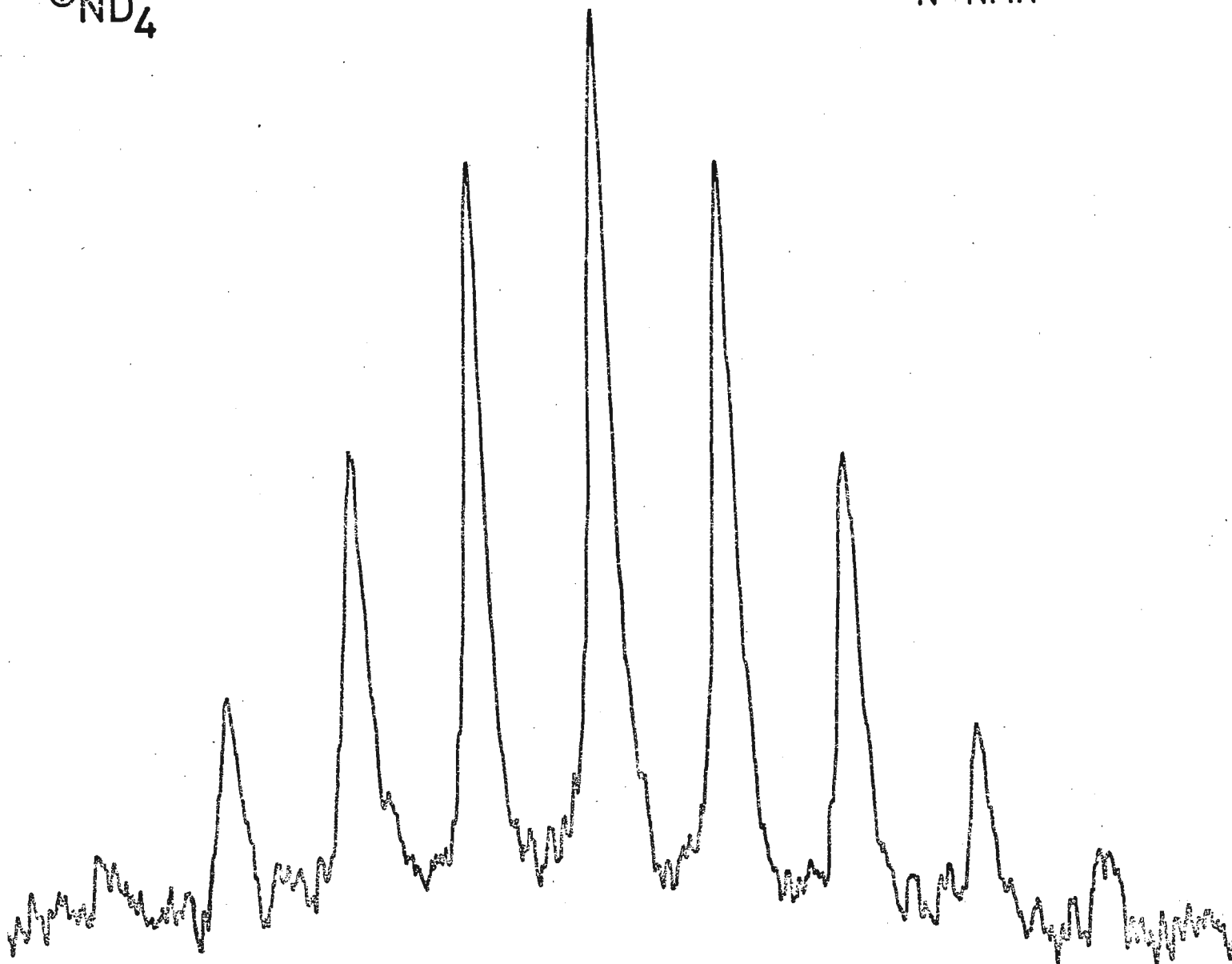
Sincerely yours,

W. Giger
W. Giger

P.S. Please credit this contribution to the
account of Professor Simon.

ND_4^+

$^{14}\text{N-NMR}$



Nitrogen-14 magnetic resonance of tetradeuteroammonium ion

10 Hz

THE UNIVERSITY OF UTAH

SALT LAKE CITY 84112

DEPARTMENT OF CHEMISTRY
CHEMISTRY BUILDINGProfessor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843Nuclear Overhauser Effect and T_1 Measurements in the ^{31}P Spectrum
of Phosphorous Acid, $\text{HP}(\text{O})(\text{OH})_2$

Dear Professor Shapiro:

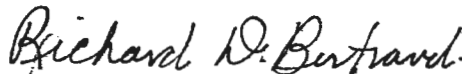
A combination of studies of the Nuclear Overhauser Effect (NOE) and spin lattice relaxation times (T_1) in high resolution NMR spectroscopy can give valuable information regarding the mechanisms of spin lattice relaxation and possibly help in understanding molecular motion in liquids.

We are determining these parameters in a series of vacuum degassed samples of phosphorous acid, $\text{HP}(\text{O})(\text{OH})_2$, in water solution. Initial results indicate that a 3.3 mole% solution at 25°C gives a NOE of 1.59 ± 0.08 and T_1 is 3.2 ± 0.3 sec under proton decoupling conditions. In the coupled case, T_1 is 2.7 ± 0.3 sec. The NOE is highly temperature dependent, being 1.4 at 53°C and 1.9 at 12°C. These data were obtained on our XL-100-15 using the Gyrocode decoupler; adiabatic rapid passage experiments were used to determine T_1 .

The theoretical maximum NOE for phosphorus with proton-phosphorus coupling is 2.23 for a dominant dipole-dipole relaxation mechanism. Using the observed T_1 at 25°C and the NOE, the contribution of this mechanism to relaxation of the phosphorus is $T_{1D} = 6.7$ sec, whereas the contribution of other mechanisms is $T_{10} = 6.1$ sec. Studies of the variation of T_1 with temperature and concentration should reveal whether these other relaxation mechanisms are due to the spin-rotation mechanism or a combination of other mechanisms such as chemical shift anisotropy, scalar coupling, or modulation of scalar coupling due to chemical exchange of the protons attached to the oxygens.

We believe this to be the first report of the magnitude of the NOE observed in phosphorus spectroscopy produced by proton decoupling. A full report giving these results and the results of the temperature and concentration dependences of T_1 of phosphorus acid will appear shortly.

Sincerely yours,



Richard D. Bertrand



David M. Grant

INDIANA UNIVERSITY

Department of Chemistry

CHEMISTRY BUILDING

BLOOMINGTON, INDIANA 47401

TEL. NO. 812-337-5513

January 21, 1971

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

Carbon-13 Spin-Lattice Relaxation Times in Complex Molecules

Dear Barry:

We were amused by a note in your Newsletter (148-37) about a carbon-13 NMR technique in which the sample is freighted back-and-forth between a superconducting solenoid and an electromagnet, the former acting as a "Boltzmann enhancer" and the latter being part of a high-resolution NMR system. This technique is only practical if ^{13}C relaxation times are at least several seconds long. Contrary to a widely held belief, carbon-13 relaxation times of protonated carbons in all but the smallest molecules are very often much less than one second. We present below (Fig. 1) a map of ^{13}C T_1 values, in seconds, of 1 M cholesteryl chloride in CCl_4 , at 42°C , obtained at 15.08 MHz, by means of partially-relaxed Fourier transform NMR¹, under conditions of complete proton decoupling. For the readers' convenience, we also include (Fig. 2) a normal proton-decoupled, natural abundance carbon-13 Fourier transform spectrum of cholesteryl chloride, showing only the region 121.0-183.5 ppm upfield from CS_2 , with assignments. This spectrum was obtained in 256 scans, using a recycle time of 21.7 (total time $1\frac{1}{2}$ hours). A spectrum of nearly equal quality can be obtained in 10 minutes, using a much faster recycle time, but then a few intensities are no longer the true equilibrium intensities.

Clearly, the T_1 values in Fig. 1 prohibit the use of intermagnet commuting, unless done by "Speedy Gonzalez". Even quaternary carbons can have relaxation times of less than 5 sec! We have measured comparably short ^{13}C T_1 values in many molecules. A preprint will soon be available upon request.

Sincerely,

A. Adam

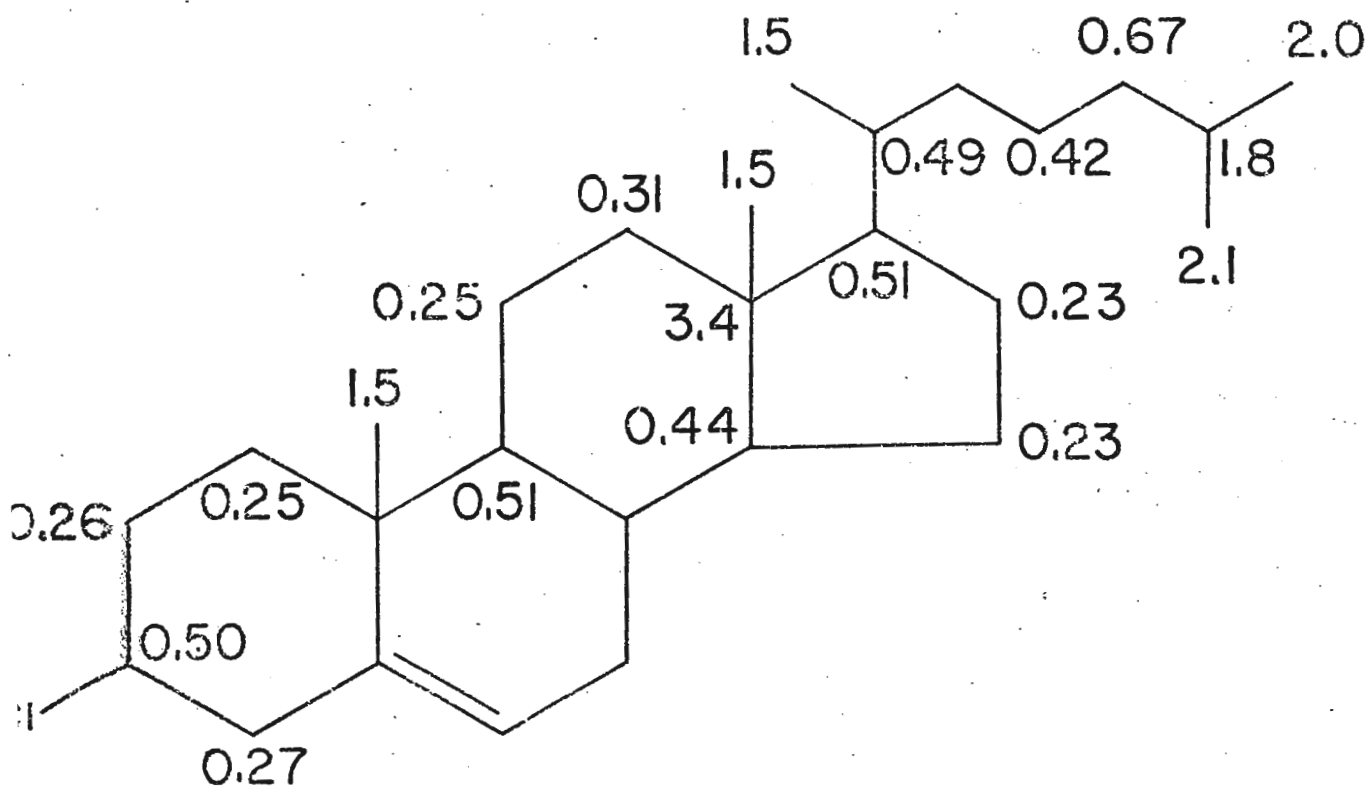
A. Allerhand

D. Doddrell

D. Doddrell

Reference:

¹ R.L. Vold, J.S. Waugh, M.P. Klein, and D.E. Phelps, J. Chem. Phys. 48, 3831 (1968).



Carbon-13 T_1 values in seconds

Fig. 1

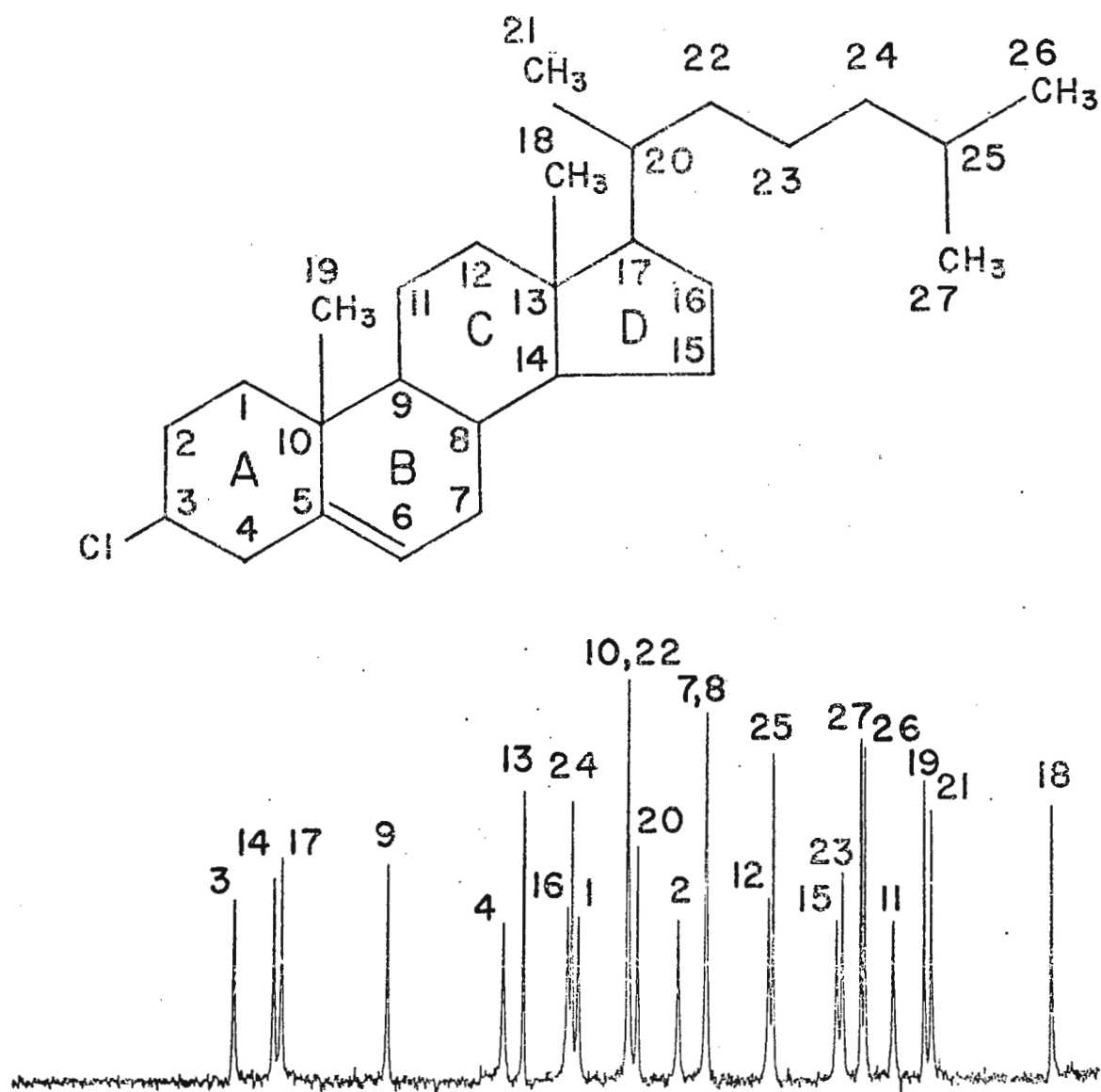


Fig. 2

COLORADO STATE UNIVERSITY

FORT COLLINS, COLORADO 80521

DEPARTMENT OF CHEMISTRY

January 21, 1971

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

Dear Barry:

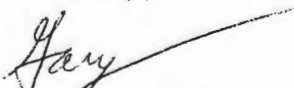
RE: External ^{19}F Lock for ^{13}C on an HA-100.

Recently we described^{1,2} modifications which incorporated an internal ^{19}F lock system for ^{13}C on an 8mm probe in the HA-100 spectrometer at U.C., Davis. We decided to extend that system to include an external ^{19}F lock system on our 5mm ^{13}C variable temperature probe. Tom Nakashima designed and carried out the modification, which is described briefly here.

The ^{19}F single coil is wound around a teflon sleeve, which is glued to the outside of the insert. The tuning circuit is housed within the probe body and is supported by a $\frac{1}{4}$ "-thick, L-shaped aluminum piece (see figure). A hole was drilled through the probe cover for access to the variable capacitor. The capacitor's and coil were varied until a double minimum was observed on the ^{19}F detector-level meter for a 360° rotation of the variable capacitor. There was no attempt at impedance matching. With this method a shim signal of $\sim 10:1$ S/N was obtained. Tuning the system is identical to that reported previously.² We chose to lock on the resonance of $\text{CF}_3\text{CO}_2\text{H}$, which is contained in a sealed 4mm pyrex tube. The sealed tube slips into the teflon sleeve, so that if one desires, the locking compound can be changed.

The convenience of the external lock is that samples can be interchanged while still maintaining a locked condition. The reproducibility of line position through a carbon resonance is ± 0.25 Hz. Long term capping increases the line width by about a factor of two.

Sincerely,


Gary E. Maciel
Professor

GEM:mln

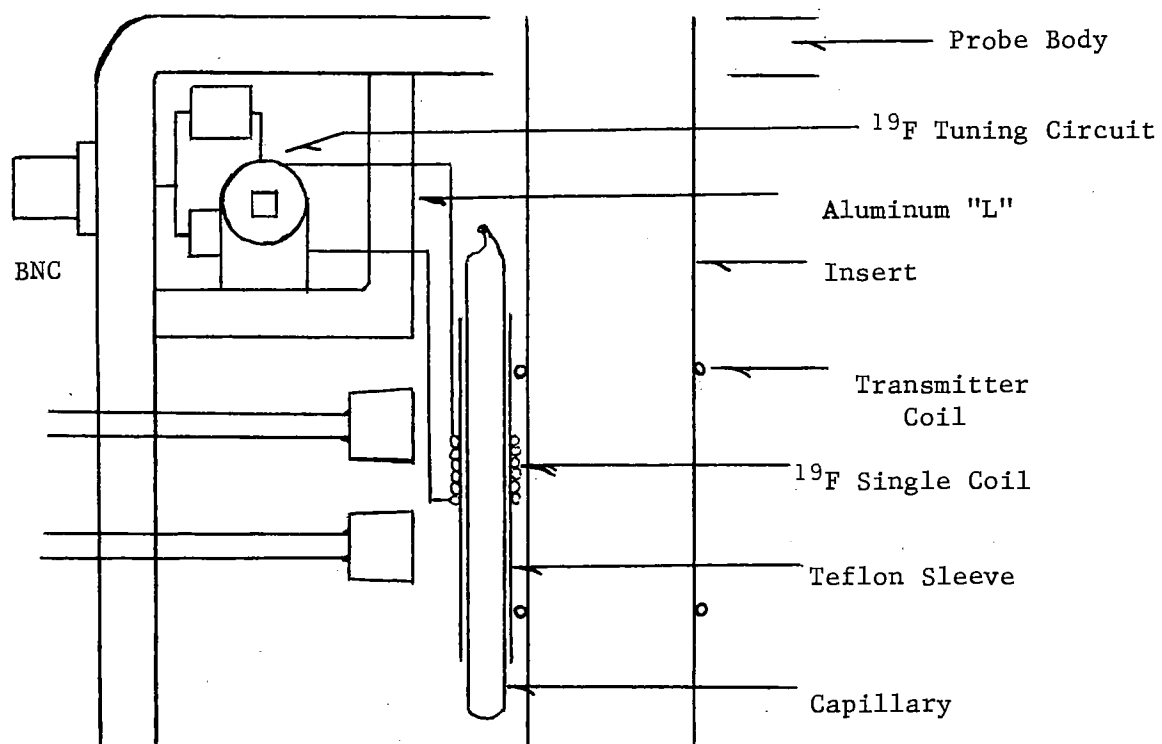


Figure of ^{19}F Lock Arrangement

1. G. E. Maciel, TAMU-NMR Newsletter, No. 136, p. 10.
2. V. J. Bartuska, T. T. Nakashima, and G. E. Maciel, Rev. of Sci. Instr., 41, 1458-62 (1970).

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

1 Berlin 12, den 1 - 26 - 1971
Straße des 17. Juni 112
Tel.: (0311) 314 (Durchwahl)

Az.:

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

U. S. A.

Re.: Temperature stability in the probe insert of our
Bruker KIS HX 90/60.
How to reference C-13 dilution and solvent shifts

Dear Professor Shapiro,

In the course of our studies on hydrogen bonding we came across the problem of the temperature stability of the thermostated probe in our Bruker KIS HX 90/60 spectrometer, which turned out to be astonishingly well performed by the Bruker Temperature Control Unit B-ST 100/700.

With a sample which shows a temperature coefficient of 6 c/s per °C (highly diluted acetic or propionic acid) we measured a line width of max. 2 c/s after averaging over a period of 12 hours with our TMC-Cat.

If the whole line width is attributed to the temperature variation in the period of 12 hours, which is certainly not quite realistic, this means that the temperature in the probe is thermostated better than $\pm 0,2$ °C over the period of 12 hours. The measurements have been performed in the temperature range from 20 °C up to 90 °C.

Measuring nmr concentration and solvent shifts will always raise the question to what extent shifts of the reference line are participating. This is particularly true in ¹³C-NMR where

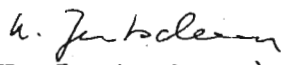
several procedures are in use. Most frequently employed are


- I) internal H or F stabilisation, directly counting ^{13}C frequencies,
- II) external H or F stabilisation, susceptibility correction
- and III) referring to internal ^{13}C of TMS or C_6H_{12} .

We have compared the respective results for diluting $\text{Ph-C}\equiv\text{C}^{13}\text{H}$, $^{13}\text{CHCl}=\text{CCl}_2$ and $^{13}\text{CHCl}_3$ in several solvents. Deviations up to 0,35 ppm are found whereas the reproducibility is $\pm 0,01$ ppm.

It seems to us that method II) is most reliable and we wonder what has been experienced in other laboratories.

Yours sincerely


(U. Jentschura)


(E. Lippert)


(D. Ziessow)

Southern Research Institute



2000 NINTH AVENUE SOUTH
BIRMINGHAM, ALABAMA 35205
TELEPHONE 205-323-6592

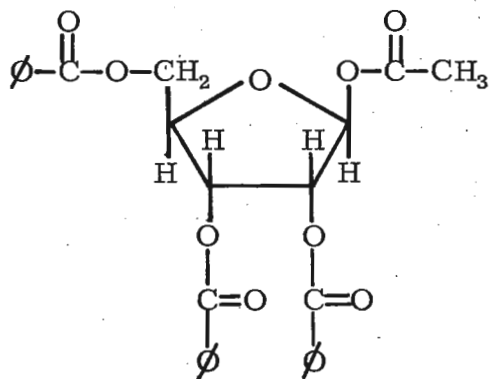
KETTERING-MEYER LABORATORY
AFFILIATED WITH
SLOAN-KETTERING INSTITUTE
FOR CANCER RESEARCH

January 26, 1971

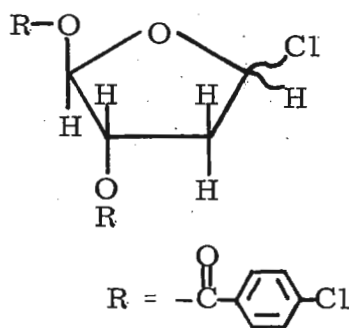
Prof. B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Dear Barry:

In view of the current interest in "shift reagents", some of your readers may be interested in our (admittedly limited) experience with $\text{Eu}(\text{DPM})_3$ [tris(dipivalomethanato)europium], in connection with some sugars.



I



II

With sugar I, the addition of $\text{Eu}(\text{DPM})_3$ produced complex but not unexpected results. Moreover, the europium complex appeared to be rather stable in the solution. After three days, the downfield shifts originally produced had decreased, and the bulk of the protons of the $\text{Eu}(\text{DPM})_3$ appeared

Prof. B. L. Shapiro
January 26, 1971
Page Two

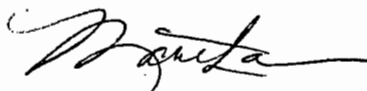
Southern Research Institute

below TMS, which we judge indicates the slow decomposition of $\text{Eu}(\text{DPM})_3$. Even at this time, however, useful results could be obtained from the spectrum.

Results with sugar II were quite different. It is, of course, a quite reactive compound, and it appeared to react so rapidly with the europium complex that no useful results were obtained. We think this reaction was too rapid to be merely the result of dehydrohalogenation of the sugar followed by acid decomposition of the complex. (Unless, of course, the presence of the $\text{Eu}(\text{DPM})_3$ assisted the dehydrohalogenation).

We have at this time no evidence as to the generality of this result with chloro-sugars. Perhaps other readers of the Newsletter will have additional information.

Sincerely,



Martha C. Thorpe
Research Chemist

Suggested title: Use of "Shift Reagents" with Sugars.

MCT: sjh

SCHEIKUNDIG LABORATORIUM
DER VRIJE UNIVERSITEIT
AMSTERDAM-Z.

De Lairessestraat 174 - Telefoon 71 7451

AMSTERDAM, 26-1-1971

Uw ref.:

Onze ref.:

Professor B.C. Shapiro,
Texas A & M University,
Dept. of Chemistry,
College Station
Texas 77843

Dear Dr. Shapiro,

NMR of Oriented Non-rigid Molecules

The manner in which a flexible molecule is oriented by a macroscopically aligned nematic solvent depends on the relative magnitudes of the lifetime of a conformation and the rotation correlation time. In this note we wish to discuss this point in connection with the interpretation of the NMR-spectra of such molecules.

As an example of a non-rigid molecule, we consider ethyliodide and assume that it interconverts rapidly between its three most stable conformations. If the internal rotation is effectively free in the experiment under consideration, the molecule will have C_{3v} -symmetry (1). On a NMR-timescale ethyliodide has indeed C_{3v} -symmetry, and the NMR-spectrum of ethyliodide in the nematic phase can be interpreted accordingly. For the rest the factorisation of the secular determinant is completely the same no matter one uses the C_{3v} -group or the composite particle approach (2).

Values of the anisotropic dipolar interactions have been reported in ref. (2). At 76°C they are: $D_{AA} (= D_{HH} [CH_3]) = 1188$ Hz, $D_{BB} = (D_{HH} [CH_2I]) = 2781$ Hz and $D_{AB} = -265$ Hz. Referred to the timescale of the reorientational motion of the molecule as a whole, ethyliodide does not need to have C_{3v} -symmetry. The values of D_{AA} and D_{BB} , which differ by more than a factor 2, indicate that ethyliodide can not be described by one orientational para-

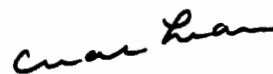
meter. If this was the actual situation D_{AA} and D_{BB} would have the same value (assuming that both H-H-distances involved are of practically the same magnitude). Instead the dipolar couplings are the weighted averages of the corresponding couplings in all possible conformations. In connection with this it may be interesting to study how far the ratio of D_{AA} and D_{BB} changes through all methylhalides.

As another example we consider cyclobutane. Recently Meiboom and Snyder published the results of a NMR study of this molecule in a nematic liquid crystal (3). They pointed out that cyclobutane has D_{4h} -symmetry if it rapidly oscillates between its two bent conformers. As a consequence it was concluded that its average orientation with respect to the magnetic field can be described by one orientational parameter. From our point of view the primary reason that a single motional constant suffices, is that each of the conformers can be described by one motional constant (4).

Sincerely yours,



J. Bulthuis



C. MacLean

References

- 1) S.L. Altmann; Proc.Roy.Soc. A 298, 184 (1967)
- 2) C.M. Woodman; Mol.Phys. 13, 365 (1967); 19, 753 (1970)
- 3) S. Meiboom and L.C. Snyder; J.Chem.Phys. 52, 3857 (1970)
- 4) H.A. Jahn; Acta Cryst. 2, 30 (1949)

Southern Illinois
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CARBONDALE, ILLINOIS 62901

Department of Chemistry

January 29, 1971

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

Lanthanide Shift Reagent Results
Dear Dr. Shapiro:

We have been investigating the practicality of using shift reagents to analyze complex nmr spectra. We are interested in seeing if it is possible to decompose the spectrum into an approximate first order one which can be more readily analyzed, followed by a reconstruction of the original complex spectrum from the coupling constants and behavior of the chemical shifts obtained on addition of the shift reagent. Difficulties are expected if the coupling constants themselves are affected by the shift reagent and if broadening of the lines tends to obscure the smaller couplings.

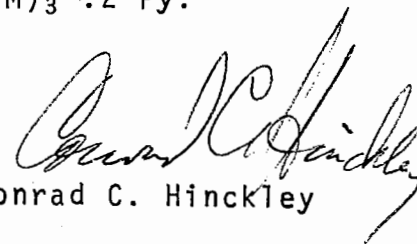
The spectrum of aniline in CCl_4 upon successive additions of $\text{Eu}(\text{DPM})_3 \cdot 2 \text{Py}$ approaches a first order one (see attached figure). Under a greater expansion than shown on the figure many of the lines due to small splittings can be discerned, albeit broadened. No evidence of significant changes in the coupling constants is evident.

We have also been investigating the effect of paramagnetic shift reagents on fluorine chemical shifts and coupling constants. The results have not been encouraging thus far, probably because the fluorine tends to reduce the basicity of the coordination site and thereby weaken the metal ligand interaction.

2-Dr. B. L. Shapiro

The fluorine chemical shifts of pentafluoroaniline and the fluorine and proton chemical shifts of 1-chloro-1, 1, 3, 3, 3-pentafluoro-2-propanol are only slightly effected by the addition of relative large amounts of $\text{Eu}(\text{DPM})_3 \cdot 2 \text{ Py}$.

Sincerely,

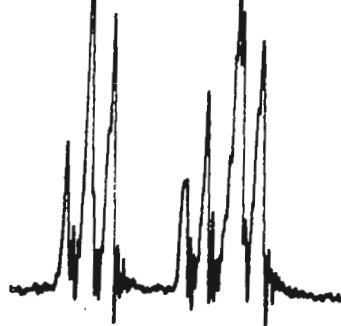
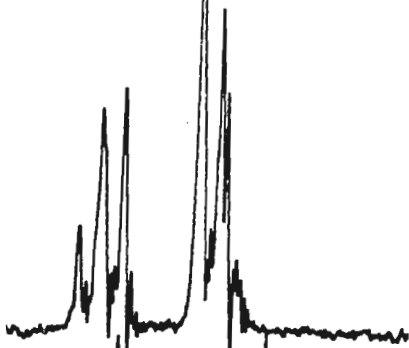
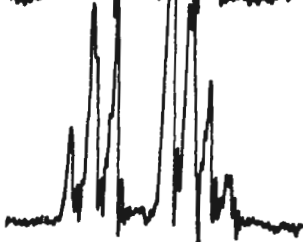
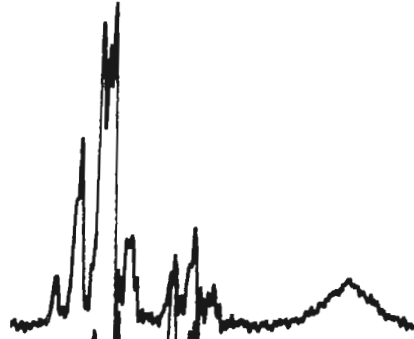
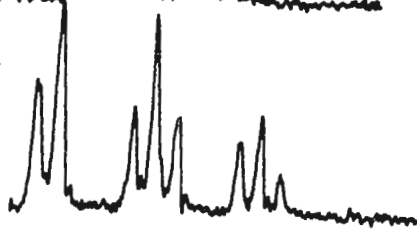
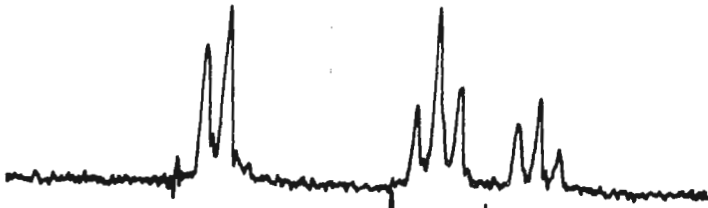
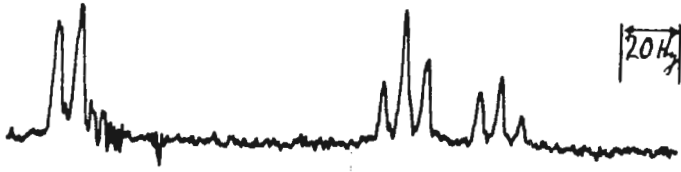


David F. Koster-Conrad C. Hinckley

DEK:vbw

A selection of references on shift reagents.

1. C.C. Hinckley, J. Am. Chem. Soc., 91, 5160 (1969).
2. J.K.M. Sanders and D.H. Williams, Chem. Commun., 422 (1970).
3. J. Briggs, G.H. Frost, F.A. Hart, G.P. Moss and M.L. Staniforth, Chem. Commun., 749 (1970).
4. P.V. Demarco, T.K. Elzey, R.B. Lewis and E. Wenkert, J. Am. Chem. Soc., 92, 5734, 5739 (1970).
5. George M. Whitesider and Joseph San Filippo, Jr. J. Am. Chem. Soc., 92, 6611 (1970).
6. G.H. Wahl, Jr., and M.R. Peterson, Jr., Chem. Commun., 1167 (1970).





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January 22, 1971

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

Chemically Induced Dynamic Nuclear Polarization - Discussion
 Dear Dr. Shapiro:- Session - July 26, 1971.

We are planning an informal evening discussion session July 26, 1971 here at the Eastern Research Laboratory on the subject of Chemically Induced Dynamic Nuclear Polarization. This meeting has been planned to coincide with the IUPAC Congress in Boston. Although three plenary lectures on the topic will be presented during the formal IUPAC Symposium, an opportunity for more detailed group discussion here seems worthwhile.

We would like to include both practicing workers in this area and novices with a serious interest. This arrangement will allow both dissemination of fundamental techniques and the exchange of recent findings among workers. We visualize structuring the discussions somewhat by selecting two or three topics and arranging for discussion leaders.

Our preliminary plans include:

5:15-6:00 P.M.	Transportation from Boston to Wayland
6:00-7:30 P.M.	Supper at Eastern Research Laboratory
7:30-10:30 P.M.	Discussion
10:30-11:00 P. M.	Transportation to Boston Hotels

As the CIDNP phenomenon is of interest to NMR spectroscopists, we would like to use the newsletter to announce this event to those subscribers planning to attend the Congress. Many of the active workers in this field will be in attendance here, and we suggest readers interested in attending write to us as soon as possible since we can host only a limited number of additional people.

With best regards,

Joe Rakshys
 J. W. Rakshys, Jr.
 Research Chemist

D. T. Dix
 D. T. Dix
 Research Chemist

pat



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH
BETHESDA, MARYLAND 20014
February 1, 1971

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

^{13}C FTNMR Studies of Peptides

Dear Barry:

We are studying peptides with the carbon-13 Fourier transform NMR technique using a Varian HA-100D/V4357 FFT system with a 620i computer and a Z-3512 proton noise decoupler. Excellent spectra are obtained at natural abundance in less than two hours, as indicated in Fig. 1.

This work is designed to form the basis to studies with proteins. We are following the titration of the ^{13}C resonances with pH (Fig. 2). We have synthesized by the Merrifield procedure the 15-amino acid peptide corresponding to the amino-terminal sequence of ribonuclease A and containing ^{13}C -enriched phenylalanine^{1,2} at position 8 (^{13}C -Phe-8]-RNase-(1-15)). This is an active derivative^{3,4} of ribonuclease-S peptide⁵, and our product after one purification step generated 28% of the activity effected with native ribonuclease S-peptide when each was added in equimolar amounts to S-protein. A comparison of spectra of the normal and the ^{13}C -Phe-8 peptide clearly indicates the enrichment in the latter case. Our use of ^{13}C enrichment is designed primarily to enable us to distinguish the residue on the peptide when it forms part of an enzymatic complex containing other such residues. This should avoid problems of the assignment of individual resonances, as encountered in PMR studies of proteins, and provide us with a "reporter" group which does not disturb the system in any significant way. We have also obtained spectra of ribonuclease A⁶ and of the C-peptide⁷ (1-13) and S-peptide⁵ (1-20), and a comparison with the (1-15) peptide should enable us to obtain definitive assignments.

A preliminary account of this work has been prepared for publication. Please consider this letter an initial contribution to the Newsletter from the Laboratory of Dr. Freedman.

Yours sincerely,

Jack S. Cohen

Jack S. Cohen, PSL, DCRT, NIH, Bethesda, Md., Murray H. Freedman, Faculty of Pharmacy, University of Toronto, Toronto, Ontario, Canada, and Irwin M. Chaiken, LCB, NIAMD, NIH, Bethesda, Maryland

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References:

1. W. Horsley, H. Sternlicht and J. S. Cohen, J. Am. Chem. Soc., 92, 680 (1970).
2. J. S. Cohen, W. Horsley and H. Sternlicht, Biochem, Biophys. Acta., 222, 521 (1970).
3. J. I. Potts, D. M. Young and C. B. Anfinsen, J. Biol. Chem., 238, 2593 (1963).
4. K. Hoffman, F. M. Finn, M. Limetti, J. Montibeller and G. Zanetti, J. Am. Chem. Soc., 88, 3633 (1966).
5. F. M. Richards and P. J. Vithayathil, J. Biol. Chem., 234, 1459 (1959).
6. A. Allerhand, I. W. Cochran and D. Doddrell, Proc. Natl. Acad. Sci., 67, 1093 (1970).
7. E. Gross and B. Witkop, J. Biol. Chem., 237, 1856 (1962).

Figure Captions:

- Fig. 1. CMR-FT spectra at 25.1 MHz and natural abundance with protein noise decoupling. a) Phe methyl ester, pH 1.86, satd. soln., 10^4 pulses (50 mins.); b) His, pH 1.14, satd. soln., 10^4 pulses; c) His-Gly, pH 3.51, 100 mg/ml, 10^4 pulses; d) His-Phe, pH 3.33, 100 mg/ml 1.5×10^4 pulses. Spectra were recorded with a pulse width of 40 μ secs and an acquisition time of 0.3 secs. Chemical shift values are in ppm downfield from external $^{13}\text{CH}_3\text{I}$.
- Fig. 2. Titration data for L-histidine. Assignments are based on the correlations deduced in ref. 1, except for C_5 (cf. ref. 6).

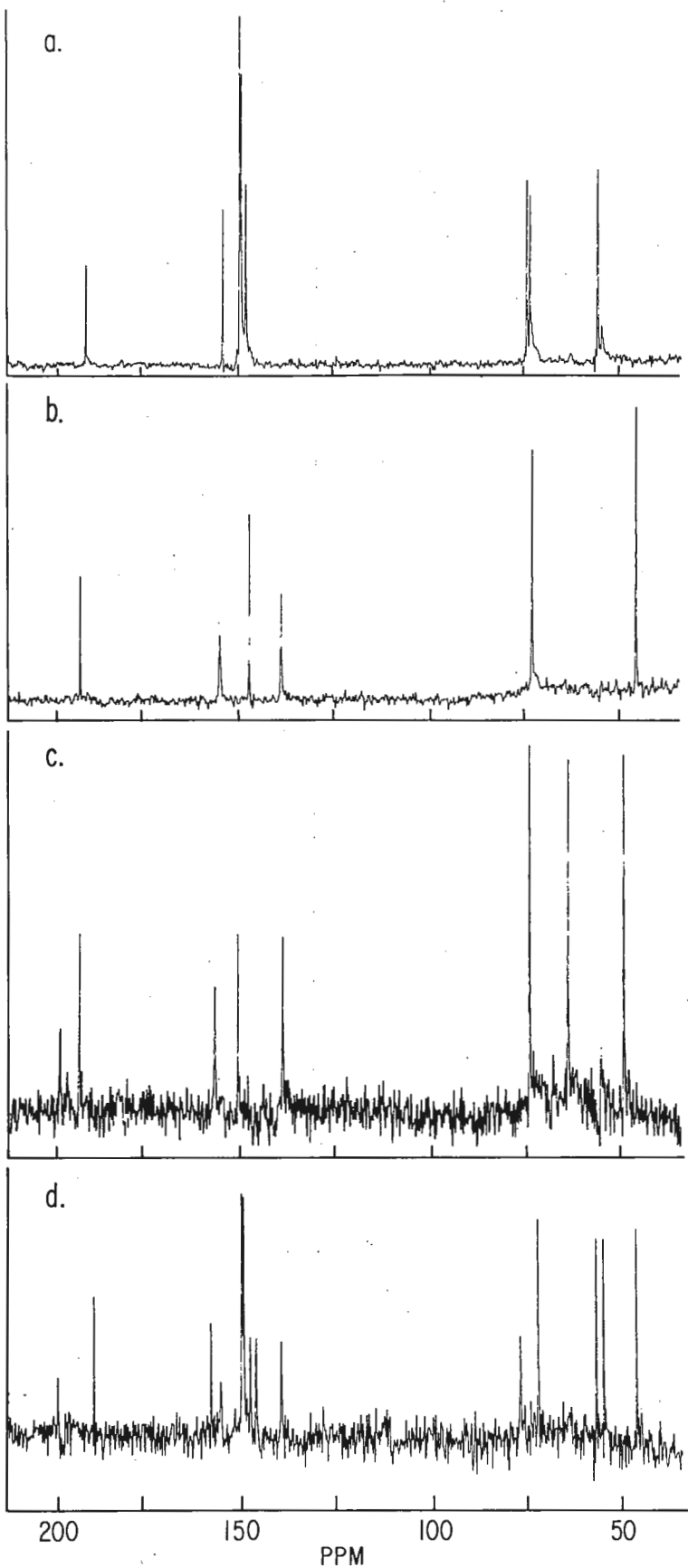


Figure I

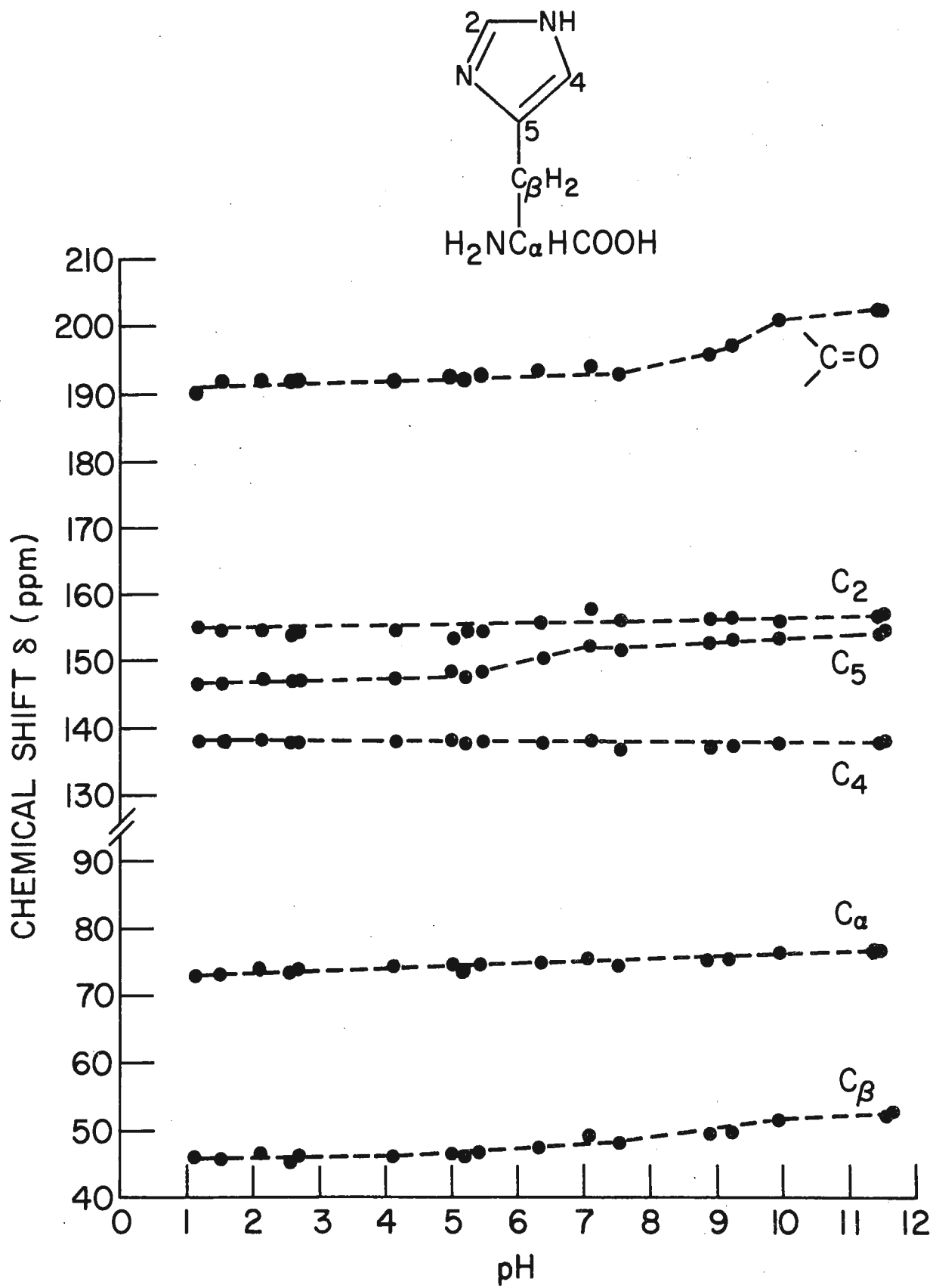


Figure II



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