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N - M - R Newsletter

No. 182

November, 1973

(Cont'd inside on p. (i))

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Deadline Dates: No. 183: 3 December 1973
No. 184: 7 January 1974

All Newsletter Correspondence, Etc. Should Be Addressed To:

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

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September 7, 1973

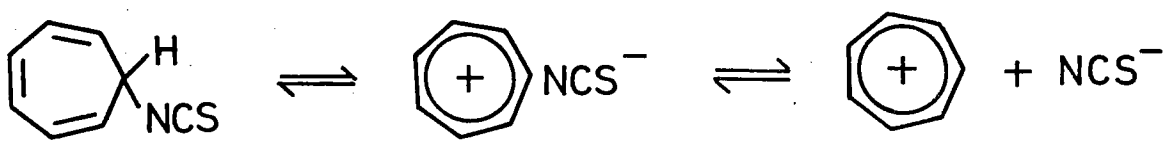
Professor
Bernhard L. Shapiro
Department of Chemistry
Texas A & M University

College Station, TX 77843
U. S. A.

Dear Dr. Shapiro:

Direct Observation of the Dissociation Equilibrium of Tropylium Salts

Hitherto, to the best of our knowledge, dissociable compounds have been observed either in nonionic or in dissociated form, but not side by side. We have found a tropylium salt that exists in solution in dissociated and undissociated forms together, these forms being separated by relatively high energy barriers. The NMR spectrum of cycloheptatrienyl isothiocyanate (1) [1] in $CDCl_3$ or ether at -40° is the usual one for 7-substituted cycloheptatrienes [δ = 6.8 (t,3-H,4-H), 6.4 (m, 2-H, 5-H), 5.6 (dd, 1-H, 6-H), and 4.1 (t, 7-H, J = 5 Hz)], but when the temperature is raised to about $+20^{\circ}C$ it is reversibly broadened and all the signals coalesce, indicating the migration of the NCS group around the whole seven-membered ring [2]. In acetonitrile, (1) dissolves only as tropylium isothiocyanate (singlet at δ = 9.2), but surprisingly both forms are observed together in $CD_3CN/CDCl_3$ at $-40^{\circ}C$.



A B C

The equilibrium between the ionized form (B,C) and the nonionized form (A) was demonstrated by irradiation at the tropylium frequency at -15°C, whereby saturation of the whole cycloheptatriene spectrum was achieved.

The intensity ratio of A:(B,C) can be modified by addition of tropylium tetrafluoroborate or by change in the composition of the solvent, but not by alteration of the concentration of the solute in the solvent mixture. The tropylium salt must therefore exist in this solvent mixture preponderantly as ion pairs B. With increasing amount of chloroform in the (originally pure) acetonitrile solvent, the position of the tropylium signal shifts to higher field and thus indicates increasing pairing of the ions. This also follows from the kinetics. Broadening of the tropylium signal in the solvent mixture is independent of the concentration (first-order reaction; $\Delta G^{\ddagger}_{243}$ = 12 kcal/mol). The barrier thus lies between the ion pair B and the cycloheptatriene A. A possible reason for its size may be seen in the aromatic tropylium system which has to be distorted on the approach of the anion [4]. Equilibria between 7-substituted cycloheptatriene and their corresponding ions were observed, just as for the isothiocyanate, with the anions N_3^-, ONO^-, and NCO^- [6]. Therefore these anions allow the study of ion recombinations [7] that will contribute to our understanding of the S_N1 mechanism.

The publication is prepared for the Angew.Chem.

Sincerely yours,

H.Kessler

A. Walter

References

[1] Prepared by the reaction of tropylium tetrafluorobarate with sodium thiocyanate. The IR spectrum of its solution in ether shows a strong band at 2060 cm^{-1} characteristic of R-NCS compounds.

[2] The same effect was observed previously with tropylium azide [3].

[3] D.S. Wulfman, L.Durham and C.E. Wulfman, Chem.Ind. (London) 1962, 859.

[4] A high barrier was also observed for dissociation of Meisenheimer complexes [5]. These also correspond to the system: aromatic compound + X.

[5] P. Caveng and H. Zollinger, Helv.Chim.Acta 50, 861 (1967).

[6] Solvent: $SO_2/CDCl_3$ for N_3^-, CD_3CN for ONO^- and NCO^-.

[7] C.D. Ritchie, Accounts Chem.Res. 5, 348 (1972).

ISTITUTO DI CHIMICA INDUSTRIALE
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Catania, 8/10/1973

Dr. BERNARD L.SHAPIRO
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Re: LIS with Organic Cations

Rose and GRAVES report (TAMUNN 180-14) on LIS with organic cations, made me remenber some puzzling data lying in my drawer from quite a while. They are shown in the table and refer to the effect of Eu $(fod)_3$ and Pr $(fod)_3$ on a series of methyl substituted benzyl-pyridinium ions.

These compounds are very soluble in chloroform and therefore it was tempting for me to look at the effect of the LSR in the hope to get hints for proton assignments.

It worked, protons were assigned, but I did not have a ready explanation for the LSR-cation interaction.

Now Rose and Graves results seem to provide a rationale also for my data, and I am looking forward to read their paper in Chem.Comm.

Figures in the Table refer to measures at 60 MHz in $CDCl_3$, 5% solutions. Values in first row are the undoped chemical shifts (ppm).

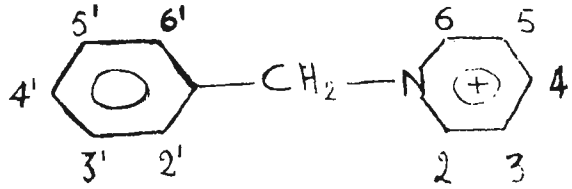
In second and third row are reported the molar LIS (ppm). The ratio of the Pr and Eu molar shifts is reported in the forth row.

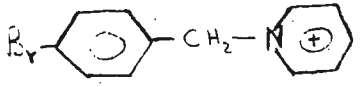
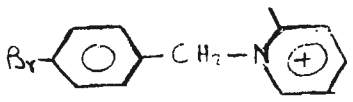
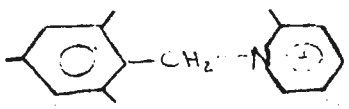
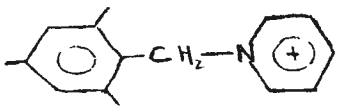
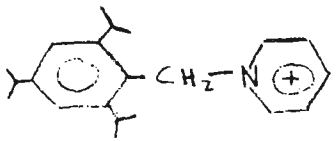
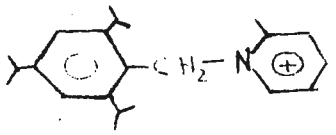
Since the conformational preference of some of these compounds is know (Tetr. Lett. 1972, 3429), one could try to speculate if data in the Table could be used to locate the anion in the molecular space by applying the fitting metods of current use (Which assume the prepoderance of the pseudocontact interaction).

Is anybody interested to adress this point?

Sincerely

Giorgio Montaudo



Compound. /= CH_3		2	3	4	5	6	2'	3'	4'	5'	6'	CH_2	CH_o	CH-p
	δ ppm	9.77	8.00	8.43	8.00	9.77	7.73	7.27	—	7.27	7.73	6.33		
	Pr(fod)3	14.13	7.29	6.08	7.29	14.13	4.44	0.99	—	0.99	4.44	10.73		
	Eu(fod)3	6.70	4.68	3.85	4.68	6.70	2.31	—	—	—	2.31	5.44		
	Pr/Eu	2.10	1.56	1.58	1.56	2.10	1.92	—	—	—	1.92	1.97		
	δ ppm	9.67	7.98	8.43	7.98	2.93	7.27	7.27	—	7.27	7.27	6.28		
	Pr(fod)3	13.92	7.24	6.78	7.24	6.23	4.96	0.81	—	0.81	4.96	10.54		
	Eu(fod)3	7.12	4.19	3.35	4.19	3.14	—	—	—	—	—	5.34		
	Pr/Eu	1.95	1.73	2.02	1.73	1.98	—	—	—	—	—	1.97		
	δ ppm	7.92	7.92	8.40	8.17	3.27	2.30	6.90	2.30	6.90	2.30	5.90		
	Pr(fod)3	4.89	8.79	10.42	10.42	6.75	2.88	0.83	0.38	0.83	2.88	5.89		
	Eu(fod)3	2.64	4.05	5.84	5.68	3.75	1.33	—	—	—	1.33	3.17		
	Pr/Eu	1.85	2.17	1.78	1.83	1.80	2.16	—	—	—	2.16	1.85		
	δ ppm	9.18	8.17	8.57	8.17	9.18	2.25	6.85	2.25	6.85	2.25	6.20		
	Pr(fod)3	10.43	9.61	9.23	9.61	10.43	2.55	0.96	0.37	0.96	2.55	6.66		
	Eu(fod)3	4.83	5.37	5.37	5.37	4.83	1.27	—	—	—	1.27	3.28		
	Pr/Eu	2.15	1.78	1.71	1.78	2.15	2.00	—	—	—	2.00	2.03		
	δ ppm	9.13	8.15	8.60	8.15	9.13	1.20	7.03	1.20	7.03	1.20	6.22	2.90	2.90
	Pr(fod)3	9.43	9.23	8.63	9.23	9.43	1.29	0.78	0.39	0.78	1.29	5.85	2.85	0.33
	Eu(fod)3	5.11	5.39	4.47	5.39	5.11	0.71	—	—	—	0.71	2.84	—	—
	Pr/Eu	1.85	1.71	1.93	1.71	1.85	1.82	—	—	—	1.82	1.85	—	—
	δ ppm	7.83	7.83	8.37	8.37	3.30	1.20	7.05	1.20	7.05	1.20	5.82	2.83	2.83
	Pr(fod)3	3.53	7.42	10.43	10.43	5.87	1.25	0.63	0.25	0.63	1.25	3.83	2.87	0.00
	Eu(fod)3	2.07	4.90	8.16	6.31	3.37	—	—	—	—	—	2.01	—	—
	Pr/Eu	1.70	1.51	1.28	1.65	1.74	—	—	—	—	—	1.90	—	—

McMASTER UNIVERSITY

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DEPARTMENT OF CHEMISTRY

September 11, 1973.

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

Slightly improved parameters for predicting ^{13}C chemical shifts in disubstituted benzenes.

Dear Barry:

The additivity of ^{13}C chemical shifts has been well established and documented. The following table is the result of the analysis of over 100 disubstituted benzenes and includes some of the data reported by Miyajima et al[1]. The following parameters are an averaged shift (relative to benzene), for a substituent located in a variety of environments and as a consequence have improved the predictability of chemical shifts in disubstituted benzenes.

Of the compounds analysed, over 70% of the observed chemical shifts were found to be within $\pm$ 0.5 ppm of the predicted value. As compared to the results of Miyajima et al, where shift parameters were derived directly from the monosubstituted benzenes, less than 50% were found to be within $\pm$ 0.5 ppm of the predicted value.

For simplicity, ortho substituent effects are not included.

Yours sincerely,

Brian Sayer

Brian Sayer.

[1] G. Miyajima, Y. Sasaki and M. Suzuki, Chem. Pharm. Bull. 19 (11) 2301, 1971.

Please consider this contribution from McMaster in the name of R.J. Gillespie.

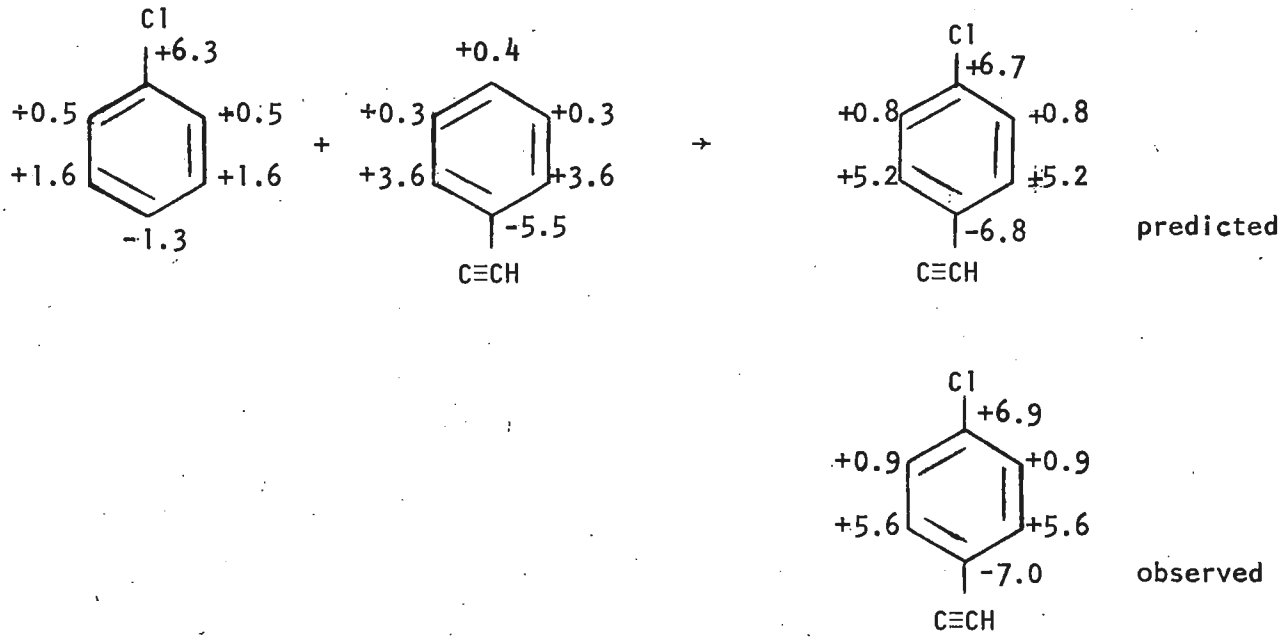
Substituent	C_1	$C_{2,6}$	$C_{3,5}$	C_4
D	- 0.3	- 0.1	(- 0.01)	0.0
F	+ 35.0	- 13.3	+ 1.9	- 4.1
Cl	+ 6.3	+ 0.5	+ 1.6	- 1.3
Br	- 5.8	+ 3.5	+ 1.9	- 0.6
* I	- 33.1	+ 9.4	+ 2.6	- 0.1
NH_2	+ 20.4	- 13.4	+ 1.6	- 10.6
NO_2	+ 20.1	- 4.7	+ 1.0	+ 6.6
* CN	- 16.0	+ 4.6	+ 1.7	+ 4.4
CH_3	+ 10.0	+ 0.8	0.0	- 2.5
OH	+ 29.5	- 12.6	+ 1.8	- 7.6
OCH_3	+ 32.2	- 14.0	+ 1.6	- 7.1
* OC_2H_5	+ 30.7	- 14.0	+ 1.0	- 7.5
CHO	+ 8.4	+ 1.3	+ 0.9	+ 5.7
* CH_2OH	+ 13.4	- 1.0	+ 0.4	- 0.8
CH_3CO	+ 9.9	+ 0.4	+ 0.4	+ 4.7
* $COOCH_3$	+ 2.6	+ 1.4	+ 0.2	+ 5.3
CCH	- 5.5	+ 3.6	+ 0.3	+ 0.4
* CF_3	+ 2.7	- 3.6	+ 0.2	+ 3.3

*Less than 5 compounds analyzed.

Positive indicates a downfield shift.

For those who are not familiar with this system, the following will serve as an example.

p Chlorophenylacetylene.



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4 October 1973

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

Dear Barry

POSITION AVAILABLE

Could I use your excellent newsletter to advertise an opening for a computer/NMR oriented man in our laboratory. We are looking for a young man with a strong computing background and interested in the experimental aspects of NMR. We are equipped with Varian XL100 and HA100 spectrometers with Fourier Transform facilities and our main interests are in biological applications of NMR. Anyone who might be interested in joining us should write to me for further details.

Many thanks for your help.

Yours sincerely

Jim Feeney

J FEENEY

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Telephone
360-2351

October 9, 1973

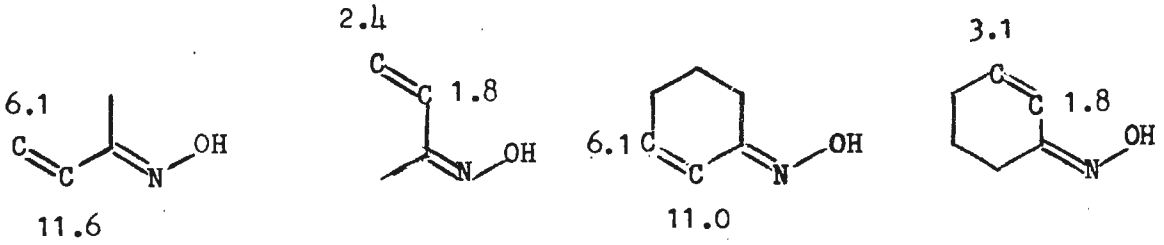
Dr. B.L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843

Title: Geometrical Dependences of Carbon-Nitrogen Coupling Constants.

Dear Barry:

With this report, please establish a subscription for me to the TAMU NMR Newsletter.

Together with Doug Dorman, we have measured ^{13}C-^{15}N coupling constants in a series of ^{15}N-enriched oximes. We were led to this study by the observation that $^{1}J_{CN}$ in enriched pyridine is almost an order of magnitude smaller than what would appear to be the electronically analogous benzalmethylamine,[1] which suggested that the one-bond coupling might be dependent on geometry and/or lone-pair orientation. The latter factor is well known to influence N-H,[2] P-H,[3] and P-C[3] couplings. Our preliminary results (see Table) show indeed that $^{1}J_{CN}$ does depend on geometry provided there is a sufficiently large presumably electronic difference in the two carbon substituents. Furthermore, $^{2}J_{CN}$ and $^{3}J_{CN}$ are enhanced by proximity of the carbon to the lone pair, as is seen by comparing the oxime isomers of 2-cyclohexenone and methyl vinyl ketone



Using finite perturbation theory in the INDO approximation, and assuming only a Fermi contact mechanism, Dr. Rod Wasylishen at NIH has calculated some representative values of J_{CN}. While these show poor numerical agree-

Dr. B.L. Shapiro October 9, 1973

ment with the experimental values, experimental trends are reproduced. Thus, the large change induced in $^{1}J_{CN}$ of pyridine upon protonation is apparent, and a negative sign calculated for $^{2}J_{CN}$ in syn-acetaldoxime is consistent with positive contributions of the lone-pair to reduced coupling constants in phosphorus[4] and nitrogen[5] systems. We feel that the numerical deviations may be attributed either to inadequate parametrization or to contributions from other spin-coupling mechanisms. These results have been discussed in more detail in a manuscript submitted for publication, and we are continuing further studies along these lines.

Cordially,

Bob

Robert L. Lichter
Assistant Professor

RLL:vg

(1) R.L. Lichter and J.D. Roberts, J. Amer. Chem. Soc., 93, 5218(1971)

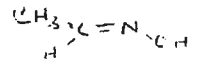
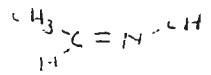
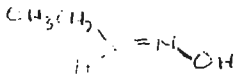
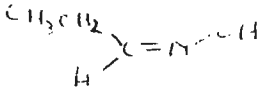
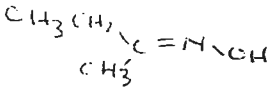
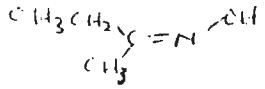
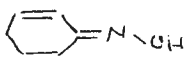
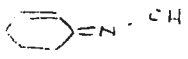
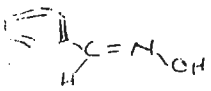
(2) J.P. Kintzinger and J.M. Lehn, Chem. Commun., 680(1967) and other papers by these authors.

(3) G.A. Gray and S.E. Cremer, J. Org. Chem., 37, 3470(1972) and references therein.

(4) M.P. Simonnin, R.M. Lequan, and F.W. Wehrli, J. Chem. Soc., Chem. Commun., 1204(1972); S. Sorensen, R.S. Hansen, and H.J. Jakobsen, J. Amer. Chem. Soc., 94, 5900(1972).

(5) W.B. Jennings, D.R. Boyd, C.G. Watson, E.D. Becker, R.B. Bradley, and D.M. Jerina, ibid., 94, 8501(1972).

Table. Carbon-13 - Nitrogen-15 Coupling Constants in Oximes

Compound	$^{1}J_{CN}$, Hz	$^{2}J_{CN}$, Hz	$^{3}J_{CN}$, Hz	$^{5}J_{CN}$, Hz
	4.0	9.0		
	2.3	1.8		
	2.4	7.3		
	1.6	1.4		
	3.6	O(CH_3) 10.5(CH_2)		
	3.4	11.1(CH_3) 1.8(CH_2)		
	5.0	11.0(=CH) 1.4(CH_2)	6.1(=CH)	
	4.0	1.8(=CH) 2.4(CH_2)	3.1(=CH)	
	4.8	7.3	2.8	0.8

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
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October 10, 1973

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

Dear Barry:

I was very much interested in the letter from Jeremy Musher (TAMUNMR 180-31). I would like to have more information as to the composition of the material that was in the nmr tube as well as its proton nmr spectrum. My main purpose in writing, however, is to point out that the parameters given (J = 80 Hz, δ = 480 Hz) will produce, not an A_2X_4 spectrum, but an A_2B_4 spectrum with pronounced second order splittings. The enclosure gives calculated "stick" plots using the parameters given, and it is apparent that the quintet, particularly, is hardly recognizable. The obvious inference is that the two fluorine spectra given by Dr. Musher do not arise from coupled sets of nuclei. The splitting of 80 Hz is only slightly larger than Dr. Brinckman and I have found in a series of XWF_5 compounds, so it is plausible that here, too, it is an F-W-F coupling. It may be that two (or more) W-F compounds are present, and that the connected spectra are in another region of the fluorine chemical shift range. We have generally found in $X\text{-}WF_5$ compounds that the axial fluorine signal is several thousand Hz (at 56 MHz) upfield from the equatorial fluorine, and much weaker as well. Perhaps speculation as to the molecule responsible for the spectrum (or spectra) should at least be deferred until the nuclear spin system is better characterized.

Yours very truly,

Rolf

Rolf B. Johannesen
Inorganic Chemistry Section

Enclosures

A_2B_4 Spectrum B Lines

J = 80. Hz . δ = 486 Hz.

3.6 Hz / line Max. intensity 100.

```
657.700   (   0) .
661.300   (   1) .XXXXXXXX
664.900   (   0) .
668.500   (   0) .
672.100   (   0) .
675.700   (   1) .XXXXXXXXXXXXX
679.300   (   0) .
682.900   (   1) .XXXXXXXXXXXXX
686.500   (   0) .
690.100   (   1) .XXXXXXXXXXXXXX
693.700   (   1) .XXXXXXXXXXXXXX
697.300   (   0) .
700.900   (   0) .
704.500   (   1) .XXXXXXXXXX
708.100   (   0) .
711.700   (   0) .
715.300   (   0) .
718.900   (   0) .
722.500   (   0) .
726.100   (   0) .
729.700   (   0) .
733.300   (   0) .
736.900   (   0) .
740.500   (   1) .XXXXXXXXXX
744.100   (   0) .
747.700   (   0) .
751.300   (   1) .XXXXXXXXXXXXXXXXX
754.900   (   0) .
758.500   (   1) .XXXXXXXXXXXXXXXXX
762.100   (   2) .XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
765.700   (   1) .XXXXXXXXXXXX
769.300   (   6) .XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
772.900   (   0) .
776.500   (   0) .
780.100   (   0) .
783.700   (   0) .
787.300   (   0) .
790.900   (   0) .
794.500   (   0) .
798.100   (   0) .
801.700   (   0) .
805.300   (   0) .
808.900   (   0) .
812.500   (   0) .
816.100   (   0) .
819.700   (   0) .
823.300   (   0) .
826.900   (   1) .XXXXXXXXXXXXXXXX
830.500   (   0) .
834.100   (   1) .XXXXXXXXXXXXXXXXXXXXXXXX
837.700   (   1) .XXXXXXXXXXXXXXXXXXXXXXXXX
841.300   (   1) .XXXXXXXXXXXXXXXXXXXXXXXXXX
844.900   (   0) .
848.500   (   1) .XXXXXXXXXXXXXXXXXXXXXXXXXXX
852.100   (   0) .
855.700   (   1) .XXXXXXXXXXXXXXXXXXX
859.300   (   0) .
```

```
1097.500
1102.500  (  0) .
1107.700  (  0) .
1112.900  (  0) .
1118.100  (  1) .XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
1123.300  (  0) .
1128.500  (  0) .
1133.700  (  0) .
1138.900  (  0) .
1144.100  (  0) .
1149.300  (  0) .
1154.500  (  0) .
1159.700  (  0) .
1164.900  (  0) .
1170.100  (  1) .XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
1175.300  (  0) .
1180.500  (  1) .XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
1185.700  (  0) .
1190.900  (  0) .
1196.100  (  0) .
1201.300  (  1) .XXXXXXXXXXXXXXXXXXXXXXXXXXX
1206.500  (  0) .
1211.700  (  0) .
1216.900  (  1) .XXXXXXXXXXXXXXXXXXXXXXXX
1222.100  (  0) .
1227.300  (  0) .
1232.500  (  0) .
1237.700  (  0) .
1242.900  (  0) .
1248.100  (  2) .XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
1253.300  (  0) .
1258.500  (  1) .XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
1263.700  (  0) .
1268.900  (  1) .XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
1274.100  (  1) .XXXXXXXXXXXXXXXXXXXX
1279.300  (  0) .
1284.500  (  0) .
1289.700  (  0) .
1294.900  (  0) .
1300.100  (  1) .XXXXXXXXXXXXXXXXX
1305.300  (  0) .
1310.500  (  0) .
1315.700  (  0) .
1320.900  (  0) .
1326.100  (  1) .XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
1331.300  (  0) .
1336.500  (  0) .
1341.700  (  1) .XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
1346.900  (  1) .XXXXXXXXXXXXXXXX
1352.100  (  0) .
1357.300  (  0) .
1362.500  (  0) .
1367.700  (  1) .XXXXXXXXXXXXXX
1372.900  (  0) .
1378.100  (  0) .
1383.300  (  0) .
1388.500  (  0) .
1393.700  (  0) .
1398.900  (  0) .
1404.100  (  0) .
1409.300  (  1) .XXXXXXXXXXXXX
1414.500  (  0) .
1419.700  (  0) .
1424.900  (  0) .
1430.100  (  1)  XXXXXXXXXXXX
```

A_2B_4 Spectrum   A Lines

J = 80. Hz   δ = 480. Hz

5.2 Hz/line   Max. Intensity 26.5

TEXAS CHRISTIAN UNIVERSITY
Fort Worth, Texas 76129

Department of Chemistry

October 12, 1973

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

Dear Barry:

Gil Persyn (Praxis Corp., 5420 Jackwood, San Antonio, 78238) stopped by yesterday to discuss a new model pulse spectrometer. For the past year we have enjoyed using a Praxis PR-102R nmr and have included the measurements of T_1 and T_2 in the undergraduate physical chemistry lab. Dean Sherry at UT Dallas has been measuring protein interactions and also lanthanide hydration numbers with theirs.

The little table unit has 90°, 90°-90°, 90°-180°, 180°, and 180°-90° pulse functions. The magnetic weights 5 lbs. and accepts 10 mm sample tubes. The rf unit operates at 10 mHz.

We have found a surprising list of analytical tasks which can be tackled by pulse nmr, and when Gil mentioned that they had several units available for academic institutions at $2,800 (about the cost of the electronics) I thought it worth a mention to the community.

Best regards,

Bill

W. B. Smith
Chairman
Department of Chemistry

WBS/dc

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^{13}C

CARBON 13

Acetates
Iodides
Cyanides
Glycine
Acetylene
Benzene-(ul)
Carbon Tetrachloride

(partial list only)

^{15}N

NITROGEN 15

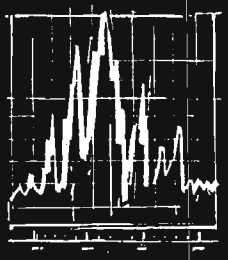
Ammonium Chloride
Nitrogen Gas
Urea
Sodium Nitrate
Aspartic Acid
Glycine

(partial list only)

LABELED BIOCHEMICALS

D-Glucose-(ul)-^{13}C
Thymine-^{13}C
Amino Acid Mixture -(ul)-D or ^{13}C
Sugar Mixture -(ul)-D or ^{13}C
Glycine-D or ^{13}C
Acetates-D or ^{13}C
L-Methionine-D or ^{13}C
L-Aspartic Acid-^{15}N

(partial list only)



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The University of Liverpool

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

16th October, 1973.

Dear Professor Shapiro,

$^{13}C - \{^{19}F\}$ NOE's

In a recent publication[1] from this laboratory on the ^{13}C nmr spectra of some fluorocarbons employing ^{19}F noise decoupling, a "significant" $^{13}C - \{^{19}F\}$ nuclear Overhauser enhancement (NOE) was reported. I have now put this comment on a more quantitative basis by measuring spin-lattice relaxation times and $^{13}C - \{^{19}F\}$ NOE factors for a few simple fluorocarbons, and the data on hexafluorobenzene is presented herein.

The measurements were made on our XL-100/15^{FT} and the "dynamic Overhauser enhancement" (DOE) technique[2] was used to measure the NOE factors as this has the advantages of rapidity (the undecoupled ^{13}C spectrum of C_6F_6 is <u>very</u> complex) and that it simultaneously provides a value for T1 which can be checked by other methods (e,g. progressive saturation[3] - PS). For the DOE method, the transient (^{13}C) signal intensity (St) is measured as a function of time (t) after switching on the (^{19}F) noise decoupler (see Figure A).

$$\ln (Soo - St) = \frac{-t}{T1} + \ln (Soo - So)$$

The NOE factor $(1+\eta)$ determined from the two points at t = 0 sec. and t = 180 sec. is 2.68 (Figure B). From the full plot (Figure C) we obtain $1+\eta = 2.75$ and T1 = 33.6 sec. (cf. progressive

saturation yielded T1 = 36 ± 2 sec. from several determinations). The maximum possible $1 + \eta$ is 2.87. Our values refer to a neat sample, degassed by freeze-pump-thaw and sealed in a 5 mm tube. A sample (12 mm tube) degassed by passage of N_2 for several minutes showed T1 = 25.6 ± 1 sec., $1 + \eta$ = 2.30 ± 0.2 (by DOE) and T1 = 27.8 ± 2 sec. (by PS). On C_6F_6 at least, careful degassing produced a significant result.

The DOE technique on C_6F_6, where good signal to noise is possible on a single transient, may be performed by manual switching of the decoupler. However, the results obtained here were from a computer controlled experiment made possible by a slight modification to the Varian 8K FT programme, thus enabling accumulation of spectra (Figure B).

Please credit this contribution to the account of Dr. R.J. Abraham.

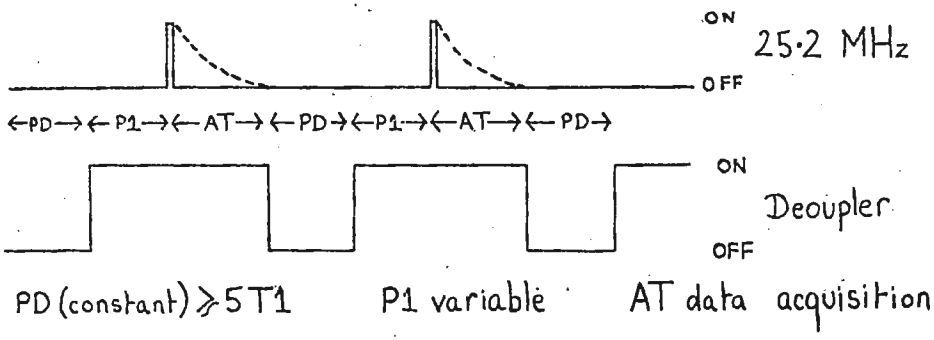
Yours sincerely,

G.E. Hawkes

G.E. Hawkes.

1) R.J. Abraham, D.F. Wileman, G.R. Bedford, and D. Greatbanks, J. Chem. Soc., Perkin II, 1733, (1972).
2) K.F. Kuhlmann, and D.M. Grant, J. Chem. Phys., 55, 2998 (1971).
3) R. Freeman, and H.D.W. Hill, J. Chem. Phys., 54, 3367, (1971).

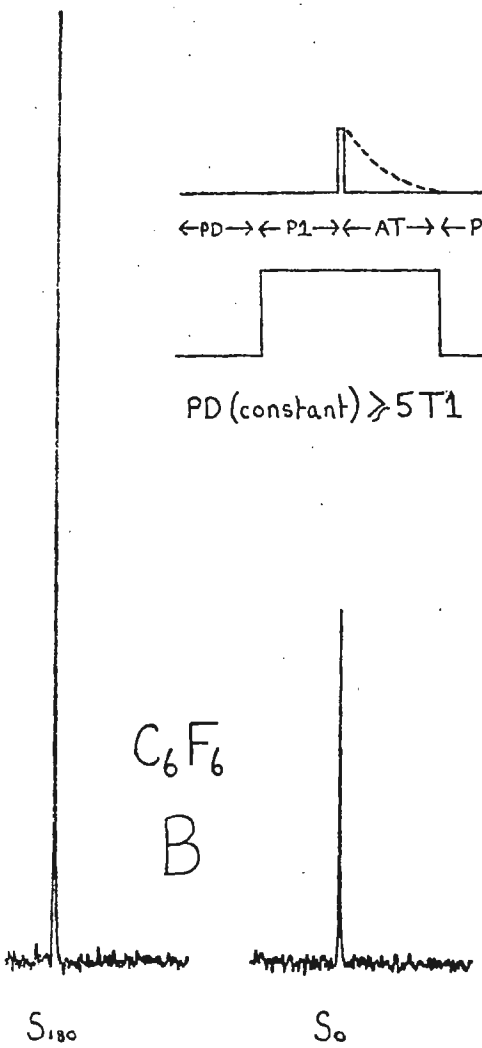
A

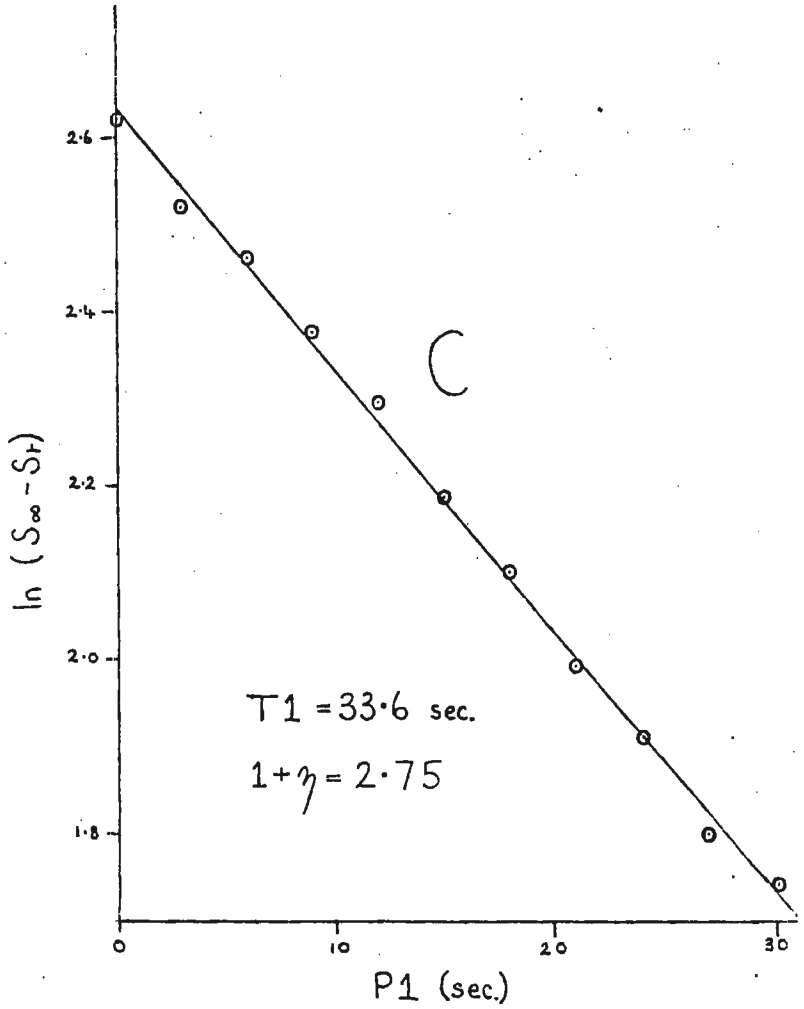


PD (constant) ≥ 5T1 P1 variable AT data acquisition

C_6F_6

B





182-2

182-22
CHEMISCHES LABORATORIUM
DER UNIVERSITÄT MÜNCHEN
INSTITUT FÜR ORGANISCHE CHEMIE

8000 MÜNCHEN 2, 15.10.1973
Karlstr. 23 - Tel. 59021

Manfred Christl

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

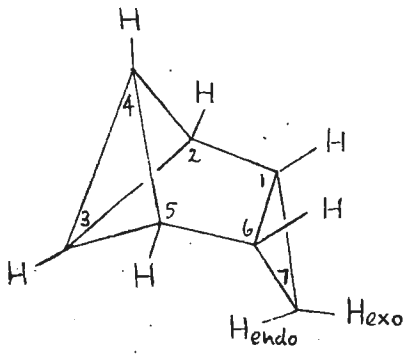
Suggested Title: ^{1}H-NMR-Parameters of Tetracyclo[4.1.0.0$^{2.4}$.0$^{3.5}$]-heptane

Dear Dr. Shapiro:

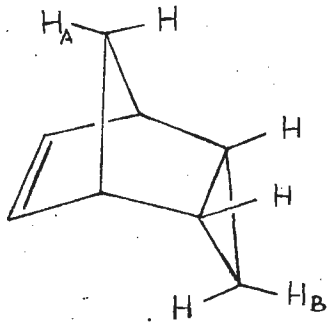
Recently we have synthesized a new isomer of cycloheptatriene, namely tetracyclo[4.1.0.0$^{2.4}$.0$^{3.5}$]heptane (1), which has an interesting ^{1}H-NMR-spectrum (see figure). Even when run only at 60 MHz this spectrum can be solved on a first order basis at least in a rough approximation. The multiplets are tentatively assigned to the different protons as shown in the figure. The most uncertain interpretation is that of the resonances of H-3 and H-4, which may possibly have to be interchanged. But that does not have any influence on the conclusion drawn later on. The following coupling constants (in Hz) have been extracted (from a more expanded and better resolved spectrum than that of the figure):

$J_{1.2} = J_{5.6} = 1.0$	$J_{1.7endo} = J_{6.7endo} = 3.3$	$J_{3.4} = 9.7$
$J_{1.3} = J_{3.6} = 0.7$	$J_{1.7exo} = J_{6.7exo} = 6.4$	$J_{4.7exo} = 2.4$
$J_{2.3} = J_{3.5} = 2.7$	$J_{2.7endo} = J_{5.7endo} = 0.4$	$J_{7endo.7exo} = 4.4$
	$J_{2.4} = J_{4.5} = 1.0$	

Further couplings either do not show up in the spectrum for reasons of symmetry, although they are expected to be in the range of 4 to 7 Hz, ($J_{1.6}$ and $J_{2.5}$) or they are below the resolution of our HA 60 IL spectrometer.



1



2

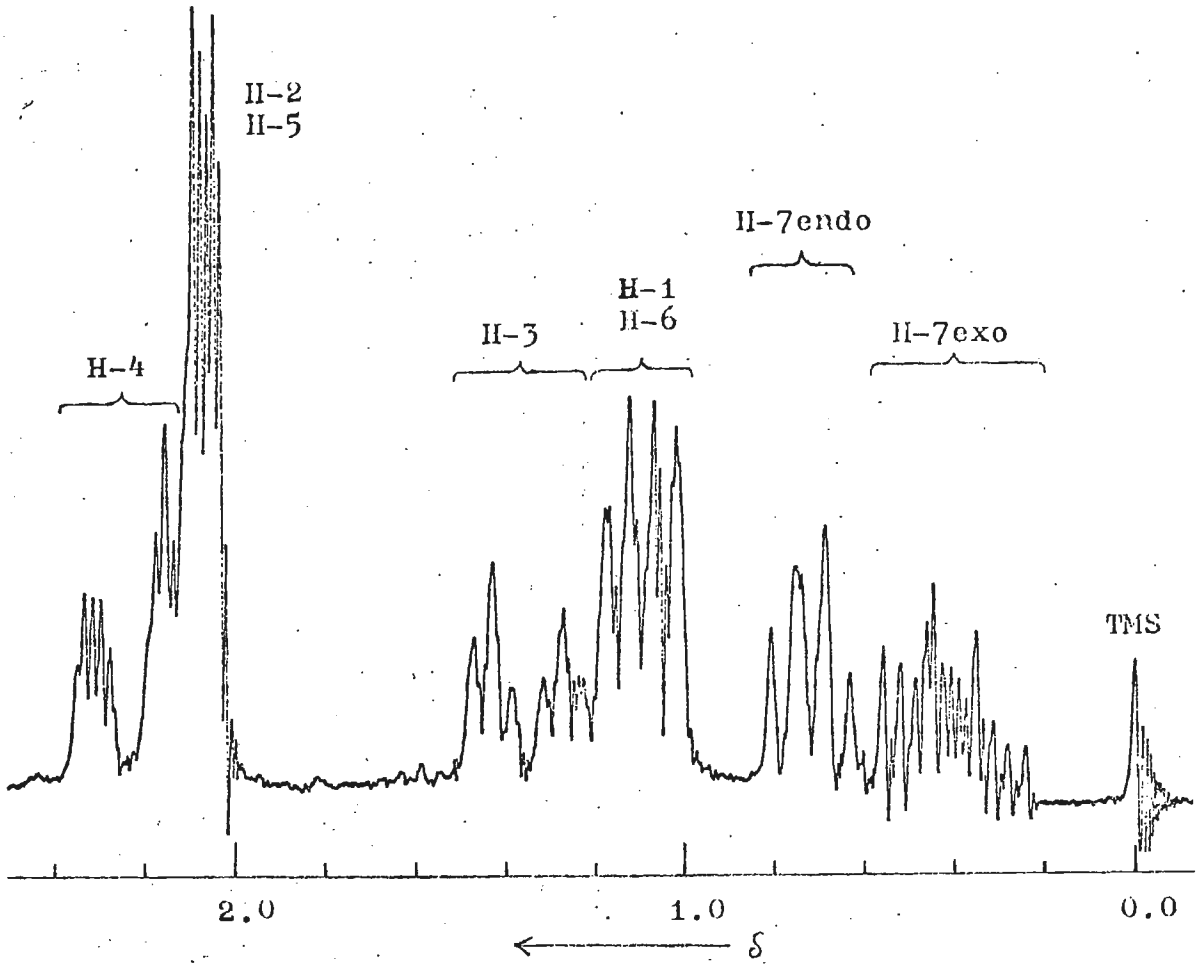


Figure: ^{1}H-NMR-spectrum of 1 in benzene solution at 60 MHz.

The most interesting feature is the $^5J_{4.7exo}$, which has been confirmed by decoupling of H-4. This long range coupling is propagated by σ bonds exclusively. An interaction of this type has also been found in 2 [1], whose coupling constant $J_{A.B}$ is nearly of the same size (2.3 Hz) as in 1. Being arranged in a perfect zigzag, the σ bonds between H_A and H_B in 2 fulfill the steric condition considered to be necessary for the existence of longrange couplings of this order of magnitude [1,2]. However, in 1 the bond between C-4 and H-4 does not fit into the zigzag path as can be seen clearly by a comparison of 1 and 2. Just in the same way the σ bonds propagating $^4J_{1.3}$ and $^4J_{3.6}$ form no zigzag (or M path). Possibly the rules concerning the arrangement of σ bonds have to be modified if a bicyclobutane frame is involved.

Sincerely yours,

Manfred Christl

P.S.: Please credit this contribution to the subscription of Gerhard Binsch.

1.) K.Tori and M.Ohtsuru, Chem.Commun. 1966, 886.

2.) S.Sternhell, Quart.Rev. 23, 236 (1969).

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LONDON E.1
Tel. 01-980 4811

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

11th October 1973

Dear Professor Shapiro,

^{15}N NMR of a Naturally Occuring Peptide

Please credit this contribution to Ed Randall's Group.

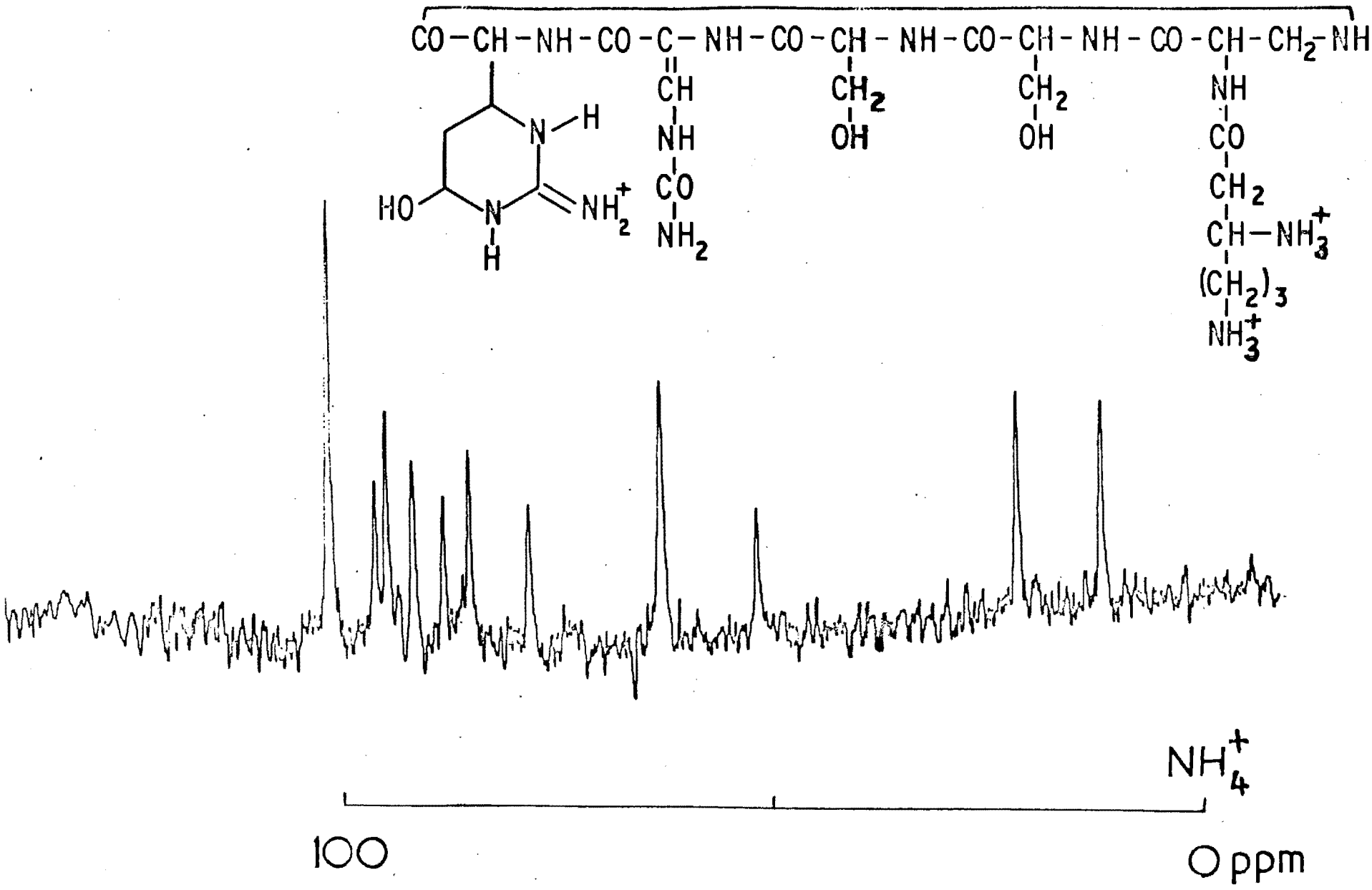
In order to extend the scope of our ^{15}N natural abundance work we have been using 13mm sample tubes instead of the usual 10mm tubes used previously. Natural abundance measurements will be of the greatest advantage where isotopically enriched samples are difficult to obtain.

The figure shows a proton decoupled spectrum of a 0.9M aqueous solution of viomycin sulphate, a bacterially produced antibiotic substance. This spectrum was obtained in about 20 hours using our Bruker HFX 13 spectrometer in the FT mode of operation. We have not yet had time to investigate the effect of variation of pulse angle, or concentration, or pH effects, but as it stands, we have only resolved 11 out of a possible 13 peaks. The linewidths result from viscosity or exchange effects rather than field inhomogeneity, since other 13mm samples give much narrower lines. I hope this preliminary result indicates the potential of natural abundance ^{15}N measurements.

Yours sincerely,

Les Farnell

Dr. L.F.Farnell.


NH4+
100
0 ppm

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Tel. 0241/422-2770

Herrn
Prof. Dr. L. Shapiro
Department of Chemistry
Texas A u. M. University
College Station
T e x a s 77843 / USA

Dear Barry:
Subject: Mobility of CH_3-Groups
- Some like it very cold -

In the last years data of NMR-measurements have been published of a temperature region down to the temperature of liquid helium. These measurements are often interpreted by a tunneling movement of the protons. We are interested in the tunneling rotation of CH_3-groups. Continuing the wide-line experiments published by R. Kosfeld and U.v. Mylius (1) we measured the spin lattice relaxation time T_1 of polyisobutylene (PIB) and polycarbonate (PC) in a temperature region from 280 K down to 4,5K. For both materials we find a high-temperature and a low temperature minimum as well. The high temperature minimum is due to the classic rotation of the CH_3-groups. The low temperature minimum is interpreted by a tunneling-rotation of the methyl-groups. Measurements of the high temperature region are published by some authors (2,3). There for fig 1 shows only the low temperature region. By means of the BPP theory we computed the activation energy of the classic rotation of the CH_3-groups

PIB $\Delta E = 7,1$ kJ/mol
PC $\Delta E = 8,8$ kJ/mol

These values are too small because the T_1 minimum occurs at relative high temperature. With regard to other autors (2,3) we estimate that for both materials the activation energy is about 1,5 kJ/mol.
There are few tunneling theroies describing low temperature T_1 measurements. The difficulty of this theory is to consider the transition from a pure quantum-mechanical to a thermally activated movement. In the theory of Clough (4) these circumstances are dealt with. His quantum mechanical description of the methyl group movement regards the interaction between the CH_3-group and the lattice.

By this he can compute the transition propabilites of"the energy Eigenwerte" and introduce a parameter p that describes the influence of the lattice on the CH_3 group. p is connected with the temperature by the equation

$$p^{-1} = p_{\infty}^{-1} \cdot e^{\frac{\Delta E_p}{kT}}$$

Other parameters of Clough's theory are the tunnel frequency ω_t and the classical correlation time τ. Fitting our measurements with this theory we find for PC

E_p = 96 J/mol

ω_t = 25 MHz

and for PIB

E_p = 125 J/mol

ω_t = 2o,3 MHz

A detailed paper will be published.

(1) R. Kosfeld, U.v. Mylius
Kolloid-Z. u. Z. Polymere 25o, 1o81 (1972)

(2) W.P. Slichter J. Polymer.Sci. Part C Nr. 14, 33 (1966)

(3) D. Mc. Call, D.R. Falcone Physics Letters 14, 262 (1969)

(4) S. Clough J. Phys. C: Solid St. Phys. 4, 218o (1971)

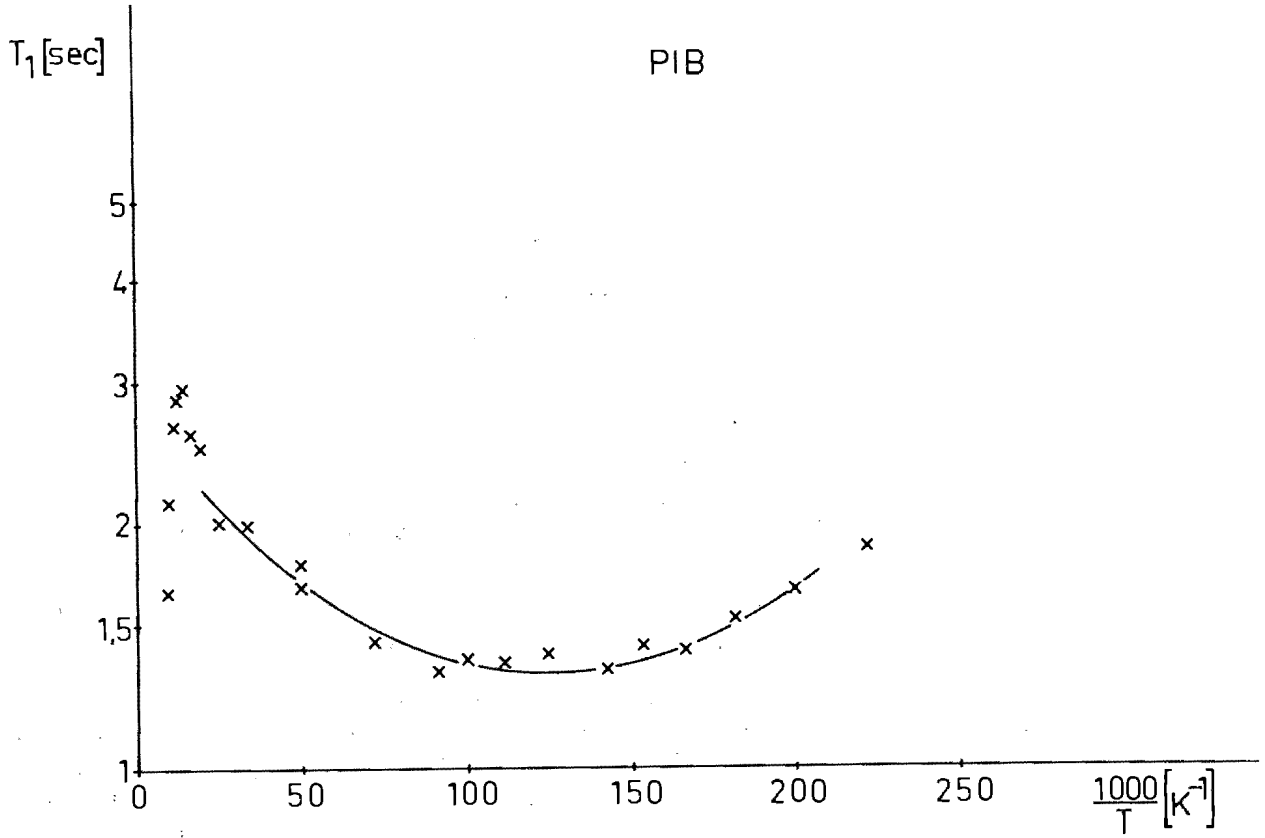
With sincerely yours

B. Lammel

B. Lammel

R. Kosfeld

Kosfeld


T1 [sec]
PIB
5
4
3
2
1,5
1
0
50
100
150
200
250
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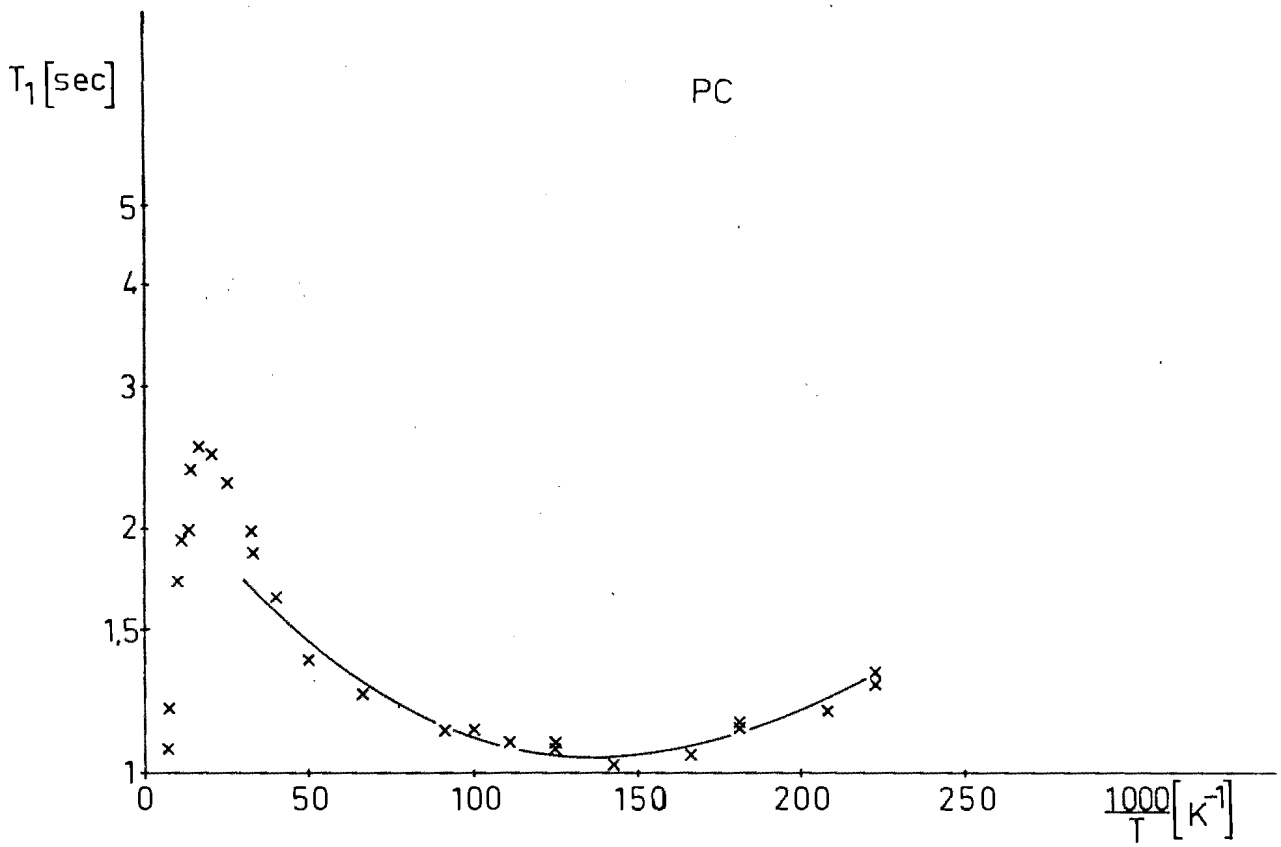
T1 [sec]
PC
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CHIMIE ORGANIQUE PHYSIQUE

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Intrinsic error in the determination of activation parameters from line shape analysis

Cher BARRY,

Etant toujours préoccupés par la précision des paramètres cinétiques déterminés par analyse des formes de raies, nous avons tenté de matérialiser le problème par des chiffres !

La précision dépend en fait de deux types d'erreurs. Le cas des erreurs liées au processus chimique (solvant, concentration, encombrement stérique, etc...) a été discuté dans la littérature (par exemple : I.O. Sutherland Annual Reports in NMR Spectroscopy vol. 4, Acad. Press 1971). Un autre type d'erreur provient de l'imprécision avec laquelle on peut mesurer les durées de vie τ et les températures T et l'erreur sur l'énergie d'activation Ea (ou l'enthalpie libre d'activation ΔH^*) peut être estimée par différenciation de l'équation d'Arrhénius (S.W. BENSON The Foundations of Chemical Kinetics, Mc Graw Hill 1960). G. BINSCH a déjà attiré l'attention sur cette question du point de vue R.M.N. (TAMU, 1972, 160, 45). En fait, les énergies d'activation (Ea ou ΔH^*) sont obtenues à partir d'une pente de droite déterminée par la méthode des moindres carrés en fonction de τ et T et un traitement statistique de l'erreur est bien approprié. Nous avons ainsi calculé par les formules statistiques classiques et au moyen d'un programme écrit pour IBM 1130, la précision accessible pour les paramètres d'activation en fonction des erreurs $d\tau/\tau$ (en %) et dT (en degrés), sur un exemple type de rotation empêchée autour d'une liaison $\rangle C{=\!=}N \langle$

Ea $\simeq$ 14,9 Kcal.mole^{-1} $\quad \Delta H^* \simeq$ 14,2 Kcal.mole^{-1} $\quad \tau_c \simeq$ 0,025 s

Log A $\simeq$ 10 s^{-1} $\quad \Delta S^* \simeq$ -15 u.e. $\quad T_c \simeq$ 390°K

$d\tau/\tau$	dT	$\pm$ d ΔH^*, dEa	$\pm$ d ΔS^*	dLog A
5 %	0,5	0,6	1,6	0,3
	1,0	0,8	2,2	0,45
	1,5	1,0	2,8	0,6
10 %	0,5	1,0	2,6	0,6
	1,0	1,2	3,2	0,7
	1,5	1,4	3,8	0,8
15 %	0,5	1,3	3,7	0,8
	1,0	1,6	4,2	0,9
	1,5	1,8	4,8	1,05

TABLEAU 1

(n = 8 $\quad \Delta T$ = 47°)

En fait, les valeurs de τ mesurées dépendent de la précision avec laquelle on peut maintenir la sonde du spectrographe à une valeur fixe. Dans l'exemple présent (T = 300 à 400°K) une régulation de la température à ± 0,5 - 1,0 - 1,5° entraine une imprécision sur τ de 5 % - 10 % - 15 % car on a sensiblement $\frac{d\tau}{\tau} \simeq 35 \frac{dT}{T}$ (réaction monomoléculaire Ces erreurs doivent être ajoutées à celles qui proviennent de l'ajustage (manuel ou automatique) des valeurs théoriques et expérimentales, de l'imprécision sur $\Delta\delta_\infty$, T_2^* etc...

Il faut aussi souligner que la précision accessible sur une pente de droite est fonction du nombre de points d'échantillonage n et de l'intervalle de température étudié ΔT.

$\Delta T(°K)$	n	dEa, d ΔH^*	d ΔS^*
47°	6	1,8	4,8
	8	1,65	4,2
	12	1,4	3,8
57°	6	1,4	4,0
	8	1,2	3,4
	12	1,1	3,1

TABLEAU 2 -

($d\tau/\tau$ = 15 % dT = 1,5°)

Habituellement, la R.M.N. dynamique ne permet donc pas d'obtenir des énergies d'activation expérimentales avec une précision supérieure à ± 15 % et la précision sur le terme preexponentiel ne dépasse pas ± 2 unités logarithmiques. Les erreurs réelles sont sans doute supérieures, spécialement dans le cas des faibles valeurs de Ea. Les corrélations structurales d'enthalpies d'activation n'ont donc souvent qu'une valeur relative . Dans de nombreux cas, les mesures entropiques ne permettent guère de fixer que le sens de variation de ΔS^* (ou de log A) et n'ont qu'une valeur statistique relative.

Veuillez nous excuser de revenir, avec pessimisme, sur un vieux problème, mais en cas d'urgence (lettre bleue!) l'ordinateur est d'un excellent secours !.

Bien amicalement.

G.J. MARTIN D. LE BOTLAN M.L. FILLEUX

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department of chemistry

October 23, 1973

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

Titles: Metal Nuclide NMR, ^{199}Hg

Dear Barry:

Since our last contribution to the newsletter we have been using most of our nmr spectrometer* time on metal nuclides (e.g., ^{207}Pb, ^{199}Hg, ^{113}Cd, ^{43}Ca and ^{25}Mg). The techniques that we've been employing are essentially those FT methods that we described at the Boulder ENC, although we've had considerably more experience with ^{25}Mg and ^{43}Ca since then.

As would be expected, the chemical shift ranges of the heavy metal nuclides are huge, whereas those of the light metal nuclides are rather small. Larry Simeral's work indicates that linewidth will be the primarily useful probe in applications of ^{25}Mg and ^{43}Ca nmr in chemical studies. Our work with ^{25}Mg has so far been done with natural abundance samples, whereas enriched materials are usually employed in the ^{43}Ca work.

As an indication of the high sensitivity of heavy-metal nuclide chemical shifts to relatively minor structural changes, some of Marie Borzo's data on the ^{199}Hg chemical shifts of bis para-substituted phenylmercury compounds may be of interest to some of your readers. The values are, for the indicated para substituents: CH_3O, 86.7; CH_3, 45.5; F, 4.3; Cl, -23.9, all in ppm with respect to $(C_6H_5)_2Hg$ (positive values correspond to lower shielding).

Sincerely,

Gary E. Maciel
Professor

* We are also having an affair now with an icr spectrometer.

GEM/rlf

CALIFORNIA INSTITUTE OF TECHNOLOGY

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DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING
GATES AND CRELLIN LABORATORIES OF CHEMISTRY

JOHN D. ROBERTS
INSTITUTE PROFESSOR OF CHEMISTRY

October 16, 1973

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

^{13}C T_1 Measurements on Dioxane–D_2O Solutions

Dear Barry,

For several months now we have devoted a lot of time and effort to the study of ^{13}C spin-lattice relaxation times under a variety of experimental conditions, such as pD, concentration and temperature, of D_2O solutions at 15.09 MHz using the PFT "Brukarian" spectrometer, and the progressive saturation technique of Freeman.[1]

It did not take long to realize that the T_1 dependencies of model systems were needed to establish standards on which to base the results. One such system was acetic acid for which the literature contains a variety of carboxyl carbon T_1 values, all reportedly obtained on degassed samples under essentially the same conditions.[2] From our studies of this system, it appears that while dissolved oxygen may play an important role in determining T_1, it alone cannot account for variable results. Farrar has recently commented on the oxygen effect on acetic acid, which suggests a contribution of about 40 sec.[2a] In trying to establish a more complete explanation, we have found that for carboxyl carbon T_1 values of ≤ 50 sec for D_2O solutions of amino acids no change in T_1 is noted upon degassing.

To establish a standard for our T_1 studies, we have determined the dioxane ^{13}C T_1 value for a range of concentrations of dioxane in D_2O. The dioxane–water is particularly advantageous to study because of its good signal-to-noise, the dominance of the dipole-dipole mechanism, and the absence of any detectable contribution to T_1 from dissolved oxygen.

The T_1 values for dioxane–water mixtures were evaluated by cutting and weighing the expanded peaks from the progressive saturation experiment. The ratio of pulse intervals b/a was chosen to equal four with a ratio of peak areas $0.65 \geq S_a/S_b \geq 0.52$ and a sweep width of 200 Hz. For each concentration of dioxane, three or more runs were made and the cutting and weighing of peaks carried out for each run by two people. The averages and deviations indicate that the resulting T_1's are probably better than $\pm 5\%$.

If the measured T_1's are multiplied by the viscosity[3] for a particular dioxane concentration and the result plotted against dioxane concentration, a near-

linear dependence, with non-zero slope, is observed. Because the dioxane ^{13}C T_1's range from 6 sec to 13 sec depending on dioxane concentration, it is apparent that the macroscopic viscosity cannot itself explain the concentration dependence. Rather, this concentration dependence may be due to intermolecular dipole-dipole interactions, contributions from other relaxation mechanisms (e. g., spin rotation), or, most likely, from changes in rotational correlations times, τ_C, which are not reflected in changes in macroscopic viscosities.[4]

For a 2:3 (v/v) solution of dioxane in D_2O, we find a ^{13}C T_1 value of 7.8 ± .8 sec at 15.09 MHz, 30° C, — this is a convenient value to measure, and we would like to see how closely others interested can check it.

With all good wishes,

Very truly yours,

Ian M. Armitage

Harry Pearson

Harry Pearson

H. Huber

Hanspeter Huber

Jach

John D. Roberts

References:

(1) Ray Freeman, H. D. W. Hill, and R. Kaptein, J. Mag. Res., 7, 82 (1972).

(2) (a) T. C. Farrar, S. J. Druck, R. Shoup, and E. D. Becker, J. Amer. Chem. Soc., 94, 699 (1972); (b) A. Olivson, E. Lippmaa, and J. Past, Est. NSV Tead. Akad. Toim. Fuus.-Mat., 16, 390 (1967); (c) T. D. Alger, D. M. Grant, and J. R. Lyerla, Jr., J. Phys. Chem., 75, 2539 (1971).

(3) Jean Timmermans in "The Physico-Chemical Constants of Binary Systems in Concentrated Solutions", Vol. 4, p. 14, Interscience Publishers, Inc., New York, 1960.

(4) I. M. Armitage, H. Huber, H. Pearson, and J. D. Roberts, full paper in preparation.

SYNTEX RESEARCH DIVISION OF SYNTEX CORPORATION, STANFORD INDUSTRIAL PARK, PALO ALTO, CALIFORNIA 94304.

182-36

19 October 1973

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

"Absolute configuration of Naproxen"

Dear Barry:

Most of the numerous literature examples of the determination of absolute configuration through the use of chiral shift reagents are concerned with compounds in which the coordinating atom is bound directly to the chiral carbon. Recently we were required to determine the absolute configuration of Naproxen[1] (1), (+)-2-(6-methoxy-2-naphthyl) propionic acid in which the potential coordinating atom is one carbon removed from the chiral center.

Naproxen was degraded in several steps to (-)-2-phenyl-1-propanol (2) which is known[2] to have S chirality. However, the rotation of 2 is only 7^{o} and additional proof of configuration was desirable. This was obtained by measuring the ^{1}H nmr spectra of (+) and (-) 2 in the presence of tris[3-(trifluoromethylhydroxymethylene)-d-camphorato]europium (3). The spectrum of (±)2 measured in $CDCl_3$ with 0.52 equivalents of 3 contains two doublets at 10.28 and 10.43 ppm which are assigned to the ortho protons of the phenyl group.

The doublet at 10.43 ppm was shown to be due to the (-) antipode by addition of a small amount of authentic (-)2. The spectrum of 2 derived from Naproxen showed only one doublet at 10.48 ppm when measured in the presence of 0.67 equivalents of 3 and this was shown to be (-)2 by addition of authentic material.

Line broadening or insufficient separation of the signals from the two antipodes prevented the use of signals from the propanol portion of the molecule being used for this determination. However, this technique may well be useful for other molecules in which the chiral center is remote from the site of coordination.

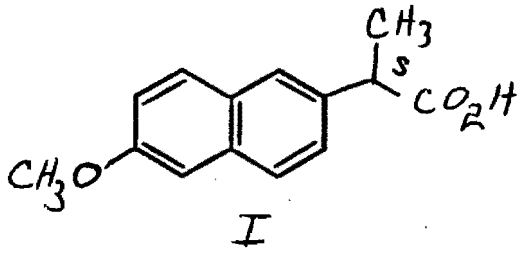
Sincerely yours,

Michael L. Maddox, Ph.D.

MLM:lo

1. I. T. Harrison, B. Lewis, P. Nelson, W. Rooks, A. Roszkowski, A. Tomolonis, and J. H. Fried. J. Med. Chem., 13 203 (1970)

2. M. B. Watson and G. W. Youngson J. Chem. Soc. Perkin I 1597 (1972)



I

Technische Hogeschool Delft

Laboratorium voor Technische Natuurkunde

Prof.Dr. B.L. Shapiro
Department of Chemistry
Texas A and M University
Texas 77843
U.S.A.

Uw kenmerk	Uw brief van	Ons kenmerk	Delft, Nederland, Lorentzweg 1, tel. 01730-33222 toestel: 5394
		015-133222	oktober 22nd 1973

Onderwerp:

Dear Professor Shapiro,

Thank you very much for your reminder of 10 oktober 1973, which prompted us (W.M.M.J. Bovée and J. Smidt) to write the following contribution :

Title : 1. T.H.D. Research Fellowships
2. Selective proton magnetic T_1 measurements on anisole derivatives

ad.1. It is possible to apply for a T.H.D. research fellowship (T.H.D.= Technische Hogeschool Delft) during the course 1974/1975.
Anyone who is interested to work in our group for a period of one year can contact me (J.S.) for further information.
The research work of the group is in the field of n.m.r. relaxation times in liquids and solids : Moreover there is activity in the field of e.s.r. of liquids and of double resonance (electron-nuclear Overhauser) in liquids.
Belonging to a technical institute of course we also have to build apparatus : a 300 MHz high resolution spectrometer and an Eldor spectrometer are under construction.

ad. 2. Selective proton magnetic T_1 measurements on anisole derivatives.

If the T_1 values of sufficient lines in a HRNMR spectrum can be selectively measured it is possible, by extending and applying Woessner's theories (1,2) for the dipolar relaxation in axially symmetric ellipsoïdal molecules, to calculate the correlation times, τ_i, for the rotation of methyl groups around their threefold symmetry axes.
This calculation can only be done with reasonable accuracy if τ_i doesn't differ too much from the overall molecular correlation time.
Over the temperature range - 20 to 80° C we determined selectively the proton T_1 values at infinite dilution in $CDCL_3$ of the compounds mentioned in the table.
There also some results are given that can be extracted from these values.

	E_A (kcal/mol)		
	methylgroup of methoxy-group 1	methylgroup of methoxy-group 4	$\frac{R_\parallel}{R_\perp}$ at 40° C
2,3,5 - trimethylanisole	3.55± 0.25	—	0.9
2,3,5 - trimethyl-4-methoxyanisole	3.01± 0.2	0.5 ± 0.4	2.3
2,6 - dimethyl-4-methoxyanisole	0.5 ± 0.4	2.75 ± 0.25	3.3

E_A is the activation energy of the Arrhenius equation for the methylgroup rotation around the C_{3v} axis in the methoxygroup.
$R_\parallel$ resp. $R_\perp$ is the rotational diffusion constant about an axis, parallel resp. perpendicular to the aryl-oxygen bond.
From this table two conclusions can be drawn :

1) The anisotropy $\frac{R_\parallel}{R_\perp}$ increases if there are two (polar) methoxy groups para to each other.
2) The E_A's are very low if the methoxy group is di-ortho substituted, and they are much larger if there is none or only one ortho substituent. This difference can be explained by the fact that in the di-ortho substituted anisoles the aromatic plane and the plane through the C-O-C bonds are perpendicular, while in the mono- or non-ortho substituted anisoles these planes are making an angle of about 20° (3,4).
   This is in agreement with INDO calculations, which give in the so called rigid rotor approximation for anisole a value of 4.65 kcal/mol, and for 2,6 dimethyl-anisole a value of 0.66 kcal/mol.
   The full results will be published elsewhere.

Sincerely yours,

Prof. Dr. Ir. J. Smidt

Drs. W.M.M.J. Bovée

1. D.E. Woessner, J. Chem. Phys. 42, 1855
2. D.E. Woessner, B.S. Snowdon, G.H. Meyer, J. Chem. Phys. 50, 719
3. M.J. Aroney, J. Chem. Soc. (1964)2954
4. W.M.M.J. Bovée, J. Smidt , Mol. Phys. to be published

182-40 CONSIGLIO NAZIONALE DELLE RICERCHE

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

Title: Conformation of dihydro-lysergic acid derivatives

Dear Prof. Shapiro,

thank you for the reminders.

During a study of lysergic acid derivatives we have assigned the ^{1}H-NMR spectra of the two stereoisomeric methyl 10β - methoxy-dihydrolysergates having the 8α-and 8β -configuration. The coupling constants of the aliphatic hydrogens are as following:

Isomer	$J_{4\alpha,4\beta}$	$J_{4\alpha,5}$	$J_{4\beta,5}$	$J_{7\alpha,7\beta}$	$J_{7\alpha,8}$	$J_{7\beta,8}$	$J_{9\alpha,9\beta}$	$J_{8,9\alpha}$	$J_{8,9\beta}$
8α	-16.2	3.0	3.6	-11.4	4.0	11.4	-12.9	4.0	12.9
8β	-16.2	10.7	6.7	-12.0	12.0	4.5	-14.1	12.9	4.2

The observed couplings in both the-CH_2CH-and the-CH_2CHCH_2-fragments can be explained in terms of the generally accepted[1] conformation I in the case of the 8α-isomer. For the 8β -isomer conformation II is ruled out because of the observed difference in the two vicinal couplings $J_{4\alpha,5}$ and $J_{4\beta,5}$ and because of the observed gauche and trans coupling of H_8 with both H_7 and H_9.[2] The coupling patterns is in agreement with the inverted conformation III in which

$J_{4\alpha,5} = J_g$; $J_{4\beta,5} = J_g$; $J_{7\alpha,8} = J_g$; $J_{7\beta,8} = J_t$; $J_{8,9\alpha} = J_g$;

$J_{8,9\beta} = J_t$

1) A.Stoll, Th.Petrzilka, J.Rutschmann, A.Hofmann, H.Gunthard, Helv. Chim. Acta 37, 2039 (1954)

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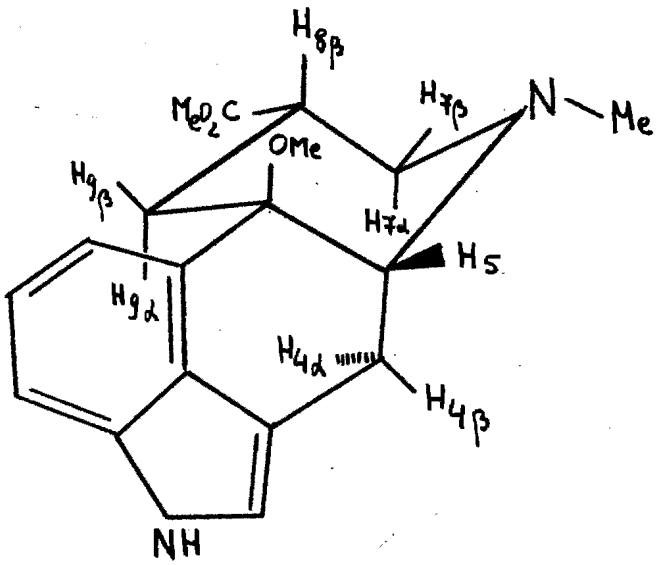

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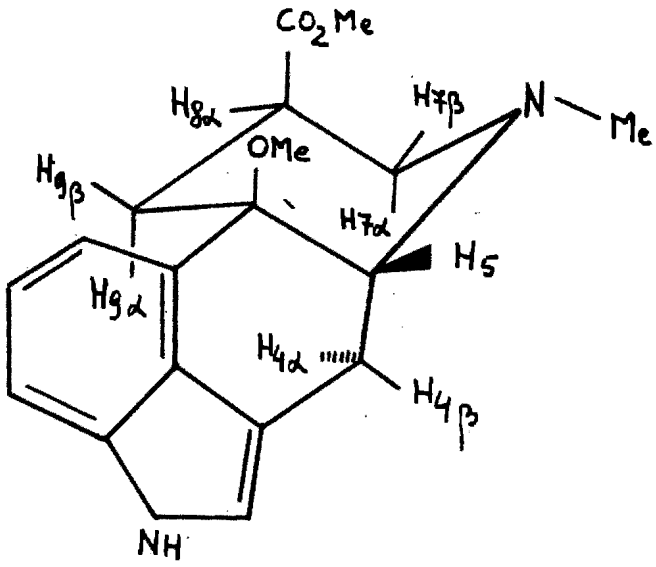

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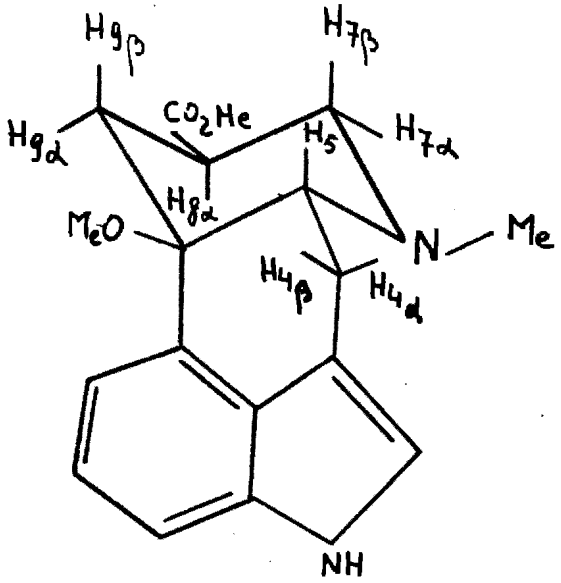

III

L. Zetta

(L. Zetta)

Yours sincerely,

G. Gatti

(G. Gatti)

182-42

UNIVERSITY OF KENTUCKY

LEXINGTON, KENTUCKY 40506

COLLEGE OF ARTS AND SCIENCES
DEPARTMENT OF CHEMISTRY
TELEPHONE 606-257-4741

October 24, 1973

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

Dear Prof. Shapiro:

I have a position available for a postdoctoral research associate (or visiting professor, etc.) beginning January 1, 1974 and terminating December 31, 1974. The individual selected should have a strong background and experience in high resolution NMR.

We presently have two (HA-60 (^{1}H, ^{11}B, ^{19}F, ^{31}P) and T-60 (^{1}H)) spectrometers and will probably have a ^{13}C FT spectrometer by spring or early summer. Current research areas include shift reagent studies of polyfunctional compounds, solvent effects, biochemical applications, and some ^{11}B work. It is possible that collaborative efforts in other areas of interest to the postdoctoral associate might be developed.

The sudden availability of this position is due to my assuming a half time administrative position. Since I will be physically absent from the chemistry department much of the time it is important that the postdoctoral associate be able to operate independently. Further, it is hoped that the individual selected will have sufficient leadership and communicating abilities that he or she can act as my substitute in day to day matters concerning operation of our NMR service program, students dropping in to ask questions, etc.

I will certainly appreciate your calling this opportunity to the attention of anyone whom you feel might be qualified. Thanks in advance for the assistance.

Sincerely yours,

Stanford L. Smith
Associate Professor of Chemistry
Department of Chemistry
University of Kentucky
Lexington, Kentucky 40506
606-258-2200

SLS/ct

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF COIMBRA
PORTUGAL

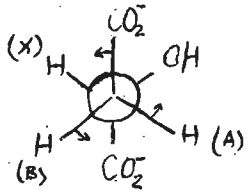
Professor B.L.Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843
U. S. A.

Coimbra, 18th October 1973

Dear Professor Shapiro

Subject: N.M.R. EVIDENCE ON THE STRUCTURE OF URANYL-MALATE COMPLEXES

Comparison of the proton chemical shifts and coupling constants for malic acid and its 1:1 complex with UO_2^{2+}, at the same pH(3.3) has led to conclusions on the conformation of the ligand in the complex and, indirectly, on the type of polymer possible. Use was made, mainly, of the vicinal coupling constants and relative chemical shifts. For 0.2 M aqueous solutions, they were found to be: J_{AX}=7.4, J_{BX}=4.2 Hz for the acid and J_{AX}=11.4, J_{BX}=1.5 Hz for the complex; higher frequency shifts $\Delta\delta_X$=2.620, $\Delta\delta_B$=0.968 and $\Delta\delta_A$=0.963 p.p.m. on going from the acid to the complex. These values require that the ligand in the complex has essentially the conformation



possibly slightly twisted in the sense indicated by the arrows. This conformation is highly suitable to the formation of a stable dimer. This dimer turns out to correspond to one of the various hypothesis given in the literature, (namely Rajan and Martell, J. Inorg. Nucl. Chem. 26, 1927 (1964)), the remaining ones being clearly ruled out by the N.M.R. results. Rigorously there can be 4 geometric isomers of such dimer; the N.M.R. spectra reveal the existence of at least two (two separate X spectra).

Yours sincerely

Victor M.S. Gil Júlio D. Pedrosa

TATA INSTITUTE OF FUNDAMENTAL RESEARCH

National Centre of the Government of India for Nuclear Science and Mathematics

Telex : 011-3009
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Telephone : 21 91 11
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September 28, 1973

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

Dear Professor Shapiro,

As Dr C.L. Khetrapal who was contributing to NMR Newsletters from this Institute has recently joined Raman Research Institute, Bangalore, and would be sending his contribution from there, the NMR Group of T.I.F.R. would like to continue its membership and expects to receive the forthcoming issues of TAMU-NMR Newsletters. These issues can be mailed to me. A brief account of the work given below is our contribution for the TAMU NMR NEWSLETTER.

We have prepared a large number of complexes of NiS_4 and CoS_4 Chromophores with heterocyctic amines, amine-N-oxides, dimethyl formamide, dimethyl sulfoxide and dimethylglyoxime. NiS_4 Chromophore adducts are hexa coordinated while with CoS_4 Chromophore both penta and hexa coordinated adducts have been isolated. The proton magnetic resonance studies on these paramagnetic adducts indicate that in Nickel (II) adducts, the observed shifts are contact in origin while there is substantial contribution from dipolar term in the Cobalt (II) adducts. The negative sign of the dipolar shifts require $g_{\parallel} > g_{\perp}$ in the dipolar equation. The mechanism of spin delocalisation in the ligand molecular orbitals is being investigated in the light of INDO calculations on the free bases. A temperature dependence of the contact shifts in the Cobalt (II) adducts, especially the penta coordinated, is expected to give interesting results. Such studies are in progress.

Sincerely yours,

M Mukherjee

ENC Inc. Fifteenth Experimental Nuclear Magnetic Resonance Spectroscopy Conference

October 26, 1973

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

FIFTEENTH ENC

Dear Barry:

It is a pleasure for me to be able to supply the readers of the Newsletter with some information concerning the Fifteenth Experimental Nuclear Magnetic Resonance Spectroscopy Conference to be held in 1974. The dates of the meeting are April 28 to May 1, and the location is Raleigh, North Carolina. The sessions will be held in the Student Union Building of North Carolina State University, and two large, modern motels adjacent to the campus will serve to house participants and to provide facilities for some of the associated activities. Dr. Charles G. Moreland, of the Department of Chemistry at NC State, is chairman of the committee which is in charge of local arrangements for the meeting.

As most of your readers probably already know, the ENC is devoted primarily to the instrumentation, methods, and principles of nuclear magnetic resonance, rather than to descriptions of results, and most of the papers are invited. The program is currently being developed and suggestions for topics of active current interest or for specific speakers who should be invited are always welcome. These suggestions can be sent to me or to any member of the executive committee. At present, we are tentatively planning for sessions on stochastic resonance, high resolution NMR in solids, pitfalls in the measurements of relaxation times, nuclei other than HFC, and operational policies for laboratories serving a varied group of customers. We hope also to incorporate a group of parallel sessions in which owners of various brands of commercial high resolution instruments can discuss the special capabilities and operating considerations of their respective spectrometers.

A mailing with further information will be distributed sometime in January by the ENC Secretary to all those who have attended the last three conferences. Anyone else who wishes to be placed on the mailing list should send a note to that effect to the Secretary.

Sincerely yours,

Wallace

Wallace S. Brey, Chairman

WSB/ewh

IWAN N. STRANSKI-INSTITUT
für Physikalische und Theoretische Chemie
der Technischen Universität Berlin
Dr. D. Ziessow

Berlin, den October 29th, 1973
Tel.: (030) 314-
Az.:

1 Berlin 12
Straße des 17. Juni 112
Ernst-Reuter-Haus

~~1 Berlin 10~~
Ernst-Reuter-Platz 7
Telefunken-Haus, ~~15. O. G.~~

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

Dear Professor Shapiro :

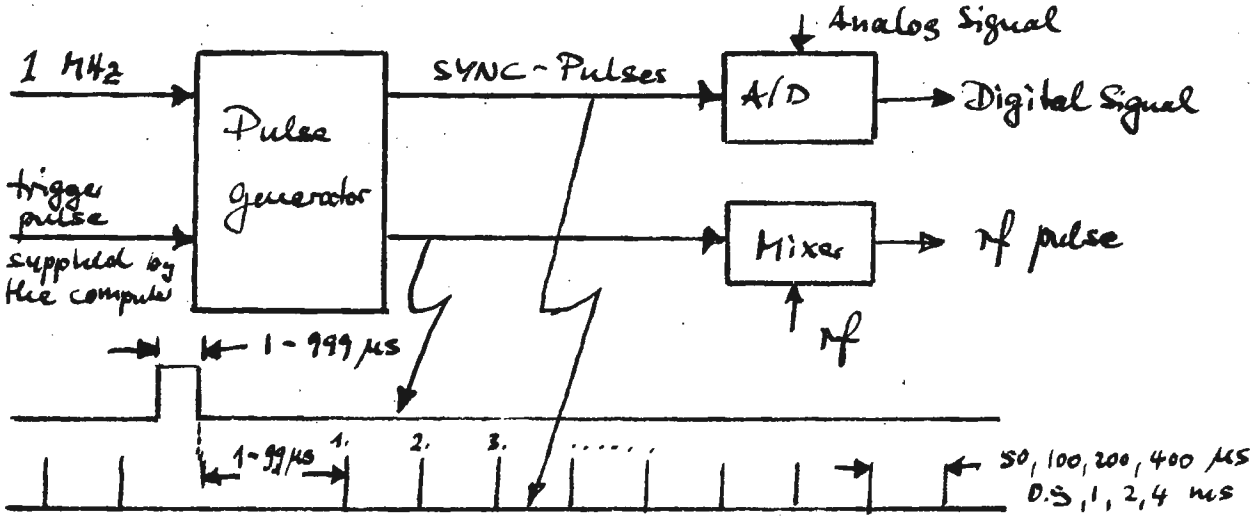
Title : C-C-coupling constants and isotope effects in fluoro-compounds.
A simple pulse generator

Continuing our work on GC coupling constants [1], we have determined magnitude and relative sign of coupling constants in several fluorinated compounds (TABLE). Line positions were measured with F-19-CW and F-19-{C-13} - CW techniques. They served as input for PDP-11 programs (on line) simulating ABX, ABXY, A2XY and A3XY type spectra. The calculated frequencies are indexed with reference to the momentum diagram. Connected transitions, therefore, are quickly accessed. High oder effects upon chemical shifts can easily be distinguished from isotope effects: erroneous ^{13}C isotope shifts do not result as is the case with first order analysis. (See e.g. [2], [3] as pointed out in [1], [4]).

The ^{13}C isotope effect on F-19 chemical shifts exhibits an additive behaviour, a fact, which has already been observed with other nuclei (see the recent review [5]). This behaviour closely correlates with the isotope effect on the vibrational zeropoint energy which has been measured to be a linear function of the number of equivalent hydrogens replaced by deuterium [6].

The C-F coupling constants show only slight changes with structure, in contrast to the C-C coupling constants. The isotope effect of the carbon bearing the F-19 atom can be roughly correlated with $^{1}J_{C-F}$ [7]. In the case of the two bond isotope effect our data exclude a similar relation ship with $^{2}J_{C-C-F}$ but indicate a rather promising correlation with J_{CC}. Further work in this area will be carried out using substituted monofluorobenzenes.

For almost a year, we have been using in our home-built HFX-90/PDP-11 set-up a pulse generator with the following features:



Interested readers can be provided with the circuit diagrams (drawn by hand !!).

Please credit this contribution to the account of Prof. E. Lippert.

Yours sincerely

(Dieter Ziessow)

[1] D. Ziessow, E. Lippert, Ber. Bunsenges. phys. Chem. 74, 568 (1970)

[2] K. Frei, H.J. Bernstein, J. Chem. Phys. 38, 1216 (1963)

[3] C.A. Reilly, TAMU-NMR 174, 46 (1973)

[4] , TAMU-NMR, (1973)

[5] H. Batiz-Hernandez, R.A. Bernheim, Prog. NMR Spectr. 3, 63 (1970)

[6] H.J. Bernstein, A.D.E. Pullin, J. Chem. Phys. 21, 2188 (1953)

[7] S.G. Frankiss, J. Phys. Chem. 67, 752 (1963)

T A B L E

	Isotope shift* F-19 [Hz]	J_{CF} [Hz]	Isotope shift C-13 [Hz]	J_{CC} [Hz]
$^{13}CF_2 = {}^{12}CCl_2$	- 8.41	- 288.67	-	-
$^{12}CF_2 = {}^{13}CCl_2$	- 2.35	+ 44.65	-	-
$^{13}CF_2 = {}^{13}CCl_2$	- 10.60 (- 10.76)	-	CF: ≈-0.3 CCl: ≈-0.6	+ 155.1
$^{13}CF_3 - {}^{12}CCl_3$	- 10.62	- 282.32	-	-
$^{12}CF_3 - {}^{13}CCl_3$	- 1.17	+ 43.08	-	-
$^{13}CF_3 - {}^{13}CCl_3$	- 11.80 (- 11.79)	-	*	85.0
$^{13}CF_3 - {}^{12}COOH$	- 10.95	- 283,25	-	-
$^{12}CF_3 - {}^{13}COOH$	- 1.40	43.73	-	-
$^{13}CF_3 - {}^{13}COOH$	- 12.24 (- 12.35)	- -	*	103.8

*) Bracketed values represent the sum of the respective single isotope shifts. F-19-Spectra were observed at 84 MHz.

UNIVERSITY OF VIRGINIA
DEPARTMENT OF CHEMISTRY
CHARLOTTESVILLE, VIRGINIA 22901

October 31, 1973

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

Dear Barry:

Plea for a program deck of LAOCOON III

Though we furnished decks of an earlier version of LAOCOON to others over a period of years, a change in computer and language has left us without a working program. We would be grateful to someone willing to furnish us a deck of LAOCOON III in Fortran IV (or extended) suitable for running on a CDC 6000 computer. We also have a complot DP-7 plotter if such an additional feature is available.

I also understand there is a version of LAOCOON III which includes magnetic asymmetry as a feature. Any information on available decks or listings of the program would be appreciated.

Phone number is (804) 924-3640.

Sincerely yours,

Bruce

R. Bruce Martin
Professor of Chemistry

RBM/dah

DEPARTMENT OF THE NAVY
NAVAL WEAPONS CENTER
CHINA LAKE, CALIFORNIA 93555

IN REPLY REFER TO:
6052/DWM:bjy
1 November 1973

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

Title: ^{13}C NMR of Hydrocarbon Gels
^{15}N NMR of Polynitrogen Compounds

Dear Barry:

Interest in gelled hydrocarbons as safe aircraft fuels has led to some interesting nmr work here. In an effort to understand the gelling process we have been looking at solutions of aluminum caprylate in benzene. At 6% concentration of $AlOH(C_7H_{15}COO)_2$ the solution forms a thick, rubbery gell which gives the alkyl ^{13}C spectrum shown below. By comparison with the spectrum of caprylic acid, it can be seen that the methylene carbons give increasingly broadened lines in going from the free end of the molecule toward the carboxyl linkage with the central aluminoxy chain. (The solvent molecules - benzene in this case - give sharp lines.) Apparently the inhibition of molecular motion by attachment of fatty acid molecules to a rigid polymeric backbone results in a variation of spin-lattice relaxation times from about 0.2 sec at one end of the molecule to about 0.02 sec at the other.

When we ordered our new XL-100 (the nmr machine - not the TV) last year, we specified an ^{15}N channel and matching probe - an act of supreme optimism, considering the fifty-fold greater difficulty of observing ^{15}N at natural abundance compared to ^{13}C. Our naive hopes have been rewarded by a steadily growing stack of nitrogen nmr spectra, which don't look much worse (nor take much more time) than ^{13}C spectra of five years ago.

As an example, the enclosed ^{15}N (natural abundance) spectrum of 2-methyl-5-cyanotetrazole shows what can be done. We are using a Transform Technology TT-100 pulse system which delivers a 1.1 kilowatt pulse, enough to flip the ^{15}N nuclei 90° in 18 μsec. All this power may not be necessary, but I think it plays a big part in achieving a near-theoretical enhancement factor for pulsed FT operation as compared with continuous wave mode.

The spectrum required 2.5 gm. of sample with 1.0 ml. of acetone-d_6 as a lock reference, and about 0.5 ml. nitromethane as a chemical shift

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1 November 1973

standard. Approximately 50 mg. of chromium acetylacetonate was added to shorten the nitrogen relaxation times from around a minute to a few seconds or less, permitting a pulse rate of 20 min^{-1}.

Assignments at first were best guesses based on assumed charge densities. Comparison with molecular orbital calculations and empirical chemical shift relationships derived by Witanowski for ^{14}N spectra have shown them to be probably correct. Variations in linewidth are not yet understood, and may arise from ^{15}N-^{14}N spin coupling.

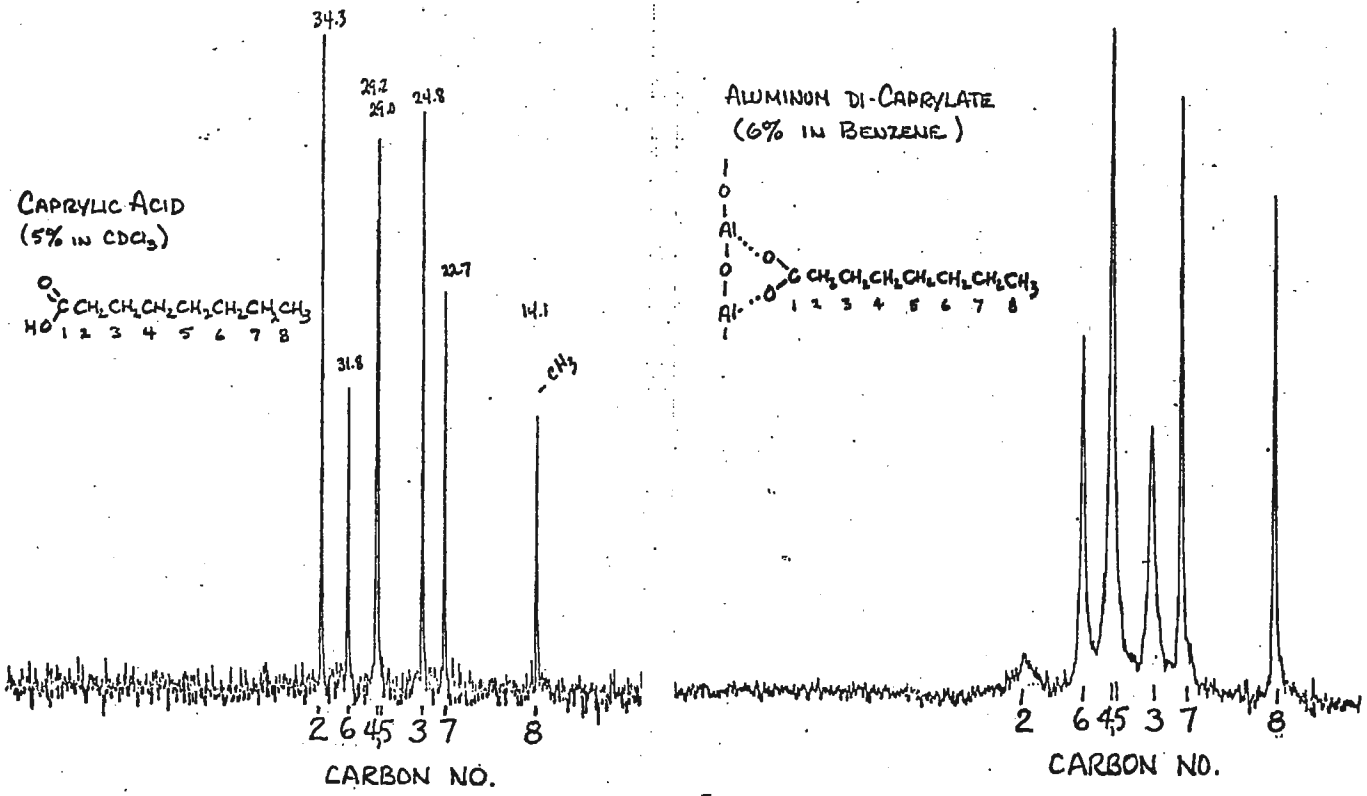
Since none of the nitrogen atoms in this molecule are proton-substituted, there was no need for ^{1}H decoupling and hence no Overhauser enhancement, positive or negative.

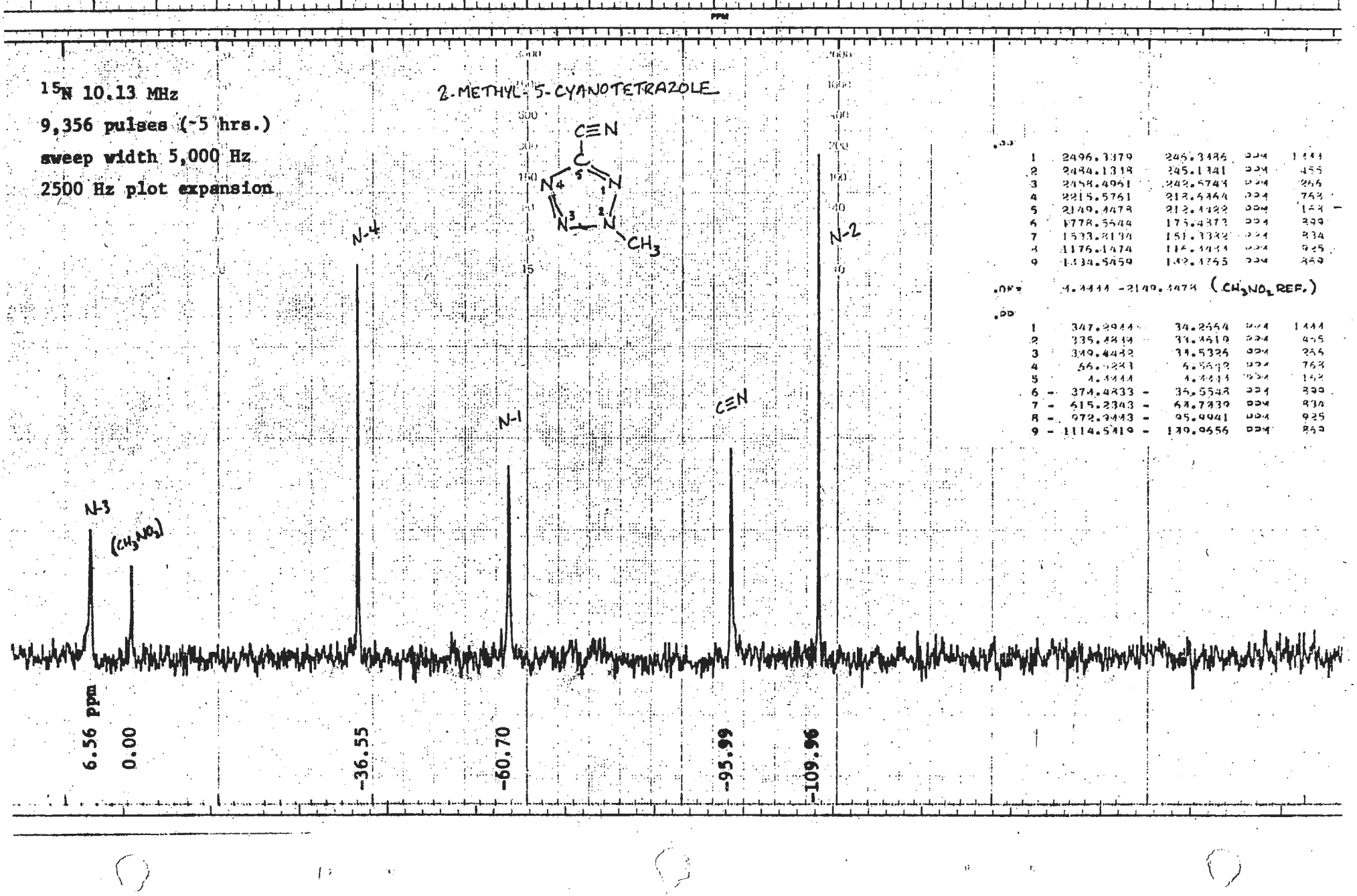
We would welcome communications from anyone else involved in this sometimes trying endeavor, and will be glad to share our own experiences.

Best regards.

Sincerely,

D. W. MOORE




15N 10.13 MHz
9,356 pulses (~5 hrs.)
sweep width 5,000 Hz
2500 Hz plot expansion
2-METHYL-5-CYANOTETRAZOLE
C≡N
N-4
N-1
C≡N
N-2
N-3
(CH3NO2)
6.56 ppm
0.00
-36.55
-60.70
-95.99
-109.96

Prof. Dr. Hanns Fischer

Physikalisch-Chemisches Institut
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CH-8001 Zürich
Rämistrasse 76
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October 31, 1973

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

U.S.A. by Airmail

Postdoctoral Position Available

Dear Dr. Shapiro,

we have an immediate opening of a post-doctoral position for research on applications of chemically induced dynamic nuclear polarization (CIDNP) and/or ESR in free radical chemistry. Facilities include HA-100, E-4 and E-9 spectrometers with on-line data processing. Applicants with some magnetic resonance background will obtain further information after sending a resume to my adress.

Sincerely

H. Fischer

Prof. Dr. Hanns Fischer

AUTHOR INDEX

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CFT-20