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Texas A&M University

N-M-R Newsletter

No. 205

October, 1975

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No. 207: 1 December 1975

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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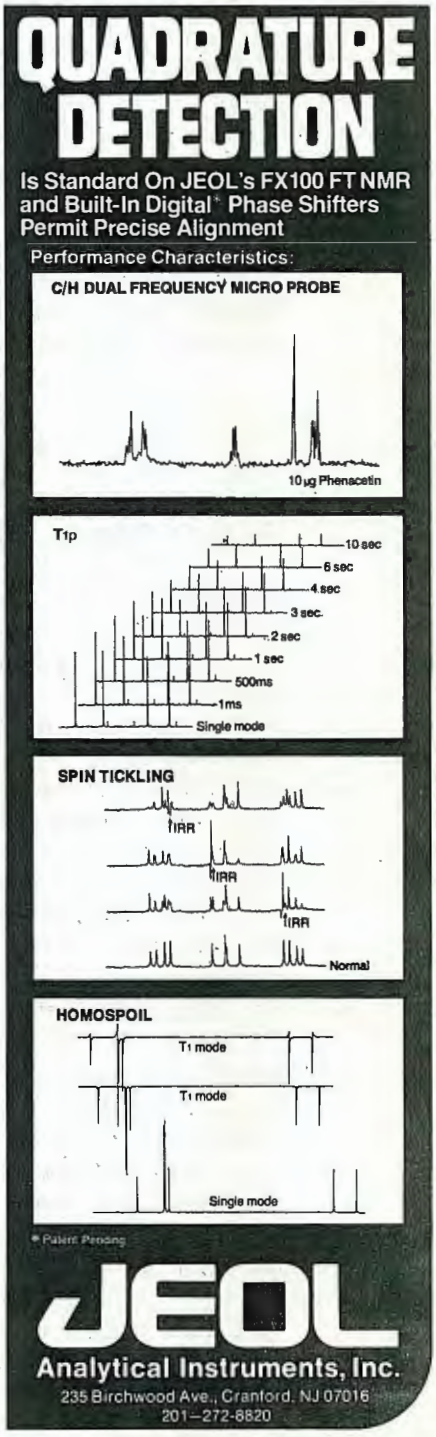

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September 22, 1975

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

CARBON-13 NMR AT THE MAGIC ANGLE

Dear Barry:

We are happy to report to you some results of combination magic-angle spinning-cross polarization ^{13}C nmr experiments performed on a wide variety of solid polymers well below their glass transition temperatures. Examples of two of the spectra, obtained at room temperautre, using rotors made from the polymers, are shown in the figure. As you can see, overlapping chemical shift anisotropies make the dipolar-decoupled, single-contact, Hartmann-Hahn CP spectra of poly-sulfone and poly(ether sulfone) virtually identical, except for the reasonably well resolved high-field line in the spectrum of polysulfone. Magic-angle spinning at 2.8 kHz, however, produces clearly different spectra which are nearly as well resolved as those obtained from the polymers in solution. The resolution is about 100 Hz. The best resolution we have obtained so far is 50 Hz and appeared to be determined by residual dipolar broadening. Note that we observe strong CP signals from non-protonated carbons as well as protonated carbons in the spinning experiment. That is, the magic-angle spinning has not totally short circuited the dipolar inter-actions needed for effective transfer of magnetization from non-bonded protons to quaternary carbons. With individual lines resolved for individual carbons we can perform various relaxation experiments and interpret the results in terms of the motions of the polymers in the solid state.

Please credit this contribution to the Monsanto subscription.

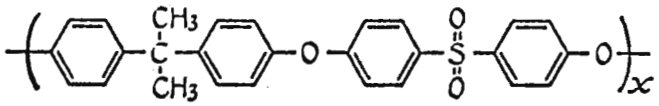
Sincerely,

Jake Ed.

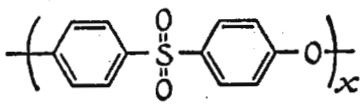
Jacob Schaefer and E. O. Stejskal

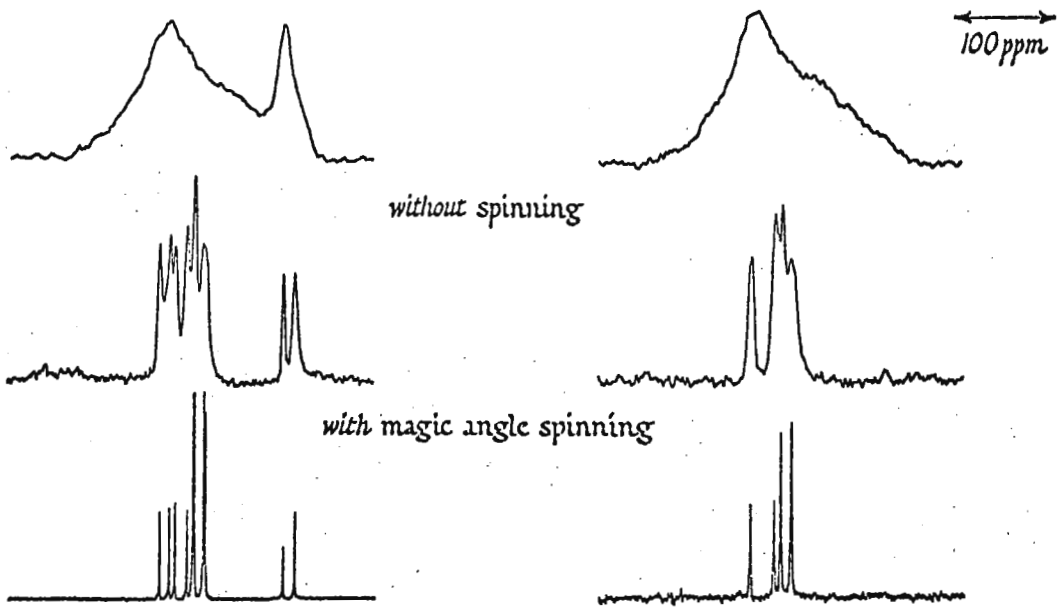
rl

polysulfone



poly(ether sulfone)





England.

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

4th September, 1975.

QUANTITATIVE NMR USING EXTERNAL REFERENCES

Dear Professor Shapiro,

When studying biological material by high resolution NMR it is important to estimate how much of the sample is giving rise to the observed signal. Internal references are often ruled out because they may bind onto and/or denature the proteins.

We have been successfully using an external reference system of a mixture of pyrazine and manganese chloride in aqueous solution sealed inside a capillary. This reference system satisfies the following requirements:-

a) The chemical shift of pyrazine ($\delta \simeq 8.6$ ppm) is separated from the normal range of protein chemical shifts.

b) The reference peak is broadened by the manganese to make it more suitable for integration against the protein.

c) The relaxation time of the pyrazine peak can be adjusted by the addition of manganese chloride so that it is equal or less than the longest relaxation time of the protein residues. This allows the acquisition parameters to be chosen for the most efficient acquisition of the spectrum of the sample without saturating the reference.

A big advantage of this reference system is that the signal intensity and relaxation time can be tailored to meet the requirements of the sample under investigation. The reference capillary is calibrated against a solution of known concentration. We have been using a solution of sodium dodecyl sulphate for this purpose.

An example of where this technique has proved useful is in the study of the thermal denaturation of proteins where it is necessary to know whether the denaturation, as monitored by the high resolution spectrum, is representative of the whole protein or only a small portion. In the particular case of glycinin (the major soya protein globulin) we have found that in the native state we observe only 7% of the aromatic and 3% of the hydrophobic methyl resonances whereas 20% of the hydrophilic residues contribute to the spectrum. On heat denaturation there is a far greater increase (~ 5 x) in the aromatic and hydrophobic methyl resonances than in the hydrophilic resonances (~ 2 x). The importance of this observation is that there are significant fractions of the protein which still do not contribute to the high resolution spectrum and thus must still be highly structured.

Please credit this contribution to Dr. J. Bus of our Vlaardingen Laboratory.

Yours sincerely,

A.G. FLOOK

CENTRO DE INVESTIGACION DEL IPN
APARTADO POSTAL 14-740
MEXICO 14, D. F.

August 28, 1975

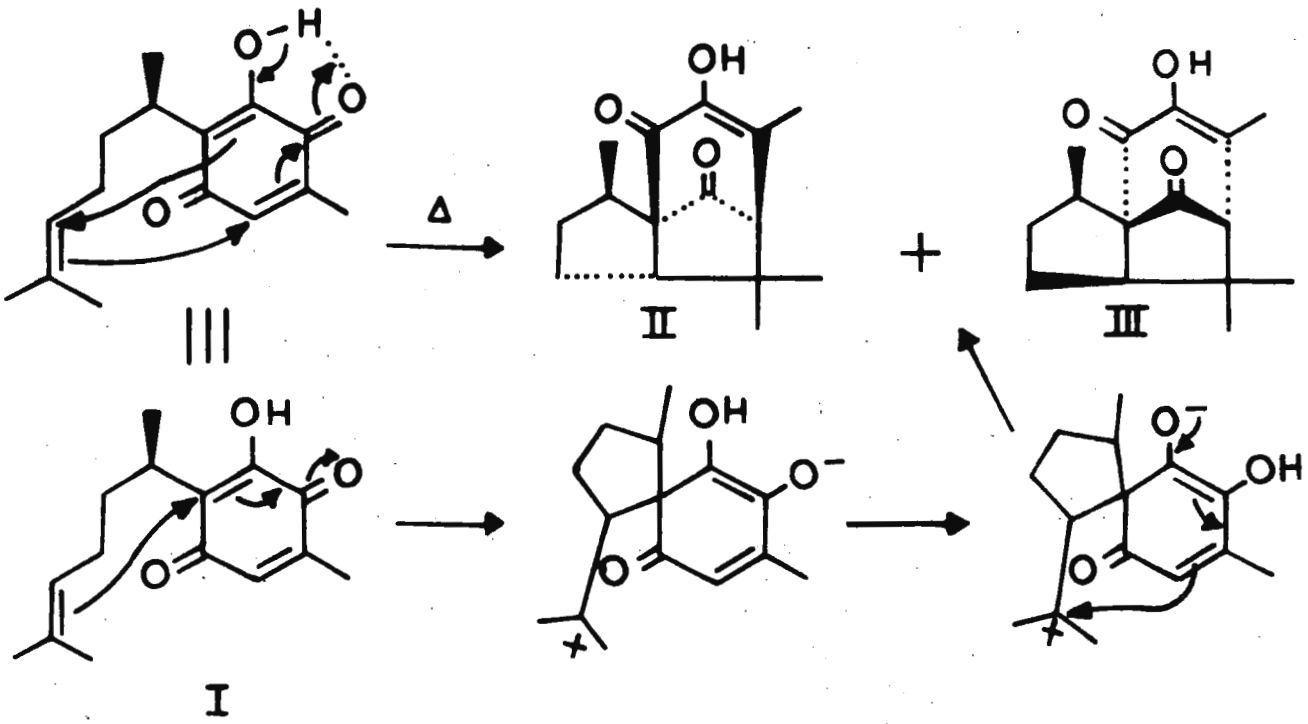
Professor Bernard L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas
U.S.A. 77843

Regioselective Deuterium Labeling for the Ellucidation of a Reaction Mechanism by PMR

Dear Professor Shapiro:

Although the transformation of perezone (I) into the mixture of α-(II) and β-pipitzol (III) has been recognized during the last century (Anschütz and Leather, Chem. Ber., 18, 715 (1885)), the structures of I, II and III were established in the last decade (Walls, Padilla, Joseph-Nathan, Giral, Escobar and Romo, Tetrahedron, 22, 2387 (1966) and references therein).

Two different mechanisms have been suggested for this transformation: A stepwise process iniciated by an intramolecular Michael addition, followed by electron and proton redistribution and ring closure (Wagner, Moss, Brooker, Heeschen, Potts and Dilling, Tetrahedron Letters, 4233 (1965)) on one hand, and on the other a concerted reaction that has been rationalized as a sigmatropic change of order (1,9) (see footnote on page 4238 of previous reference) or a class B cycloaddition (Woodward and Hoffmann, The Conservation of Orbital Symmetry, Verlag Chemie, p. 87 (1970)) in accordance with our original suggestion (Walls, Salmón, Padilla, Joseph-Nathan and Romo, Bol. inst. quím. univ. nal. autón. Méx., 17, 1 (1965)). These two mechanisms are summarized bellow:



In order to distinguish these two paths we have transformed perezone into regioselectively deuterium-labeled perezone as can be seen in the pmr spectra of figure 1.

When the D-labeled compound was heated at ∿200°C, it transformed into the mixture of the pipitzols (II + III), which after benzoylation gave the pmr spectrum shown on the second trace of figure 2. This spectrum is compared with that of a plain mixture of pipitzol benzoates and with those of the individual materials, permiting to conclude that the concerted mechanism is operating, since otherwise due to the carbonium ion of the intermediate in the stepwise process, the deuterium would appear on all the methyl groups of the gem-dimethyl of both molecules.

Sincerely yours,

Pedro Joseph-Nathan
Professor of Chemistry

Virgilio Mendoza
Graduate Student

Esther García G.
Graduate Student

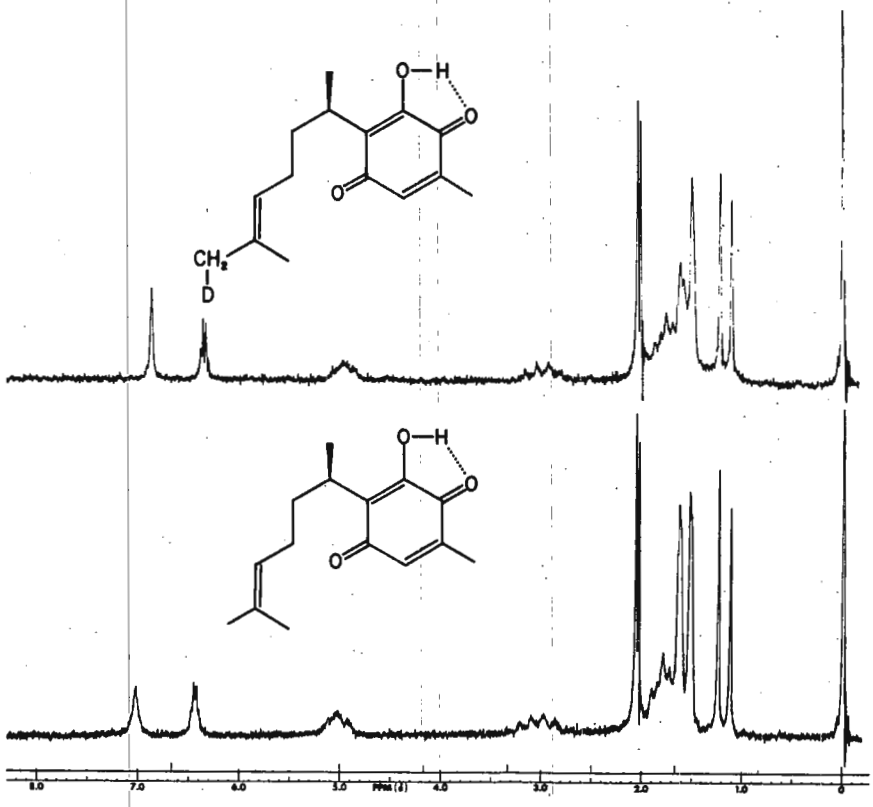


Figure 1.- The 60 MHz PMR spectra of perezone and perezone-D.

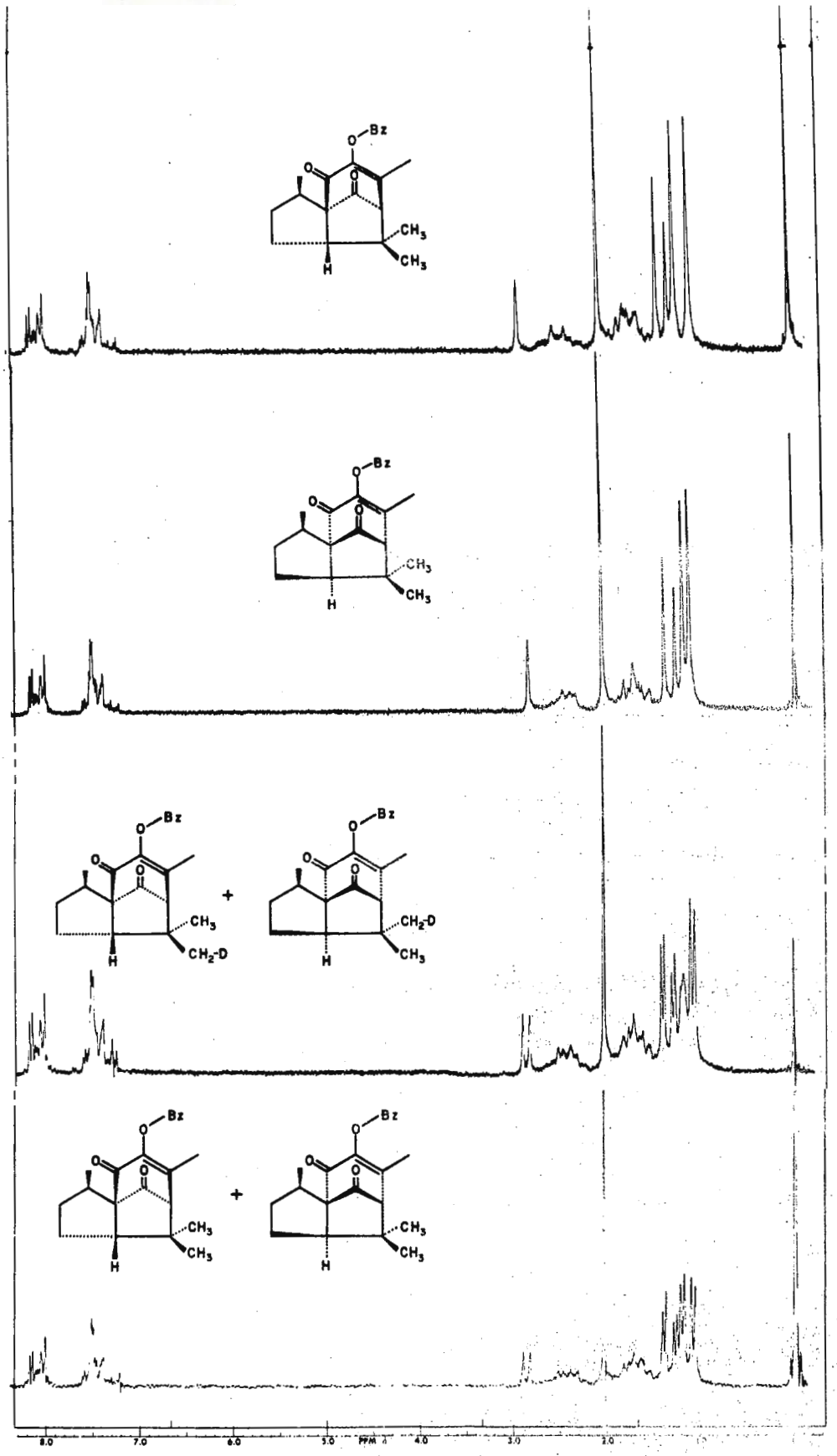


Figure 2.- The 60 MHz PMR spectra of pipitzol benzoates.

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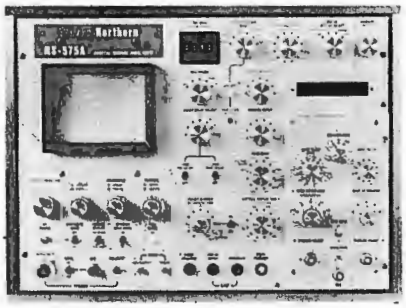

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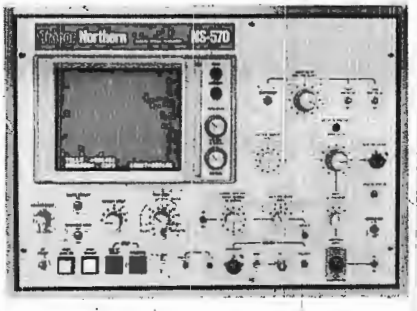

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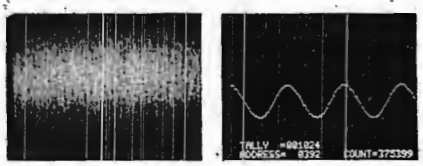

Left: NS-570 in a direct averaging application examines a severe noise environment. Right: Sine wave is detected after 1024 sweeps (real time = 20 sec.).

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THE UNIVERSITY OF TEXAS AT AUSTIN
AUSTIN, TEXAS 78712

Department of Chemistry

September 19, 1975

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

Title: "Frequency Dependence of Proton Relaxation in Liquid Crystals"

Dear Barry:

The relaxation rate (T_1^{-1}) of protons in liquid crystals has been of interest for several years, in part because T_1^{-1} varies as $\nu^{-\frac{1}{2}}$ for nematogens (PAA for example) and as $\nu^{\frac{1}{2}}$ for some others (such as MBBA for example).

The $\nu^{-\frac{1}{2}}$ dependence is often credited to relaxation by collective modes in the field oriented mesophases. Theory indicates this intramolecular mechanism often gives $\nu^{-\frac{1}{2}}$ dependence, and it is frequently observed for protons in p-azoxyanisole (PAA). A diffusion mechanism (intermolecular) predicts a $\nu^{\frac{1}{2}}$ behavior and such is observed in MBBA.

It is in principle possible to separate these two contributions by studying the intermolecular (T_{1r}^{-1}) and intramolecular (T_{1a}^{-1}) contributions to T_1^{-1}. This can be done with isotopic dilution studies (1). In collaboration with Bing Fung at the University of Oklahoma, we have determined the frequency dependence of T_{1r}^{-1} and T_{1a}^{-1} in PAA - $(CD_3)_2$ at 120°C over a range of 5 to 100 MHz. Analysis of the data indicates that T_{1r}^{-1} has a strong frequency dependence (not $\nu^{\frac{1}{2}}$), that T_{1r}^{-1} becomes more important at lower frequencies, and that some mechanism in addition to those discussed above is probably important.

Yours truly,

Charles G. Wade
Associate Professor

CGW:dj

1) E.T. Samulski, C.R. Dybowski, and Chas. G. Wade, Phys. Rev. Letters 29, 340, 1050 (1972); Molecular Crystals and Liquid Crystals 22, 309 (1973).

205-9 St. Berger

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Professor B. Shapiro
TAMU NMR
College of Science
Texas A+M University
College Station, Texas 77843

Dear Dr. Shapiro:

^{15}N-FT-Experiments on CIDNP

The ^{15}N-sensitivity of our XL-100 (serial No 149) is certainly not the best, so we have to try harder in order to get good spectra in a short time. On the opposite page we should like to show your readers ... trace A an aniline spectrum (one transient, enriched material) and i... e B a 6 hours run of a saturated solution of 98% α-^{15}N-labelled ph... nium tetrafluoroborate taken at 0°. Trace C contains essenti... since it consists of only 100 transients of the same solut... Trace D, however, represents again 100 transients of the ... after rapid addition of about 1 ml of saturated NaOH in ... final trace E shows again 100 transients after the reac... the end (1).

Obviously, the diazonium salt is "resynthesized" dur... tion as we already found by means of ^{13}C-FT-CIDNP ... however, is the fact that both nitrogens at 174.5 ... respect to aniline) are polarized, their ratios ... termine, because of the different relaxation ti... α-ß-nitrogen exchange did take place within a ... reaction, containing the phenyldiazene struc... the phenyldiazene radical).

During ^{15}N-FT-CIDNP experiments the phase ... ficult... than in ^{13}C-FT-CIDNP, since the sign of ... al-... tered depending on whether one decoupl... h it is ... now accepted to record even decoupled ... spectra ... are phase corrected with respect to ... ne peak ... in order to comply with the KAPTEIN ...

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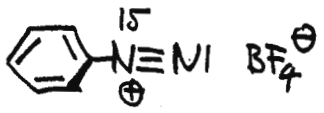
(1) All spectra in a 1... CH_3OH/CH_3CN, 6000 ... iz, ... flip angle 30 de... 566 sec, pulse delay 1 sec, ... 8k FT, external ... decoupling.
(2) S. Berger, S. ... Rieker, Tetrahedron Letters ... 1972, 2581.
(3) Bob Lichter



174.5 ppm

0.0 ppm

A

B

C

353 ppm

252.8 ppm

D CIDNP

E

205-11

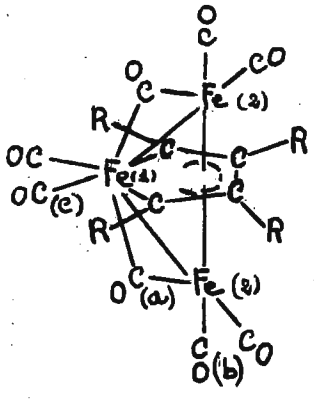
ISTITUTO CHIMICO
della
UNIVERSITÀ DI TORINO

10125 TORINO, 18th September 1975
CORSO MASSIMO D'AZEGLIO, 48
Tel. 65 21 02 - 68 28 92 - 65 58 31 - 65 58 32

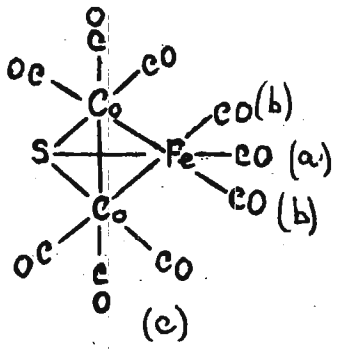
Prof. B.L. Shapiro
TAMUNMR NEWSLETTER
Department of Chemistry
Texas A & M University
College Station, TX 77843
U S A

Dear Prof. Shapiro,

^{13}C-n.m.r. is proving to be a powerful tool in the study of the fluxional behaviour of metal carbonyls. Former observations have shown that in some instances (e.g. $Fe_3(CO)_{12}$) the energy required for the scrambling of the CO is so low that even at temperature below -100°C the limiting spectra cannot be obtained. Substitution of the carbonyls, however, increases the energy of the averaging process so that is possible to have a complete picture in the n.m.r. experimental range of temperature.
Two nice examples are the ^{13}C variable temperature spectra of $Fe_3(CO)_8(C_2R_2)_2$ (I) and $FeCo_2(CO)_9S$ (II).



I



II

The limiting spectrum of I at -53°C exhibits three resonances for the carbonyls that can be assigned from their integrated intensities and chemical shifts (CO_a 255.1; CO_b 205.8; CO_c 204.2). Raising the temperature localized scrambling is occurring between CO_a and CO_b whereas up to +90°C CO_c don't partecipate in any exchange process. These observations indicate an opening of the longer bonds of the CO bridge with $Fe_{(1)}$ and that the different nature of the bonds of $Fe_{(1)}$ and $Fe_{(2)}$ with the ligand is strongly influencing the exchange process of the CO respectively associated with $Fe_{(1)}$ and $Fe_{(2)}$. The same mechanism is observed in $Ru_3(CO)_8(C_2R_2)_2$ with an higher activation energy.

Three resonances (216.4, 210.3, 198.9) with integrated intensities 1 : 2 : 6 are observed in the ^{13}C-n.m.r. spectrum of (II) at -88°C, which are assigned to CO_a, CO_b and CO_c respectively. At -65°C CO_a and CO_b coalesce to a single peak; eventually at -12°C a single peak is obtained that remains broad in raising the temperature owing to the spin-spin coupling with cobalt. The scrambling of the carbonyls is therefore occurring in three different stages: the lowest energy barrier is for CO bonded to cobalt; a second process is axial equatorial interchange at iron; complete scrambling at higher temperature should involve bridge intermediates.

Silvio Aime

Silvio Aime

Luciano Milone

L. Milone

Title:

"Stereochemically non rigid metal carbonyl derivatives".

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North Texas State University
Denton, Texas 76203
Department of Chemistry

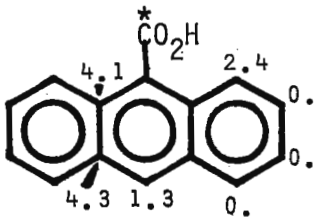
September 22, 1975

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

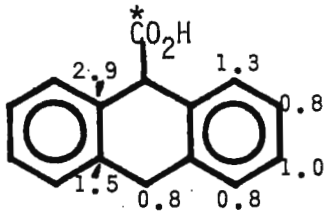
Dear Barry:

Some recent developments in our carbon-carbon coupling work indicates that π-contributions to carbon-carbon coupling may be more pronounced when the coupling path is more nearly analogous to the classical "allylic" type rather than when a continuous conjugated system is involved. Specifically, in compound 1 no longer-range (more than three-bonds) couplings are observed, while in compound 2 all longer-range couplings are significant. The CO_2H group in 2 is axial, and thus a "hyperconjugative" effect (see 5) appears to exist. We have done the INDO-FPT calculations for a model compound of 2 (see 6), and these data also suggest such a π-mechanism.

EXPERIMENTAL C-C COUPLINGS TO THE $\overset{*}{C}O_2H$ CARBON FOR 1-4:



1



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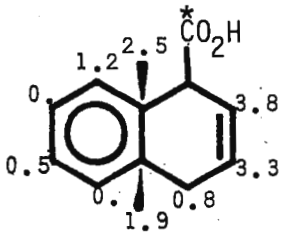

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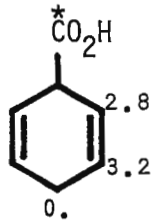

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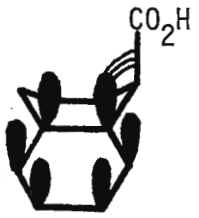
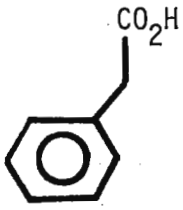


5



6

We were hoping that the expected ^3J(C-C) dependence would allow a conformational analysis of the series 2-4. These couplings, however, do not follow a monotonic trend toward planarity. Apparently π-contributions (which are maximum at greatest puckering) and σ-contributions (which are greatest with a flat molecule -- σ-contributions would be maximum with a puckered conformation with an equatorial substituent, but such an orientation is not assumed) as a net total are roughly the same throughout the series. However, that longer-range couplings are more significant in 2 than in 3 indicates the former compound is more highly puckered.

Sincerely,

Jim

James L. Marshall and Mike Barfield
(University of Arizona)

TITLE: π-Contributions to Long-Range Carbon-Carbon Coupling

Koninklijke/Shell-Laboratorium, Amsterdam

Shell Research B.V.

Prof. Bernard L. Shapiro
Department of Chemistry
Texas A&M University
COLLEGE STATION, TEXAS 77843
U.S.A.

Uw ref.:

Onze ref.: 1992

Amsterdam, September 23rd, 1975
Postadres: Postbus 3003
Tel. via telefoniste (020) 20 91 11
Tel. rechtstreeks (020)
Hr/Mw

Title: structural analysis of a sulfylide by ^{13}C NMR

Dear Professor Shapiro,

Though receiving pink letters makes a nice break from the normal black and white mail, it does not compensate for not receiving our beloved TAMUNN. Therefore we wish to report on the rather interesting ^{13}C NMR data of the sulfylide $CH_3(CH_3)S = CH-\overset{O}{\overset{\|}{C}}-O-C(CH_3)_3$

The ^{13}C data are given in Table 1.

Table 1 ^{13}C NMR data * of the sulfylide :

$(1)CH_3(1')CH_3S = CH - \overset{(3)}{\overset{O}{\overset{\|}{C}}} - O - \overset{(4)}{C}(\overset{(5)}{CH_3})_3$ (2)

C-atom no	S(ppm)	J_{C-H}	multiplicity
$C_1 + C_{1'}$	28.7	142	quartet
C_2	29.7	183	doublet
C_3	169.5	---	(long range)
C_4	74.8	---	(long range)
C_5	28.3	126	quartet

* in toluene-d_8 ; shifts relative to TMS

Koninklijke/Shell-Laboratorium, Amsterdam

d.d. September 23rd, 1975

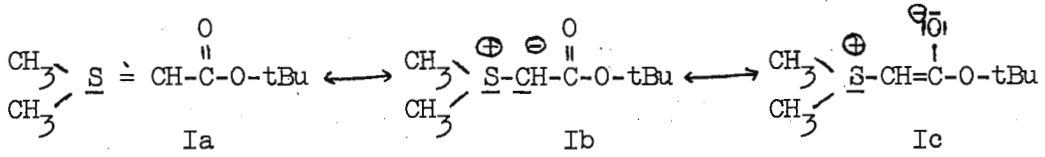
For comparison the ^{13}C NMR data for $(\overset{1}{CH_3})_3 P = \overset{2}{CH_2}$ are given below [1]):

δ C(2) = -1.5 ppm ; J (C^2-H) = 149 Hz
δ C(1) = 19.7 ppm ; J (C^1-H) = 127 Hz

The following comments on these data can be made :

- At first sight one would expect two absorption lines for the two different methyl groups on sulfur (Z and E position). However, down to -90°C a single absorption line is observed for both methyl groups, indicating a relative fast rotation around the S-C^2 bond.
- Carbon atom 2 resonates at rather high field (29.7 ppm), but is still at relatively low field compared to C(2) in the phosphorus compound.
- The coupling constant J (C^2-H) is very large for carbon atoms absorbing at this high field.

The above mentioned facts can be rationalized on the basis of the possible resonance structures :



Ia Ib Ic

- Carbon 2 resonates at very high field, when considered as an olefinic carbon atom. Therefore an important contribution from resonance structure Ib has to be considered.
- The large coupling constant J (C^2-H)=183 Hz rules out a possible sp^3-hybridization of C(2), because both sp^3-hybridization and high non-π-electron density result in a coupling constant much lower than 145 Hz. In fact the observed coupling constant is as expected for a -S-CH=C structure element. These facts favor a strong contribution from Ic.
- The rapid rotation around the S-C(2) bond can be accounted for by structures Ib or Ic only.

In conclusion one can say that the resonance structures Ib and Ic make the major contributions to the structure of the sulfylide.

1) H. Schmidbauer, W. Buchner and D. Scheutzow, Chem. Ber. 106 (1973) 1251

Yours sincerely,

(J.P.C.M. van Dongen, A.D.H. Clague, A. Reinink)

P.S. Please credit this to the Shell account in Dr. R. Prins's name.

205-17

UNIVERSITY OF GRONINGEN

DEPARTMENT OF ORGANIC CHEMISTRY
ZERNIKELAAN, GRONINGEN
THE NETHERLANDS

HEAD: PROF. DR. H. WYNBERG
TEL.: 050 - 11 43 45

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

Groningen, September 25, 1975.

Dear Professor Shapiro:

Our continuing interest in unsaturated sulphones led us to study the properties of dibenzothiophene dioxide (I). The ^{1}H-NMR spectrum was analysed by means of the INDOR technique and simulated as an ABCD spectrum with the following parameters:

	δ (ppm)	J (Hz)
H_A	7.860	$J_{AB} = J_{BC} = J_{CD} = 7.3$
H_B	7.730	$J_{AC} = J_{BD} = 1.3$
H_C	7.626	$J_{AD} = 0.9$
H_D	7.498	

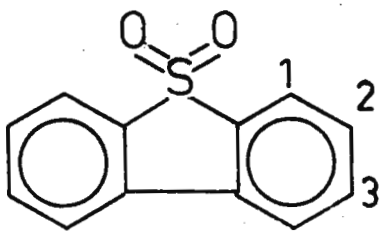
The problem of assigning the absorptions to the different protons was elucidated by adding the paramagnetic shift reagens Eu(Fod)$_3$. The ratio of the shifts for the different absorptions was:

$$H_A : H_B : H_C : H_D = 5.3 : 1.0 : 1.1 : 1.9$$

These data show that the resonance H_A belongs to the proton H-1, and thus H_B, H_C and H_D to H-2, H-3 and H-4. The order of the shifts is somewhat unexpected, therefore we calculated the proportionality of the shifts at different positions of the Europium complex, using the relation $\Delta\delta = (1-3\ \mathrm{ros}^2\ \Theta)/r^3$ and assuming a 1:1 complex.

When Eu is located on the bisectric of the O-S-O angle no correlation is found between the calculated and measured values although several Eu-O distances were tried. However, exact agreement was obtained when Eu was coordinated with one oxygen atom, at a linear arrangement of the atoms S-O-Eu and a Eu-O distance of 2.0 Å. The probability that the Eu complex coordinates with either O-atom is by symmetry equal.

When Eu was moved in either direction, the correlation coefficient decreased. The same results were obtained for a number of dithienothiophene dioxides. This linear arrangement of the Eu-O-S atoms is comparable to the linear arrangement found for the ketones from your analysis assuming a 1:2 complex (LS_2).[1] It is however strange that in the sulphone case, the LS_2 complex should be viewed as a Eu molecule coordinated with two sulphone groups, in stead of the sterically more favourable coordination with two oxygens of one sulphone group. On the other hand this type of complexation is in accordance with theoretical predictions on hydrogen-bond complexation to sulphones.



I

Sincerely Yours,

Drs. J. Runsink.

1. B.L. Shapiro and M.D. Johnson, Jr., J. Amer. Chem. Soc., 94, 8185 (1972).

Please credit this contribution to Dr. W.D. Weringa's subscription.

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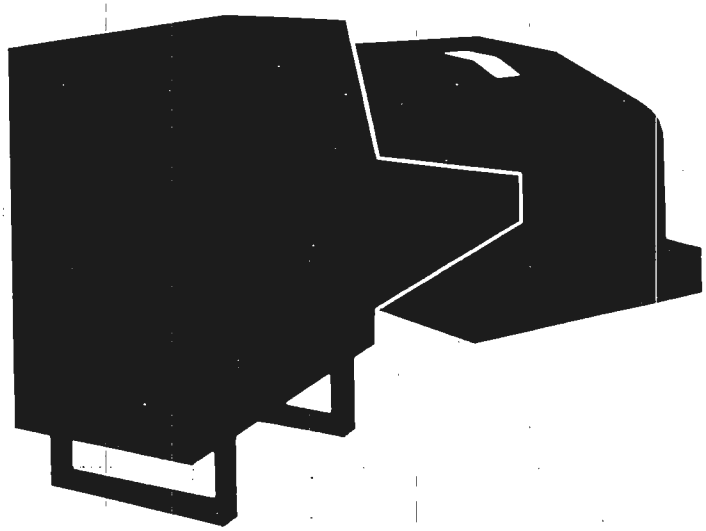

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Prof. Bernard L. SHAPIRO
Dept. of Chemistry
College of Science
Texas A & M University
COLLEGE STATION Texas 77843

^{1}H NMR with ^{13}C probe for speeding up ^{13}C selective decoupling experiments

Dear Professor Shapiro,

With the increasing use of ^{13}C NMR as a structural tool, it is very often required for assigment purposes to do selective proton decoupling. In this case, one needs to know very accurately, the "absolute" decoupler offset of the proton being irradiated on the tube and solution used for ^{13}C spectrum to avoid side effects as solvent shifts, etc... We found handy to use a very simple modification which allows the WP 60 users to perform ^{1}H NMR with the ^{13}C probe. What they need is only one coaxial cable, 1 meter long, and 2 minutes of their research time for doing the following :

- plug in the ^{1}H emitter into the console and the ^{1}H cascode amplifier into its socket in lieu of the ^{13}C emitter and cascode.
- connect the BU1 ^{1}H cascode output to the broad band decoupler input on the ^{13}C probe. BU2 and BU3 outlets on the ^{1}H cascode being normally connected to BU2 and BU3 cables, BU1 cable coming from the ^{13}C coil being left loose.
- after the probe has been lowered down and automatically positionned the spectrometer is ready for ^{1}H operation. The ^{1}H spectrum being recorded, the decoupler offset is given immediately on the WP 60 DS by the D command in the EP subroutine, cursor mode. With the BNC 12 computer, one has only to assign the leftmost address (carrier frequency) to zero frequency and points out the peaks with the cursor. The decoupler offset is then the difference between the f_1 offset and the peak frequency given by the A command; after switching the WP 60 back to ^{13}C mode, The programming of the f_2 frequency with the determined proton offsets will give an automatic stacked plot of the different selectively proton decoupled ^{13}C spectra.

The attached example shows selective decoupling on Indene which allows and unambigous assignment of the ethylenic carbons C2 and C3 by successive irradiation of the AB components of the ethylenic hydrogens in agreement with ref. 1.

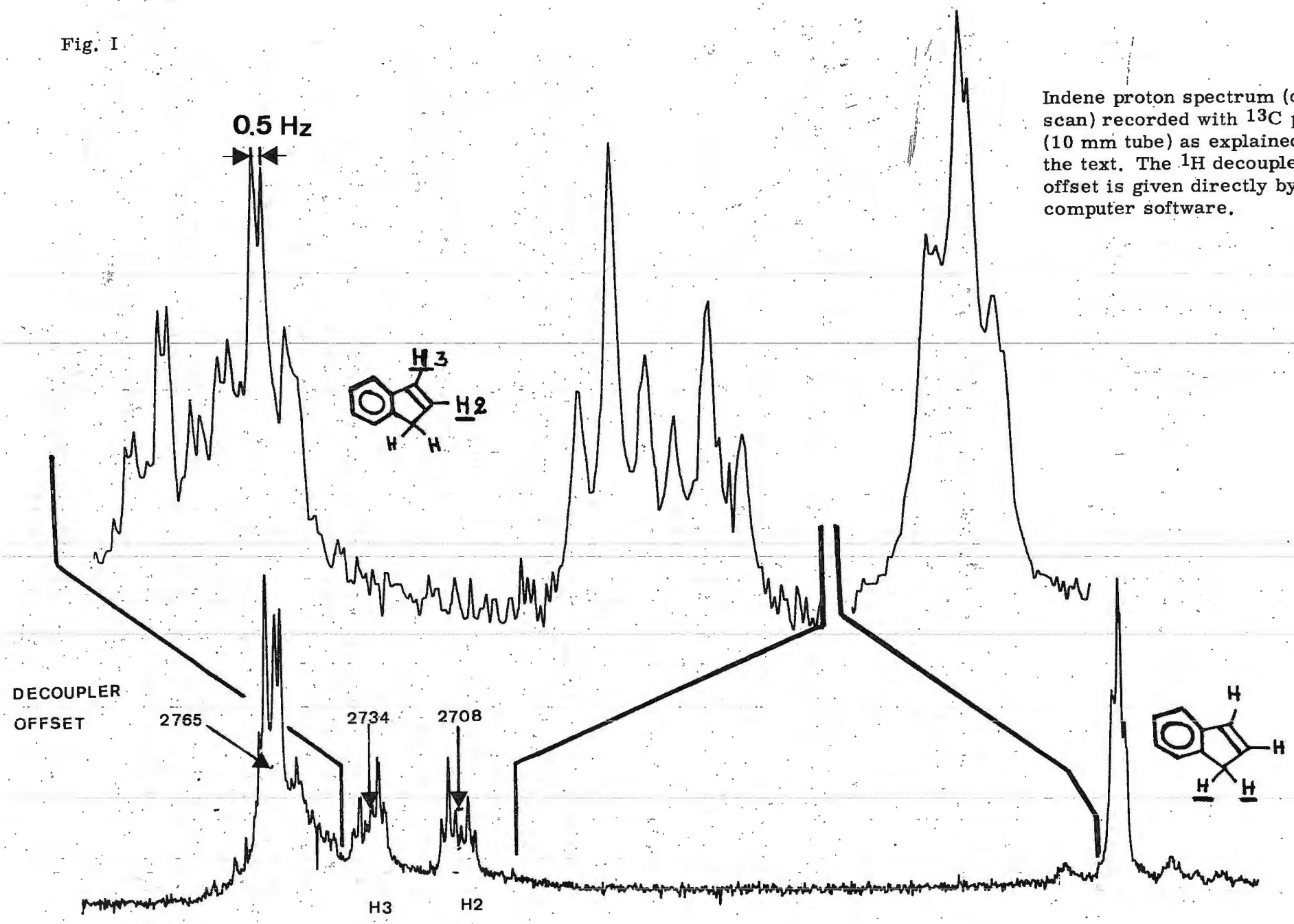
The resolution of ^{1}H spectra recorded in this way is good, as exemplified by the 0,5 Hz, long range coupling seen on the low field component of the AB doublet of triplets and the suggested modification could be used to record ^{1}H spectra of rather insoluble products taking into account the increase in tube diameter. I hope this contribution will allow the Wissembourg Lab not being on your pink list. Hoping to see you sometimes in Alsace.

With best wishes,

C. BREVARD

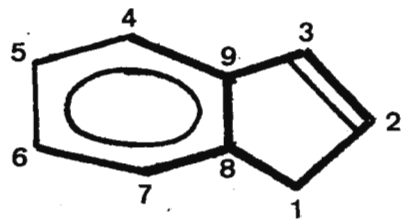
1 - N. PLATZER, J. J. BASSELIER, P. DEMERSEMAN :
Bull. Soc. Chim. 5, 6 , 905, 1974.

Fig. I

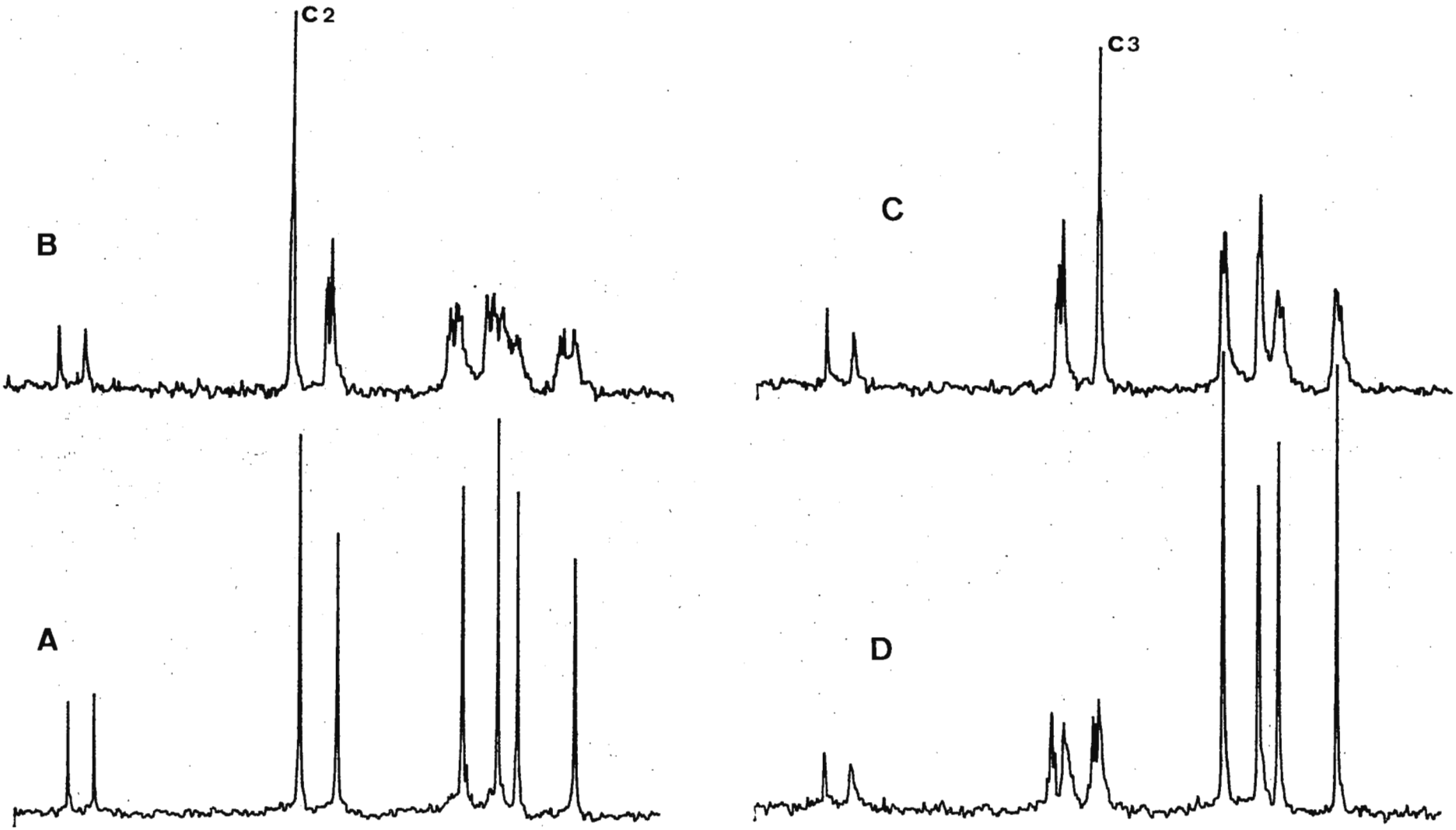


Indene proton spectrum (one scan) recorded with ^{13}C probe (10 mm tube) as explained in the text. The ^{1}H decoupler offset is given directly by the computer software.

Fig. II



Indene ^{13}C spectrum. Same tube as in I. Spectrum A : Broad band decoupling
Spectra B, C, D : Selective decoupling with proton decoupler offset respectively set at 2708 Hz, 2734 Hz and 2765 Hz.



205-23

UNIVERSITY OF UMEÅ
Department of Organic Chemistry

Title: The CSA Relaxation of Carbons in Organic Molecules and T_1 Studies of Carbanions in Solution.

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

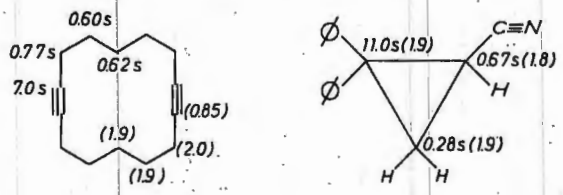
Dear Barry,

After having left the bright sun of Florida (?) far behind and changed the football back to a spherical top one I have started some carbanion projects again. But first I would like to mention some late preliminary findings resulting from my stay with G. C. Levy, Florida State University.

In many typical organic compounds we noticed that the relaxation due to the CSA mechanism could be of a comparable magnitude to the DD relaxation pathway for nonprotonated sp^2 carbons at high magnetic field ($\geq$50 kG) Even at moderate field strengths ($\leq$30 kG) the CSA mechanism could give significant contribution to the relaxation rates of these carbons. As for our study of compounds containing nonprotonated sp-carbons , 1,8-cyclotetradecadiyne (A) turned out to be as close as we could get in our efforts to find an isotropically tumbling molecule.

As indicated in Fig 1 the CSA mechanism is the major cause of the relaxation of the sp carbons with a chemical shift anisotropy tensor being ~300 ppm. In compound (B), however, the partially sp^2 hybridized ring carbon C-1 did not show any significant relaxation due to the CSA mechanism judging from the enhancement factor. Low field data confirmed our results for these compounds.

^{13}C T_1's and NOE's ( )
at 38°C and 67.9 MHz



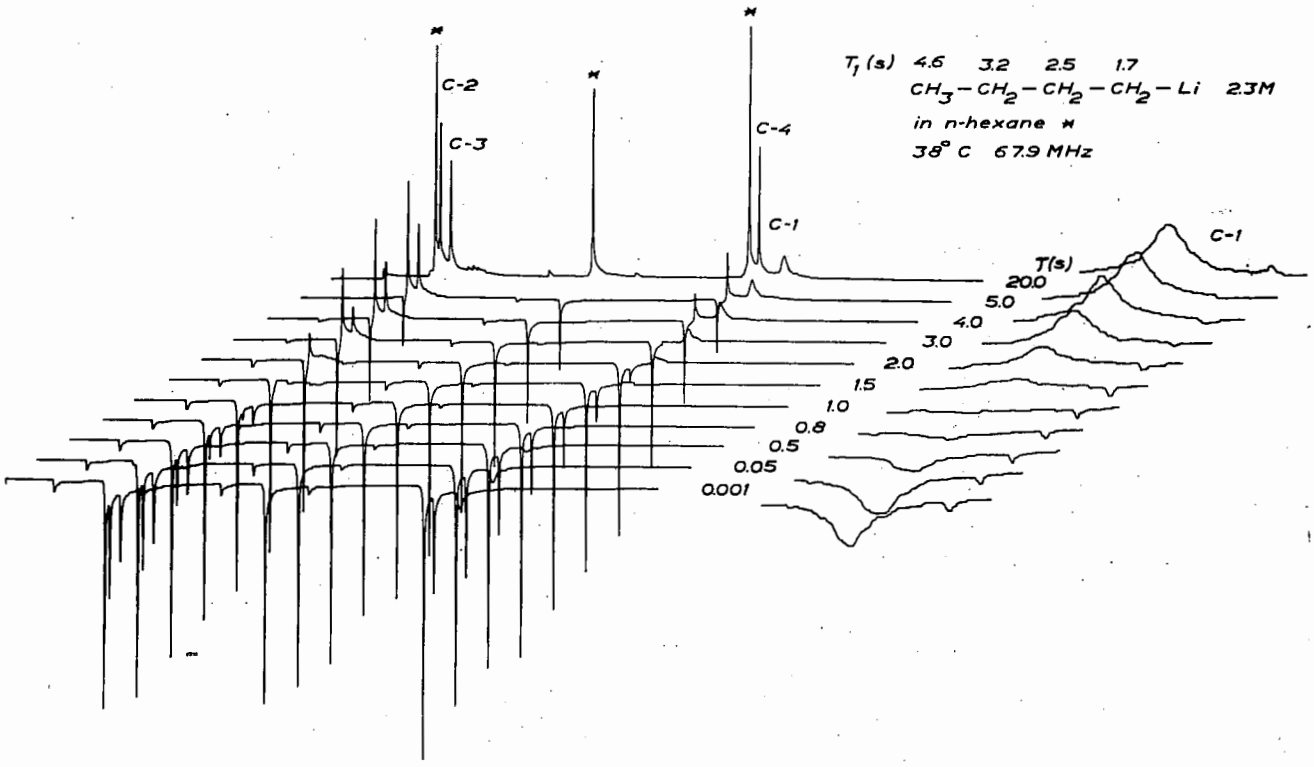
A
2.5M

B
2.0M

in tetrachloroethane-d_2

Currently we are investigating the characteristics of delocalized carbanions in solution as a function of solvent and concentration mainly by means of T_1 data. Addition of chelating agents will be subject to future investigations. For lithium phenylacetylide we observed strong association tendencies in THF and dioxane based on the o,m / p T_1 ratio.

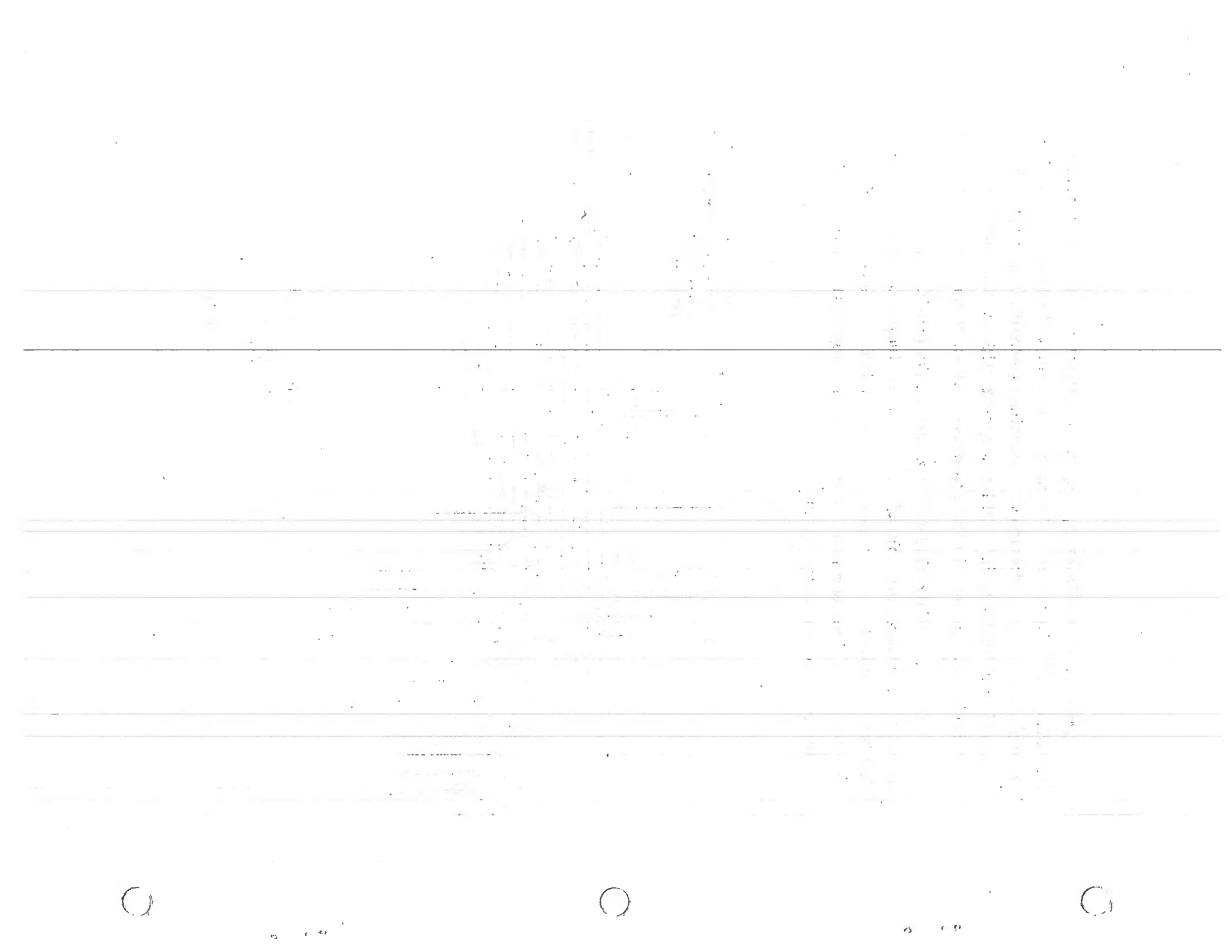
Even simple alkyllithium compounds, like n-BuLi, revealed a T_1 pattern indicating intermolecular association (segmental motion). Data for this compound were mentioned earlier in TAMU Newsletter (Prof. G. Fraenkel) but since our results are in some disagreement with his it could be worth mentioning again.



Yours sincerely

Ulf

Dr Ulf Edlund



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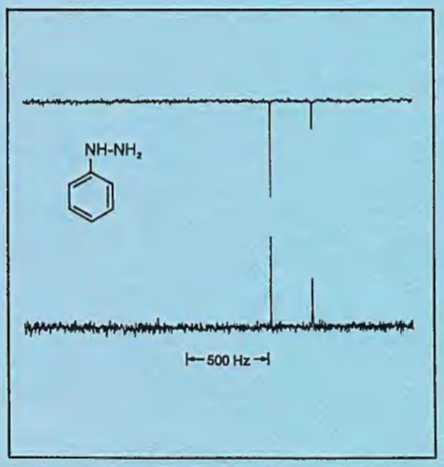
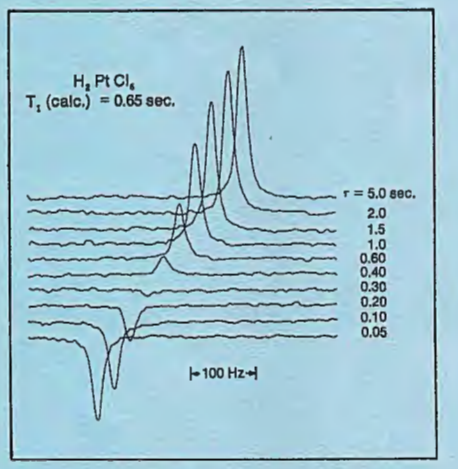


The nucleus observed for this spectrum is ^{15}N, at 10.1 MHz. The upper trace shows 500 transients ($\alpha = 90°$) of a proton noise-decoupled spectrum of phenylhydrazine in C_6D_6. The negative magnetogyric ratio of ^{15}N produces negative NOE, hence the inverted lines in the trace. The lower trace shows 2000 transients of phenylhydrazine ($\alpha = 90°$); the decoupler was on during acquisition and off during the pulse delay. This technique makes it possible to measure NOE while retaining the advantages of a ^{1}H noise-decoupled spectrum.



In this spectrum, the new accessory allows the observation of ^{195}Pt at 21.5 MHz; the sample was aqueous hexachloroplatinic acid. An inversion recovery ($180°$-τ-$90°$) pulse sequence was used in the automatic measurement of the spin-lattice relaxation time (T_1) for the ^{195}Pt nucleide.

We wish to acknowledge the cooperation of Professor Paul Ellis, of the University of South Carolina, whose early experimental work contributed to development of this capability of the XL-100.

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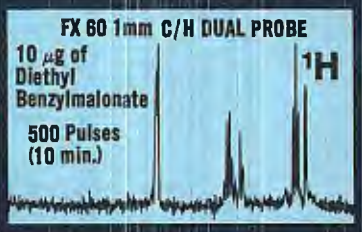

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