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Illinois
Institute of
Technology
N – M – R
Newsletter

No. 87
DECEMBER, 1965

cf. also No. 88 p. 66

Deadline Dates: No. 88: 18 January 1966
                No. 89: 18 February 1966

SOCIETÀ EDISON

SOCIETÀ PER AZIONI CON SEDE IN MILANO
CAPITALE SOCIALE L. 375.000.000.000 - INTERAMENTE VERSATO

LABORATORIO RICERCHE DI BOLLATE

AZIENDA CHIMICA

BOLLATE 16 November 1965

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Nella risposta citare il N° 3513/Cav/td
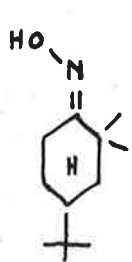
Associate Prof. B.L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Ill. 60616

Subject: Solvent Effects in the 4-tert.butyl,2.2-dimethyl
cyclohexanonoxime.

Dear Professor Shapiro,

we have continued our
study of the chemical shifts induced by solvents
in oximes, and we continue to find rather interest
ing results. Since our last contribution (see
Newsletter 77/40) we have extended our observations
to other oximes, in particular to some ɑ-methyl-
cyclohexanonoximes. We wish to report some
results giving the N.M.R. data of the most repre-
sentative compound, the 4-tert.butyl,2.2-dimethyl
cyclohexanonoxime. (*)

The methyl positions of
this oxime (in c.p.s. from TMS) in CCl_4, benzene
and Pyridine as solvents are reported in the table
below:

Solvent	2-CH_3		CH_3-t.butyl
	ɣ equatorial	ɣ axial	ɣ
CCl_4	68.0	68.0	52.0
C_6H_6	76.8	59.0	43.4
C_6H_5N	81.4	69.6	49.0

(*) We are indebted to Dr Jean-Claude Richer of
Montreal University, who kindly supplied us with
a small quantity of the corresponding cycloketone,
from which the oxime was prepared.

The values are accurate to
±0.5 cps. The NMR spectra are collected in the
figure hereby attached; a), b), and c) are
relative to CCl_4, C_6H_6 and C_6H_5N solutions respec-
tively. All spectra were run at 60 Mc on an
A56/60 Varian spectrometer at probe temperature
($\sim 37°C$), employing microcells (25 μl. microtube
NMR Specialities Inc.). Sample concentrations were
5% (or less) mole fraction.

The only conceivable form
for this cyclohexanonoxime is that one which presents
the $>C = NOH$ group in anti-configuration to the
α.methyls. The anti form is in fact suggested both
by steric considerations and by the appearance of
the H.6 equatorial proton signal at low field,
$\Upsilon = 6.70$ in CCl_4 (see Newsletter 69/26). In addition
the ring is locked predominantly in one conformation
because of the equatorial direction of the bulky
t.butyl group.

The most interesting fact
revealed in the NMR data of this oxime is that where
as in the CCl_4 solution the α.methyls are not differen
tiated, in the C_6H_6 and the C_6H_5N solution exhibit
large chemical shift differences, which must be
clearly imputed to some complex formation involving
solute and solvent molecules. The assignments for
the α.methyl peaks in the C_6H_6 and the C_6H_5N solutions,
as given in the table are justified from the NMR
observations of other methyl cyclooximes and from the
already known solvent effects results in corresponding

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AZIENDA CHIMICA

ketones $^{(+)}$. That is to say, we are thinking that
the equatorial methyl is displaced to lower fields
both in the C_6H_6 and in the C_6H_5N solution. The
α.axial one on the contrary is shifted to higher
fields in C_6H_6, but remains almost unaffected in
C_6H_5N.

Yours sincerely,

L. Cavalli

Luciano Cavalli

(+) a) N.S. Bhacca, D.H. Williams, "Applications of
        NMR spectroscopy in Org. Chem.", pp. 159-181,
        Holden Day 1964

     b) D. H. Williams, Tetrahedron Letters 2305, 1965.
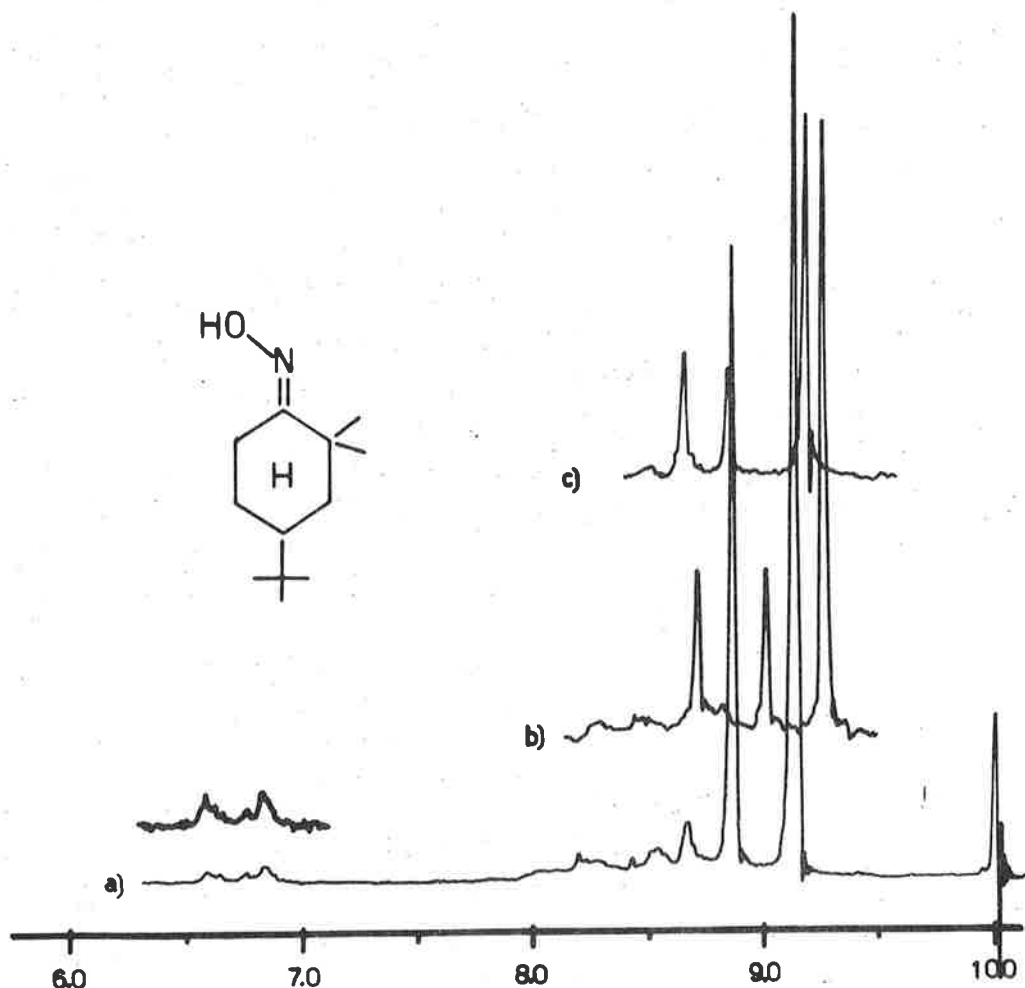
UNIVERSITÉ DE STRASBOURG
Faculté des Sciences
—

INSTITUT DE CHIMIE
—

Boîte postale 296
Téléphone 36.63.51 à 53

STRASBOURG, le October 22nd 1965
1, Rue Blaise PASCAL

Dr. B.L. SHAPIRO

Department of Chemistry

Illinois Institute of Technology

CHICAGO   Illinois 60616

Dear Dr. Shapiro,

Here is our contribution, the first one since we have moved in our new quarters . Some readers will no doubt appreciate what is involved in making a new Institute chemically operational !!

1) Conformational equilibrium in a diazepinone derivative .

We have detected a conformational rate process in the following compound :
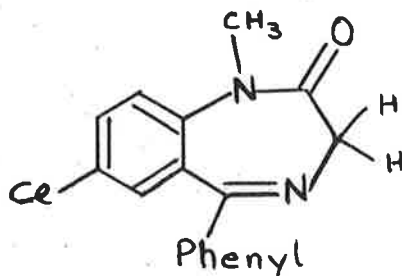
At room temperature (in tetrachloro-ethylene) the CH_2 group shows a spectrum of the AB type with doublets at 3.65 and 4.75 p.p.m. (J = 11 c.p.s.) . When the temperature is increased the AB system collapses to a broad singlet at 4.2 p.p.m. . The coalescence temperature lies around 85°C , but a very accurate determination is difficult because of the breadth of the signal . One calculates an approximate activation energy of ca. 17.5 k.cal./mole .

We are finishing up this study .

2) Methyl groups non-equivalence .

In the prize running for the "largest chemical shift between non-equivalent methyl groups of an isopropyl group" we would like to present the following horse :
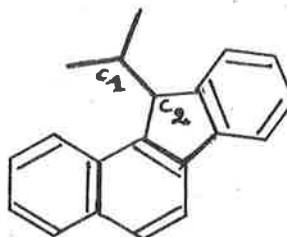
In this compound the CH_3 groups of the isopropyl are non-equivalent, giving a doublet at ca. 0.08 p.p.m. and a doublet at ca. 1.53 p.p.m. (in $CHCl_3$) . This leads to $\Delta\delta = 1.45$ p.p.m. !
Studies at different temperatures give some insight into the preferred conformation around the C_1-C_2 bond .

3) Chemical shift constants for CH_3 groups in Triterpenes .

Some time ago we had compiled from our work on triterpenes, a list of chemical shift constants for the methyl groups of a variety of triter-penic substances (from the Lupane, Dammarane, Allobetulane and Hopane series) as a function of the substituents present . We will send a copy of this list to anyone who might be interested in it .

Yours sincerely,

Jean-Marie LEHN

THE UNIVERSITY OF LIVERPOOL
DEPARTMENT OF ORGANIC CHEMISTRY

~~FROM PROFESSOR A. R. KATRITZKY~~

THE ROBERT ROBINSON LABORATORIES,
OXFORD STREET,
LIVERPOOL 7.
TELEPHONE: ROYAL 6022

11th November, 1965

Professor B.J. Shapiro,
Illinois Institute of Technology,
Chicago,
U.S.A.

Dear Barry,

Solvent Dependence of Rotational Isomerism

I am sorry to have been such a long time in com-
municating to MELLON that I have lost my hitherto
unblemished record of no reminders! I hope this
communication may interest MELLON readers. In
association with Drs. L. Cavalli and K. Pachler,
I have been working on a theory which would quan-
titatively explain how the energy difference between
two rotational isomers in a substituted ethane varies
with the solvent. Obviously, this theory would need
first to explain the known differences between the
energies of the rotational isomers in the vapour
and liquid states.

We have managed to develop such a theory by
adding to the previously known expression for the
energy of the molecular dipole field the energy
of the molecular quadrupole field. Considering the
simplest case of a 1,2 disubstituted ethane, in
which there will be only two distinct rotational
isomers, the trans and gauche forms, we obtain
the following expression for the energy difference
between the isomers in a medium (s) of dielectric
constant ε.

$$\Delta E^s = E_g^s - E_t^s = \Delta E^v - \frac{k \mathcal{X}}{1 - \frac{2 \alpha \mathcal{X}}{a^3}} + \frac{3 \hbar \mathcal{X}}{5 - \mathcal{X}} \qquad \underline{1}$$

$$\Delta E^v = E_g^v - E_t^v \quad ; \quad \mathcal{X} = \frac{\varepsilon - 1}{2\varepsilon + 1} \quad ;$$ α is the molecular
polarisability and a the solute radius.

The factors k and h are constants which depend on the differences in the dipole and quadrupole moments of the isomers.

e.g. for each isomer

$$k_i = \mu^2/a^3$$

$$h_i = \frac{3}{2a^5}\left\{4(q_{xx}^2 + q_{zz}^2 - q_{xx}.q_{zz}) + 3(q_{xz} + q_{zx})^2\right\}$$

where μ is the dipole moment and the q's are quadrupole moments of the isomer. Thus it is necessary to calculate k and h for each isomer. The values of k and h in equation 1 are the differences between these values.

For the molecules we considered ($CH_2Cl.CH_2Br$, $CH_2F.CH_2Br$ and $CH_2F.CH_2Cl$) the dipole moment of the trans isomer is zero, thus k equals $\mu^2 g/a^3$. h was calculated assuming point dipoles midway along the c - x axes. As all the other constants in equation 1 are known, this gives us ΔE^s in terms of ΔE^v and x (i.e. ϵ) the dielectric constant of the medium. The results of our calculations are shown in Table 1 from which it can be seen that there is excellent agreement between calculated and observed $\Delta E^v - \Delta E^1$.

Table 1

Calculated and Observed Energy Differences

for some 1,2 Disubstituted Ethanes ($CH_2X\ CH_2Y$)

X - Y	k kcal/ mole	h kcal/ mole	ϵ (pure liqd)	Dipole term kcal/ mole	Quad. term kcal/ mole	$\Delta E^v - \Delta E^1$	Observed $\Delta E^v - \Delta E^1$
F Cl	4.83	5.37	21.1	2.85	1.65	1.20	-
F Br	4.59	5.32	16.3	2.74	1.60	1.14	-
Cl Cl	4.51	5.47	10.66	2.53	1.55	0.98 (1.62)	1.20
Cl Br	4.31	5.45	7.17	2.26	1.43	0.83 (1.28)	0.98
Br Br	4.14	5.46	4.85	1.92	1.27	0.65 (0.97)	0.86

The two values of $\Delta E^u - \Delta E^1$ in the last but one column of the table are due to the fact that equation 1 shows that ΔE^1 is not independent of temperature (both the solute radius a which is dependent on the density and the dielectric constant are functions of the temperature) and thus the measurements of ΔE^1 (mainly by I.R.) have to be corrected for this. These are the bracketed values.

We can use equation 1 with measurements of the coupling constants of these molecules in different solvents to obtain the coupling constants in the distinct isomers. Any observed coupling J is given by

$$J = n_g J_g + n_t J_t$$

where

$$n_g / n_t = 2 \exp(-\Delta E^s / RT)$$

and

$$n_g + n_t = 1$$

Thus the plot of J vs $x \left(\frac{t-1}{2t+1}\right)$ can be fitted by only two unknowns (J_g and J_t) if ΔE^u is know, or by the three unknowns if ΔE^u is not known.

We have measured the spectra of the three compounds in a variety of solvents and obtained the following molecular parameters.

X	Y	trans isomer			gauche isomer		
		J_g^{HH}	J_t^{HH}	J_g^{HF}	J_g^{HH}	$(J_t + J_g)^{HH}$	$(J_t + J_g)^{HF}$
Cl	Br	5.1	13.3	–	2.7	14.8	–
Br	F	5.5	12.2	3.8	2.7	13.2	55.6
Cl	F	5.5	12.1	3.0	2.2	13.0	56.6

The couplings are shown schematically opposite.
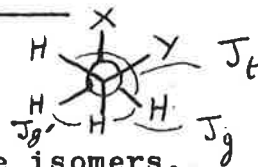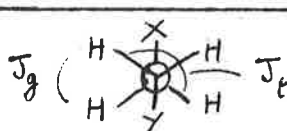
We note a) The values of J_g vary widely between the isomers.

b) These variations in J_g parallel those in cyclic systems (e.g. J_{ae} and J_{ea}).

c) The large value of J_t^{HF}, ca. 50 c/sec.

All this is being slowly written up although some of it was presented at the Sardinia S.I.P.S. conference last year.

With best wishes.

Yours sincerely,

R. J. Abraham

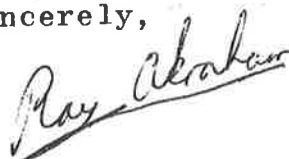# THE PENNSYLVANIA STATE UNIVERSITY
1-112 RESEARCH BUILDING
UNIVERSITY PARK, PENNSYLVANIA 16802

Materials Research Laboratory *

November 18, 1965

Dr. Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois   60616

Re: Magnetic Anisotropy of Metallocenes and Ring Currents.

Dear Barry:

Thank you for your letter of September 20th, which I received a few weeks ago on my return from a trip to Japan and India. I had an opportunity to present a paper dealing with N. M. R. and the magnetic susceptibility anisotropy of some single crystals of Ferrocene, Ruthenocene, and Osmocene, at an international symposium on N. M. R. in Tokyo last September. In this letter I will be very brief with regard to our results which should be of interest to the readers of the "NMR Nesletter". (cf. Musher, IIT Newsletter 83-18, August 65) The anisotropy work was done in collaboration with Mr. Withstandley, a graduate student in my laboratory. An extended communication is scheduled to appear in J. Chem. Phys. in the near future. I will be happy to send preprints to anyone who may be interested in this work. At a later date, I expect to write to you again giving you appropriate graphs and more information:

For studying variations in chemical bonding and ring-current effects on chemical shifts in Proton Resonance Spectra in the homologs, ferrocene, Fe $(C_5H_5)_2$, ruthenocene, Ru $(C_5H_5)_2$, and osmocene, Os $(C_5H_5)_2$, the diamagnetic susceptibility anisotropies referred to the crystallographic axes of single crystals were measured by the flip-angle technique. The ferrocene anisotropies were established by me and Fox (J. Chem. Phys. 38, 760, 1963). These values and known orientations gave molecular anisotropies by Lonsdale and Krishman's method. The π-electron densities are: Ferrocene, 4.6 (reported before); Ruthenocene, 3.1; Osmocene, 2.6.

* Laboratory for Interdisciplinary Research in Chemistry, Physics, Planetary Sciences, etc. Participating in a Graduate Research Program devoted to Solid State Science.

Bernard L. Shapiro--November 17, 1965--Page 2

These show increasing trend for π-electron withdrawal from the Cp ring with 6 electrons; thus electronegativity increases in the progression 1.4 : 2.9 : 3.9 for Fe, Ru, and Os. This disagrees with most scales, but supports recent M.O. calculations of Batsanov (1962).

These π-electron densities correlate as anticipated with chemical reactivity and thermal properties, but show unexpectedly negative correlation with Proton Magnetic Resonance Chemical Shifts (J. Org. Chem. $\underline{28}$, 3225, 1963). We propose an hypothesis depicting increasing shielding effects from (i) expanding d-orbitals of metal atoms interacting with the bonding in C_5H_5 and (ii) increasing metal-core diamagnetism.

I hope that you will find my first contribution helpful, at least to a degree which will allow you to keep me on your mailing list.

Sincerely yours,

L. N. Mulay
Associate Professor

LNM/blg

P.S. Research workers in the magnetic suscepticility-N. M. R. area may be interested in the following publications which appeared some time ago.

1. L. N. Mulay "Magnetic Susceptiblility: Analytical Applications", in Chapter 38 in Part I, Vol. IV "Treatise On Analytical Chemistry", Ed. Kolthoff and Elving John Wiley, 1963.

2. L. N. Mulay and I. L. Mulay, "Magnetic Susceptibility: Trends in Instrumentation, Research and Applications." Analyt. Chem 36, 404R (1964) (Another review is expected to appear in the April 1966 review issue.)

הטכניון - מכון טכנולוגי לישראל

TECHNION – ISRAEL INSTITUTE OF TECHNOLOGY

23 November 1965

הפקולטה לכימיה
DEPARTMENT OF CHEMISTRY

Profesor B.L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616
U. S. A.

Dear Profesor Shapiro,

Cation resonances in Ferri-and Ferrocyanides Solutions.

We are extending the investigation of complex cyanides (Inorg. Chem. 4, 358, 361, (1965)) in various directions. One of the problems is the cause of linewidth variations in both ferri-and ferrohexacyanides as various counter-cations are used, cf. Table **II** in paper II referred above. Our guess was that since the anions are strongly complexed with the cations, the latter could change the effective radius of the complex and/or affect the electrical field gradient at the N^{14} nucleus.

To gain more information on this problem we studied some cation resonances in these solutions and the results are presented in the following Table:

Cation	$Fe(CN)_6^{-3}$		$Fe(CN)_6^{-4}$	
	Shift (ppm)	Width (cps)	Shift (ppm)	Width (Cps)
Li^+ (reference LiCl)	-130	13.8	+131	7.4
Cs^+ (reference CsBr)	-11.7	2.4	-3.3	5.3
Mg^{++} (reference $MgCl_2$)	~0	20±10	~0	40±10

-2-

The width of the cations in the LiCl, CsBr and $MgCl_2$ solutions are approximately 4; 2; and 13 cps respectively. In neither solution is the position of the N^{14} resonance affected as compared to its position in $K_3Fe(CN)_6$. Equimolar mixtures of the ferri-and ferrocyanide solutions show average width and position.

The narrow resonances of the cations seem to indicate that they are not bound tightly enough to the anion to slow down their rotational motion or to be broadened by the electrical field gradient of the anion. The cations probably occupy an "averaged position" on the anion which permits free motion various considerations seem to rule out a simple "complexed cation-free bulk cation" exchange model.

Other componnds studied in this connection are the $Fe[(CN)_5NH_3]^{-3}$ and $Fe[(CN)_5 NH_3]^{-4}$.

Thank you for sending us your most valuable newsletter.

Yours Sincerely

A. Loewenstein

A. Loewenstein

UNIVERSITÉ DE NANTES

FACULTÉ DES SCIENCES

B. P. 1044 NANTES

Laboratoire de Chimie Organique-Physique
38, Boulevard Michelet - Nantes
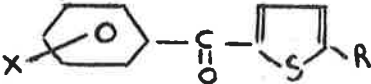
Nantes, le 26 Novembre 1965.

N M R determination of angular deformations in benzoylthiophènes.

Cher Professeur SHAPIRO

Nous avons montré que la résonance magnétique du proton peut-être utilisée, au même titre que celle du carbone 13 (1) pour étudier les angles de torsion résultant de gênes stériques dans des systèmes conjugués.

Dans les molécules (R = H ou C_2H_5 ;

X = H, F, Cl, Br, I, CH_3, OCH_3; X substitué en ortho ou para) la conjugaison des groupes thienyle -2, C=O, et phényle tend à imposer une structure plane (2). Cependant cet effet peut être contrarié par la substitution, en ortho de C=O, d'un groupement encombrant.

L'analyse des spectres A B C ou A B du motif thiofénique montre que les déplacements chimiques des protons 4 (et 5) sont peu influencés par la nature de X et sa position sur le cycle. De même les modifications d'effets électroniques du substituant en <u>para</u> de C=O ne se répercutent que faiblement sur le déplacement chimique δ_5 ; en admettant l'intervention de ces seuls effets on peut donc supposer qu'il en est ainsi pour la position ortho de X .

Or on observe un déplacement notable de δ_5 vers les champs forts lorsque le substituant X, placé en <u>ortho</u> de C=O, varie dans la série.

$$H < F < O\text{-}CH_3 < CH_3 < Cl < Br < I$$
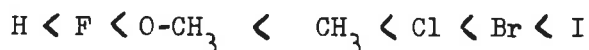
Cet ordre, qui ne coincide d'ailleurs pas avec celui que l'on pourrait attendre d'une transmission des effets mésomères et inducteurs de X, suit de façon satisfaisante l'accroissement des rayons de Van der Waals (figure 1).

Les variations de déplacement chimique δ_3, entre les positions para et ortho de X, sont donc reliées aux angles de torsion provoqués par effet stérique du substituant et nous nous proposons de les utiliser pour la détermination de ces angles.

Si on néglige, en première approximation, les effets de X sur $H_{(3)}$ à travers l'espace, deux phénomènes de même sens sont susceptibles d'expliquer cette perturbation sélective de δ_3

— d'une part, une modification de l'effet de cycle intra moléculaire dû à la circulation électronique dans le noyau benzénique.

— d'autre part une variation, par inhibition de résonance, de l'effet électronique transmis au thienyle.

Nous tentons maintenant d'évaluer l'importance relative de ces deux phénomènes.

Bien cordialement.

Maryvonne MARTIN   et   Gérard MARTIN

(1) DHAMI K.S STOTHERS J. B.   Tetrah. Lett. 631 - 1964

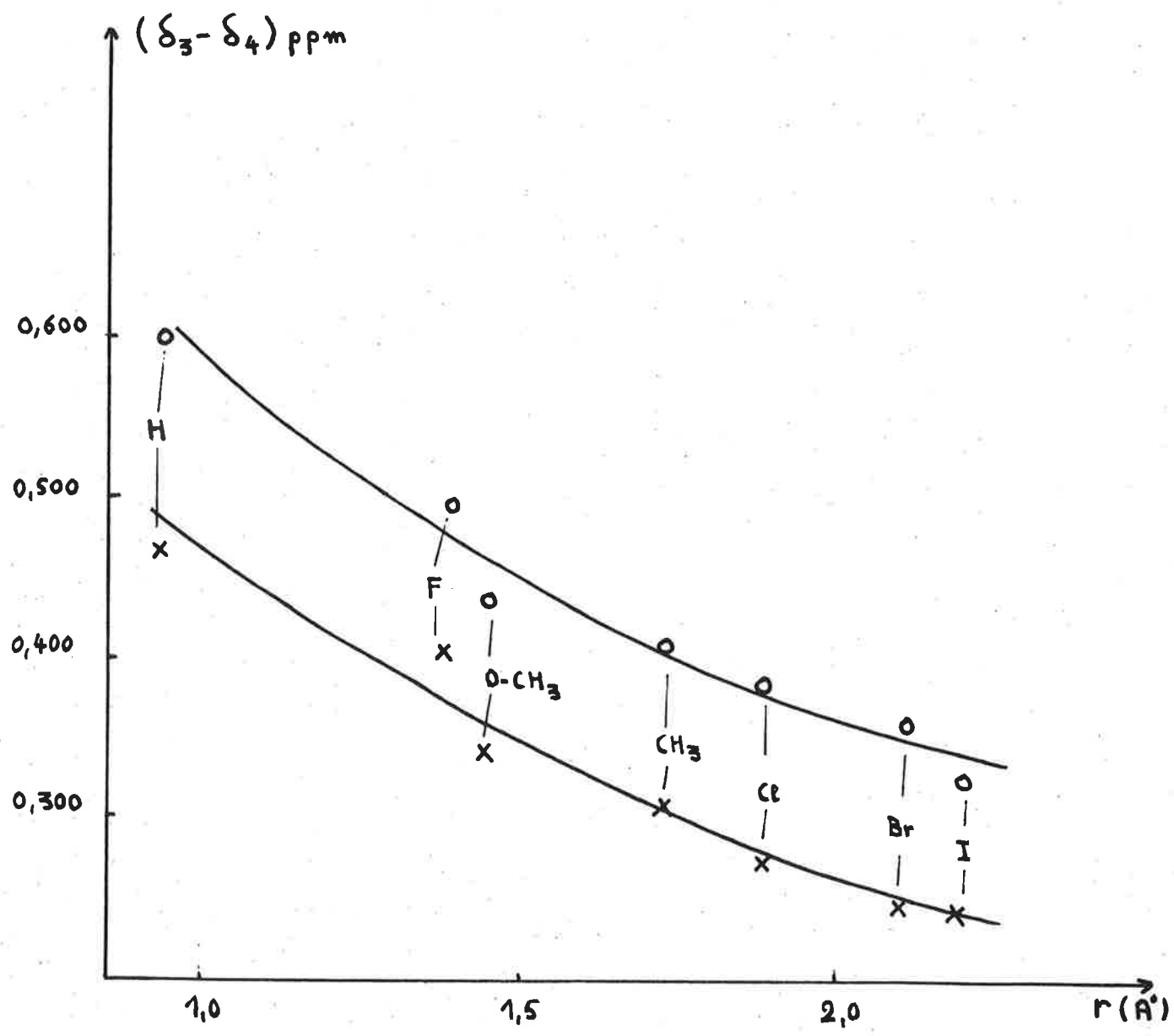(2) ANDRIEU C. BERTIN D. LUMBROSO H.   C. R. Acad Sci 260 - 131 - 1965

2

Fig.I:Variation de l'écart de déplacements chimiques $(\delta_3 - \delta_4)$ dans les composés ortho-substitués du benzoyl-2 thiophène,en fonction du rayon de Van der Waals du substituant ortho.

INDIANA UNIVERSITY

BLOOMINGTON, INDIANA 47405

DEPARTMENT OF CHEMISTRY
CHEMISTRY BUILDING

AREA CODE 812
TEL. NO.

November 30, 1965

Professor Bernard L. Shapiro
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Barry:

Tabulations of [11]B chemical shift data have appeared recently in several reviews,[1-4] notably in one by Schaeffer.[1] We have been measuring [11]B chemical shifts recently for a number of $C_2B_2N_2$ heterocyclic compounds, and have found it very helpful to abstract [11]B chemical shift values from as many pertinent sources as possible and set them down in a table of the sort used by N. B. Colthup for infrared data, and later widely emulated by others. In the thought that other of your readers might find this tabulation useful, I enclose a copy in this letter.

The table is organized into tri- and tetra-coordinated boron compounds, and further subdivided according to the nature of the substituents on the boron atom. Thus, "BCN_2" represents a tricoordinate boron with one carbon and two nitrogen atoms bonded to it. The number in parentheses indicates the number of examples represented. When two values were available for the same compound, both were included. Values were included for measurements carried out in neat liquids and solutions. Measurements for highly deshielded tricoordinate systems in solvents known to function well as Lewis bases were not included. Except for these cases, the nature of the solvent had only a small effect on chemical shifts, where data were available to compare. We have included only those compounds with one type of boron atom, and have not recorded the chemical shift data for systems with bridge hydrogens. For this we apologize to the boron hydride chemists.

Certain trends and consistencies are obvious from inspecting the table. Tri- and tetra-coordinated systems are sharply divided. Shielding generally increases with increasing number of unshared electron pairs on atoms bonded to boron, especially within a series, but there are clear exceptions to this when these atoms are of the third or higher row. There is no apparent general relationship between chemical shift and atom electronegativity.

Sincerely yours,

Joseph Casanova, Jr.
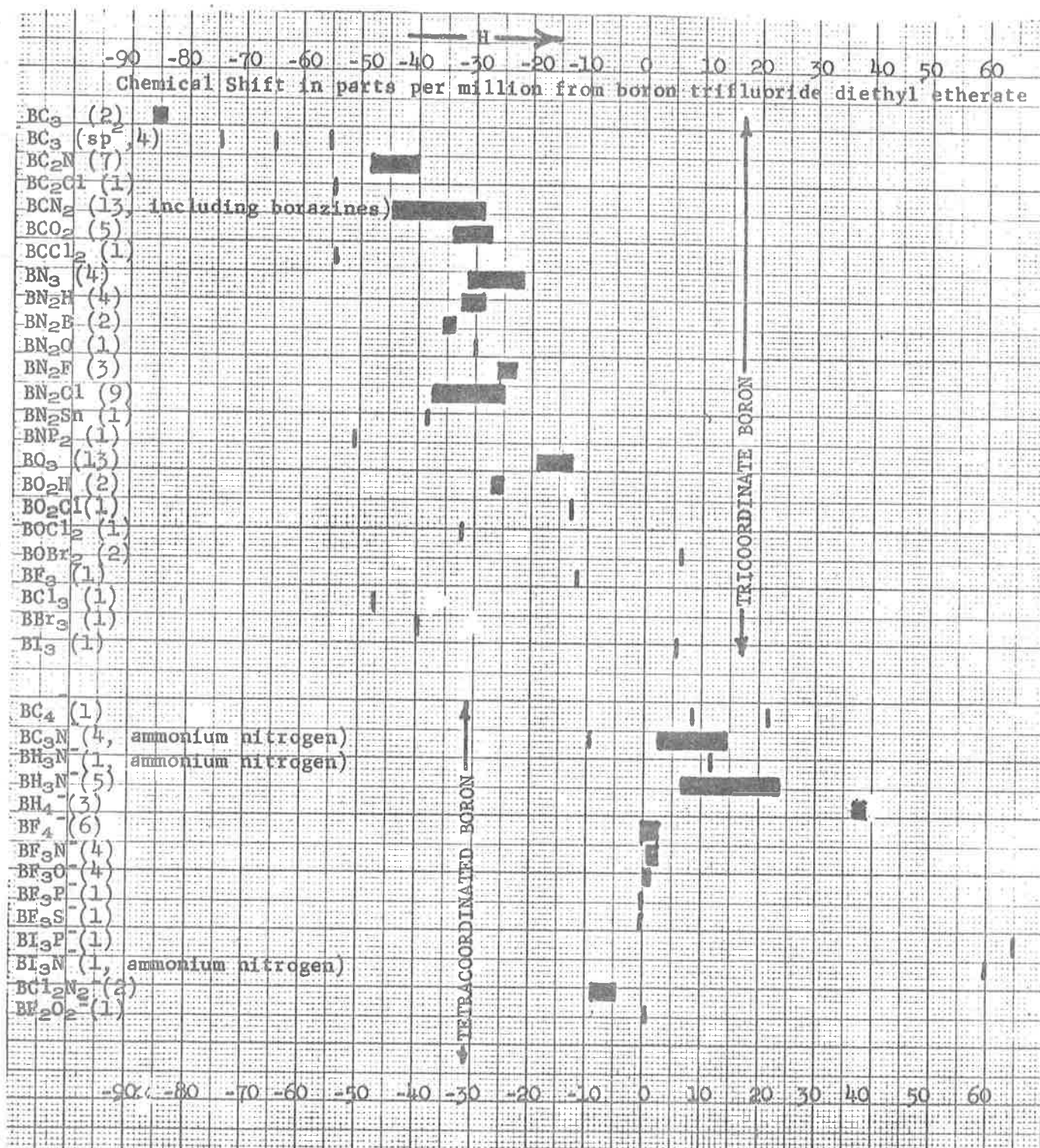Visiting Associate Professor

JC:sjc

Dr. Shapiro
Page 2
November 30, 1965

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Chemical Shift in parts per million from boron trifluoride diethyl etherate

UNIVERSITY OF ILLINOIS

Department of

CHEMISTRY AND CHEMICAL ENGINEERING

URBANA

61803

The William Albert Noyes Laboratory

December 1, 1965

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

Dear Barry:

We have found n.m.r. studies of <u>ortho</u>-substituted triarylmethane derivatives to be very interesting. Increased bulk of <u>ortho</u>-substituents greatly slows the rotation about the bond joining the aromatic ring to the central carbon. The most hindered derivative we have prepared has four <u>o</u>-methyl substituents and two <u>o</u>-methoxyl groups. At room temperature this compound shows two <u>o</u>-methoxyl peaks (τ 6.35 and 6.85) which coalesce at higher temperatures in accordance with $\Delta H\ddagger$ = 18 kcal./mole, $\Delta S\ddagger$ = -10 e.u., and $\Delta G\ddagger$ (176°) = 22 kcal./mole. These values also correctly describe the coalescence of <u>meta</u>-proton peaks on the same methoxylated aromatic ring.
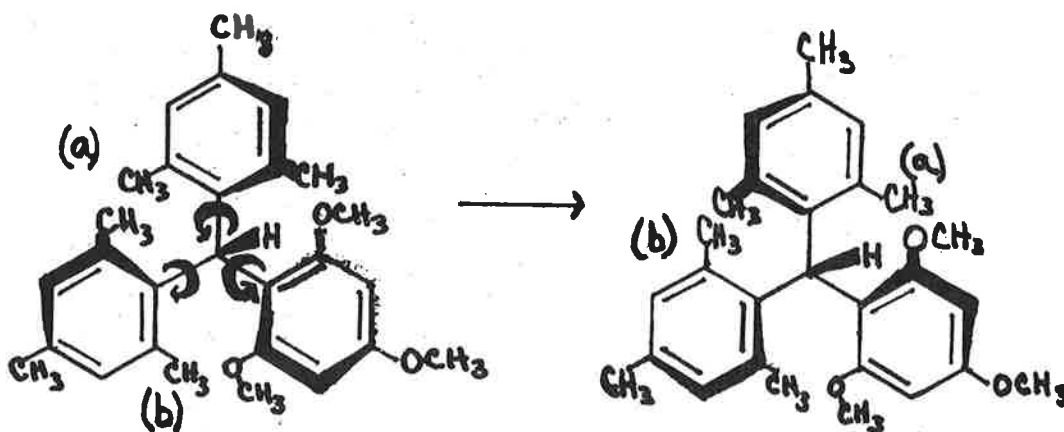
Dr. B. L. Shapiro   - 2 -   December 1, 1965

     The high energy of the transition state for the process interconverting the two ortho-methoxyls presumably reflects the large non-bonded interaction between o-methyls on different rings, (those marked a and b in the pictured process). In this process, converting the molecule from one distorted "propeller" conformation to another, these methyl groups approach each other closely. The exchange of o-methoxyl groups can proceed only through such a transition state. Exo-endo exchange of o-methyl groups, on the other hand, occurs through a transition state involving the smaller interaction between a methoxyl and methyl group. Thus, the non-equivalence of o-methyl groups is seen in the spectrum only at temperatures below -20° * where evidence for four nonequivalent o-methyl substituents is evident. Studies of this compound, and of its analogs with larger ratios of o-methoxyl groups to o-methyl groups, are consistent with this picture.

Yours,

J. C. Martin

(with M. J. Sabacky)

JCM:MJS:psh

     * To press this half page into service in the interests of reform, may I point out that the temperature -20°C. may be expressed as + 390,444 p.p.m. from the m.p. of TMS (-91.1°C). An alternative temperature scale, which has the advantage of avoiding negative numbers, defines the m.p. of TMS as 1,000,000. Thus, -20°C. becomes 1,390,444 °T.

Milan, november, 30th, 1965

Prof.Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois   60616

Dear Professor Shapiro :

for our contribution to the IIT NMR Newsletter we would
like to give results of a study on keto-enol tautomerism in 4-sub-
stituted 1,2-diphenyl-3,5-pyrazolidindiones(1).
The 4-amino-alkylidene derivatives show some interesting
features: only a few examples of vinylogous amides (that are sta-
bilized in a mesomeric dipolar structure) were studied,whereas
hindered rotation in amides is well known.
Among the tree structures :
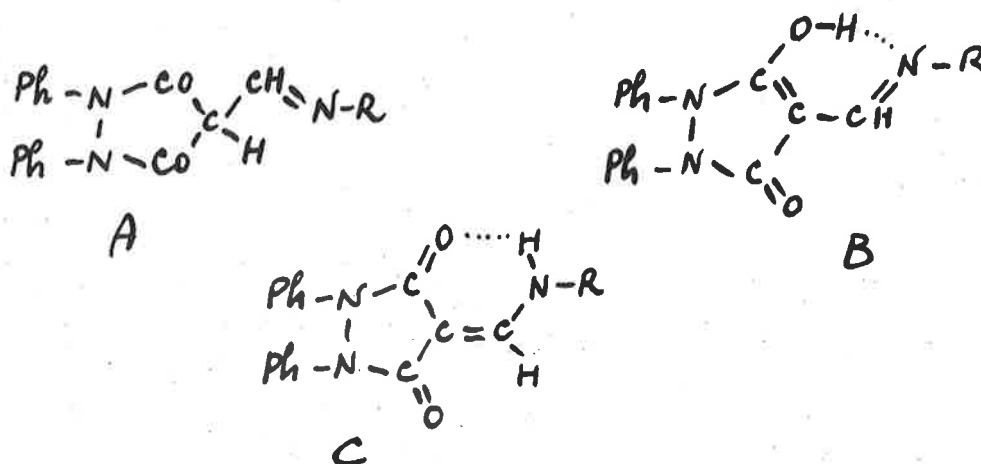
C is preferred for both R=Alkyl and R=Aryl,with a high contri-
bution of the polar structure D :
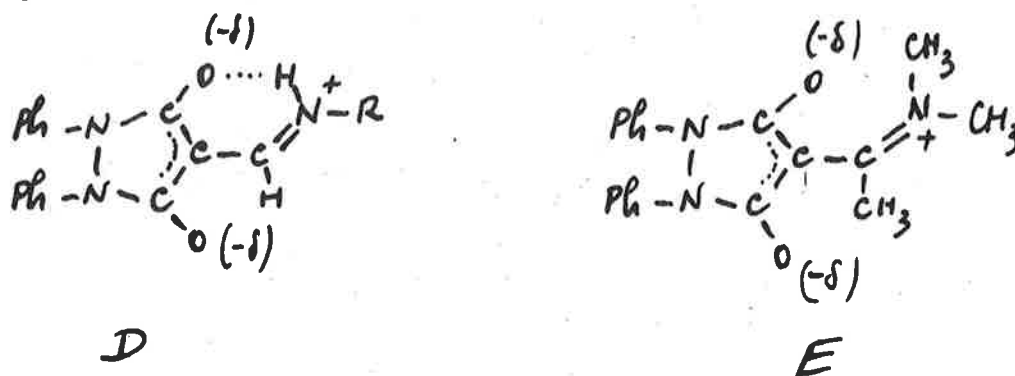
| R | DMSO-d$_6$ | | | TFA | | |
	CH=	NH$^+$	CH$_2$	CH=	NH$^+$	CH$_2$
Ethyl	8.05 D.J=15	9.6 w=24	3.50 Quint. J'=J"=5.5	8.55 D.J=15	10.15 w=30	3.83 Quint. J'=J"=6.5
Phenyl	8.50 D.J=13.5	11.18 D.J=13.5		9.0 D.J=15	11.0- -12.0 a	

a) under solvent.

Similar behavior is shown in CDCl$_3$ and acetone.

This is supported by :

1) the large values of $J_{NH,CH}$ (14-15 cps), explained with a π contribution, due to the partial localisation of double bond between C and N. Only the _trans_ isomer is present; to its stabilisation contributes the intramolecular H-bonding.

2) the lack of protonation in TFA and

3) the very low chemical exchange(2) of the amino hydrogens, as can be seen from observable $J_{NH,CH}$ and J_{NH,CH_2} (see table), thus proving the partial localisation of positive charge on N. In compound E:

4) the hindered rotation between C-N bonds makes the N-methyls non equivalent (3,29 and 3,38 δ in DMSO-d$_6$) at 38°C ; at 80-90°C the two CH$_3$ signals coalesce. Further, homoallylic couplings (J=0,6 and J<0,4) are visible.

With best regards

R. Mondelli

R.Mondelli

(1) The paper, in press in Gazzetta Chimica Italiana, includes also derivatives :

R = H, Alkyl, CHO, COCH$_3$, NO$_2$

Ph-N-CO
| X H
Ph-N-CO   R
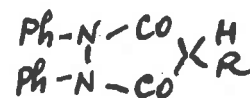
The diketo form prevails when R=H, Alkyl; enolic structures are predominant for electron-withdrawing substituents: intramolecular H-bonds and conjugation with R contribute to their stabilisation.

(2) Sometimes coupling constants were not observable: we think that a trace of basic impurity, sufficient to catalise the exchange, could be present in DMSO-d$_6$.

NORTHWESTERN UNIVERSITY

EVANSTON, ILLINOIS

60201

DEPARTMENT OF CHEMISTRY

December 1, 1965

Associate Professor Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Barry:

By means of an n.m.r. method, we have been able to determine
the conformational preference of the electron lone pair in piperidine.
There has been a long-standing controversy between groups that
maintained that the lone pair is equatorial[1] or axial.[2] Hamlow[3]
and Bohlmann[4] observed that, when a lone pair is constrained to
the axial position, the axial-equatorial chemical-shift difference
between the α-protons is significantly enhanced (0.9 p.p.m. in
quinolizidine; about 0.45 p.p.m. in cyclohexane and protonated
quinolizidine). We applied this test to the spectra of piperidine-
3,3,5,5-d_4 (I), N-methylpiperidine-3,3,5,5-d_4 (II), and N-t-
butylpiperidine-3,3,5,5-d_4 at temperatures for which ring
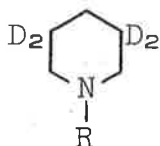
I: R = H
II: R = CH_3
III: R = $\underline{t}$-C_4H_9

inversion is slow (see the figure). For all three compounds, δ_{ae}
(γ) is about 0.5 p.p.m. For piperidine, however, $\delta_{ae}(\alpha)$ is about
0.45 p.p.m., but for the N-methyl and N-t-butyl compounds, the
value is close to 1.0 p.p.m. The large up-field shift of the
α-axial protons in II (the low-field quartet) is quite evident in
the figure (upper spectrum is II, lower is I). These values are
consistent with a predominantly axial lone pair in II and III,
but a predominantly equatorial lone pair in I. Since we get

Dr. Bernard L. Shapiro
Page 2
December 1, 1965

identical results in methanol-d_4 and in cyclopropane, our conclusions seem to be independent of solvent polarity. We are continuing this work with similar heterocyclic systems.

<div style="text-align: right;">

Yours sincerely,

Joseph B. Lambert

Joseph B. Lambert

Robert G. Keske

Robert G. Keske

</div>

JBL/kc

(1)   M. Aroney and R. J. W. LeFèvre, _J. Chem. Soc._, 3002 (1958).

(2)   N. L. Allinger, J. G. D. Carpenter, and F. M. Karkowski, _J. Am. Chem. Soc._, 87, 1232 (1965).

(3)   H. P. Hamlow, S. Okuda, and N. Nakagawa, Tetrahedron Letters, No. 37, 2553 (1964).

(4)   F. Bohlmann, D. Schumann, and H. Schulz, _ibid._, No. 3, 173 (1965).

(a)

(b)

50cps
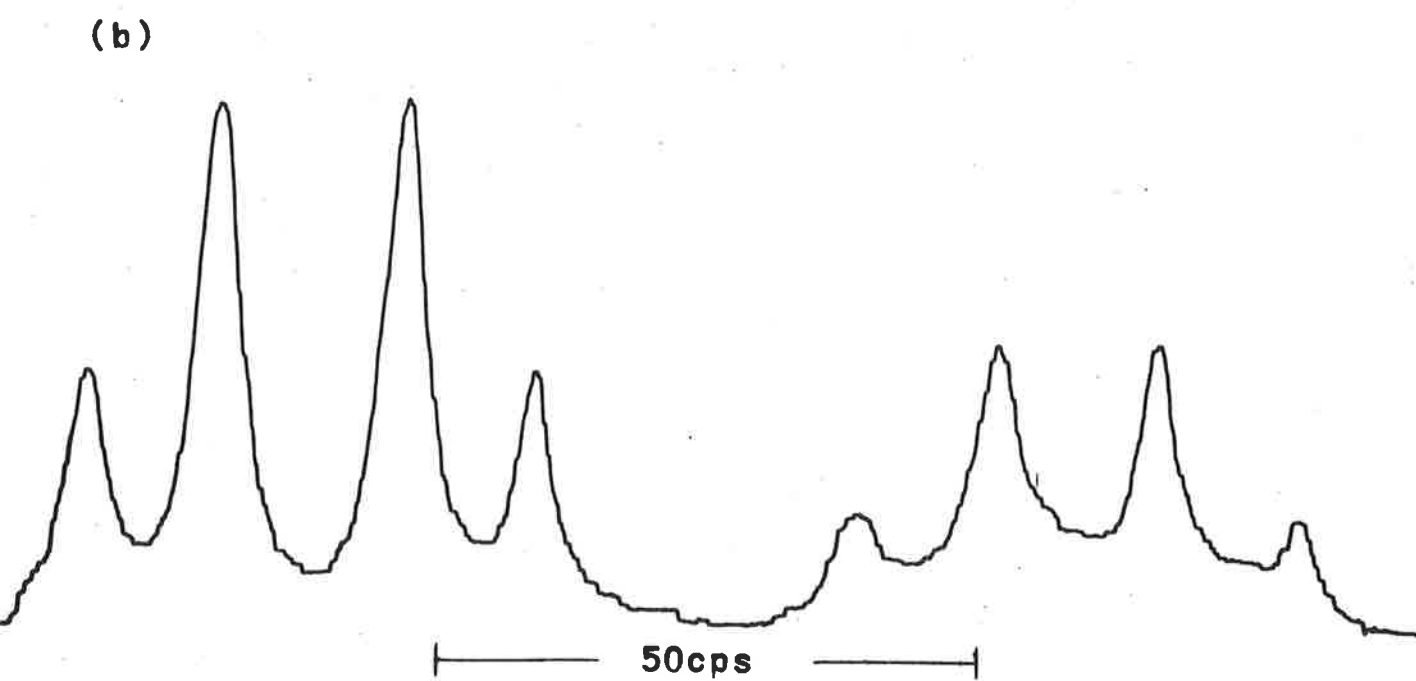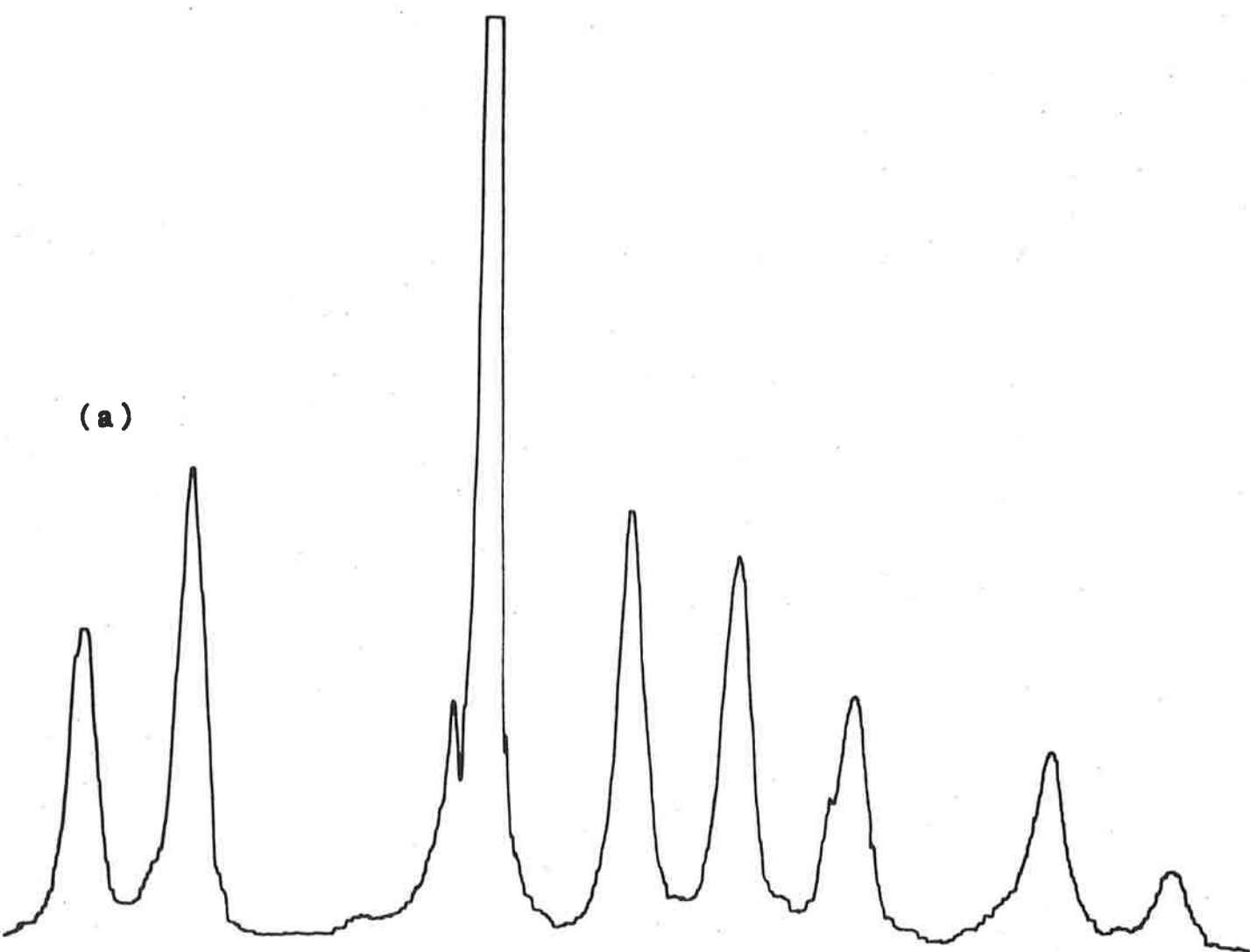
GENT, December 2nd. 1965.
J. Plateaustraat, 22   Tel. 23.38.21

Professor B. L. SHAPIRO,
Department of Chemistry,
Illinois Institute of Technology,

CHICAGO.   ILLINOIS 60616.
U. S. A.

DIFFICULTIES IN USING METHYL KETALS OF ALKYL SUBSTITUTED CYCLOHEXANONES AS MODELS FOR CONFORMATIONAL ANALYSIS.

Dear Prof. B. L. Shapiro,

Since our short communications (1,2) have appeared, we have examined further the title compounds, using the shifts of the methoxy protons. The main problem lays in the unreliability for any value of the "theoretical maximal" shift, value which one should expect to obtain from reference substances with fixed conformation. In fact variable shift difference values between equatorial and axial methoxy protons are obtained for different rigid models.

Moreover there is another troublesome phenomenon. Except for two rigid systems, the others of this class show increasing splitting with decreasing temperature, in the range +150/-105° (~ 30 %). One could have expected an opposite effect, if any. It was indeed found that the shift differences under consideration do not find their equivalent in extend, when compared with the difference between cis- and trans-4-t.Bu-cyclohexyl methyl ether, the latter value being substantially smaller. Clearly there is some mutual interaction between the methoxy groups in the ketals, the axial methoxy groups in the latter compounds being forced to spend some more time above the hexacycle than in the trans (single methoxyl) substituted ether.

.../...

.../...

Thus one should have expected increasing population of the
least hindered rotamers of the axial group at lower tempera-
ture, resulting in a shift decrease.

For analoguous reasons an opposite trend than the one ob-
served would have been expected when twist conformers occur,
as far as these are not present in larger amounts as the chair
forms. Actually we are checking some other systems in order
to evaluate if this temperature dependance is a pecularity for
the gem dimethoxy compounds only. If this was a general beha-
viour it is clear that it is very hazardous to take shift va-
lues obtained e.g. beneath coallescence temperature and to use
them as reference at some other temperature.

Because of the foregoing phenomenon, we could not decide
if the mobile systems can be frozen in (except for 4,4-dimethyl-
1,1-dimethoxy cyclohexane and dimethyl cyclohexanone ketal (3)),
nor could we evaluate from low temperature data the needed "ma-
ximal" shift value.

It was further noted that the distance from an axial me-
thoxy peak towards the peak observed for the (unsubstituted)
cyclohexanone ketal is somewhat greater (ca. 0.4 c/s) than the
one measured between the equatorial methoxy group and the same
reference. It also interesting to note that these behaviour
was found to be the same ($\pm$ 0.05 cps) for all compounds inves-
tigated (in CS_2), except in bicyclic systems (4). There seems
to occur a slight deformation of the hexacycle by introducing
a substituent, which - regardless of the nature of this (except
by "bridging") - the result is grosso modo identical.
Although the original goal has not been obtained, we will do
some further work in this field, especially with 4,4-dialkyl
cyclohexanone methyl ketals.

It is perhaps the occasion here to point upon a mistake
which appeared in Angewandte Chemie (5), where, referring to
our paper (1), the conformational energy value of 1.2 Kcal
has been attributed to $-OCH_3$. This of course regards $-CH_3$
and not $-OCH_3$. Some comparable work has now been achieved in
heterocyclic systems too.

.../...

.../...

We have further the intention to look at gem-difluoro cyclohexane derivatives (2) also, but as the preparation of these compounds creates great difficulties, we actually try to develope other synthetic routes.
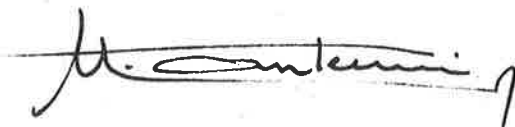
Meanwhile some other PMR work has been done at these laboratories. Please find the list of papers which will be published in the very near future (Bull.Soc.Chim.Belges) :

- The Humulinic Acids-methyl <u>allo</u>humulinic Acid D (hops chemistry)
- Locked Acetyl Group in $N_{(6)}$-Acetylcytidine.
- Shift values of Aromatic Aldehyde Protons.
- NMR Experiments on Ketals. V. The Conformation of 2-substituted-1,3-dioxolanes (treating the results of the (human) analysis of several A_2B_2 systems in 2-substituted-1,3-dioxolanes).

Sincerely yours,

Drs. D. Tavernier

M. Anteunis
Assoc. Prof.

(1) M. Anteunis; Bull.Soc.Chim.Belg., <u>73</u>, 731 (1964).

(2) M. Anteunis, D. Tavernier; Tetr.Letters, n° 52, 3949 (1964).

(3) H. Friebolin (Freiburg) also communicated me he finished studies on these compounds, where he evaluated $F^{\ddagger}$.

(4) Prof. E. Eliel (Notre Dame, Ind.) reported me that he found no difference in shift between the middle of 4-t.Bu ketal and the unsubstituted compound, but that he does on the contrary for 3-t.Bu (solvent not stated). Our results however were checked several times, using as well the unsubstituted compound as internal reference, as other reference material. We found that results must be handled with care caused by shift-concentration dependance.

(5) H. Feltkamp, N.C. Franklin; Angew.Chem., <u>77</u>, 806, table 1 (1965).

C.S.I.R.O. DIVISION OF COAL RESEARCH - P.O. BOX 175, CHATSWOOD, N.S.W., AUSTRALIA
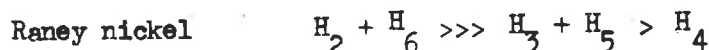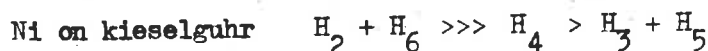
3rd December, 1965.

Professor B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Technology Center,
CHICAGO, ILLINOIS 60616, U.S.A.

Dear Professor Shapiro,

PYRIDINE - DEUTERIUM HYDROGEN EXCHANGE

The nickel catalysed deuterium-hydrogen exchange reaction of pyridine in D_2O, using nickel on kieselguhr[1] and a degassed Raney nickel catalyst, exchanged the H_2 and H_6 protons preferentially to other protons present. However, on longer reaction times there appears to be a different preferential exchange of the remaining protons.

Fig. 1 shows the spectrum for the H_3, H_4 and H_5 protons of pyridine (exchanged with D_2O over Ni on kieselguhr) and Fig. 2 the corresponding spectrum using degassed Raney nickel. In both cases an A_2B and an AB system are present, indicating the species 2,6-pyridine d_2 and 2,3,6-pyridine d_3. However, the Ni on kieselguhr spectrum shows an A_2 (or A) system (high field) due to the species 2,4,6-pyridine d_3 (or 2,3,4,6-pyridine d_4), whereas the Raney nickel run does not show this. The above, together with the areas involved, indicates the following order of exchange:-

Ni on kieselguhr $H_2 + H_6 >>> H_4 > H_3 + H_5$

Raney nickel $H_2 + H_6 >>> H_3 + H_5 > H_4$

Yours sincerely,

P.J. Colin.

P.J. Collin

1. Macdonald, C.G. and Shannon, J.S.
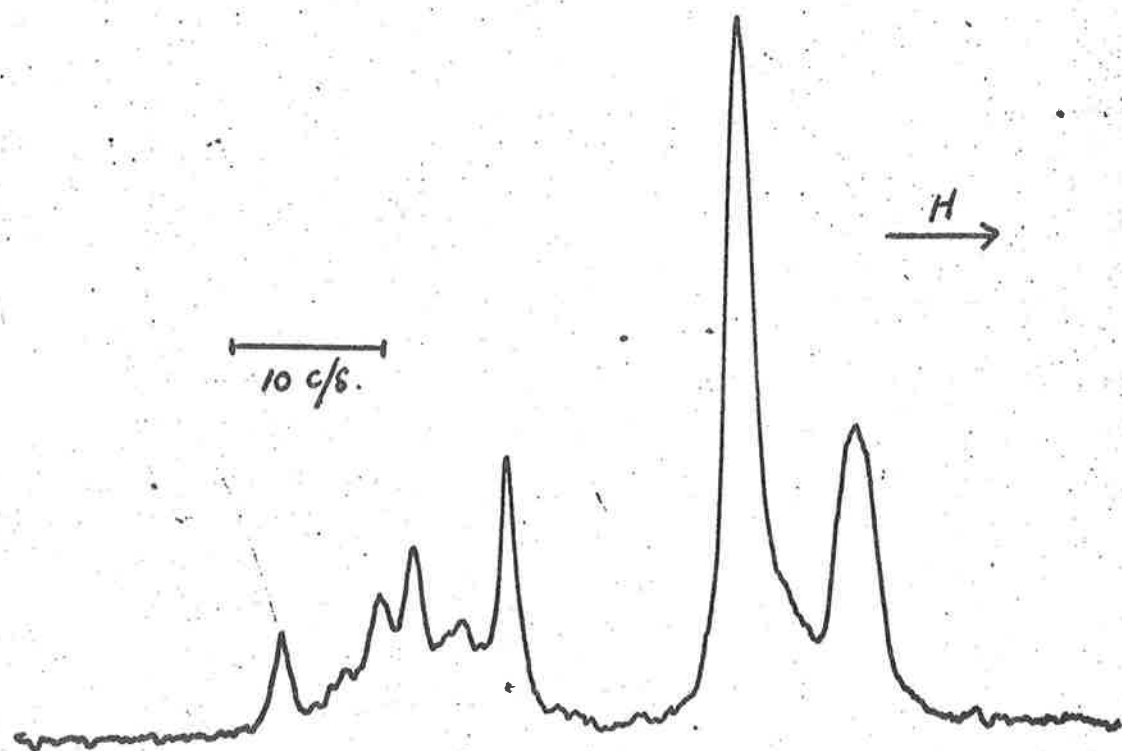   Tetrahedron Letters No. 45, 3351-54 (1964)

Fig.2

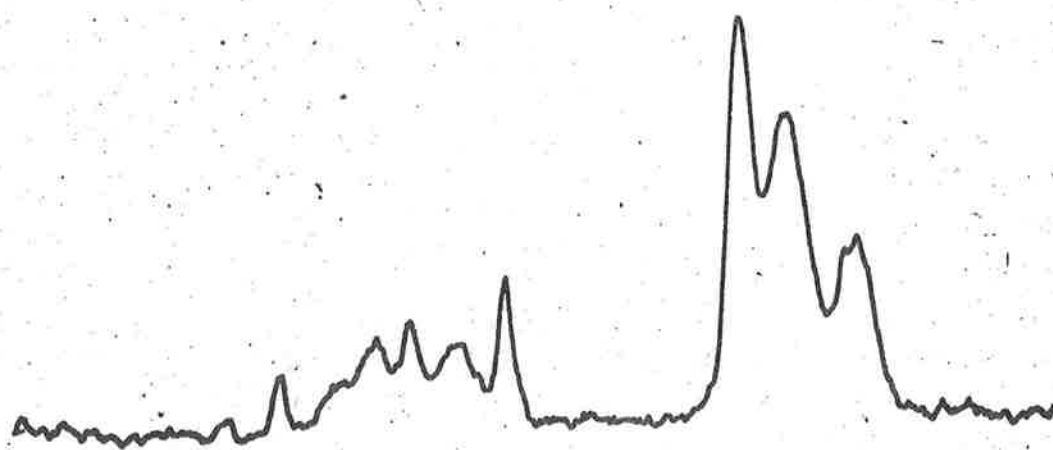

Fig.1

CHEMISCHES LABORATORIUM
DER UNIVERSITÄT MÜNCHEN

INSTITUT FÜR ORGANISCHE CHEMIE
Gerhard Binsch

8000 MÜNCHEN 2, Germany
Karlstr. 23 - Tel. 55 79 76

December 6, 1965

Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago 16, Illinois

What means "magnetically nonequivalent"?

Dear Professor Shapiro:

After having been a postdoc at Caltech and the ETH in
Zürich I have just returned to the University of Munich and
I expect to get some NMR work done in the near future. I hope
the following remarks will put me on the mailing list of
IITNMR Newsletters.

On several recent occasions I noticed that the term
"magnetic nonequivalence" and its associated physical con-
sequences have caused quite a confusion in the minds of
students (and of supposedly more sophisticated people as well).
It turns out that you cannot blame them for it, since some
ambiguities still persist when you look up the research papers
in this particular field. In fact, when you come to think of
it, magnetic nonequivalence might be understood to characterize
three entirely different situations.

Suppose that nuclei with the same chemical shift form a
group. Then one might want to distinguish between

1. nuclei in different groups,
2. nuclei in the same group which are unequally coupled to
   certain nuclei in another, and
3. nuclei in the same group, all of them having equal coupling
   constants to all nuclei of any other, but unequally coupled
   among themselves.

Case 3 could be discarded as being purely academic, since it
is well known that such a difference is principally unobservable.
But even then it becomes obvious that, for being concise, we
need an additional specification.

Since it is also desirable to have some means of expressing
the relationship between the magnetic environment of the nuclear
spins and the chemical structure of the molecule in which they
are incorporated, the following definitions are recommended.

1. We call nuclei chemically equivalent if and only if they are related by molecular symmetry (otherwise chemically nonequivalent).
2. Nuclei with the same chemical shift are called isochronous, regardless whether this is a consequence of their being chemically equivalent or not (otherwise anisochronous).
3. We speak of magnetically nonequivalent nuclei whenever they differ in chemical shift, or in coupling constants to spins in another group of isochronous nuclei, or in both; magnetically equivalent nuclei, however, may still differ in their coupling constants within a group of isochronous spins.

There is nothing new about these terms. Almost all of them have appeared in the pertinent literature, albeit not with precisely this meaning. If we would decide to stick to these definitions, we could differentiate the following five cases (the minus sign designates the contrary)

1. CE   IS   ME
2. CE   IS   -ME
3. -CE   IS   ME
4. -CE   IS   -ME
5. -CE   -IS   -ME

By applying the principle of maximum coincidence we see that it would suffice to speak of anisochronous spins, whereas, e.g., the observation that isochronous spins are magnetically equivalent does not necessarily imply that they are also chemically equivalent, etc, etc.

I am considering to put all these things neatly together, show their consequences, decorate them with a few illustrative examples, and send it to J. Chem. Ed. Before I do so it would comfort me to know that I find myself in agreement with the community of NMR spectroscopists. Comments to the contrary are hereby encouraged.

Sincerely,

Gerhard Binsch

CONFIGURATION OF AMIDE GROUPS IN CYCLIC ANILIDES

After our Research Centre recently secured a Varian 60 NMR spectrometer, we have looked at the NMR spectra of a number of cyclic anilides. In the course of this study, we have come across data which may be of some interest to NMR fans.

Restricted rotation in simple amides has been the subject of detailed studies in the past[1]; recently NMR evidence has been presented for the stable conformation of N-methylacetanilide[2], in comparison with that of acetanilide. In a study which we hope to publish elsewhere, we have looked at the NMR spectra of some N-acylindolines and N-acyltetrahydroquinolines. We find that the preferred, perhaps exclusive, configurations of the amide bond in the two groups in $CDCl_3$ solutions are respectively as depicted in I and IIIa.
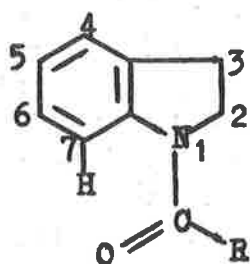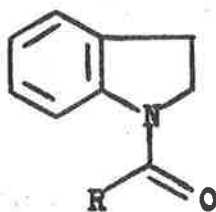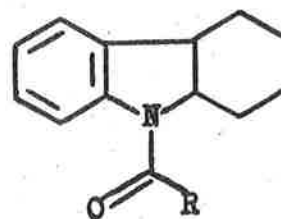

| I | Ia | II |

The literature already records[3] NMR data for simple N-acylindolines, which would indicate that I is the preferred configuration. This is inferred from the large down field shift found for the aromatic proton at position 7 on the indoline ring eg., in N-acetyl-3,3-dimethyl-indoline (fig.1, δ 8.2 from TMS). The magnitude of the chemical shift (0.8 - 1.3 ppm) of this proton relative to the rest arising from the field effect of the carbonyl group would suggest full or nearly complete coplanarity of the amide and benzene planes. A similar down field shift of this aromatic proton signal has been found for N-acylhexahydro-carbazoles (II)[4,5]. In special cases, as for kopsine[5], the down field shift is not observed, because of the N-acyl group being bound in the opposite configuration (Ia).

In the spectra of N-acyltetrahydroquinolines, eg., N-acetyltetrahydroquinoline (fig.2), the signals of all the 4 aromatic protons are seen as an ill-resolved multiplet, centred around δ 7.2. On the other hand, the methylene protons at C-2 appear as a triplet (rapid inversion of the tetrahydropyridine half chair[6]) at δ 3.8. The protons at C-2 in the model compound IV, that was readily available to us at the time, are seen as

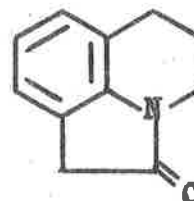a triplet at δ 3.73. We would like to consider this as strong evidence for the proposed orientation of the carbonyl group in IIIa.
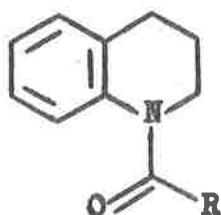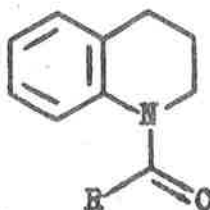
III   IIIa   IV

The NMR spectrum of N-acetyltetrahydroquinaldine (fig.3) illustrates this even better. All the 4 aromatic protons again appear as one multiplet. The shift of the methine proton at C-2 (δ 4.83) from its position in tetrahydroquinaldine is 1.58 ppm. This not only supports our thesis, but also incidentally indicates that the tetrahydropicoline ring exists almost exclusively with the methine hydrogen in the equatorial and methyl group in the axial conformations (cf. Bohlmann and Schumann[7]). This may be considered to be further substantiated by a simple analysis of the signals from the C_2-H. The observed sextet (J $\sim$ 7 cps) would be easily explained by three H-CH$_3$, one H_e-H_e and one H_e-H_a couplings, all of them equal in magnitude or nearly so. Of course, the e-e and e-a couplings are on the larger side. Models indicate unfavourable interaction between the methyl group in the equatorial conformation, with the carbonyl group. Hence the preference for the axial conformation.

The preferred configurations of anilides are known to be influenced by substituents on the nitrogen atom[2]. In our case, we would like to speculate from a study of Dreiding models that as compared to N-acyltetrahydroindolines, there is greater interaction in the case of N-acyltetrahydroquinolines, of the R group with the protons at C-2 in the configuration III. This would tend to destabilize III in favour of IIIa.

Lastly, we would like to mention the abnormal position (δ 1.43) of the signal from the methyl group in N-acetyl-1,2,3,4-tetrahydro-8-phenylquinoline, which would suggest that it has structure V with a twisted diphenyl system, with the methyl group poised over the 'hole' in the 8-phenyl group.
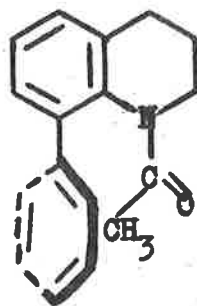
V

We hope to study in the near future the influence of temperature on the NMR spectra of these derivatives.

References:

1. M.T. Rogers & J.C. Woodbrey, J. Phys. Chem., 66 (1962), 540.

2. B.F. Pedersen & B. Pedersen, Tetrahedron Letters, 1965, 2995.

3. S. McLean, Canad. J. Chem., 38, 2278 (1960).

4. W.G. Kump, D.J. LeCount, D.R. Battersby & H. Schmid, Helv. Chim. Acta, 45 (1962), 854.

5. T.R. Govindachari, B.R. Pai, S. Rajappa, N. Viswanathan, W.G. Kump, K. Nagarajan & H. Schmid, Helv. Chim. Acta, 45 (1962), 1146.

6. H. Booth, J. Chem. Soc., 1964, 1841.

7. F. Bohlmann & D. Schumann, Tetrahedron Letters, 1965, 2435.

CIBA Research Centre   Dr. K. Nagarajan
Bombay 62 - India   Dr. M.D. Nair

FIG.1

(sweep offset +50cps)

FIG.2

FIG.3

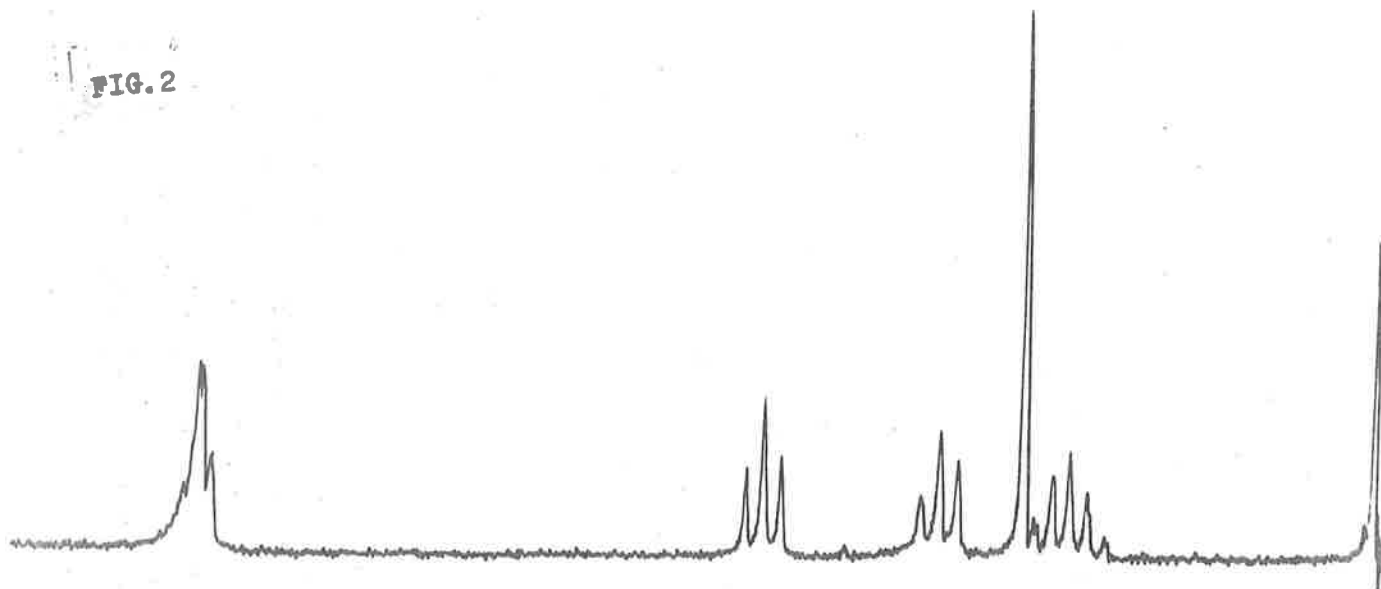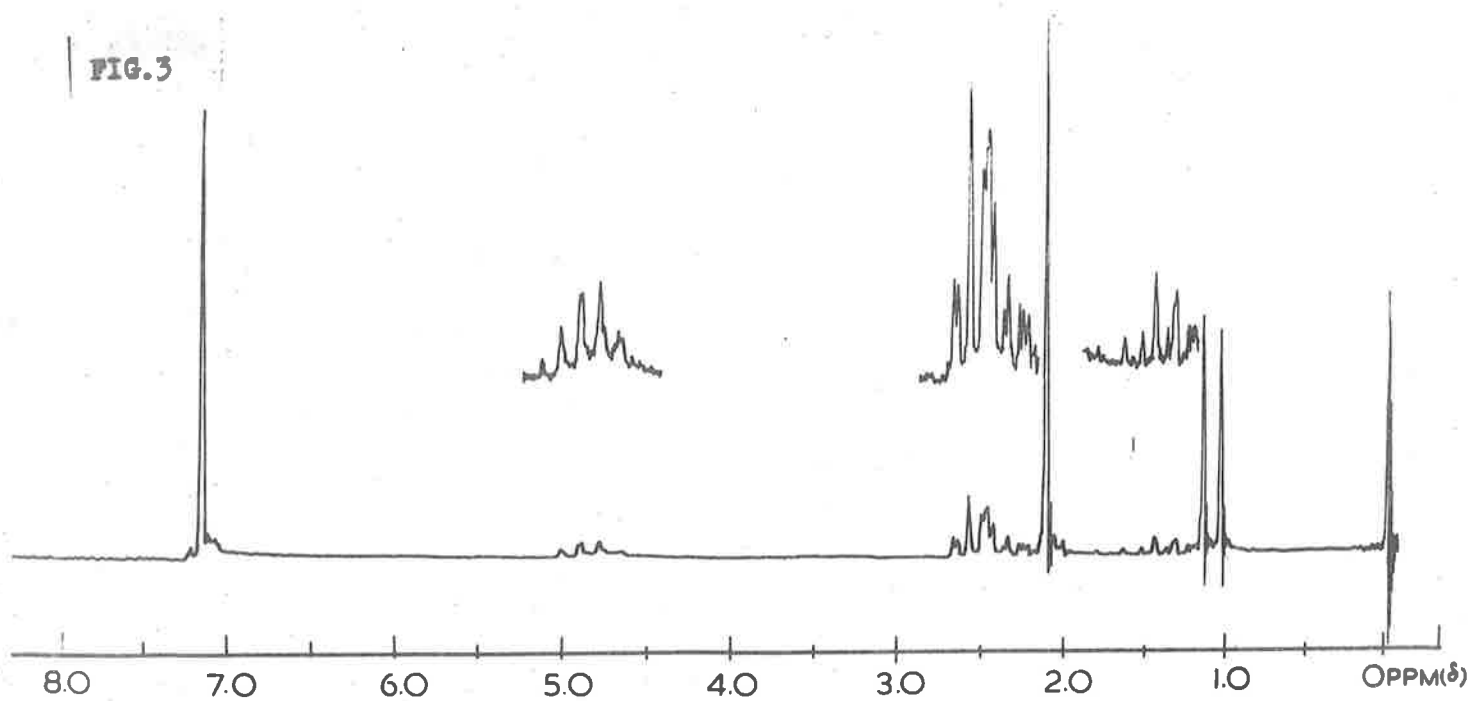87-37

8.0   7.0   6.0   5.0   4.0   3.0   2.0   1.0   OPPM(δ)

THE UNIVERSITY OF NEW BRUNSWICK
FREDERICTON, N. B.
CANADA

DEPARTMENT OF PHYSICS

December 8, 1965

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

Feedback Spectrometer

Dear Barry:

Thank you for your patience regarding my contribution to the news-
letter. While I was at Shell Development Company we investigated in
some detail the behaviour of a regenerative feedback loop consisting
of the n.m.r. spectrometer and a narrow band filter. Such a loop can
be established in principle by connecting the receiver coil through a
narrower band amplifier to the transmitter coil of the crossed-coils
probe. Oscillations occur when the Larmor frequency of the nuclei in
the sample is passed by the filter in the feedback amplifier, provided
that the loop gain and phase shift are properly adjusted. Scanning of
the magnetic field brings one sample resonance after another into the
passband of the filter, and a recording of the oscillation amplitude
vs. field strength resembles the sample spectrum. A detailed study of
the dynamics of the system, based on the Bloch equations, was carried
out with an analog computer.

In order to obtain adequate resolution, the filter band width must
be comparable with the n.m.r. line width, and this is difficult to
achieve with a filter in the r.f. range. A practical solution may be
obtained by operating with side band resonances (see Rev. Sci. Instr.
33, 495, 1962) so that the filter may operate in the audio frequency
region.

The interesting feature of such a feedback system is that it can
produce spectra with enhanced signal/noise ratio without using multiple
scan averaging techniques or an excessively slow scan rate. Some
features are similar to the rapid adiabatic passage method, but the
resonance lines are not significantly broadened beyond their slow-
passage width. The attached recording shows C^{13} spectra in natural
abundance of benzene on the left, and of p-dioxane on the right, both
obtained with the feedback spectrometer using a 4 mm i.d. sample tube
at 24 K gauss.

Sincerely yours,

R. Kaiser
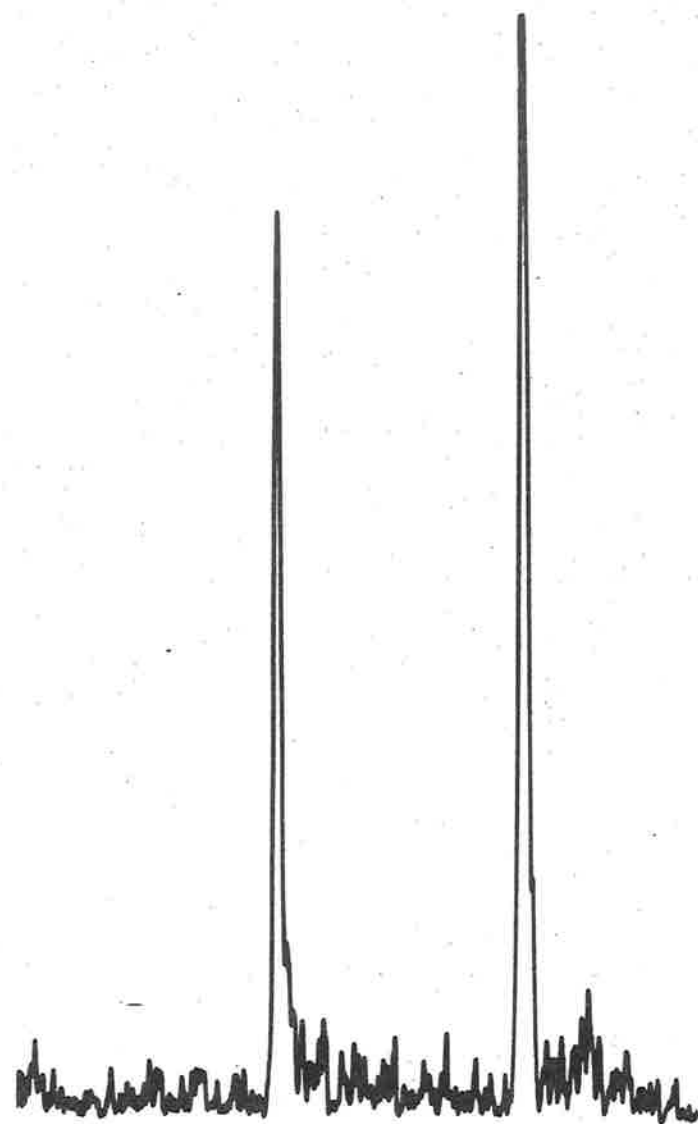
C[13] spectra in natural abundance

benzene
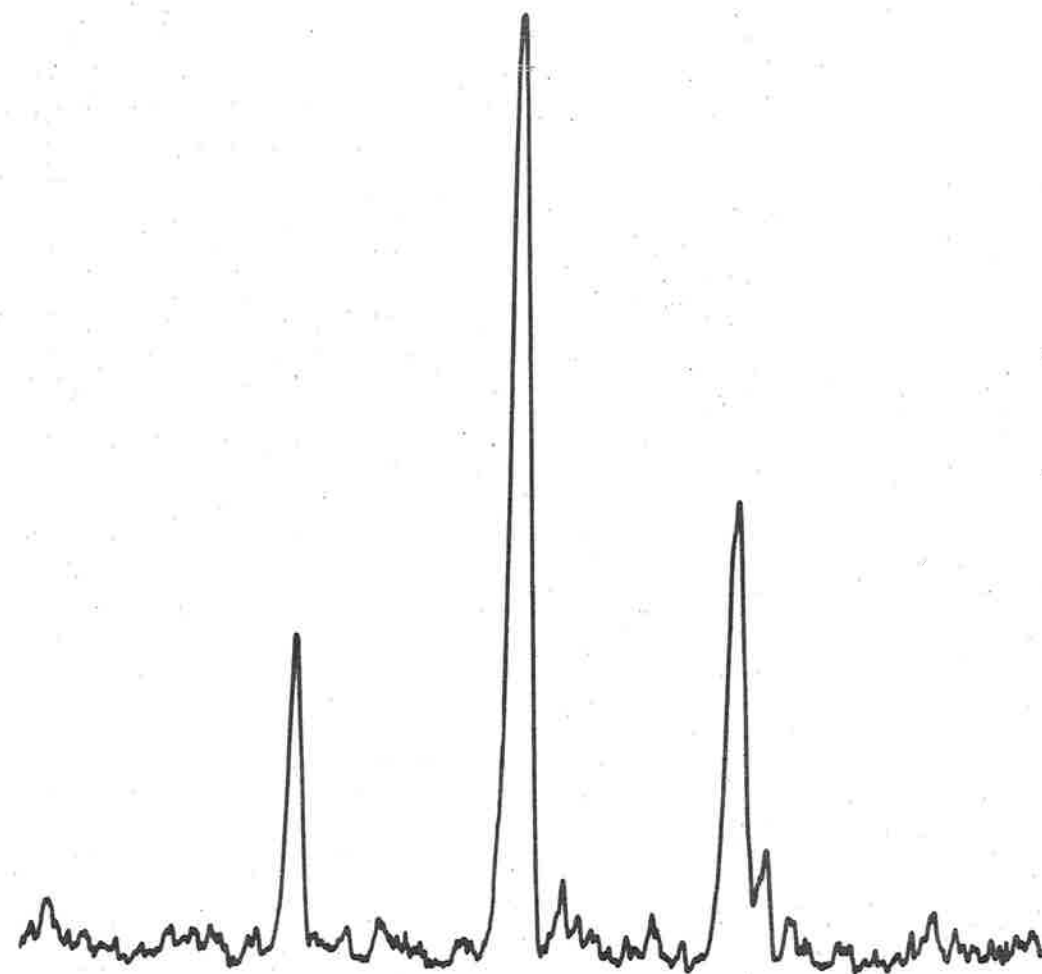
. p-dioxane

UNIVERSITY COLLEGE OF SWANSEA.
(UNIVERSITY OF WALES)
SINGLETON PARK, SWANSEA.

Telephone : SWANSEA 25678.

**DEPARTMENT OF
CHEMISTRY.**

**PROFESSOR C. H. HASSALL,
Ph.D., F.R.I.C.**

9th December 1965.

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

Dear Professor Shapiro,

In reply to your appeal in October's issue of the newsletter for a source of tetramethylsilane, I thought that it might interest readers to hear of our experience in Swansea.

A few months ago we also wanted to replenish our stock of T.M.S. but found that the sole manufacturer in Britain (L. Light and Co. Ltd.) had deleted this item from their list. On looking into possible sources of TMS in Europe we were able to find only two manufacturers who could supply high purity material; Fluka A.G., Buchs S.G., Switzerland and E. Merk A.G., Darmstardt, Western Germany. However, the cost of imported high purity material from either manufacturer was in fact greater than the new prices which you have quoted for manufacture in the U.S.A. We had to order a small quantity from one of these manufacturers to tide us over and in desperation we became interested in whether we could make the stuff ourselves.

We contacted a friend in a local silicone plant for advice and he was able to tell us that the plant probably made vast quantities of TMS each year but that it was not economic to separate it off and it generally went to waste. However he mentioned that it was comparatively easy to prepare TMS by the reaction of trimethylsilyl chloride with methyl magnesium bromide when TMS was the sole product.

Trimethylsilyl chloride, being an intermediate in silicone production, should be relatively easy to obtain at reasonable cost and for those of your readers who have the time or have a tame organic chemist handy, I enclose the recipe.

(cont'd. ....

Professor B. L. Shapiro   9th December 1965

Methyl magnesium bromide was prepared in the usual way
from methyl bromide (380 g.) and magnesium (96 g.) using di-n-butyl
ether (2000 ml.) as solvent. Trimethylsilyl chloride (445 g.) was
added over 1 hour to the stirred cooled solution (0° C.) with the
provision of efficient reflux condensers. The reaction was allowed to
warm up gradually with continued agitation and was finally heated under
reflux for 1 hour. After cooling to 0° C., the complex was decomposed
by the addition of dilute hydrochloric acid. The solvent layer was
separated, washed with water and dried over anhydrous magnesium
sulphate. The product was then separated from the di-n-butyl ether
with an efficient fractionation column, when TMS was obtained as
the fraction b.p. 26-30° C. A second distillation gave tetramethylsilane
b.p. 26-27° C. (140 g. 40% yield) which was homogeneous in the nmr
spectrometer.

Yours sincerely,

J. A. Ballantine

J. A. Ballantine.

UNIVERSITY OF CALIFORNIA, LOS ANGELES

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DEPARTMENT OF CHEMISTRY
LOS ANGELES, CALIFORNIA   90024

December 15, 1965

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

Dear Barry:

Ring Inversion in Cyclohexane-d_{11}

The recent spin-echo work of A. Allerhand, F-M. Chen and H. S. Gutowsky[1] on the conformational isomerization of cyclohexane and cyclohexane-d_{11} gave a much lower value of $\Delta H^{\ddagger}$ (and E_a) than previous measurements based on the high-resolution method. Tony Bourn and I have now made new measurements at 60 Mc./sec. with improved instrumentation by the latter method. A field-frequency lock was used to obtain reproducible sweeps at very low sweep rates (e.g., 0.06 c.p.s./sec.) and at constant resolution.

Temperature gradients along the vertical axis of the sample tube were kept to less than 0.3°/cm. by means of a rapid flow of nitrogen for cooling and by the use of a sample tube which had been modified by sealing a 5 mm glass sphere to the bottom end (this prevented the sample from being in the region of the Nylon cup at the bottom of the insert, where cooling is relatively inefficient). Temperature measurements were made with copper-constantan thermocouples (30 gauge) and a Leeds-Northrup potentiometer (Cat. no. 8687). The thermocouples were calibrated against a platinum resistance thermometer and were also checked at the sublimation temperature of Dry Ice (-78.6°). The temperature of a liquid at the level of the receiver coil in a tube modified as above was about 1.5° higher than the temperature indicated on a thermocouple sealed to the insert about 2 cm. above the receiver coil. This difference was very reproducible from day to day at a given flow-rate of cooling gas. We estimate that the temperature of the sample at the level of the receiver coil can be measured to an accuracy of better than $\pm$ 0.3°. (Deuterium decoupling did not affect the temperature of the sample.)

Since the value of $\Delta H^{\ddagger}$ is largely dependent on measurements of k at the temperature extremes of the temperature range used, we made measurements at about -35°, when the line is still sufficiently wide (about 1.5 c.p.s.) that its width can be

-2-

measured accurately, and at about -82°, when two lines of about
1.5 c.p.s. each are obtained. The line-width of internal TMS
under these conditions varied from 0.28 c.p.s. (at -35°) to 0.36
c.p.s. (at -82°). Since the sample was carefully degassed and T_1
was quite large, these widths were due largely to magnetic field
inhomogeneities. The coalescence temperature was also determined.
The results are as follows:

Temperature	Line Width	k (sec^{-1})
	(corr. for reference peak width)	
-35.3°	1.24 $\pm$ .05 c.p.s.	1,040 $\pm$ 40
-62.0°	(coalescence)	63.6
-82.3°	1.18 $\pm$ .05 c.p.s.	3.70 $\pm$ .15

E_a=10.85 $\pm$ 0.3 kcal./mole; $\Delta H^{\ddagger}$=10.45 $\pm$ 0.3 kcal./mole

The data of ACG give E_a=9.5 $\pm$ 0.1 kcal./mole, and $\Delta H^{\ddagger}$=9.1 $\pm$
kcal./mole.

We have carefully considered various possible sources of errors
but can see none which could reduce the activation energy to the
value found by ACG. In particular, the line-width at -82.3°
gives a value of k (3.70 sec^{-1}) which should be reliable, but
which is well off that expected from the data of ACG. (k=5.8 sec^{-1})

Our present results are in excellent agreement with those of Bovey
et al[2], and with our own previous results[3].

We hope to obtain further data at temperatures of about -100°,
using the double irradiation method of Forsen and Hoffman[4].

Yours sincerely,

F. A. L. Anet

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    and should be multiplied by 2. This correction lowers the
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4) S. Forsen and R. A. Hoffman, J. Chem. Phys., 39, 2892 (1963).

TEXAS CHRISTIAN UNIVERSITY
Fort Worth, Texas 76129

Department of Chemistry   December 9, 1965

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

Dear Dr. Shapiro:

Perhaps the readers of I.I.T.N.M.R. should be informed of two
positions available in the department here at T. C. U. One is for
a physical chemist, and the other (presumably an analytical chemist)
is for someone with a special interest in teaching the senior course
in instrumental analysis.

Our department is small (nine men), extremely well equipped,
and our graduate program is growing (now twenty-six graduate students).
Stipends are competitive, and fringe benefits well above average. A
new building is in the offing. Teaching and research are equally
emphasized with one or two courses the normal load. Contracts are
for forty two weeks; so there's no sweat about summers.

Interested persons may contact me for further information.

Yours sincerely,

W. B. Smith
Chairman
Department of Chemistry

WBS/dc
Enclosure

P. S.   Our current NMR is an A-60 with variable temperature probe and
a spin decoupler on order.

THE UNIVERSITY OF IOWA

IOWA CITY, IOWA   52240

Department of Chemistry   December 17, 1965

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

Dear Barry:

I hope this note will keep my name on the mailing list of your stimulating newsletter. A short title is "Chelated Enol Protons".

Enolic protons which are chelated, as in 1, have chemical shifts ranging from 10.6 ppm (downfield from TMS) for methyl salicylate and 14.9 ppm for acetylacetone to 16.7 ppm for dibenzoyl methane. Paramagnetic deshielding and paramagnetic anisotropy must be operating in a concerted manner for such unusual downfield positions.
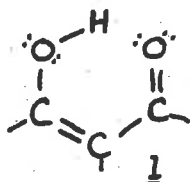
We have examined the NMR spectra of some enolized β-diketones:
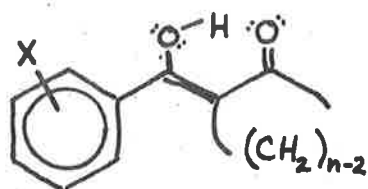
C-5 (n=5)
C-6 (n=6)
C-7 (n=7)
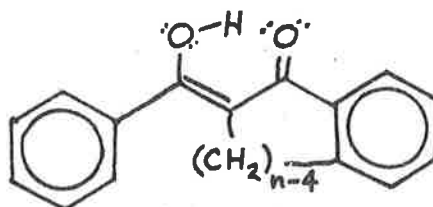
B-5 (n=5)
B-6 (n=6)
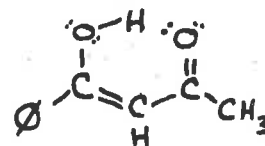
A

Table I Enol Proton Shifts and Line Widths

Compound	Shift in CCl_4	$W\frac{1}{2}$
A (Benzoylacetone)	15.52 ppm	5 cps
B-5 (2-Benzoylindanone)	14.18	3.5
B-6 (2-Benzoyl-1-tetralone)	16.61	2
C-5 (2-Benzoylcyclopentanone)	14.0	12
C-6 (2-Benzoylcyclohexanone)	16.31	1
C-7 (2-Benzoylcycloheptanone)	16.88	1.5

Prof. B. L. Shapiro
December 17, 1965
Page 2

    Our experiments (Table I) show that the oxygen-oxygen distance is critical. In the open-chain and six and seven membered ring cases, the internal angles in the chelate ring can be the optimum 120°. In C-5 and B-5 cases these angles are distorted to ~128°, the system O-H---O is stretched, and an upfield shift occurs, accompanied by broadening of the signal to $w_\frac{1}{2}$ = 12 cps. in C-5. It appears that the proton experiences an electrical field gradient as it tunnels between the two oxygen atoms at a rate in the range of proton relaxation time. We have no measure of $\Delta \nu$ for the two proton positions. We intend to extend our solvent studies and do some temperature studies as well, to get at ν_A and ν_B. Any suggestions would be gladly received.

    It is also possible that in these compounds (Table I) the enol proton experiences a decreasing paramagnetic anisotropy as it is removed to greater distance from the center of the chelating ring system. This suggests that in B-6 and B-7 the proton is almost in a straight line between the chelating oxygens, and in B-5 it is moved outward due to weaker chelation.

    We also find substantial solvent effects with 2-benzoyl-1-tetralone (B-6). The enol proton appears at 17.15 ppm in pyridine, 16.76 in acetone, and 16.56 in carbon tetrachloride. The downfield shift in pyridine is due to anisotropy of oriented solvent molecules.

    Substituents which favor enolization in the benzoyl cyclopentanones (C-5) cause an upfield shift in the enol proton signal (Table II). One might predict a down field shift due to additional proton deshielding for substituents which are electron withdrawing (o-Cl, p-NO$_2$). One

Table II Substituted Benzoylcyclopentanones in CDCl$_3$

Substituent	none	p-OCH$_3$	p-Cl	p-NO$_2$	o-Cl	o-CH$_3$
Shift (ppm.)	14.16	14.53	14.30	14.25	12.34	12.78

explanation for the result observed is that as the pi electron density in the chelate ring increases, the increased anisotropy causes a greater paramagnetic shift. This paramagnetic effect is intense in all of these compounds.

Sincerely yours,

Richard D. Campbell
Department of Chemistry
University of Iowa
Iowa City, Iowa 52240

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