July 65

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Institute of
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Newsletter

No. 81
JUNE, 1965

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STEVENS INSTITUTE OF TECHNOLOGY

HOBOKEN, NEW JERSEY

Department of
Chemistry and Chemical Engineering

May 18, 1965

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

Signs of $J(C^{13}CH)$

Dear Barry:

Using the Varian Integrator as a spin decoupler, we have been investigating the C^{13} satellites of methyl protons. Based on $J(C^{13}H)$ being positive, we find $J(C^{13}CH)$ to be +27.1 cps and -2.8 cps for acetaldehyde and 1, 1-dichloroethane, respectively. (The C^{13} is the methyl carbon.) The negative sign of the latter compound is particularly interesting; expecially so, since Freeman (Mellon Newsletter 55-15) reports a value of +1.1 cps for sym-tetrabromoethane.

We are very much interested in hearing from anyone who has been using the Varian Model C-1024 Time Averaging Computer on HR-60 or DP-60 spectrometers, not equipped with a Proton Stabilization Control Conversion Kit.

Respectfully yours,

Edmund R. Malinowski

Edmund R. Malinowski
Assistant Professor
of Chemistry

ERM:jef

CARNEGIE INSTITUTE OF TECHNOLOGY
SCHENLEY PARK
PITTSBURGH 13, PENNSYLVANIA
DEPARTMENT OF CHEMISTRY

May 19, 1965

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

Dear Barry:

Diamagnetic Anisotropies of Substituent Groups

IITNMR readers may be interested in a set of substituent diamagnetic anisotropies which we have obtained from the in-plane susceptibilities of substituted benzenes, naphthalenes and anthracenes. The table gives the susceptibility increments parallel to and perpendicular to a C-X bond relative to the C-H bond in the unsubstituted aromatic hydrocarbon. Such increments must, of course, be combined tensorially in a polysubstituted compound. The numbers were obtained by assigning fixed increments for each substituent in both directions and making a least-squares fit to all available experimental data. Only in-plane susceptibilities were used, as changes in the susceptibility perpendicular to the molecular plane arise partly from the change in ring currents caused by the substituent.

	$10^6 K_{\parallel}$	$10^6 K_{\perp}$	$10^6 (K_{\parallel} - K_{\perp})$
Me	-12.46	-9.91	-2.55
Br	-34.37	-20.54	-13.83
Cl	-20.99	-9.21	-11.78
OH	-9.65	-2.72	-6.93
NO_2	-14.13	-0.78	-13.35
NH_2	-4.66	-10.38	+5.72
= O	+1.52	+2.70	-1.18
COOH	-10.10	-16.80	+6.70

Three features are worth particular note.

1. The results for Me indicate that the C-C single bond has its axis of highest diamagnetism along the bond (that is, assuming no anisotropy for the C-H bond). This is in agreement with the magnetic birefringence

result of Buckingham, Pritchard and Whiffen, but in disagreement with the anisotropy usually deduced from the NMR data.

2. Carbon-Halogen bonds have their excess of high diamagnetism along the bonds.

3. The carbonyl group is paramagnetic relative to C-H for both in-plane directions.

With best wishes,

Yours sincerely,

John A. Pople
Carnegie Professor of
Chemical Physics

JAP:kos

81-4

CABLE ADDRESS "RESEARCH"

IN YOUR REPLY PLEASE QUOTE

FILE No. .....

NATIONAL RESEARCH COUNCIL

CANADA

DIVISION OF APPLIED CHEMISTRY

OTTAWA 2,

May 20, 1965.

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

Dear Barry,

Your reminder letter was waiting on my desk when I returned from a months visit to the Soviet Union. Since my mind is still full of this visit perhaps your readers would be interested in an account of the state of high resolution NMR in the Soviet Union. Only a few people were aware of the existence of IITNMRN. They said that they were not allowed to send unpublished material from Russia. Others were eager to subscribe and asked for your address. There was much evidence of widespread photocopying of entire journals and I suspect that this would also be the fate of IITNMRN.

The highest operating frequency for any Soviet made spectrometer is 40 Mc. for protons. There is very little investigation of other nuclei. About equal numbers of installations were using permanent magnets as electromagnets. The best resolution was about 0.3 c.p.s. and was obtained with both types of magnets. Shim coils were attached to the probe itself which was moved to find the best spot in the field. The final adjustments were then made with the electric shims.

There were two installations using field-frequency control. One used a Japanese electromagnet and the other a Soviet electromagnet, which looked very similar to the Japanese model. Both systems used a separate reference sample but there the similarity ended. The system designed by Dr. Lubimov (Institute of Organic Chemistry, Moscow) used the error signal from the reference sample to change the magnetic field. The stability of the field-frequency ratio was not as good as in the A-60 since

.....

signal-noise ratio improvement could not be done by integrating for a given time at discrete spectral intervals (SNAIL?).

The system designed by Dr. Lippmaa (Institute of Cybernetics, Tallin) was located in the center of a busy city and quite near tram lines. It therefore had to handle large transient fields and have a very fast response time. The output from a crystal oscillator of the appropriate frequency went to three separate frequency synthesizers. The frequency of the output of these units was adjusted by audio oscillators. A fluctuation of magnetic field would alter the frequency of an audio oscillator and adjust the frequency for the control and for the sample. The spectrum was obtained by an additional frequency sweep of the sample frequency synthesizer. The third frequency synthesizer could be used with the same control system for proton-proton double resonance. The performance of the unit seemed very good but maintenance was difficult and complex.

Many Japanese instruments at 40, 60 and 100 Mc. were seen, and one Trub-Tauber unit at 25 Mc. The Russians have great difficulty getting spare parts, vacuum tubes, etc., for these instruments. It appears that they are still a long way from their own spectrometer operating at 60 Mc. The embargo on American electronic apparatus generally and Varian instruments in particular is very effective. They were all very keen to get Varian instruments and many have tried in a variety of unsuccessful ways to obtain one. There is much interest in pulse techniques for getting relaxation times and some very versatile pulsers have been built. There is still not much use of solid state devices in their electronic construction.

I hope the next letter will tell more of my own work.

Yours truly,

Syd Brownstein

S. Brownstein.

SB/cm

81-6

TELEPHONE NO. 78555

Department of Chemistry,
THE UNIVERSITY,
SHEFFIELD, 10.

20th May, 1965,

Dr. B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
CHICAGO, Illinois,
U. S.A.

Dear Dr. Shapiro,

Molecular Orbital calculations of the proton coupling constants in aromatic molecules.

We have calculated the proton coupling constants (J_{HH}) in benzene and pyridine using the M.O. treatment due to Pople and Santry (Mol. Phys., 8, 1 (1964)). This theory is particularly suitable for studying nuclear spin coupling constants in large molecules or when electronegativity effects are present. It predicts that the Fermi contact term in J_{HH} is proportional to the mutual polarizability of the 1s atomic orbitals of the hydrogen atoms in question, providing changes in the 1s densities at the proton positions are neglected. In our calculations the basis for the σ -molecular orbitals and the parametrization were the same as those used by Pople and Santry in their theory of σ -electron delocalization in saturated hydrocarbons (Mol. Phys., 7, 269 (1964)). The correlation between the Coulomb integrals of nitrogen and carbon atomic orbitals (2s and 2p) was $\alpha_N = \alpha_C - 1.0$ eV. The values obtained for the contact contributions in benzene are as follows:

$$J_{ortho} = 7.7 \text{ c.p.s.}, \quad J_{meta} = 2.5 \text{ c.p.s.}, \quad J_{para} = 1.8 \text{ c.p.s.}$$

The agreement with experiment is excellent. The outstanding features in the pyridine results as compared to benzene are:

$$J_{23} = J_{56} = 4.7 \text{ c.p.s.}, \quad J_{26} = 0.7 \text{ c.p.s.}$$

Experience shows in fact that substitution of a CH group in benzene (1 position) by the more electronegative N atom leads to an appreciable decrease in $J_{23} = J_{56}$ and in J_{26} (for pyridine, $J_{23} = 5.5$ c.p.s. and $J_{26} = 0.4$ c.p.s.)

It is hoped that, by studying smaller molecules and molecular fragments, we will be able to show how J_{HH} depends on the various interactions (resonance integrals). This is of particular interest in the understanding of the effect of geometrical arrangement on proton coupling constants. Indeed, an expression has already been obtained relating $J_{vicinal}$ (contact) to the various resonance integrals (future communication).

Yours sincerely,

Victor M.S. Gil

V.M.S. Gil J.N. Murrell

81-8

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
WASHINGTON, D.C. 20234

25 May 1965

IN REPLY REFER TO: 313.01

*

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

Dear Barry:

Thanks for the recent letter reminding me that an NMR contribution is due. Tom Coyle and I here at the National Bureau of Standards have collaborated with Earl Whipple and Tom Brown to measure the relative signs of the coupling constants in $^{1}H^{11}B^{19}F_2$ via the Freeman-Whiffen double resonance "tickling" experiment. The results for the reduced* coupling constants, K_{XY}, are:

$$K_{BH} = \pm\ 58.2 \times 10^{20}\ cm^{-3};\ J_{BH} = \pm\ 211\ Hz$$

$$K_{BF} = \mp\ 23.2 \times 10^{20}\ cm^{-3};\ J_{BF} = \mp\ 84\ Hz$$

$$K_{HF} = \pm\ 29.8 \times 10^{20}\ cm^{-3};\ J_{HF} = \pm\ 108\ Hz.$$

If one assumes J_{BH} to be positive then ^{11}B in $^{1}H^{11}B^{19}F_2$ corresponds to ^{13}C in $^{1}H^{13}C^{19}FCl_2$ (see G. V. D. Tiers, J. Am. Chem. Soc., 84, 3972 (1962)), and the results support the prediction that couplings between first-row elements and directly bonded ^{19}F are negative.

Sincerely,

Tom

Thomas C. Farrar
Inorganic Chemistry Section

* J. A. Pople and D. P. Santry, Molecular Physics, 8, 1 (1964).

Max-Planck-Institut für Biochemie

München 15, den Goethestraße 31
Fernruf 59 42 61/63
Postschließfach 64

13.5.1965

Dr. Bernhard L. Shapiro
Illinois Institute of
Technology

C h i c a g o 60616

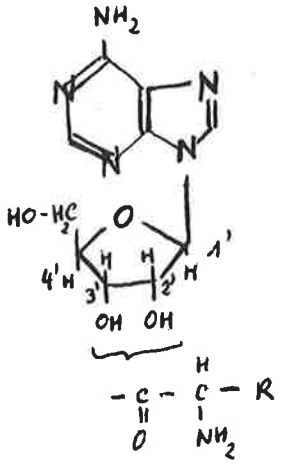
Sehr geehrter Herr Dr. Shapiro !

Neben unseren Untersuchungen zur Systematik substituierter Chinoline versuchten wir uns in einer biochemischen Problemstellung:

2'- oder 3'-Aminoacyladenosin in Aminoacyl-sRNA

In einer Zwischenstufe der Proteinbiosynthese sind die Aminosäuren mit der 2'- bzw. 3'-Hydroxylgruppe des Riboseanteils eines terminalen Adenosins der s-RNA verestert. In wieweit 2'- bzw. 3'-Veresterung vorliegt, konnte bisher nicht eindeutig entschieden werden.

Die NMR-Spektroskopie scheint zur Lösung der Fragestellung geeignet, einmal, da die Signale der Adenosinwasserstoffe identifiziert sind[1], zum andern, weil aufgrund der Verschiebung der Signale in den Adenosinmonophosphaten[2,3] gegenüber Adenosin angenommen werden darf, daß das Signal desjenigen Wasserstoffs, der an demselben C-Atom sitzt wie die veresterte Hydroxylgruppe, die stärkste Verschiebung zu niederem Feld erleidet und die weiterhin benachbarten CH-Gruppen deutlich schwächer beeinflußt werden.

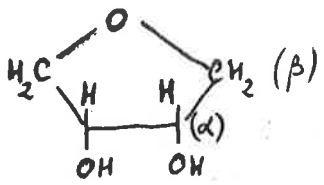


Die Verschiebung der CH_2-Resonanz des Äthanols bei Veresterung mit Valin, Tryptophan, Tyrosin und Cystein beträgt 26, 21, 29 und 28 Hz.
Bei den Adenosinphosphaten beträgt die Verschiebung des Wasserstoffsignals an dem Ribose-C-Atom, das die veresterte Hydroxylgruppe trägt, 36-46 Hz und für das nächststehende tertiäre Wasserstoffatom 7-17 Hz.
Als weitere Modellsubstanzen wurden verwendet: Essigsäure-, Glycin- und Valinester des Hydroxycyclopentans, 3-Hydroxy-tetrahydrofurans und der entsprechenden vicinalen Dihydroxyverbindungen.

Max-Planck-Institut für Biochemie

2. Blatt zum Schreiben vom 13.5.1965 an Dr. B.L.Shapiro, Chicago

Das der Ribose nächststehende Modell, das cis-Dihydroxytetrahydrofuran, zeigt bei der Veresterung mit Glycin bzw. Valin Verschiebungswerte von 72 und 70 Hz für das α-H-Atom und 21 und 22 Hz für die ß-H-Atome.



Synthetische Aminosäureester des Adenosins wurden vermessen und die Signale unter Berücksichtigung der zu erwartenden Verschiebungen geordnet. Die Intensitätswerte waren für die Zuordnung wesentlich, da stets Gemische von 2'- und 3'-Ester bei der Synthese entstehen. In der Tabelle sind die beobachteten Signale geordnet.

Bemerkenswert sind die isoliert stehenden Dubletts für die jeweiligen 1'-Wasserstoffe. Aus ihrem Intensitätsverhältnis entnehmen wir, daß bei den synthetischen Aminoacyladenosinen ca. 30 % 2'-Ester und 70 % 3'-Ester vorliegen. In Aminoacyl-adenosin, das aus einer enzymatisch mit mehreren Aminosäuren beladenen RNA isoliert wurde, fanden wir <10 % 2'-Ester und >90% 3'-Ester.

Daß isoliertes Aminoacyladenosin mehr 3'-Ester enthält als synthetisches, könnte auf einen 3'-Ester in Aminoacyl-sRNA hindeuten. Eine Verschiebung des 2'-/3'-Verhältnisse während der Isolierung konnte unwahrscheinlich gemacht werden[4]. Die Ergebnisse sind überraschend angesichts der von mehreren Autoren betonten schnellen Acylwanderung bei derartigen Estern.

Für manche Messungen standen nur 1-2 mg Substanz zur Verfügung; mit unserem A-60 mußten wir die Spektren wiederholt aufnehmen, um verläßliche Intensitätswerte zu ermitteln. Ein Teil der Spektren wurde mit "Crutchfield-Technik" aufgenommen.

Für die Verspätung unseres Beitrages zu den IITNMR-Letters bitten wir um Nachsicht.

H.G. Zachau H. Feldmann Johann Sonnenbichler

(H.G. Zachau) (H. Feldmann) (J. Sonnenbichler)
Institut für Genetik, Köln Max-Planck-Institut für Biochemie

1) C.D.Jardetzky, J.Amer.chem.Soc. 84, 62 (1962)
L.Gatlin und J.C.Davis, J.Amer.chem.Soc. 84, 4464 (1962)
2) O.Jardetzky, J.Amer.chem.Soc. 85, 1823 (1963)
3) J.Sonnenbichler, H.Feldmann und H.G.Zachau, Z.f.physiol.Chem. 334, 283 (1963)
4) J.Sonnenbichler, H.Feldmann und H.G.Zachau, Z.physiol.Chem., im Druck.

Tabelle

Signallagen+ der Wasserstoffatome des Riboseanteils in Adenosin und Adenosinestern in Hz bezogen auf TMS bei 60 MHz in Hexadeuterodimethylsulfoxid.

		1'-H	2'-H	3'-H	4'-H	5'-H
Adenosin		354 [1.0]	278 [1.2]	250 241 (zusammen 2,2)		219 [2,4]
Valyl-	2'-Anteil	369 [0.27] (15)	341 [0.29] (63)	269 [0.37] (19)	250 [0.95] (9)	222 [1.8] (3)
Adenosin	3'- "	357 [0.73] (3)	298 [0.75] (20)	319 [0.78] (69)		
Methionyl	2'- "	369 [0.27] (15)	340 [0.28] (62)	-	248 [-] (7)	222 [1.8] (3)
Adenosin	3'- "	355 [0.73] (1)	294 [0.62] (16)	318 [0.64] (68)		
Alanyl-	2'- "	366 [0.31] (12)	339 [0.32] (61)	-	249 [1.09] (8)	221 [1.81] (2)
Adenosin	3'- "	355 [0.69] (1)	295 [0.62] (17)	319 [0.95] (69)		
Aminoacyl-	2'-"	368 (schwach) (14)	343 (schwach) (65)	-	249 [0.89] (8)	222 [2.12] (3)
Adenosin	3'- "	358 [1.00] (4)	298 [1.00] (20)	320 [0.89] (70)		

+In runden Klammern sind die Differenzen der Signallagen gegenüber Adenosin angegeben. Die in eckigen Klammern angegebenen Intensitäten sind Mittelwerte aus mehreren Einzelmessungen; sie sind auf I = 1.00 für die Summe der Intensitäten der 1'-H-Signale bezogen. Beim Aminoacyladenosin wurde die Intensität des Signals bei 358 Hz gleich 1.00 gesetzt. - Wegen der Überlagerung durch die Wasserbande ließen sich die Signale unter 280 Hz in einigen Fällen nicht beobachten, in einem anderen Fall konnte die Intensität nicht genau genug bestimmt werden (in der Tab. mit - bezeichnet).

81-12

THE JOHNS HOPKINS UNIVERSITY

SCHOOL OF MEDICINE

725 N. WOLFE STREET · BALTIMORE, MARYLAND 21205

DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY

TELEPHONE 955-5000
AREA CODE 301

May 21, 1965

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

Dear Barry,

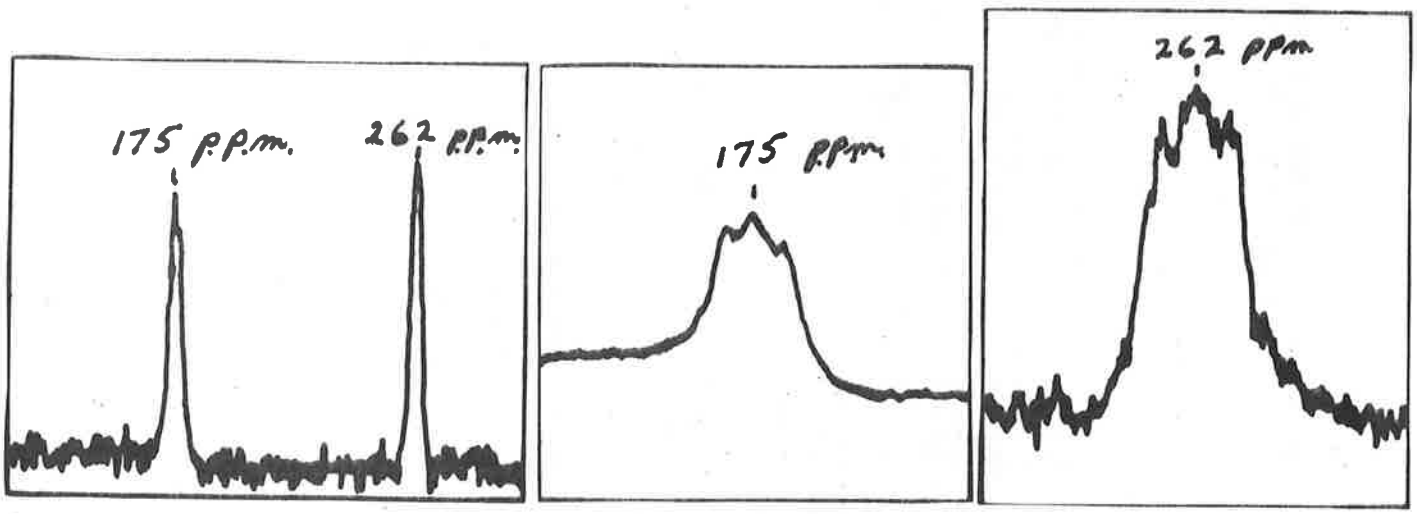
To initiate our subscription to the IIT NMR Newsletter, I would like to report some N^{14} NMR work which I did at Stanford and Varian several years ago and which may interest some readers.

Using an especially made Dewar-jacketed. 2.88 Mc insert equipped with a two liter gas reservoir, the N^{14} NMR spectrum of N_2O liquid was obtained. Sufficient N_2O gas was admitted into the reservoir to give about three mls. of liquid when condensed by immersing an attached coldfinger in liquid nitrogen. This coldfinger could then be placed into the precooled Dewar insert which would then allow about five minutes for observation of the N^{14} spectrum while the N_2O slowly evaporated into the reservoir. The spectra obtained are shown below. Two lines were found shifted 262 and 175 ppm respectively upfield from the NO_3^- resonance of saturated aqueous NH_4NO_3. The expanded traces show that the two lines are actually triplets which presumably result from N^{14}-N^{14} coupling. The measured triplet splitting is 5 cps. As far as I know this is the only N^{14}-N^{14} coupling which has been observed directly so far. Has anyone else such an example?

Sincerely yours,

Don

Donald P. Hollis



TEXAS CHRISTIAN UNIVERSITY
Fort Worth, Texas 76129

Department of Chemistry

May 28, 1965

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

Dear Dr. Shapiro:

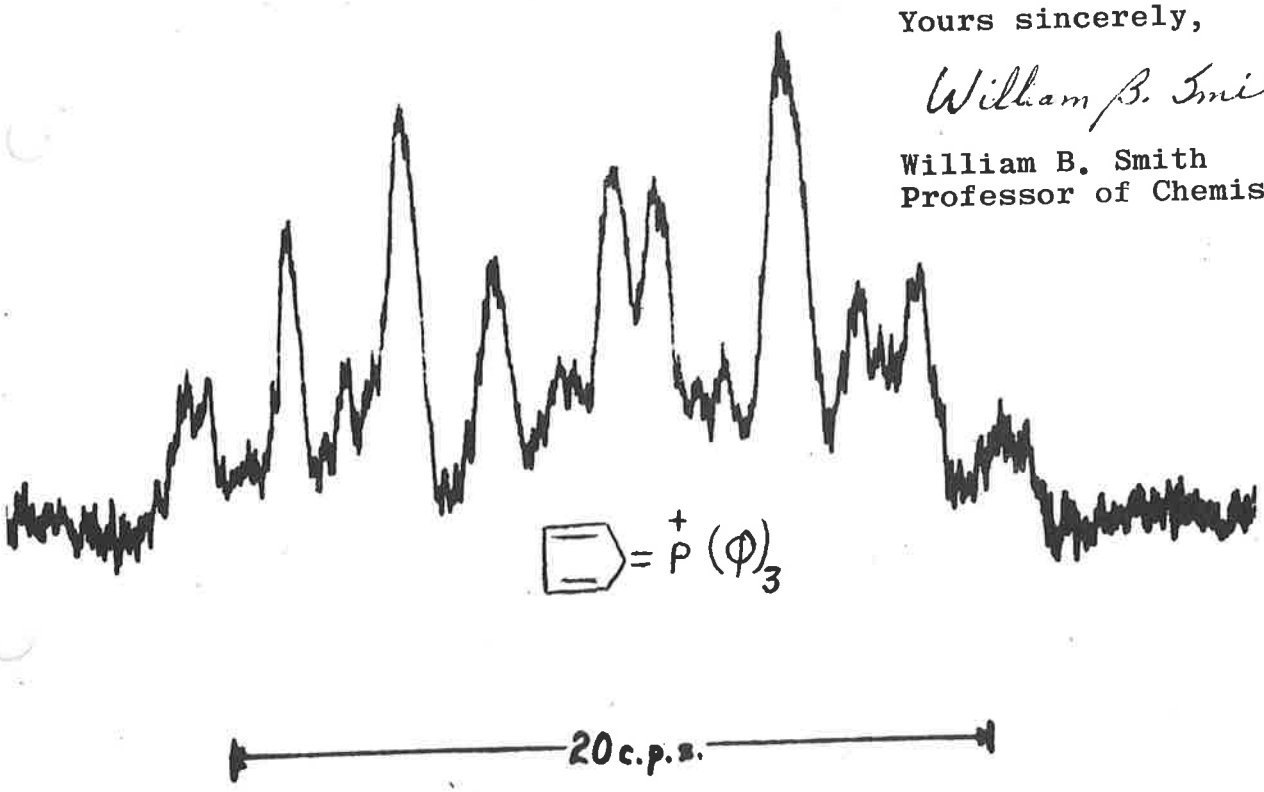
Since you like to have titles for the items in I. I. T. -NMR perhaps this should have the heading "Help!".

The spectrum below is the five ring in the compound shown. Our sample has physical properties which agree with the literature values for this interesting substance. Presumably the ring spectrum is complicated due to the coupling of the protons with the phosphorous. It would help us a great deal if we could get the phosphorous decoupled spectrum of these protons determined. Since we do not have the proper equipment to do this experiment, I would like to inquire if any of your readers might be willing to render us this service. If so, we would be more than willing to send a sample to the interested party. This could be either as the pure solid or in deuterochloroform.

Yours sincerely,

William B. Smith

William B. Smith
Professor of Chemistry



81-14

CALIFORNIA STATE COLLEGE AT LOS ANGELES

Department of Chemistry

5151 State College Drive, Los Angeles, California 90032
(San Bernardino and Long Beach Freeways Interchange)
Telephone 225-1631 (Area Code 213)

May 26, 1965

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

Dear Barry:

At the present time I am completing some studies of the effect of electrolytes on solvent mixtures, including solvents of biological importance. Although the interpretations are not yet complete, I would like to discuss briefly some interesting data compiled in several solvent systems and shown in Tables 1 and 2. In these tables, the δ values listed are defined by $\nu_P - \nu_M$ where ν_P represents the resonance frequency of a particular proton (water protons, for example) in the pure solvent mixture, and ν_M the resonance position of the same signal in the solvent mixture with salt added. The salt concentrations were 2 M in all cases. An A60 Spectrometer was used for these measurements.

Consider first the water shift data in Table 1. All shift displacements of the water signal upon salt addition with two exceptions are positive, that is, the signal is usually displaced to lower field in the presence of salt. Several processes can occur, simultaneously or selectively, when salt is added to a solvent mixture. The added particles can destroy, to some extent, hydrogen bonds already existing in solution. Also, the ions can interact with either or both solvent components. Empirically one can state that if a proton is involved in a hydrogen bond or if the molecule to which the proton belongs is in-

volved in complex formation of some sort, the proton resonance is displaced to lower field. This statement is justified in view of the tremendous amount of NMR data compiled for systems in which hydrogen bonding is extensive. Applying this rule to Table 1 leads to the conclusion that in almost all mixtures, a structure-making process dominates, at least with respect to water. That is, addition of salt usually leads to a more ordered water structure, presumably through solvation processes. Both salt and non-aqueous solvent influence the degree to which the ordering occurs. For example, in the $BeCl_2$ solutions, the largest water resonance-shift displacements are observed in the dioxane and acetone systems, the next-largest in the ethanol, dimethylformamide, and dimethylsulfoxide, and smallest in the methanol and N-methylformamide mixtures. A similar trend is observed in the remaining alkaline earth solutions, solutions of $ZnCl_2$, $CdCl_2$, $SnCl_2$, $AlCl_3$, $InCl_3$, and $LaCl_3$. The data available for $GaCl_3$ indicate this salt will not demonstrate the above correlation. A preliminary interpretation of the trend discussed above indicates that competitive solvation is responsible for the differences observed for the water chemical shift displacements. Thus, in mixtures with either acetone or non-polar dioxane, water is able to interact most strongly with ions, as evidenced by the large downfield displacement of this resonance signal. The next series of solvents DMF, DMS, and ethanol, compete with water for added ions, since the water proton signal is not displaced as far downfield in these mixtures as in the previous two. Finally, methanol and NMF compete most effectively with water for ions, as can be deduced by the much smaller shifts exhibited by water in these mixtures. It might be mentioned that this evidence for competitive solvation is remarkable when one considers that the nonaqueous component is present in such a small molar ratio.

Included in Table 2 are the chemical shift data for the nonaqueous components of the mixtures previously discussed. In contrast with the water results which can be correlated with interactions occurring in solution, the shift displacements for several of the solvents were remarkably similar in the presence of many electrolytes. Compare, for example, the results shown for acetone, dioxane, methanol, and possibly dimethylsulfoxide. Shifts observed with the remaining solvents, dimethylformamide, ethanol, and N-methylformamide, are more encouraging. In these molecules, the presence of two types of protons permits the observation of selective shift displacements. Thus, the CH_2 proton signal of ethanol displaced approximately twice the amount of the CH_3, and the CHO signal displacement in both amides is twice that of the CH_3 proton signal in each molecule. Thus, in the alcohol and these two amides, the oxygen end of the molecule apparently is the active site for ionic interactions.

Striking evidence of interactions between the organic solvent components and ions was provided by $AlCl_3$ solutions. Al ion is so strongly solvated in solution separate signals were observed for bulk and complex solvent molecules. This occurred in aqueous mixtures of dimethylformamide, N-methylformamide, and dimethylsulfoxide. This is in direct contrast to the water results, and, in fact, to most studies of solvent interactions, wherein rapid exchange produces only an average resonance signal. Peak areas of bulk and complexed solvent vary as a function of concentration, as expected, and the separation, usually 10 - 15 cps, decreases with increasing temperature. This feature of the results is presently being thoroughly explored.

Studies of paramagnetic $CoCl_2$ in these solvent mixtures also provided conclusive evidence that strong interactions were occurring

between cations and the non-aqueous solvent components. For example, 0.3 M Co ion displaced the water signal downfield more than 220 cps in the acetone and dioxane solutions, but to a much smaller extent in the remaining mixtures. This agrees well with the diamagnetic results previously discussed. However, even at the low concentration of salt, the Co ion, due to the strong magnetic moments of the unpaired electrons, also displaced the organic component resonance signals. Acetone and dioxane displacements were slightly upfield, indicating again that these solvents are inactive with regard to ion-dipole interactions. The significant shift displacements of the remaining solvents led to a determination of the complexing site in the molecule.

At the present time this work is being readied for publication and I'll gladly send along preprints to any interested parties. I also have a limited number of preprints of a study recently completed on the effect of electrolytes in dl-and β alanine aqueous mixtures.

Sincerely,

A. Fratiello

Anthony Fratiello

TF/es

TABLE 1

H_2O Shift Displacements, $\delta = \nu_P - \nu_M$ in Solvent Mixtures (H_2O/Solvent = 10:1) Salt = 2 M

Chlorides	Be	Mg	Ca	Sr	Zn	Cd	Sn	Al	Ga	In	La
Solvent Acetone	69	24	13	5	20	17	22	107		35	45
Dioxane	71	24	12	4	21		22	111	71	36	49
Dimethyl formamide	61	20	10	2	17		16	83		27	34
Dimethyl Sulfoxide	62	19	9	0	15		12	86		24	32
Ethanol	57	17	8	1	15	14	19	90	68	31	39
Methanol	51	13	5	-3	14	11	17	75	70	27	33
N-methyl formamide	49	11	5	-5	10		8	72		20	24

TABLE 2

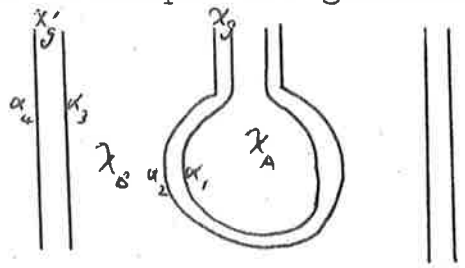
Solvent Shift Displacements ($\delta = \nu_P - \nu_M$) Aqueous Mixtures

Chlorides	Be	Mg	Ca	Sr	Zn	Cd	Sn	Al	Ga	In	La
Solvent Acetone	5	5	5	5	4	5	3	7		5	9
Dioxane	5	2	5	4	6		4	8	7	7	7
DMF CH_3	8	3	5	3	5		5	6		8	7
CHO	12	6	10	7	10		12	13		14	12
DMS	8	4	6	5	6		9	9		11	11
Ethanol CH_2	7	5	7	5	7	8	6	10	11	8	10
CH_3	4	3	4	4	3	4	3	6	6	4	7
Methanol	5	2	5	3	6	5	4	6	9	6	8
NMF CH_3	4	1	4	3	2		3	2		4	5
CHO	9	3	9	6	10		12	10		14	10

Unilever Ltd.,
Colworth House,
Sharnbrook,
Bedford.

A Spherical External Reference

Having found an external spherical reference to be a convenient standard in aqueous solutions (1), requiring no bulk susceptibility corrections, we have attempted to extend the theory of such a system using the classical approach of P.S.B. (2). It is important to ascribe separate geometrical factors to both the inside and outside surfaces of the reference cell, and although a spherical system is shown, the equations developed are generally applicable.



If the observed shift between compounds A and B is δ^{o}_{B-A}, then the true separation is given by :

$$\delta^{T}_{B-A} = \delta^{o}_{B-A} - \left[\left(\tfrac{4\pi}{3}-\alpha_1\right)\chi_A + (\alpha_1-\alpha_2)\chi_g + \left(\alpha_2-\tfrac{4\pi}{3}\right)\chi_B\right]$$

The geometry of the outside tube does not enter the equation. When $\alpha_1 = \alpha_2 = \alpha$ the expression reduces to

$$\delta^{T}_{B-A} = \delta^{o}_{B-A} + \left(\alpha - \tfrac{4\pi}{3}\right)(\chi_B - \chi_A)$$

and $\left(\alpha - \frac{4\pi}{3}\right)$ is the so-called g factor (3). Then for a cylindrical reference, where $\alpha = 2\pi$, the well-known susceptibility correction equation results,

$$\delta^{T}_{B-A} = \delta^{o}_{B-A} - \tfrac{2\pi}{3}(\chi_B - \chi_A)$$

For a perfect sphere, where $\alpha = \frac{4\pi}{3}$, the observed shift is then the true separation. However, we have found that for the majority of spheres that can be blown, $\alpha_1 \neq \alpha_2$. This has been demonstrated by measuring the separation between two compounds when first A (and then B) is in the sphere, and B and A outside respectively. Then the sum of these values, $\delta^{o}_{B-A} + \delta^{o}_{A-B}$ (where $\delta^{T}_{B-A} = -\delta^{T}_{A-B}$), according to a simple g factor expression, should be zero. In practice we found that this was non-zero, and could be represented by

$$\delta^{o}_{B-A} + \delta^{o}_{A-B} = (\alpha_1 - \alpha_2)\left[2\chi_g - (\chi_A + \chi_B)\right]$$

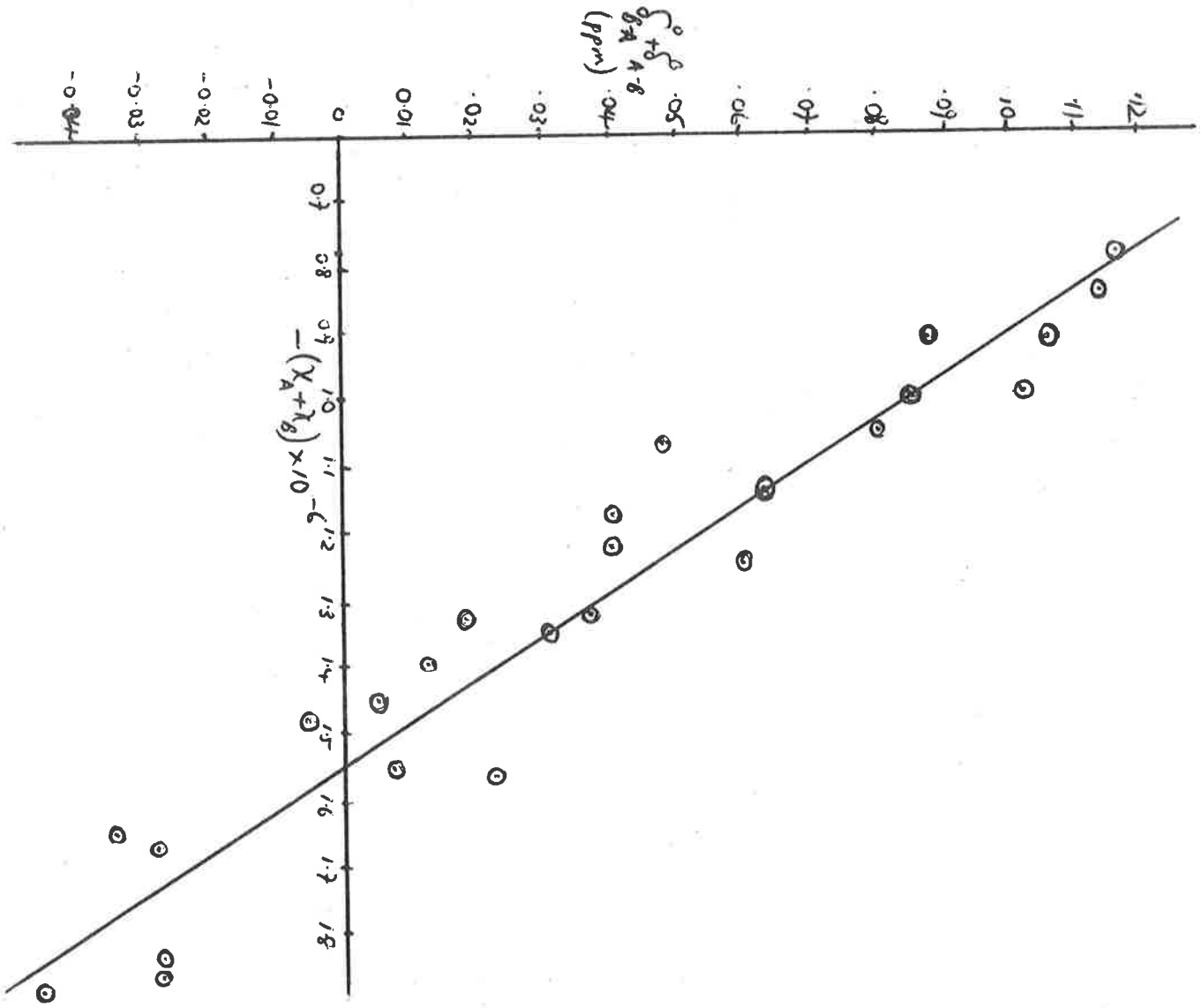
derived from the equation developed above. Using an obviously imperfect sphere, we obtained a linear plot of $\delta^{o}_{B-A} + \delta^{o}_{A-B}$ vs $(\chi_A + \chi_B)$ of slope 0.150 and crossing the $(\chi_A + \chi_B)$ axis at -1.550×10^{-6}. This represents a value of $\chi_g = -0.775 \times 10^{-6}$, which compares with previously reported (4) values.

We now conclude, therefore, that in the use of a spherical external reference, unless the sphere is perfect, the errors involved depend upon the magnetic susceptibilities of the solution, the reference compound and the material from which the sphere is made.

1. Frost,D. & Hall, G.E. Nature, 205, 1309, (1965)
2. Pople Schneider & Bernstein - High Resolution N.M.R. p.81-2
3. Frei,K. & Bernstein,H.J. J.Chem.Phys. 37, 1891, (1962)
4. Fratiello,A. & Douglas,D.C. J.Mol.Spect. 11, 465, (1963)

Gordon Hall.

David Frost



81-22

EMORY UNIVERSITY
ATLANTA, GEORGIA 30322

DEPARTMENT OF CHEMISTRY

May 26, 1965

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

Dear Barry:

We have recently completed an exact analysis of the spectrum of biphenyl and have used the results to obtain, under certain assumptions, an estimate of the dihedral angle in this structure. Taking into account the necessary anisotropy contributions, it is possible to correlate the chemical shifts in benzene, biphenyl and para-terphenyl to within 3 cps. It was necessary to assume, however, a decrease in ring current of about 5% for each attached phenyl ring.

At 60 Mc/sec, and in $CDCl_3$ solution the experimental chemical shifts are at 28° C, relative to internal TMS: benzene, -441.2 cps; biphenyl, -455.4 (o), -444.8 (m), -439.3 (p); p-terphenyl, -460.0 cps (central ring). Our present estimate for the dihedral angle in biphenyl is 42°, but essentially identical results are also obtained if free rotation is assumed.

We hope to have the complete results available very shortly.

Sincerely yours,

J. H. Goldstein

R. E. Mayo
J. H. Goldstein

CHEMSTRAND
RESEARCH CENTER, INC.

Box 731
Durham, N. C. 27702
Telephone 549-8111
Area Code 919

May 25, 1965

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

$\bar{M}_n$ Determinations of α,ω-Polymeric Glycols

We have recently investigated NMR methods of measuring number average molecular weights of polymeric glycols. In many instances, a molecular weight determination of a polymeric glycol can be best accomplished by measuring the area of the resonance signal of the methylene protons adjacent to the hydroxyl group and comparing this area to that of a repeating unit within the polymeric glycol. In the case of some glycol polyethers, the repeating methylene unit and end methylene groups overlap thereby making such an approach impossible. Such an example is α,ω-polytetramethylene glycol (PTMG). Earlier workers have used pyridine to complex the hydroxyl end groups so as to shift the $-CH_2OH$ resonance from the $-CH_2O-$ resonance (1). We have found that by "capping" the hydroxyl end groups with acetic anhydride using a trace of sulfuric acid as a catalyst, the $-CH_2OH$ end groups are efficiently converted to $-CH_2O(CO)CH_3$ and the end group appears in the case of PTMG as a well-defined triplet apart from the $-CH_2O-$ resonance.

With glycol polyester ethers, an $\bar{M}_n$ determination can be made by comparing the peak area ratios of the $-CH_2O-$ and $-CH_2O(CO)$ resonances both before and after capping with acetic anhydride.

Please accept our apologies for the tardiness of this contribution.

Sincerely yours,

James C. Randall

SA/65-42/tc

1. T. F. Page, Jr. and W. E. Bresler, Analytical Chemistry 36, 1981 (1964).

81-24

MELLON INSTITUTE

4400 FIFTH AVENUE

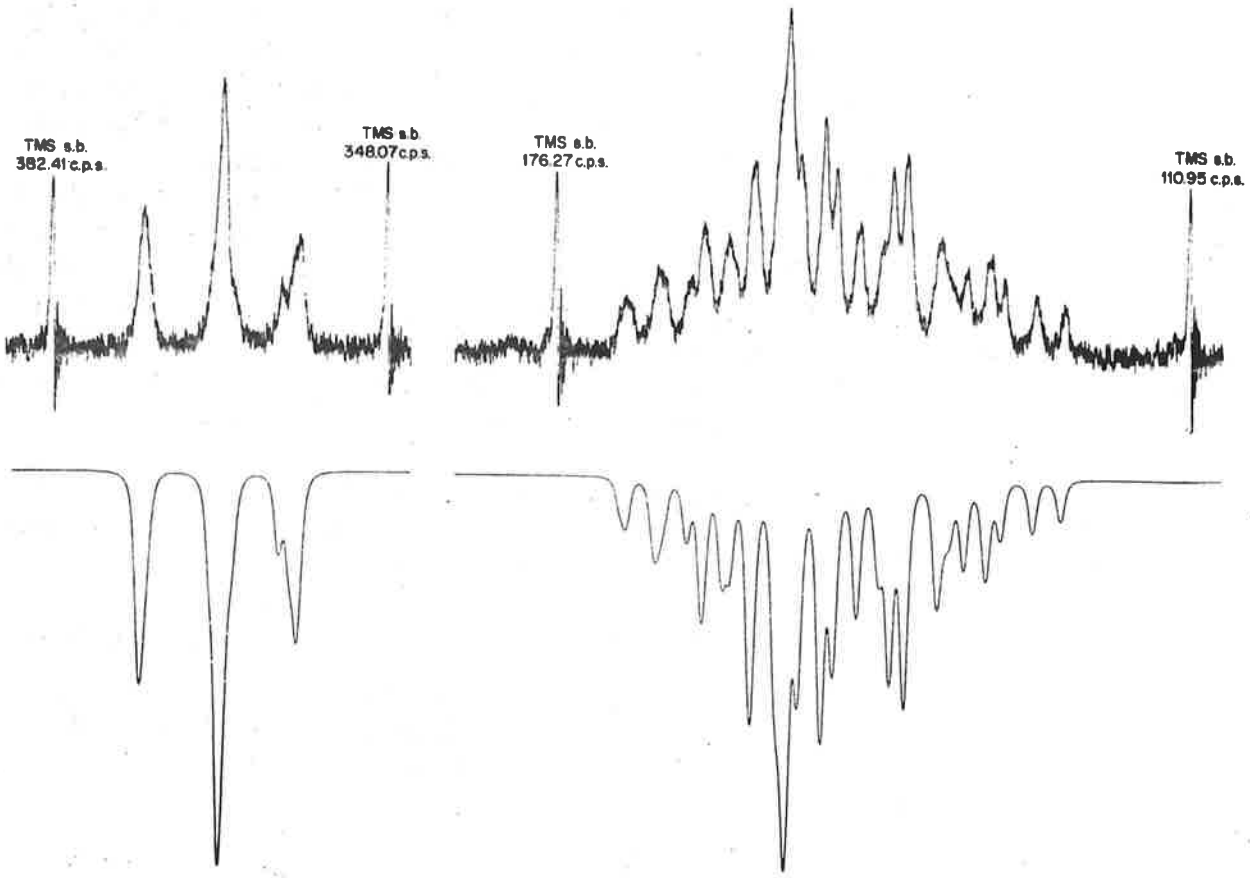
PITTSBURGH, PA. 15213

3 June 1965

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

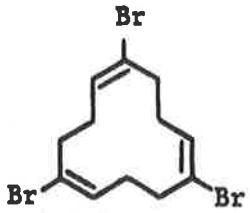
Dear Barry:

Recently one of us synthesized 1,5,9-tribromo-cis,cis,cis-1,5,9-cyclododecatriene (I). As part of the structural proof, the calculated n.m.r. spectrum was utilized. The n.m.r. spectrum was analyzed exactly as a 5-spin problem, using the computer program LAOCOON II [S. Castellano and A. A. Bothner-By, J. Chem. Phys., 41, 3863 (1964)]. The calculated curve displayed is the result of a separate subroutine, prepared by Dr. D. Jung, which converts the read-out of the program into a smooth curve plot. A resolution factor of 0.5 c.p.s. band width at half peak height was used.

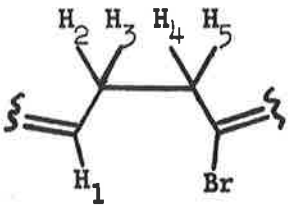


MELLON INSTITUTE

The tribromotriene is interconverting between equivalent conformers and the coupling constants listed are averaged values.



I



$J_{12} = J_{13} = 8.41$ c.p.s.
$J_{14} = J_{15} = -0.31$
$J_{23} = -13.03$
$J_{45} = -13.13$
$J_{25} = J_{34} = 10.54$
$J_{24} = J_{35} = 5.55$

The magnitude of the vicinal coupling constants, i.e., $J_{25} = J_{34}$, $J_{24} = J_{35}$, strongly favors an s-trans arrangement for the ethano-hydrogens of I.

Turi and I are sorry we will miss you during your June visit to Pittsburgh.

Sincerely yours,

S. Castellano
Turi
K. G. Untch
Karl
J. Lorenc
Jack

81-26

UNIVERSITY OF FLORIDA
GAINESVILLE, 32603

DEPARTMENT OF CHEMISTRY

June 2, 1965

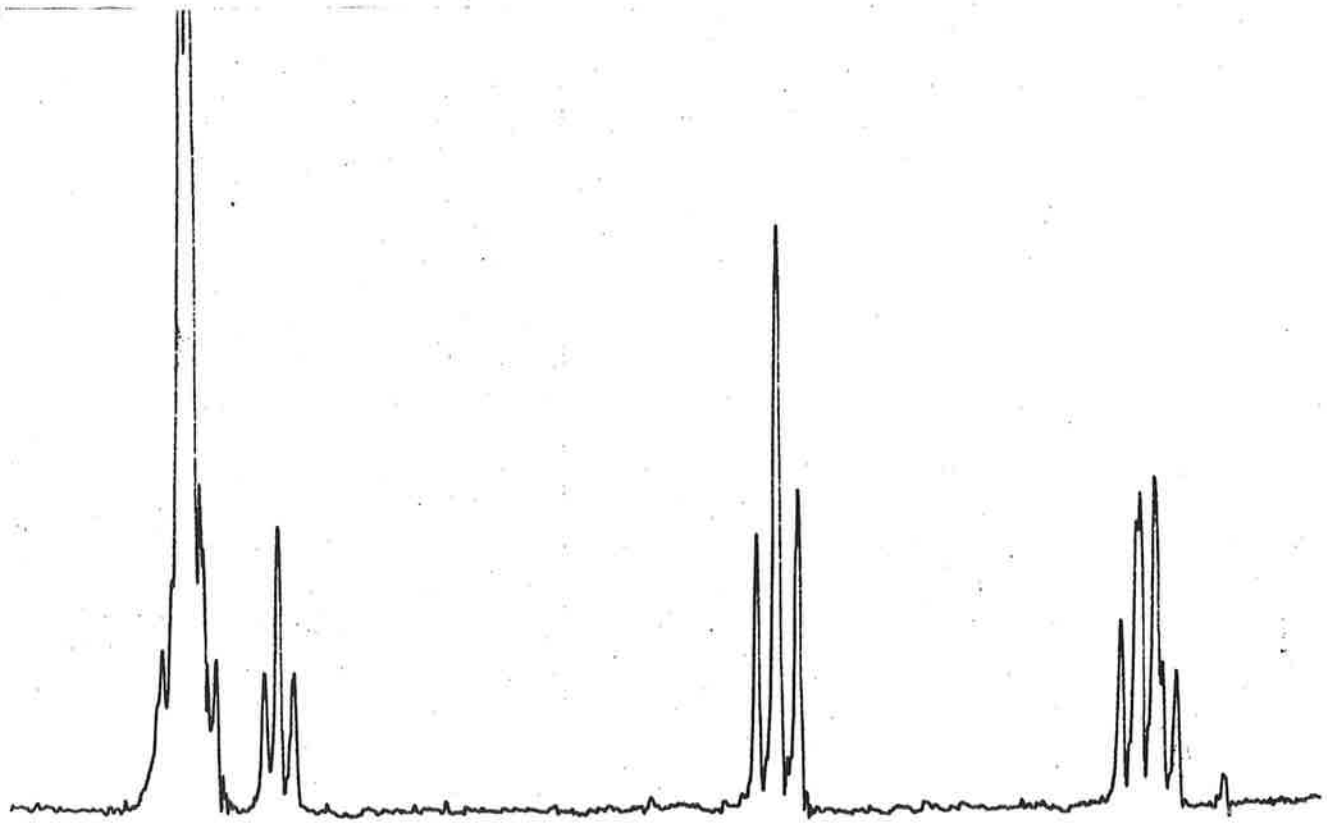
Dr. B.L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry:

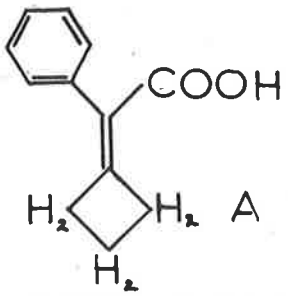
As our contribution to the IITNMR Newsletter, I should like to describe a few interesting results of several types that have turned up recently.

NONEQUIVALENCE IN A CYCLOBUTYLIDENE COMPOUND-The chemists at Peninsular ChemResearch recently supplied us with a sample of a material produced as a byproduct in one of their reactions. The formula is shown as A below. In the NMR spectrum, the cyclobutane ring proton peaks are multiplets which approximate triplets at 6.73 and 7.18 τ and a pentet at 7.92 τ. I think it is rather interesting that the pair of protons on the side of the ring having a cis relationship to the phenyl group is not equivalent to the pair on the side of the ring cis to the carboxyl. The splitting of the multiplets corresponds to an average J between vicinal ring protons of about 7.5 cps.

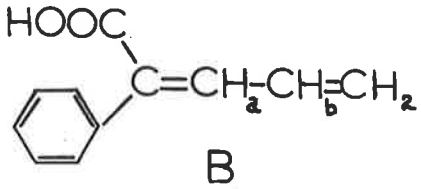
THE CASE OF THE STRANGE COINCIDENCE-After the four-membered ring compound above was mastered by NMR and supporting data from other techniques, the PCR synthetic chemists decided to attempt preparation of the corresponding cyclopropylidene compound. They were quite disconcerted when the reaction product displayed the following spectrum, indicating the presence of a phenyl group, one olefinic hydrogen, and four other hydrogens, none of which had a shift suitable for the cyclopropyl ring.



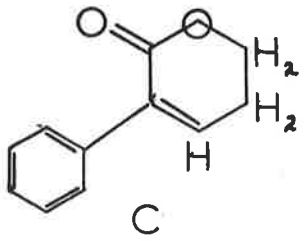
The alert reader may feel that this spectrum if familiar, and indeed he may well have seen it before, in Varian's "NMR AT WORK" Series (No. 91 in J. Am. Chem. Soc., Aug. 20, 1964; No. 92 in J. Am. Chem. Soc., Oct. 20, 1964), where it did present some difficulties. By good fortune I happened to notice the similarity, and subsequent work has shown that Varian's structure C (marked C below, as well) is correct. Hydrolysis of the material leads to a compound for which the NMR spectrum, in a very straightforward way, confirms structure B. In B, the atom H_a has a resonance well downfield at 2.38 τ and is coupled to H_b by 11 cps, which is a rather large coupling constant.



A

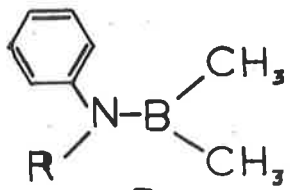


B

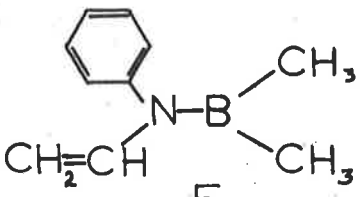


C

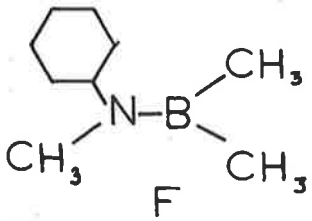
MAGNETIC ANISOTROPY OF THE CYCLOPROPYL RING-We thought that a nice way of demonstrating the existence of a "ring current" in the cyclopropyl ring would be to show that the ring contributed to nonequivalence of the methyl groups in a B-dimethyl aminoborane. We found earlier that in compounds D and E the methyl groups are nonequivalent, presumably as the result of the phenyl ring current, while in molecules such as F, without the phenyl group, the methyls are equivalent.



D



E



F

Drs. Kurt Niedenzu and Peter Fritz at Duke were kind enough to prepare for us a sample of cyclopropylaminodimethylborane. The spectrum of this compound at room temperature is very unenlightening, but cooled below room temperature, the methyl peaks become distinguishable, and the two methyl groups are indeed found to be nonequivalent. One might suspect that this molecule dimerizes, thus producing the nonequivalence or generating two ring isomers in which the methyl shifts are different. However, the boron chemical shift indicates that it exists in the monomeric form.

POSTDOCTORAL POSITION OPEN-We will have an opening in our NIH-supported research project for a postdoctoral research associate with interest and, preferably, training in NMR, beginning September, 1965 or January, 1966. The research is concerned with spectra of nitrogen heterocycles, including double resonance, study of solutions of proteins and polypeptides, and measurement of relaxation times by spin-echo methods.

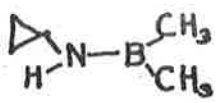
Cordially yours,

Wallace S. Brey, Jr.

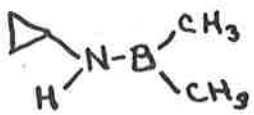
Katherine N. Scott

Katherine N. Scott

33°



-68°



GOODYEAR

The Goodyear Tire & Rubber Company

AKRON 16, OHIO

RESEARCH DIVISION
142 GOODYEAR BLVD.

June 8, 1965

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

SUBJECT: Flush the A-60 Magnet Cooling Coils

Dear Dr Shapiro:

Thank you for your subscription reminder.

As a precautionary step, we have recently flushed our Varian A-60 Spectrometer's magnet cooling coils. As pointed out by Professor Roberts (IITNMRN 70-18), the trapped magnetic oxide by the magnetic field inside the coils cannot be flushed out while the magnet is energized and that in the A-60 there is no water flow through the coil when the magnet current is shut off. We have found that one of the handy ways to flush the coils is to turn on the spectrometer with the fuse F1608 for the magnet current removed. The fuse is located on the cold plate and is easily accessible. It seems to us that the spectrometer did not experience any ill-effect after such a treatment. It seems desirable to flush the cooling system with the three-way solenoid valve on both to by-pass and to heat exchanger positions.

With best wishes.

Sincerely,

Hung Yu Chen

Spectroscopy Section
RESEARCH DIVISION

H Y Chen
bj

81-30

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
BETHESDA, MD. 20014

NATIONAL INSTITUTES OF HEALTH
AREA CODE 301 TEL: 656-4000

June 10, 1965

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

Dear Barry:

I thought you might be interested in some measurements I've made on the effect of hydrogen bonding on the N^{15}-H coupling constant in aniline-N^{15}. The values of J for fairly dilute (~ 0.2 M) solutions of aniline-N^{15} in several solvents are as follows:

Solvent	J(cps)
$CDCl_3$	78.0
Cyclohexane-d_{12}	78.0
CCl_4	78.0
Pyridine	81.4
Acetone	82.1
Dimethylformamide (DMF)	82.3
Dimethylsulfoxide (DMSO)	82.3

The coupling constant is seen to increase by about five per cent on hydrogen bonding. This is the same sort of change found by Evans for J(C^{13}-H) in $CHCl_3$ [J. Chem. Soc. 5575 (1963)], but the preliminary results reported by Reuben and Samuel for J(O^{17}-H) in methanol [IITNMR 72, 6] show no such simple correlation with hydrogen bonding. Of course, the observed value of J represents an average of the values of hydrogen bonded and free forms; the real change in J on hydrogen bonding may be somewhat larger. I haven't yet determined equilibrium constants for all these systems, but Mel Hanna (University of Colorado) has given me some data indicating that in pyridine at room temperature nearly 90 per cent of the aniline is hydrogen bonded.

There is an interesting point of technique that I learned in doing these experiments. In all the above solvents except DMF (the DMF was Matheson, Coleman, Bell Spectro Grade) the $N^{15}\underline{H}$ signal initially was a broad singlet like that in ordinary aniline. Apparently the exchange is due to traces of water, for I found that I could obtain the expected doublet by adding alumina directly to the sample tube, shaking, and letting the alumina settle. Bill Moniz (Naval Research Lab.) had previously told me that he found this technique helpful in obtaining vicinal proton-proton splitting in the OH peak of some primary alcohols.

At least a dozen people at NIH regularly read the Newsletter and find it very helpful. Keep up the good work!

Sincerely,

Ted

Edwin D. Becker
Laboratory of Physical Biology
National Institute of Arthritis
and Metabolic Diseases

81-32

FACULTE DES SCIENCES
DE MONTPELLIER

SERVICE CHIMIE M.P.C. 1

R. JACQUIER
Professeur

E.N.S.C.M., 8 Rue de l'Ecole Normale

Tél. 72-28-60
72-49-19
72-97-16

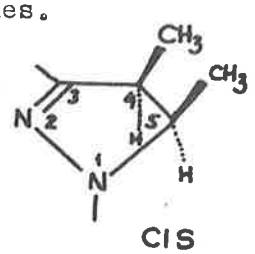
MONTPELLIER, le 3 Juin 1965

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

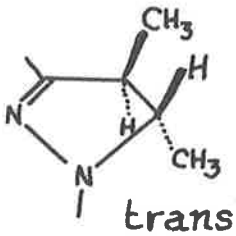
PROBLEMES DE CONFIGURATION DANS LE CYCLE PYRAZOLINE-2

Cher Dr. Shapiro,

Nous nous intéressons actuellement avec le Dr. Elguero, à certains problèmes stériques dans la série de la pyrazoline-2 Etant donné la vitesse élevée d'inversion de l'azote, seule la disubstitution en 4,5 est susceptible de conduire à deux isomères configurationnels distincts. Il faut d'autre part tenir compte de la possibilité d'une interconversion rapide entre deux conformations symétriques résultant de la vibration du carbone 5 de part et d'autre du plan constitué par les quatre autres atomes cycliques ; l'examen des modèles montre cependant que cette déformation est faible et qu'un dérivé disubstitué-4,5 cis est en moyenne plus proche d'une conformation éclipsée que d'une conformation gauche. Si les substitutions sont constituées par des groupes méthyles, on doit s'attendre dans ces conditions à observer des glissements différents selon que ces CH_3 seront ou non en vis-à-vis ; au contraire, une déformation plus importante du cycle les rendrait en moyenne équivalents, et ne permettrait plus de différencier sur cette base l'isomère cis du trans, comme c'est le cas pour d'autres systèmes hétérocycliques.

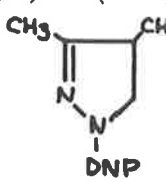


cis

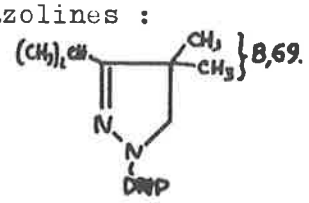


trans

Nous donnons ci-dessous les glissements chimiques (dans $CDCl_3$; valeurs en τ) des méthyles de quelques (dinitro-2'4'phényl)-1 (DNP) pyrazolines :



I



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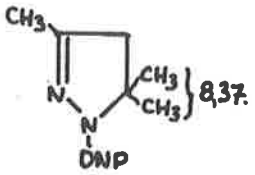
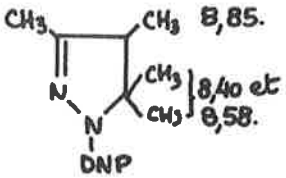


III



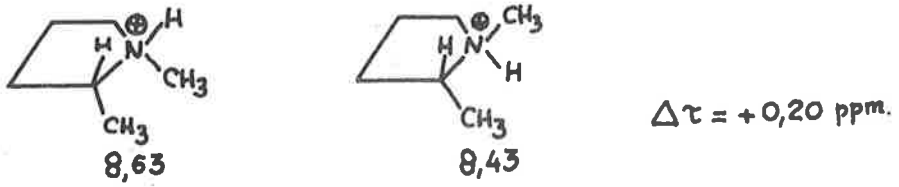
IV

On trouve ainsi des glissements chimiques moyens de : 8,70 τ pour un méthyle en 4 en vis-à-vis d'un proton (I et II)
8,37 τ pour un méthyle en 5 en vis-à-vis d'un proton (III)
8,85 τ pour un méthyle en 4 en vis-à-vis d'un méthyle (IV)

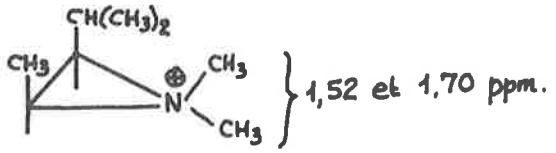
Des deux signaux du gem-diméthyle en 5 de (IV), il est donc logique d'attribuer celui de 8,40 τ au méthyle en vis-à-vis du proton par analogie avec (III) ; la valeur de 8,58 τ correspond au méthyle en 5 vis-à-vis du méthyle.

On voit ainsi qu'un CH_3 exerce sur un groupement identique en vis-à-vis un blindage de 0,15 à 0,20 ppm.

Dans un travail récent, Becconsall, Jones et McKenna (J. chem. Soc., 1965 p. 1276) ont démontré l'existence du chlorhydrate de diméthyl-1,2 pyrrolidine sous deux configurations, et ils ont attribué la structure trans à l'isomère le plus abondant. Le spectre RMN (dans $CDCl_3$) de ce produit, que M. le Professeur McKenna nous a obligeamment communiqué confirme nos résultats, car le C-méthyle cis est plus blindé que le trans :



Dans un autre travail récent, Bottini et VanEtten (J. Org. Chem., 1965, 30, 575), en étudiant la quaternarization d'aziridines, ont décrit le spectre RMN (solvant D_2O, référence interne H_2O) du produit



Nous pensons en accord avec ce qui précède que le signal situé aux champs forts (1,70 ppm) est celui du méthyle qui est cis par rapport aux deux C-substitutions.

En espérant que cette contribution me permettra de recevoir les I.I.T.N.M.R. Newsletter, recevez, Cher Dr. Shapiro, l'assurance de mes sentiments les meilleurs.

R. JACQUIER.-

81-34

THE SCHOOL OF PHARMACY

UNIVERSITY OF LONDON

PHARMACEUTICAL CHEMISTRY
PROFESSOR W. B. WHALLEY
D.Sc., Ph.D., F.R.I.C.

29/39, BRUNSWICK SQUARE
LONDON, W.C.1.
TELEPHONE TERMINUS 7651/8

WBW/CLS

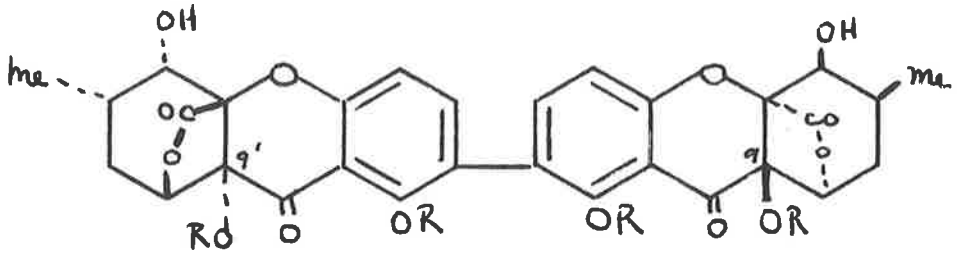
11th June 1965

Dear Dr. Shapiro,

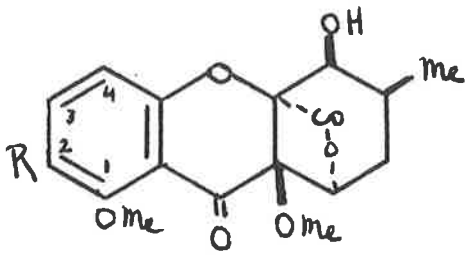
The Conformation of Ergoflavin

Thank you for your recent reminder that our subscription is due. I hope the following contribution will be satisfactory.

For some years we have been working upon the constitution of the non-alkaloidal pigments associated with ergot and have recently substantially completed their structural elucidation. The principal pigment, ergoflavin [1], has the structure and absolute stereochemistry (I; R = H). On general grounds, it would be anticipated that the two halves of the ergoflavin molecule would be non-planar. This deduction is confirmed by the N.M.R. spectral evidence. Thus, the methoxyl signals in 2-methoxycarbonyl-di-O-methylhemiergoflavin (II; R = CO_2Me)



(I)



(II)

/cont.....

and in di-O-methylhemiergoflavin (II; R = H) occur in the regions τ 6.1 and 6.6, whereas the corresponding signals in tetra-O-methylergoflavin (I; R = Me) and its derivatives are located in the regions τ 6.45 and 6.6. In both series, it is apparent that the signal at τ 6.6 is that of the C_9 methoxyl group. The diamagnetic shift (0.36 p.p.m.) of the C_1 methoxyl signal of tetra-O-methylergoflavin relative to that of di-O-methylhemiergoflavin is indicative of a large dihedral angle between the two benzene rings of the diphenyl nucleus which results in a mutual shielding of the C_1 methoxyl residue in one half of the molecule by the aromatic ring of the other half. This up-field shift of signals associated with methoxyl residues in "hindered" diphenyl systems has been previously observed [2,3,4] in a very limited number of other natural products.

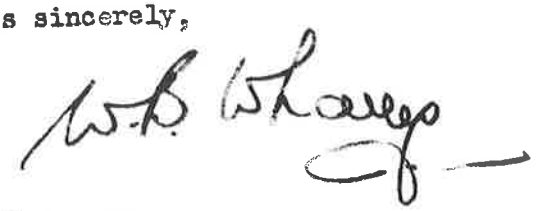
Additional evidence for a large dihedral angle between the aromatic rings of ergoflavin and its derivatives is provided by the N.M.R. spectral data of its various acetyl derivatives.

N.M.R. spectroscopy has made a very considerable contribution towards the solution of this structural problem. The details will be reported in full in various papers which should appear within the next few months.

May I say how much I and my colleagues enjoy receiving your I.I.T. N.M.R. Newsletter. We look forward to remaining on your circulation list for a long time.

With very best wishes,

Yours sincerely,



W. B. Whalley

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1. J.W. ApSimon, J.A. Corran, N.G. Creasey, K.Y. Sim and W.B. Whalley, Proc. Chem. Soc., 1963, 209; J.D.M. Asher, A.T. McPhail, J.M. Robertson, J.V. Silverton and G.A. Sim, Proc. Chem. Soc., 1963, 210.
2. R.C. Cambie, W.R.J. Simpson and L.D. Colebrook, Tetrahedron, 1963, 19, 209.
3. S.M. Books, R.C. Cambie and T. Takchasi, Tetrahedron, 1963, 19, 1109.
4. S. Goodwin, J.N. Schoolery and L.F. Johnson, Proc. Chem. Soc., 1958, 306.

Dr. Bernard L. Shapiro,
Associate Professor,
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Chicago,
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U.S.A.

CARNEGIE INSTITUTE OF TECHNOLOGY
SCHENLEY PARK
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DEPARTMENT OF CHEMISTRY

TELEPHONE: 621-2600
AREA CODE 412

June 16, 1965

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

Dear Barry:

In the course of our work on relative signs of coupling constants in olefins, we came across some curious variations in long-range C-H couplings. Further studies of such couplings uncovered regularities and led us to some general speculations, a few of which we would like, after several years, to mention to IIT NMR readers.

Our first observations on polybromo and polychloroethylenes revealed the existence of a rather good additivity relationship among the two-bond CH coupling constants, from which we could infer the values of the three such couplings in vinyl bromide. We later found that the proton spectrum of a C^{13} enriched sample of the latter compound had been studied by Mrs. R. M. Lynden-bell.(1) She regarded her results as rather surprising, but they turned out to be completely consistent with our work in the polyhalides, as shown in Table 1. The numbering system is given below:

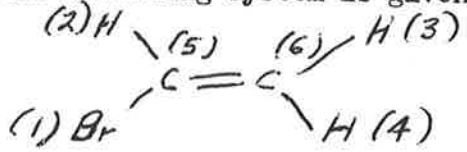

TABLE I

Compound	J_{CCH} (cps) Observed	Calculated
$CHBr = CH_2$ (J_{35})	+7.5[a]	—
(J_{45})	-8.5[a]	—
(J_{26})	+5.8[a]	—
<u>cis</u> CHBr = CHBr	+15.1[b]	+15.7
<u>trans</u> CHBr = CHBr	+0.4 or +1.2[c]	-0.3
$CH_2 = CBr_2$	d	+1.4
$CHBr = CBr_2$	7.7[e]	+9.6

a Sign determined relative to ^{J}CH by spectral analysis.
b Sign determined by double resonance.
c Sign determined by spectral analysis (see below).
d Absolute value $\lesssim$ 2.5 cps in $CH_2 = CCl_2$.
e Sign unknown.

The coupling constants in the corresponding chlorine compounds are very similar, and some data on them have been reported by Nobby Muller[2]. As he found, the inner satellites in the spectrum of the trans-dichloride are exactly superimposed, but this implies a coupling of +0.8 cps rather than zero if one takes into account the fact that they are parts of two AB systems. A slight splitting of the corresponding peaks in the trans-dibromide is observed, leading to two possible values for the coupling.

The two-bond CH couplings in maleates and fumarates are small and nearly equal, as Muller also noted[2], but we have been unable to measure them in an acrylate and cannot make a comparison similar to that in vinyl bromide. We can, however, compare the one-bond couplings in those compounds and in the chloro- and bromoethylenes, and the results are shown in Table II.

TABLE II

Compound	J_{CH} (cps) Observed	Calculated
ethyl acrylate (J_{25})	163.1	—
(J_{46})	159.7	—
(J_{36})	159.3	—
methyl maleate	166.7	166.0
methyl fumarate	167.7	166.4
vinyl chloride (J_{25})	195.0	—
(J_{46})	160.0	—
(J_{36})	161.0	—
cis CHCl = CHCl	198.5	199.6
trans CHCl = CHCl	199.1	198.6
$CH_2 = CCl_2$	166.0	164.6
$CHCl = CCl_2$	201.2	203.2
vinyl bromide (J_{25})	196.1	—
(J_{46})	163.8	—
(J_{36})	159.6	—
cis CHBr = CHBr	198.0	199.3
trans CHBr = CHBr	202.2	203.5
$CHBr = CBr_2$	201.6	206.7

A good additivity relationship is evident, although it begins to break down with tribromoethylene, as it did for the two-bond couplings. The two-bond carbon-hydrogen coupling in vinylene carbonate is 17.6 cps, even larger than in the corresponding chloro and bromo compounds, but we have not been able to measure the two-bond couplings in vinyl acetate or to find a corresponding trans compound for comparison.

The explanation for these results is not clear. Accordingly, we have restricted ourselves to attempts to find very general, essentially phenomenological, models consistent with the observed additivity relationships. A model in which the substituent effects are the result only of additive changes in the ψ^2 (0) involved in the contact interaction is not consistent with the two- and three-bond couplings, but a "pathways" model in which the coupling is transmitted through no more than one intervening atom is adequate.

For example, for the mono-substituted compound, for the one-bond couplings one may write

$$J_{36} = d + g + c' + t' \quad (x)$$
$$J_{46} = d + g + c' \ (x) + t'$$
$$J_{25} = d + g \ (x) + c' + t'$$

and for the two-bond couplings

$$J_{26} = d' + g' \ (x) + c + t$$
$$J_{35} = d' + g' + c + t \ (x)$$
$$J_{45} = d' + g' + c \ (x) + t$$

where d, d', g, g', c, c', t, t' stand for contributions to the coupling constants from the following pathways:

d (direct) 

c (cis) 

d'(") 

c'(") 

g (gem) 

t (trans) 

g'(") 

t'(") 

and where d (x), g (x), etc., are contributions with a substituent x in the given position (●). Similar equations may be written for the di- and tri-substituted compounds. Thus, given the coupling constants in ethylene

$$(J\ (C^{13}\text{-H}) = 156.4 \text{ cps, or } J\ (C^{13}\text{-C-H}) = -2.5 \text{ cps})$$

and three of the seven coupling constants (either one-bond or two-bond) in the substituted vinyl compounds, one may predict the other four coupling constants.

Unfortunately, we have not yet been able to find a theoretical or experimental test to distinguish between the above "pathways" model and a simple additivity rule.

The differences in couplings among the haloethylenes suggested that similar effects might be present in the haloalkanes. We have accordingly looked for solvent effects on the two-bond CH couplings in 1,2-dichloroethylene and 1,1,2,2-tetrachloroethylene, in which the relative amounts of trans and gauche rotamers should be concentration dependent. The changes observed were small and seem to be real, but further work will be necessary to completely confirm the dependence on solvent and concentration expected from the results of measurement of HH couplings.

(1) Ruth M. Lynden-Bell, Mol. Phys. 6, 537 (1963)
(2) N. Muller, J. Chem. Phys. 37, 2729 (1962)

Yours truly,

Robert J. Kurland
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Carnegie Institute of Technology
Pittsburgh, Pennsylvania 15213

Paul C. Lauterbur
Department of Chemistry
State University of N. Y.
Stony Brook, Long Island, N. Y.

81-40

NORTH CAROLINA STATE
OF THE UNIVERSITY OF NORTH CAROLINA
AT RALEIGH

SCHOOL OF PHYSICAL SCIENCES
AND APPLIED MATHEMATICS
DEPARTMENT OF CHEMISTRY

P. O. BOX 5247
RALEIGH, N. C. 27607

June 16, 1965

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

Dear Dr. Shapiro: NMR Spectral Parameters of the Ring Protons for Some Cyclopentadienylmanganese Tricarbonyl Derivatives

Thank you for your subscription reminder. Recently Dr. G. G. Long of this department and I have completed work on some cyclopentadienylmanganese tricarbonyl derivatives. The n.m.r. portion of this work should be of some interest to your readers.

The n.m.r. data for some of the cyclopentadienylmanganese tricarbonyl derivatives are summarized below. In compounds I to IV the resonance signals of the α- and β-protons appeared as apparent triplets with a plane of symmetry between them, in accordance with an A_2B_2 system. In compounds V, VII, and IX the α- and β-protons appeared as broad singlets.

	Ring Substituent	τ Values of the Ring Protons	
		α	β
I	-CHO	4.22	4.75
II	$-COCH_3$	4.26	4.84
III	$-CONH_2$	4.36	4.99
IV	-COOH	4.42	4.89
V	$-CCH_3{=}NOH$	4.70	5.09
VI	>PO.OH	4.48	4.76
VII	-SO.OH	4.55	4.95
VIII	-H	5.04	
IX	$-CH_3$	5.21	5.21

The presence of the carbonyl group in the substituent of compounds I to IV is reflected by a deshielding of both the α- and β-protons. The more deshielded protons were assigned as being alpha to the carbonyl group by analogy to the benzene series where the deshielding effect of the carbonyl is greater at the ortho positions than at meta positions. The chemical shift difference between the ortho and meta protons in benzoic acid is 0.53 ppm which is very close to the difference observed for the α- and β-protons in

compounds I to IV. The deshielding of the α- and β-protons in these compounds with respect to the parent cyclopentadienylmanganese tricarbonyl is the same order as the deshielding in the analogous benzene series. In compound V, the α-protons were assigned to the lower τ value since the oxime substituent would be expected to have a similar but less pronounced deshielding effect than the carbonyl group.

In compound VI, the presence of phosphorus is indicated by the appearance of a doublet ($J = 14.0$ cps) for one of the resonance signals of the ring protons. This doublet was assigned to the α-protons since long range coupling of the type $P^{31}-C-C-H^{1}$ is usually about 5 to 15 cps. Based on this assignment, it appears that the α-protons are more deshielded than the β-protons in this compound. This is consistent with the observation that the phosphinico group is an electron withdrawing substituent when attached to benzene. Similarly, it appears that α-protons are more deshielded than β-protons in compound VII, since the sulfino group is also known to be an electron withdrawing substituent.

The methyl substituent in compound IX produces an upfield shift of 0.17 ppm for both the α- and β-protons. This effect is similar to that in toluene where the ortho and meta protons show identical chemical shift values, 0.10 ppm upfield from benzene.

Sincerely,

Charles G. Moreland

Charles G. Moreland
Assistant Professor

CGM/jk

81-42

TELEPHONE : MW 0522.

Dr. B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Technology Center, Chicago Ill.
UNITED STATES OF AMERICA.

16th June, 1965.

The University of Sydney

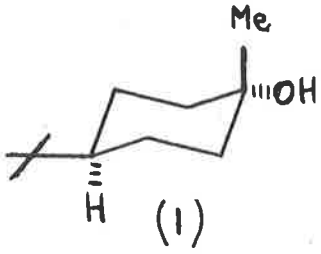
SYDNEY, N.S.W.

IN REPLY PLEASE QUOTE : DEPARTMENT OF ORGANIC CHEMISTRY.

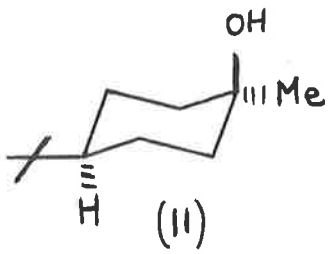
LINE WIDTHS OF TERTIARY METHYL GROUPS

Dear Barry,

In connection with our work on long-range coupling involving the angular methyl groups in steroids[1] we have examined the NMR spectra of cis-4-t-butyl-1-methyl-cyclohexanol [I], trans-4-t-butyl-1-methylcyclohexanol [II], their acetates and the corresponding 2,2,6,6-tetradeutero compounds. The tabulated results show that the axial methyl groups are always broader, that some broadening of equatorial groups occurs and that the protons responsible are at C_2 and C_6. This is in broad agreement with the known relationships in rigid systems[2] but, unfortunately, the accuracy of the measurements is insufficient to say much about the smaller broadening of the equatorial methyl groups and possible long-range coupling with deuterium. However, together with the results obtained in steroids[1, 3, 4, 5] decalins[4] and miscellaneous compounds[4] these data should be useful in assigning configurations and conformations in systems with undistorted six-membered rings. Not unexpectedly, the relationship does not hold for the geminal dimethyl groups in α-pinene where the two methyl groups are of approximately the same line widths [1.2-1.3 c/s].



(I)



(II)

With best regards,

C.W. Shoppee Charles Shoppee
F.P. Johnson Frank Johnson
R.E. Lack Ruth Lack
S. Sternhell Saul Sternhell

1] Shoppee, Johnson, Lack and Sternhell, Tetrahedron Letters 2319 [1964].

2] Barfield, J. Chem. Phys., 41, 3825 [1964] and refs. therein.

3] Bhacca, Gurst and Williams, J. Amer. Chem. Soc., 87, 302 [1965].

4] Williamson, IITNMRN 79, 50.

5] Shoppee, Johnson, Lack and Sternhell, unpublished data.

LINE WIDTHS AT HALF HEIGHT(C/s) Averages for at least 6 scans on A60 spectrometer. Approximately 20% in $CDCl_3$. [a]: Machine at the University of NSW, [b] Machine at CSIRO Division of Coal Research [c] Machine at the University of Sydney. We thank Mr. V.A. Pickles and Mr. P.J. Collin respectively for cooperation.

COMPOUND	OAc	t-Bu	Me	TMS	Me-TMS
trans-4-t-butyl-1-methylcyclohexanol [a]	-	0.55 ± 0.02	0.61 ± 0.02	0.40 ± 0.03	0.21 ± 0.05
ditto [b]	-	0.66 ± 0.03	0.69 ± 0.01	0.42 ± 0.02	0.27 ± 0.03
ditto 2,2,6,6-d_4 [c]	-	0.60 ± 0.07	0.62 ± 0.09	0.49 ± 0.04	0.13 ± 0.13
trans-4-t-butyl-1-methylcyclohexyl acetate [a]	0.41 ± 0.02	0.50 ± 0.02	0.64 ± 0.02	0.38 ± 0.01	0.26 ± 0.03
ditto 2,2,6,6-d_4 [b]	0.42 ± 0.01	0.54 ± 0.01	0.54 ± 0.01	0.40 ± 0.01	0.14 ± 0.02
cis-4-t-butyl-1-methylcyclohexanol [a]	-	0.62 ± 0.01	1.05 ± 0.03	0.45 ± 0.03	0.60 ± 0.06
ditto [b]	-	0.59 ± 0.03	0.99 ± 0.05	0.40 ± 0.01	0.59 ± 0.06
ditto 2,2,6,6-d_4 [c]	-	0.60 ± 0.09	0.57 ± 0.13	0.40 ± 0.04	0.17 ± 0.17
cis-4-t-butyl-1-methylcyclohexyl acetate [a]	0.41 ± 0.01	0.51 ± 0.02	1.29 ± 0.05	0.38 ± 0.01	0.91 ± 0.06
ditto 2,2,6,6-d_4 [b]	0.50 ± 0.01	0.57 ± 0.01	0.56 ± 0.03	0.45 ± 0.03	0.11 ± 0.06

81-44

Dr.R.F.Zürcher c/o

C I B A

LIMITED

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

4000 Basel, June 11, 1965

What causes proton chemical shifts?
(when a substituent is introduced into a given molecule)

Dear Professor Shapiro:

Substituents may bring about additional chemical shifts of nearby protons in the same molecule and as we did not have the patience to wait until "the chemical shift concept is derived in a correct way from the first principles of quantum mechanics"(Primas et. al. IIT NMR Newsletter 79-26), we tried some less fundamental principles in the meantime and are quite pleased with "the success of those semi-empirical concepts".

There are some clearcut cases with no strongly polar groups where it is safe to assume that the anisotropy of the magnetic susceptibility of a substituent X is the cause of a proton chemical shift (X = phenyl, -C=C-, -C≡C-, etc.). In many other cases (X = halogens, -C≡N, >C=O, -OH, etc.) it has become the custom to do so without inquiring if the change of the proton screening constant under the influence of the electric field due to the polar substituent might not be a better explanation of the chemical shift. The electronegativity concept fails to account for chemical shifts of protons some bonds away. In addition chances are good that the well-known electronegativity correlations may be explained by more fundamental quantities [see below and J.I.Musher: J.Chem.Phys. 37, 34 (1962)].

In order to decide this question at least for non-conjugated and non-aromatic molecules we have tried to explain chemical shift increments $\Delta\delta$ of nearby protons due to the replacement of hydrogen atom(s) by a substituent X in rigid cyclic compounds with known geometry in terms of its anisotropic magnetic susceptibility and electric dipole moment:

$$\Delta\delta = \Delta\delta_{el} + \Delta\delta_{magn} \qquad (1)$$

$$\Delta\delta_{el} = \varkappa \cdot e_z \cdot 10^{-12} \qquad (2)$$

[A.D.Buckingham: Canad.J.Chem. 38, 300 (1960)] where

$\Delta\delta_{el}$: that part of the measured additional chemical shift due to the electric dipole moment of the substituent

e_z: the component of the electric field in C-H bond direction due to a substituent with unit dipole moment (1 debye)

$\varkappa = k \cdot \mu$ (μ = dipole moment in debye)

$\varkappa, k$: proportionality factors

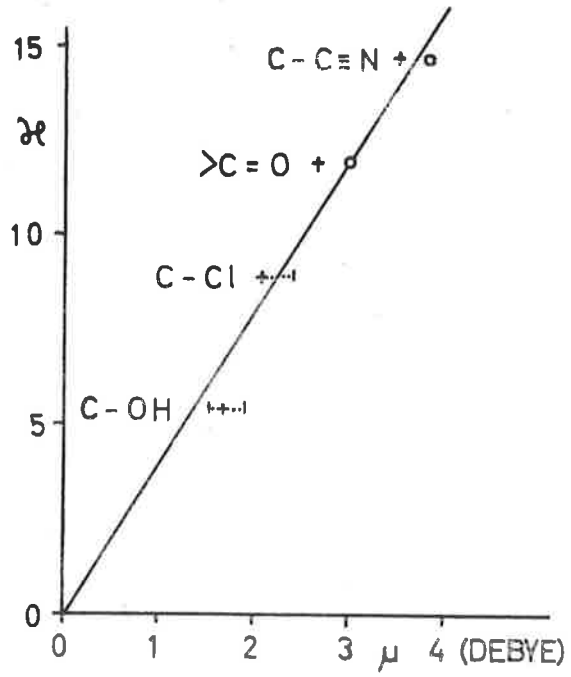
$$\Delta\delta_{magn} = \tfrac{1}{3} R^{-3} \left[\Delta\chi_x (3\cos^2\gamma_x - 1) + \Delta\chi_y (3\cos^2\gamma_y - 1)\right] \qquad (3)$$

(J.A.Pople, W.G.Schneider and H.J.Bernstein, High Resolution NMR, McGraw-Hill, New York 1959, p. 176 - 183)

where $\Delta\chi_x = \chi_x - \chi_z$ and $\Delta\chi_y = \chi_y - \chi_z$. For axially symmetric substituents $\chi_y \equiv \chi_z$ and $\Delta\chi_y \equiv 0$. In eq. (2) a quadratic term in e as well as the influence of the so-called reaction field have been omitted, the former because there are good reasons to expect it to be small at distances bigger than 2.5Å, and the latter because at present no reliable model for its assessment exists (see e.g. P.Laszlo and J.I.Musher, J.Chem.Physics 41, 3906 [1964]).

If the relative spatial positions of the proton and the substituent, as well as the chemical shift caused by its introduction, are known, the geometrical factors in eqs. (2) and (3) may be calculated, and the two (or three) unknown quantities $\varkappa$ and $\Delta\chi_x$ (and $\Delta\chi_y$) may be determined for each substituent by a least-squares treatment. This was done mainly with tertiary methyl groups of steroids and bicyclic compounds and the substituents >C=O, -OH, -Cl and -C≡N.

The result was surprising. The chemical shift increments of the tertiary methyl protons due to a carbonyl group at each position of the steroid frame could not be reproduced with either the anisotropic susceptibility or the electric dipole moment model alone, nor was this possible with both together if the methyl groups were assumed to be freely rotating. But as soon as the calculations were done for a preferred staggered position of the methyl groups the experimental data for eight different ketosteroids could be fitted. In the case of the hydroxy-, chloro- and nitrilo-compounds it turned out that no fit was possible with the anisotropic susceptibility model. On the other hand a good fit was achieved with the electric dipole model. Taking the magnetic susceptibility into consideration did not improve the results markedly. So with one quantity ($\varkappa$) the methyl shifts of 12 chloro compounds and with other $\varkappa$'s those of 12 hydroxy- and 5 cyano-compounds could be reasonably well fitted. What really convinced us that this is not an artefact is the following: the four $\varkappa$'s (for the four different substituents) are quantities found by least-squares calculations. They simply connect the experimental $\Delta\delta$'s with the purely geometrical quantities e_z, but $\varkappa = k \cdot \mu$, a fact which has not been considered up to this point. So $\varkappa$ should be proportional to the substituent dipole moment μ as determined by dielectric constant measurements, which is the case (see Figur).



The relationship between æ and the electric dipole moment μ of the substituents.

Thus in molecules with polar substituents their electric field and not their anisotropy of the magnetic susceptibility seems to be the dominant cause of proton chemical shifts in most cases.

A last word on electronegativity. It is strange that the internal chemical shifts between methyl and methylene protons in ethyl derivatives and the methyl shifts in substituted methanes [J.R.Cavanaugh and B.P.Dailey, J.Chem.Phys. 34, 1099 (1961)] correlate well with substituent electronegativity, but that the methyl shifts in ethyl derivatives themselves do not. With the same æ's and $\Delta\chi$'s (for >C=O) as determined above the right chemical shifts are predicted for methyl protons in ethyl derivatives (ethanol, ethyl chloride and cyanide, also acetone) but not in methyl derivatives. It does not come as a surprise that the latter ones evade such a simple calculation. Other effects possibly become important at short distances, one of them, but not the only one may be the quadratic term in e . These results make it appear likely that electronegativities finally may be explained by more fundamental quantities.

A preliminary account of this work will appear sometime this year in the Proceedings of the 48th Meeting of the Italian Society for the Advancement of Science (NMR in Chemistry), Academic Press, New York.

With best regards.

Sincerely yours,

R. F. Zürcher

R. F. Zürcher

Institut für Elektrowerkstoffe

INSTITUTSDIREKTOR:
PROF. DR. R. MECKE

Herrn
Professor B.L. Shapiro
Chemystry Department,
Illinois Institute
of Technology

C H I C A G O
Illinois, 60616

TELEFON 0761/45514

78 FREIBURG I. BR.
ECKERSTRASSE 4

Ihre Zeichen	Ihre Nachricht vom	Unser Zeichen	
		Frie/Ob.	den 10.6.65

Sehr geehrter Herr Dr. Shapiro!

Konformative Beweglichkeit flexibler Ringsysteme.

Wir möchten hier über einige Ergebnisse unserer Messungen an 1,3-Dioxanen, 1,3-Dithianen und 1,3-Oxathianen berichten (s. Tabelle). Diese Untersuchungen sind, wie schon in unserer früheren Mitteilung in Tetrahedron Letters 1962, 683 angekündigt, eine Weiterführung unserer Arbeiten über den Einfluss von Substituenten auf die Geschwindigkeit der Ringinversion, die Aktivierungsenergie, sowie die Konformation von Heterocyclen. Zur Bestimmung der Werte bzw. der Arrhenius'schen Aktivierungsenergie E_a benutzten wir die Linienbreiten, unterhalb der Aufspaltungstemperatur T_a $(=T_c)$ außerdem auch den Abstand der Maxima (Dublett oder AB-Quartett) und das Intensitätsverhältnis (Linienhöhe zur Höhe des zentralen Minimums). Bei mehreren der in der Tabelle angeführten Heterocyclen konnten wir an derselben Verbindung die Signale der CH_3-Gruppen (Dublett) sowie die AB-Quartette der geminalen Protonen an C-2 oder C-4,6 auswerten. Wir erhielten sehr gut übereinstimmende Werte für die Aktivierungsenergien und die Frequenzfaktoren. Ausserdem fanden wir eine z.T. sehr starke Temperaturabhängigkeit der Eigenbreite der Signale, d.h.

desjenigen Anteils der Linienbreite, der nicht vom Austauschprozess beeinflusst ist. So ist z.B. beim 5,5-Dimethyl-1.3-dioxan bei + 25°C die Linienbreite des CH_3-Signals 0,5 Hz, ($k \sim 10^5$ sec^{-1}) bei - 75°C jedoch 2,1 Hz ($k > 1$ sec^{-1}). Bei diesen Temperaturen erfolgt keine Verbreiterung mehr durch die Ringinversion. Ebenfalls ist die Verbreiterung nicht auf ein schlechteres Auflösungsvermögen des Geräts (DP 60) bei den tiefen Temperaturen zurückzuführen, wie leicht am Referenzsignal TMS zu sehen ist. Wie wir gefunden haben, muss bei Vernachlässigung dieser Temperaturabhängigkeit der Eigenbreite immer dann mit besonderm grossen Abweichungen des E_a-Wertes gerechnet werden, wenn zusätzlich zu einer starken Temperaturabhängigkeit die chemische Verschiebung der beobachteten Signale klein ist. Eine ausführlich Arbeit ist z.Z. im Druck (Spectrochimica Acta). Die in der Tabelle angegebenen Fehler sind nadh dem Fehlerfortpflanzungsgesetz aus den Fehlern aller gemessenen Größen berechnet.

Wie wir kürzlich aus Ihren Mitteilungen ersahen (IIT NMRN Nr. 77 (1965)) hielt es auch Herr Dr. J. Anderson, Straßburg, für notwendig, unsere Arbeit über 1,3-Dioxane zu ergänzen: " it appeared worthwhile to extend the studies of Maier et al (Tet. Lett., (1962) 16, 683) in the 1,3-dioxane series ".
Die von ihm bestimmten Werte der Aktivierungsenergie weichen z.T. erheblich von den von uns gefundenen ab. Diese Abweichungen sind vermutlich darauf zurückzuführen, daß Dr. Anderson die Temperaturabhängigkeit der Eigenbreite nicht berücksichtigt hat. Sollte Herr Dr. Anderson die 50 Meilen zwischen Freiburg und Straßburg, seinem derzeitigen Arbeitsort, nicht scheuen, so böten wir ihm gern die Möglichkeit, die von uns ausgearbeitete Verfeinerung des Auswerteverfahrens zu studieren.

Mit freundlichen Grüßen

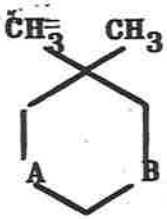
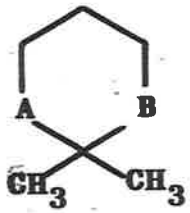
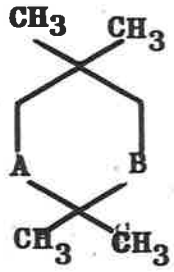
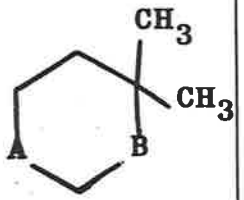
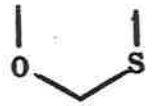
H. Friebolin

(Dr. H. Friebolin)

H. Schmid

(H. Schmid)

Aktivierungsenergien in kcal/Mol

					
 A = B = S	11,8 [1]	12,2 ± 1,2	11,5 ± 1,0	13,5 ± 2,0	
 A = B = O	14,4 [1]	13,5 ± 1,2	13,2 ± 2,7 [1]	10,6 ± 1,5	11,7 ± 1,7 [2]
 A=O, B=S	10,2	11,9 ± 1,3	10,6 ± 1,2	12,5 ± 1,0	

1) Eine genaue Auswertung unserer Meßergebnisse der unsubstituierten Heterocyclen mit Fehlerrechnung ist noch nicht vollständig abgeschlossen.

2) Wir sind z.Zt. mit der Darstellung und der Untersuchung dieser in 4- bzw. (und) 6-Stellung methylsubstituierten Heterocyclen beschäftigt.

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