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DEPARTMENT OF CHEMISTRY

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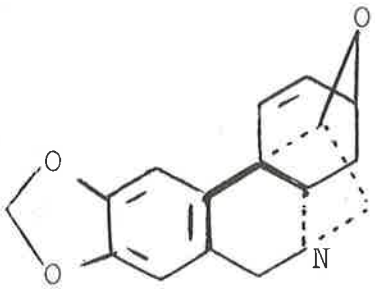
March 7, 1966

Coupling Constants of the Olefinic Hydrogens in Apohaemanthamine.

Dr. Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago 16, Illinois

Dear Dr. Shapiro:

In a recent general study[1] of proton magnetic resonance characteristics of Amaryillidaceae alkaloids of the 5,10b-ethanophenanthridine series we reported that the C(1), C(2) and C(3)-hydrogens in the strained cyclic ether apohaemanthamine (I) showed coupling constants of unusual magnitude. The values ascribed ($J_{1,2}$ = 12.6 c/s; $J_{2,3}$ = 6.5 c/s) from the 60 mc spectrum were, in the first instance, abnormally high[2] for olefinic protons in a six-membered ring. And secondly, the 6.5 c/s coupling of the C(2) and C(3)-hydrogens was in poor agreement with their subtended dihedral angle of ca.5°.



I

The 100 mc spectrum[3] of the ether (I) has permitted the reassignment of the coupling constant at $J_{1,2}$ = 8.5 c/s, $J_{2,3}$ = 4.6 c/s and also reveals the presence of allylic coupling $J_{1,2}$ = 1.6 c/s (see figure). The presence of allylic coupling serves to distinguish the signals of the C(1) and C(2) hydrogens and thus makes the above assignments of $J_{1,2}$ and $J_{2,3}$ unequivocal. However, since the coupling constant of 4.6 c/s for the C(2) and C(2)-hydrogen is much smaller than the predicted[4] value of 8 c/s for a dihedral angle of ca. 5° double resonance studies were carried out to corroborate the assigned couplings. Saturation at the C(3)-hydrogen resonance frequency gave rise to a

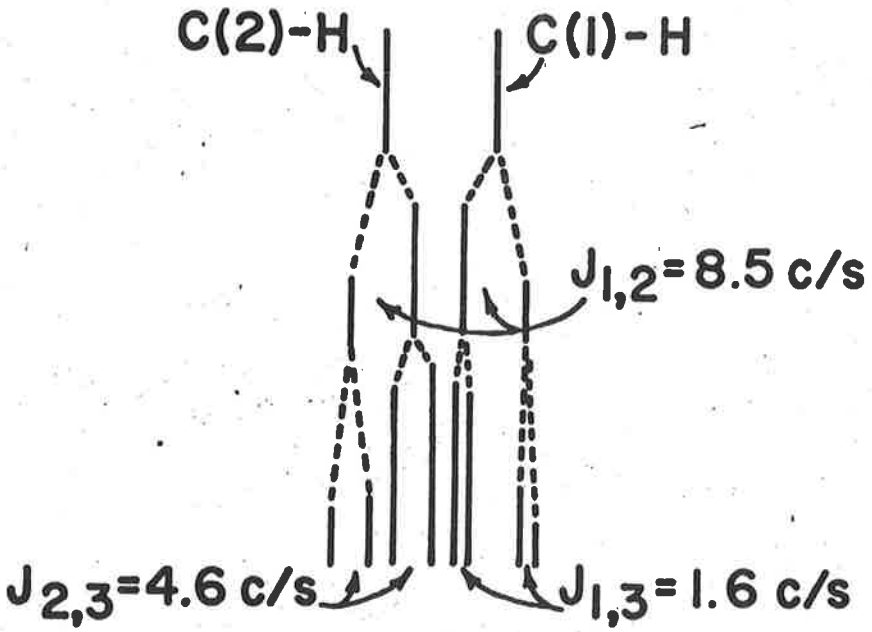
typical AB pattern (see figure) for the olefinic hydrogens; caused by the collapse of both the small allylic coupling of 1.6 c/s in the C(1) hydrogen signal and the 4.6 c/s coupling in the C(2) hydrogen signal.[5] The vicinal coupling constant for the C(1) and C(2)-hydrogens in I is somewhat smaller than the lower limit of the values recorded for the vicinal coupling of olefinic hydrogens in cyclohexene systems (range 9.9 - 10.3 c/s)[2]. However its value still exceeds the maximum value reported for the analogous hydrogen coupling in cyclopentene systems (range 5.1 - 7.0 C/S). Therefore it is suggested that the most probable reason for the low value of $J_{1,2}$ = 8.5 c/s in apohaemanthamine is due to a small decrease in the internal angle of C(1) and C(2). This presumably occurs in order to accommodate the relief of strain in the most equitable manner in this rigid ring system. At present no satisfactory explanation is available for the large deviation of the observed coupling constant of the C(2) and C(3)-hydrogens from that of the calculated value. Undoubtedly the inherent strain present in this molecule affects the hybridization of C(2) and C(3) but whether this is sufficient to account for such a large reduction in magnitude of the coupling constant of these hydrogens is debatable. If anybody has a good explanation for these results I would be interested in hearing from them.

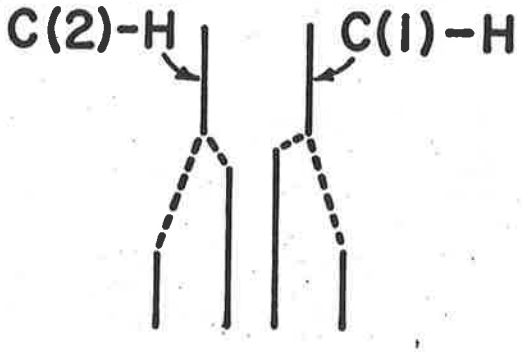
Sincerely yours,

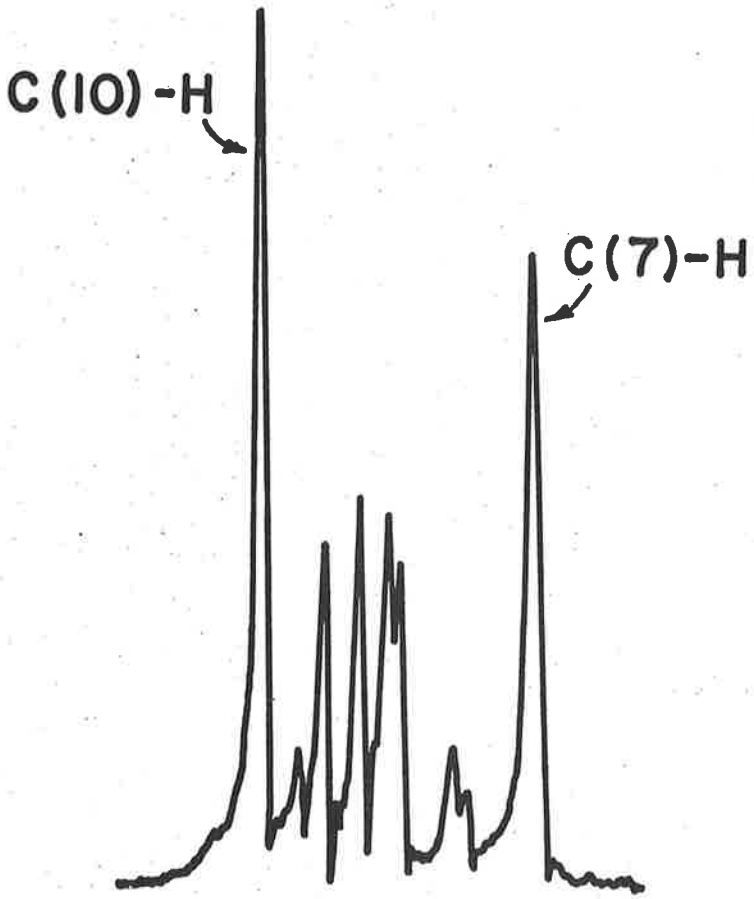
Peter W. Jeffs

Peter W. Jeffs

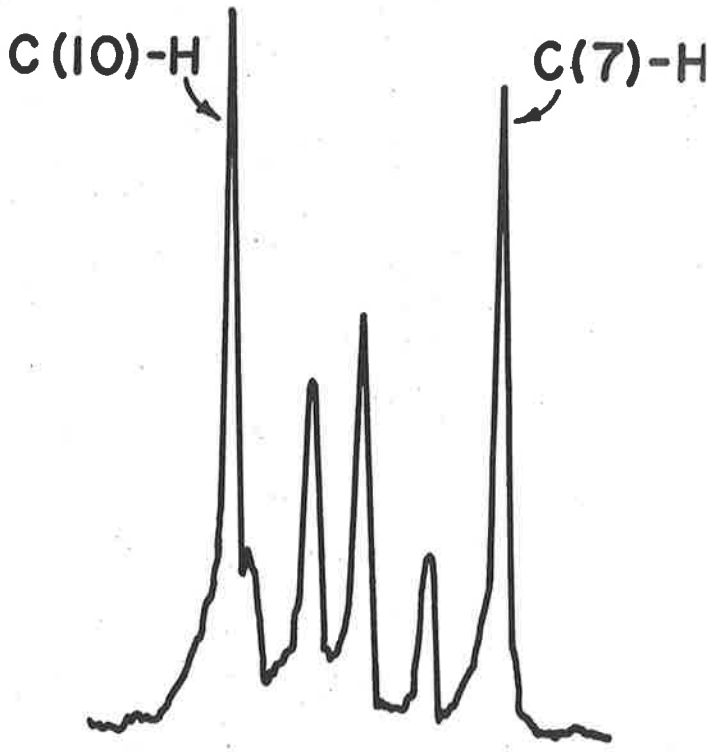
PWJ/dgv







(a)



(b)

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LABORATOIRE DE SPECTROSCOPIE HERTZIENNE
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PARIS, le 7 Février 1966
ODÉ. 24-13 POSTES 484, 483 et 263

Dr. SHAPIRO
Department of Chemistry
Illinois Institute of Technology
CHICAGO Illinois 60616
U.S.A.

Sujet : Résonance magnétique nucléaire et absorption infra-rouge.

Mon Cher Collègue,

Dans une publication précédente (1), nous avons souligné qu'il existe une relation entre les données de la résonance magnétique nucléaire et celles des spectres d'absorption infrarouge.

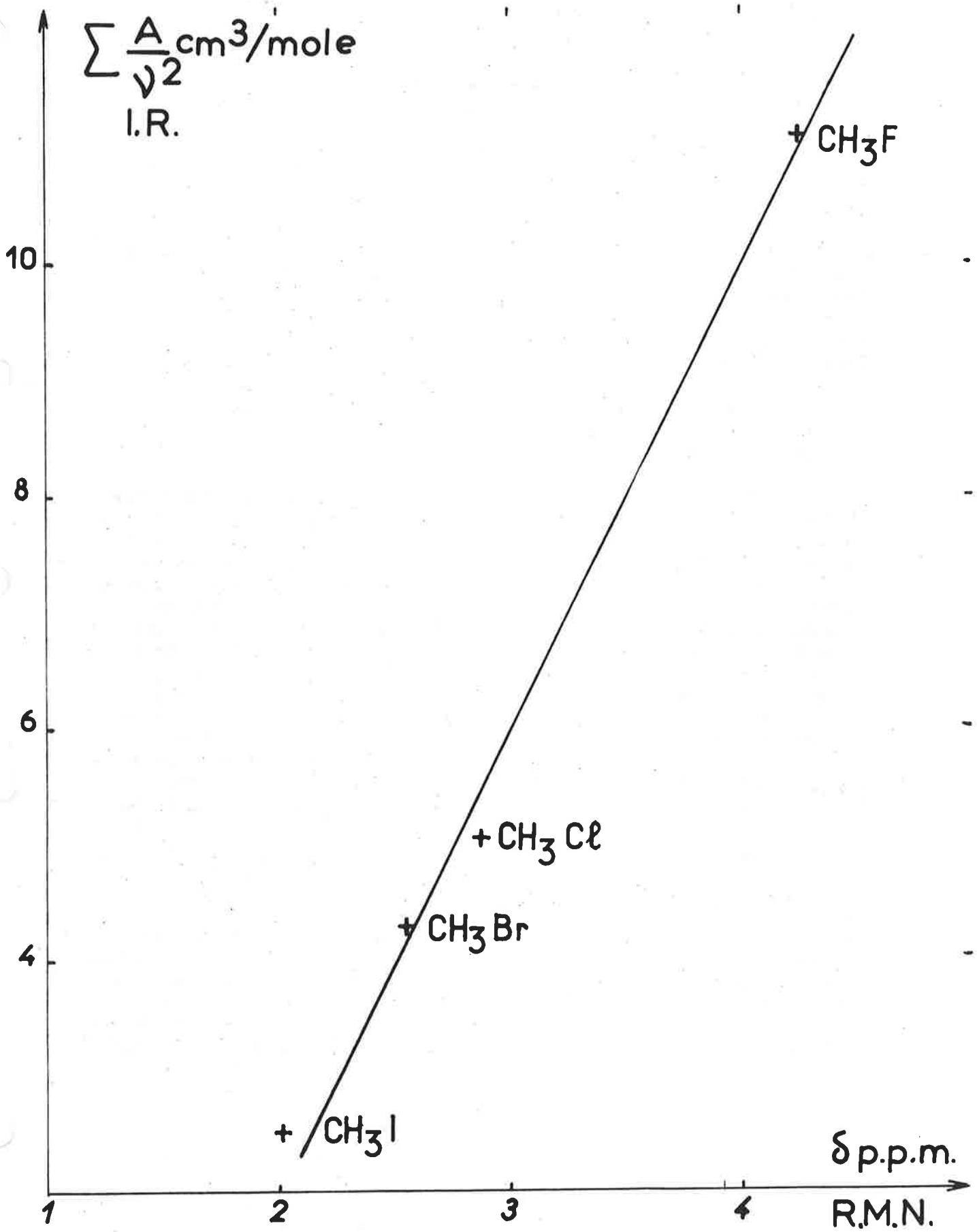
Ce travail était basé sur l'hypothèse suivante : d'une part le déplacement chimique δ du proton CH est directement lié à la charge q portée par ce proton; d'autre part l'intensité de l'absorption infrarouge $|A|$ du vibrateur CH est liée, par l'intermediaire du moment de transition, à cette charge q (1). Il devait donc exister une relation entre $|A|$ et δ. Comme l'avait montré P. JOUVE (1)(2), cette relation $|A|$, δ, existe bien mais elle n'est pas linéaire.

Or, Crawford (3) et Buckingham (4), comparant des composés deutériés ont introduit pour les fréquences de vibration ν, 2ν, $n\nu$, le paramètre $\Sigma A/\nu^2$, $\Sigma A/\nu^3$, $\Sigma A/\nu^{n+1}$ ($|A|$ intensité, ν fréquence fondamentale de vibration, Σ somme pour toutes les vibrations de même symétrie de la molécule).

Le paramètre $\Sigma A/\nu^2$ a été relié par P. Jouve (1) au déplacement chimique δ pour les halogénures de méthyle, les hydracides, les alcools, les composés acétyleniques, etc... : Comme le montre la figure ci-jointe, on obtient une relation sensiblement linéaire. Ceci montre la validité de l'hypothèse de départ.

Bien cordialement.

1. R. Freymann - Colloque Cagliari-Sassari (Nuclear Magnetic Resonance in Chemistry, 1 vol. 1965 Academic Press, p. 13 à 34)
2. P. Jouve - Colloque Ampère Louvain - (Nuclear Magnetic Resonance and Relaxation in solids, 1 vol. North Holland 1965, p. 307)
3. B.L. Crawford J. - Chem. Phys. 20, 977, 1952
4. A.D. Buckingham - Proc. Roy. Soc. A 248, 169, 1958


$\sum \frac{A}{\nu^2}$ cm³/mole
I.R.
10
8
6
4
+ CH3F
+ CH3 Cℓ
+ CH3 Br
+ CH3 I
δ p.p.m.
R.M.N.
1
2
3
4

McMASTER UNIVERSITY

HAMILTON COLLEGE

HAMILTON, ONTARIO, CANADA

DEPARTMENT OF CHEMISTRY—BURKE CHEMICAL LABORATORIES

March 7, 1966

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

The Interpretation of the ^{19}F N.M.R. Spectrum of VF_5

Dear Professor Shapiro:

This note outlines a procedure that we have used for the interpretation of "structureless" spectra which actually contain information on coupling constants and quadrupole relaxation times. As an example we consider VF_5 which has a ^{19}F n.m.r. spectrum at room temperature consisting of a single symmetrical broad line which we found to have a width of 250.9 ± 1.6 c/sec at half-height. (Figure 1) If VF_5 has a trigonal bipyramidal structure like PF_5 it might be expected to give rise to two ^{19}F n.m.r. signals; a triplet of relative intensity three and a quartet of relative intensity two. Even at low temperatures (using a solution of VF_5 in an inert solvent) it was not possible to resolve any fine structures in the spectrum (1). We propose that rapid intramolecular exchange occurs as in PF_5 (2). Such exchange would cause n.m.r. equivalence of the five fluorine atoms while retaining vanadium fluorine spin-spin coupling. The observed spectrum can be interpreted as a partially collapsed multiplet (octet of equal intensities) due to coupling with the ^{51}V nucleus (I = 7/2) which is undergoing electric quadrupole relaxation (3).

Using an extension of the theory previously reported (3,4) theoretical line shapes may be calculated as a function of $\eta = 2\pi J\tau$ where J is the V-F coupling constant in c/sec and τ is the quadrupole relaxation time for the ^{51}V nucleus. In order to facilitate the process of obtaining a calculated spectrum in agreement with the observed spectrum it was necessary to have approximate values of J and τ to start with. These were obtained in the following manner: A value of the V-F coupling constant of 116 c/sec has been previously determined for the

species VOF_4^- (5) and so this value was used for our initial calculations. We have recorded the ^{51}V spectrum of VF_5 using the high-resolution audio side-band method previously utilized in our laboratory for ^{77}Se resonances (6). It was found to be a broad symmetrical band approximately 2000 c/sec wide at half-height. As the line-width is several times the vanadium-fluorine spin-spin coupling constant all fine structure is lost and the width at half-height may be taken to be $1/\pi\tau$, therefore, $\tau = 1.6 \times 10^{-4}$ sec and hence $\eta = 0.12$. Theoretical spectra were calculated using values of η near to 0.1. The best agreement with the observed spectrum was obtained for $\eta = 0.230$. The accuracy of the fit between observed and calculated spectra can be conveniently tested by comparing the ratio of the line widths at three-quarters and at half-height. For $\eta = 0.230$ this was found to be 0.6050 compared with the experimental value of 0.6049±0.0057. (We may note that for a simple Lorentzian line shape this ratio has the value of $1/\sqrt{3} = 0.577$.) The theoretical spectrum for $\eta = 0.230$ has a width of 2.856J c/sec at half-height. Hence we obtained J = 88±5 c/sec and $\tau = 4.2 \pm 0.7 \times 10^{-4}$ sec (7). The limits of precision on these values were obtained by considering the error in the experimental value for the ratio of the line widths at three-quarters and at half-height.

Yours sincerely,

J. Bacon | R. J. Gillespie | U. R. K. Rao

1. R. J. Gillespie and J. W. Quail, unpublished results.

2. E. L. Muetterties, W. Mahler, R. Schmutzler, Inorg. Chem., 2, 613 (1963).

3. J. Bacon, R. J. Gillespie and J. W. Quail, Can. J. Chem., 41, 3063 (1963).

4. M. Suzuki and R. Kubo, Mol. Phys., 7, 201 (1964).

5. J. V. Hatton, Y. Saito and W. G. Schneider, Can. J. Chem., 43, 47 (1965).

6. T. Birchall, R. J. Gillespie and S. L. Vekris, Can. J. Chem., 43, 1672 (1965).

7. We earlier reported at the Chemical Institute of Canada Symposium on Structural Inorganic Chemistry, Halifax, N.S., Sept., 1965, an interpretation using the same method, but only one VF_5 ^{19}F spectrum. This gave $J_{VF} = 78$ c/sec, $\tau = 5.1 \times 10^{-4}$ sec.

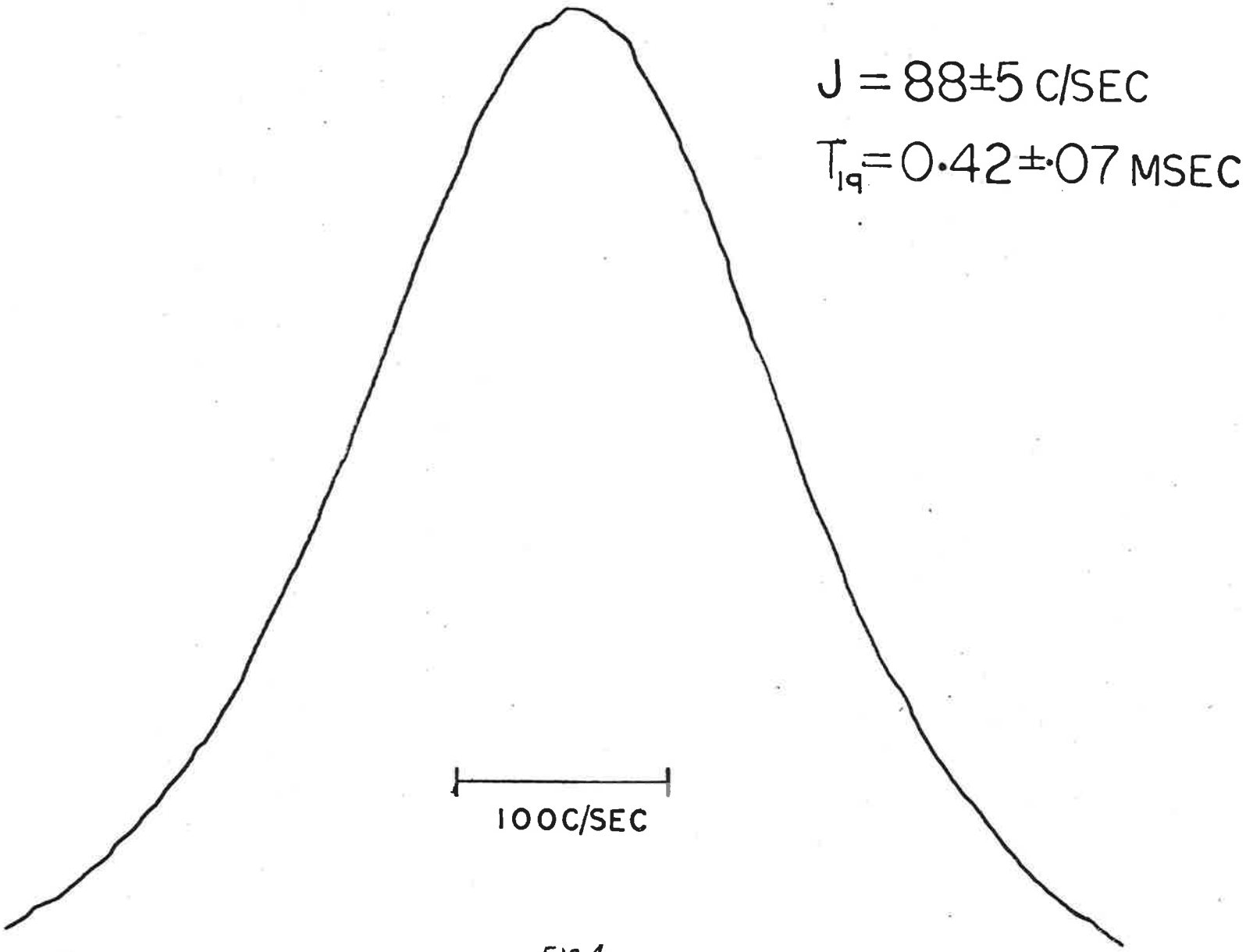


FIG 1.

^{19}F n.m.r. spectrum of VF_5 at [illegible]m temperature

Telephone No. 24161 (Ext.)

SCHOOL OF CHEMISTRY,
THE UNIVERSITY,
BRISTOL 2.

10th February, 1966.

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

Dear Professor Shapiro,

Conformation and Proton Couplings in some D-Ribopyranose Derivatives

We have recently completed an investigation of the ring conformations of some 2,3,4-Tri-O-benzoyl-D-ribopyranosyl derivatives and one or two related compounds. PMR spectra were measured on A-60 and HA-100 spectrometers and the chemical shifts and coupling constants obtained are summarised in Tables 1 and 2. The spectrum (Fig. 1c) of α-D-ribopyranose tetrabenzoate (not known in pure form) was obtained by subtraction of the 100 Mc. spectrum (Fig. 1a) of its pure β-anomer from that (Fig. 1b) of the anomeric mixture, using the Varian C-1024 time-averaging computer. (We are indebted to Dr. K.A. McLauchlan for considerable help with this experiment). From the proton couplings it may be deduced that the β-1-cyanide, β-acetamidomethylene derivative, α-1-halides and α-1-benzoate exist predominantly in the C1 conformations A, B, and D respectively, whereas the β-1-halides, -glycosides, and -benzoate are mainly in the 1C conformation C. The operation, or non-operation of the 'anomeric effect'[1] appears to be the principal energetic factor determining the predominating chair conformation. Thus the halides, glycosides, and 1-benzoates which contain an electron-rich atom bonded to C_1 adopt predominantly the conformation in which the substituent at C_1 is axial.

From Table 2 it can be seen that certain couplings are characteristic of each chair conformation. Thus although the protons in the pairs H_2-H_3, and H_3-H_4 have the same type of gauche orientation in the two chair conformations, the values of $J_{2,3}$ and $J_{3,4}$ in the C1 chair are characteristically smaller than those in the 1C form. It does not appear possible to rationalize these differences by means of the trans-coplanar electronegativity effect.[2] Since the proton pairs H_2-H_3, and H_3-H_4 in conformation C possess more electronegative atoms in trans-coplanar orientation than they do in A, B, or D, it might be expected that the values of $J_{2,3}$ and $J_{3,4}$ in C would be smaller than those in A, B, and D; i.e., the opposite of that observed. It seems necessary therefore, to explain these results in terms of dihedral angle. Flattening of chair C resulting from repulsion of the syn-axial acyloxy groups at C_2 and C_4 could cause

$\phi_{2,3}$ and $\phi_{3,4}$ in C to be smaller than in D. There appears also to be a conformational dependence of the geminal coupling $J_{5e,5a}$. For instance, the numerical values of $J_{5e,5a}$ in the α-halides (D) are appreciably smaller than those in the β-halides (C). Assuming that these couplings have negative sign, the results agree with the predictions of the recent M.O. theory of geminal coupling,[3] namely, that CH_2 protons in vicinal gauche-trans orientation to an electronegative substituent (chair C) should show a geminal coupling more negative than that of protons both in gauche relationship with the substituent (chair D).

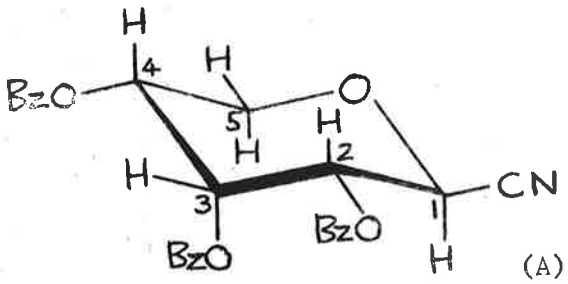
Yours sincerely,

B. Coxon.

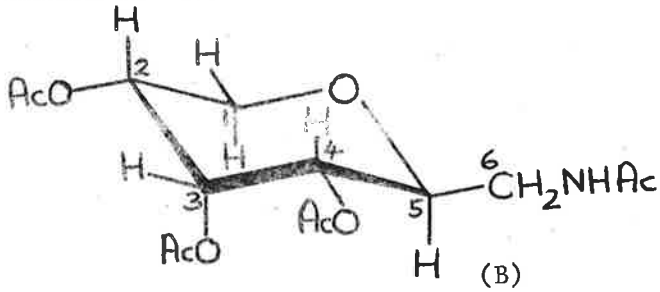
1. J.T. Edward, Chem. and Ind., 1102 (1955); R.U. Lemieux, Molecular Rearrangements (Edited by P. de Mayo) part 2; p. 735, Interscience, New York (1963).

2. D.H. Williams and N.S. Bhacca, J. Amer. Chem. Soc., 86, 2742 (1964); H. Booth, Tetrahedron Letters, 411 (1965).

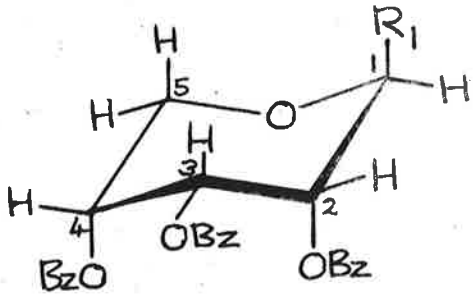
3. J.A. Pople and A.A. Bothner-By, J. Chem. Phys., 42, 1339 (1965).



(A)

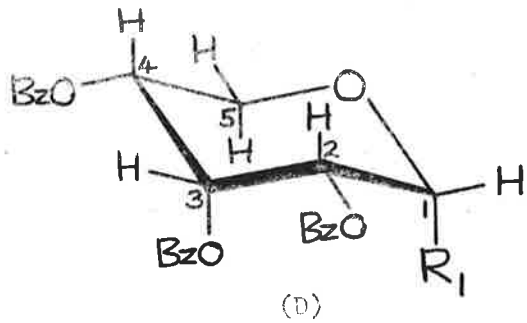


(B)



(C)

R_1 = F,Cl,Br,I,OMe,OCH_2Ph,OBz.



(D)

R_1 = F,Cl,Br,OBz.

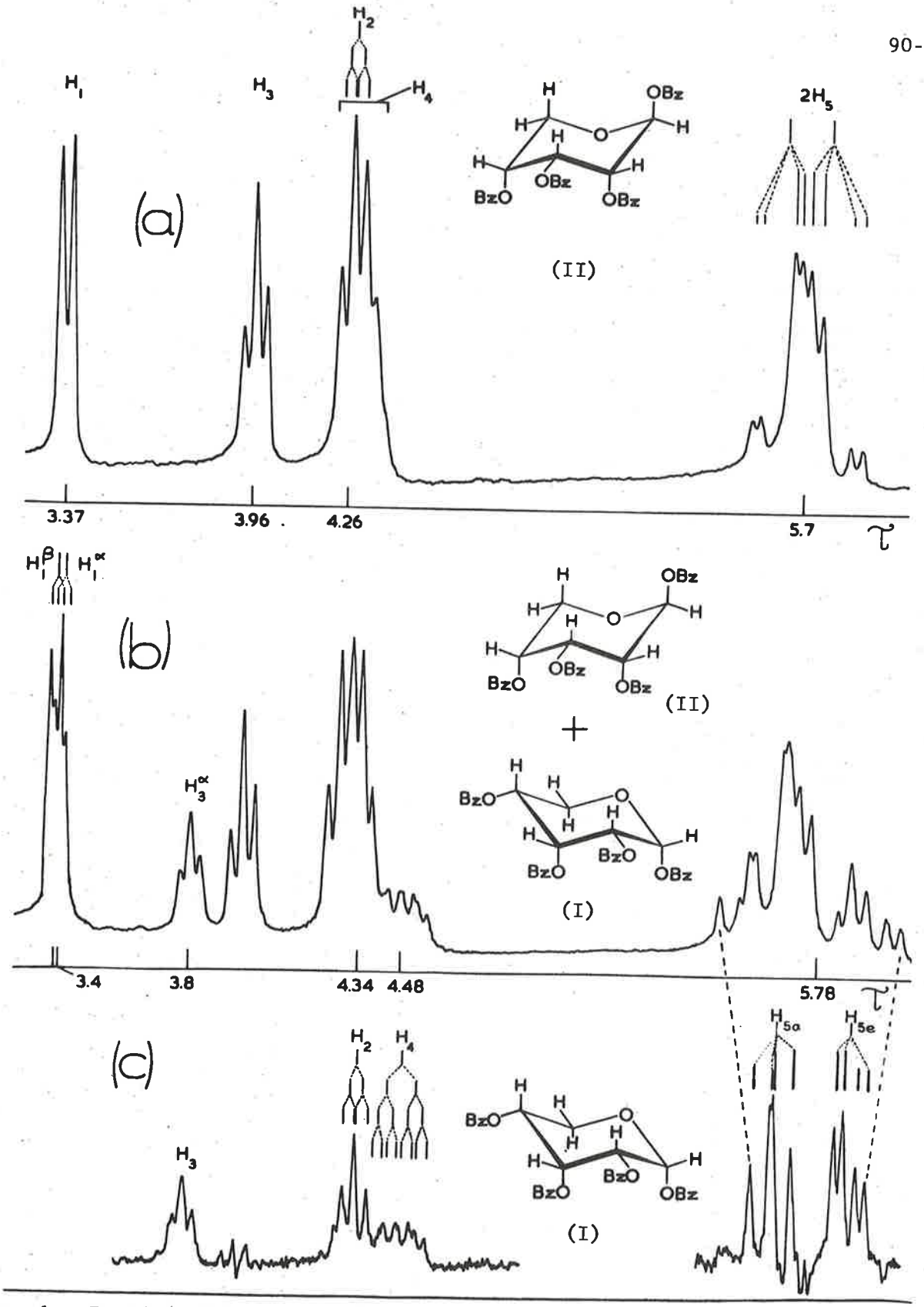


Fig. 1. Partial PMR spectra of 1,2,3,4-tetra-O-benzoyl-D-ribopyranoses in $CDCl_3$ at 100 Mc/s, (a) pure β-anomer (II), (b) mixture of α- and β-anomers (I and II), (c) α-anomer (I), obtained by electronic subtraction of (a) from (b).

TABLE 1

1st Order Chemical Shifts (τ values) of 2,3,4-tri-O-benzoyl-D-ribopyranosyl Derivatives and related Compounds in $CDCl_3$

Compound	R_1	H_1	H_2	H_3	H_4	H_{5e} & H_{5a}	$\tau_{5a} - \tau_{5e}$[c]	R_1	$R_2 = R_3 = R_4 = OBz$
I[a,d]	α-OBz	3.40d[e]	4.34t	3.80t	4.48sx(at least)	5.78o	-0.375	1.72 - 3.05m	
II[a]	β-OBz	3.37d	4.26t	3.96t	≈4.28[f]	5.70o	-0.139	1.90 - 2.91m	
V[b]	β-CN	4.96d	4.34q	3.90t	≈4.44[f]	5.78o	0.159	—	1.60 - 2.89m
		4.26d[g]	3.71q[g]	3.36t[g]	4.02qi[g]	5.51sp[g]	0.110[g]	—	1.65-1.98m, 2.32-2.88m[g]
IX[b,h]	β-OAc	3.95d	4.98q	4.25t	≈4.95[f]	5.74m(H_5+2H_6)	—	$R_1 = R_2 = R_3 = R_4 = R_6 = OAc$ 7.81(R_3), 7.87, 7.92, 7.97(x2)(R_1,R_2,R_4,R_6)	
XII[b] a	β-F	4.12q	4.10 —	—	4.41[f]	5.69sp	—	—	1.89 - 2.97m
		≈4.2[f]	4.17 - 4.45[f]		≈4.35[f]	5.75o	0.149	—	1.98 - 2.93m
XIII[b]	β-Cl	3.66d	4.30q	3.97t	≈4.3[f]	5.62o	0.272	—	1.85 - 2.94m
IV[b]	β-Br	3.25d	4.16q	3.82t	≈4.19[f]	5.57o	0.174	—	1.80 - 2.88m
XIV[a]	β-I	2.94d[f]	4.23q[f]	3.88t	≈4.25[f]	5.82o	0.128	—	1.97 - 2.93m
XV[a]	β-OMe	5.04d	4.49q	4.21t	≈4.44[f]	5.91o	-0.119	6.60	1.96 - 2.89m
XVI[b]	β-OCH_2Ph	4.80d	4.41[f]	4.14t	≈4.4[f]	5.83sp	-0.163	5.29q(CH_2),2.69m(Ph)	1.93 - 2.97m
XVII[a]	α-F	4.19q[f]	4.72sx[f]	3.84m	4.56qi(at least)[f]	5.81o+t	-0.349	—	1.84 - 2.85m
XVIII[a]	α-Cl	3.67q	4.54q	3.84m	4.58sx(at least)[f]	5.80o+t	-0.428	—	1.75 - 2.86m
XIII[b]	α-Br	3.27d	4.53q	3.75m	4.48sx(at least)[f]	5.73o+t	-0.356	—	1.62 - 2.91m
	R_5	H_5	H_4	H_3	H_2	H_{1e} & H_{1a}	$\tau_{1a} - \tau_{1e}$	R_5	$R_4 = R_3 = R_2 = OAc$
VII[a,i]	β-CH_2NHAc	6.13-6.91[f]	5.36q	4.44t	5.13o	6.13-6.91[f]	—	6.13-6.91[f](CH_2) 3.44t[j](NH) 8.06(NAc)	8.01(x2) (R_2 and R_4) 7.89(R_3)

[a] Measured at 100 Mc/s.

[b] Measured at 60 Mc/s.

[c] δ_{AB} derived by ABX analyses of the H_{5e} and H_{5a} multiplets. The positive signs given for the β-halides are not definitely proven.

[d] Measured from the mixture of (I) and (II).

[e] Signal multiplicities are symbolized by d(doublet), t(triplet), q(quartet), qi(quintet), sx(sextet), sp(septet), o(octet), and m(complex multiplet).

[f] Unresolved.

[g] Measured in pyridine-d_5 solution.

[h] 1,2,3,4,6-Penta-O-acetyl-β-D-allopyranose.

[i] 6-Acetamido-2,3,4-tri-O-acetyl-1,5-anhydro-6-deoxy-L-alditol. The shifts are arranged under those of the corresponding protons in the D-ribopyranosyl derivatives.

[j] Broad multiplet.

TABLE 2

1st Order Proton Coupling Constants (c/s) of 2,3,4-tri-O-benzoyl-D-ribopyranosyl Derivatives and related Compounds in $CDCl_3$

Compound	R_1	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5e}$ [c]	$J_{4,5a}$ [c]	$J_{5e,5a}$	$J_{1,3}$	$J_{3,5e}$	Predominant Chair Conformation
I[a]	α-OBz	3.7	3.4	3.2	4.6 (4.51)	9.3 (9.39)	10.9	—	—	C1
II[a]	β-OBz	3.5	3.6	3.6	3.9 (4.12)	2.5 (2.27)	12.95	—	—	1C
V[b]	β-CN	6.7	3.2	3.2	4.3 (3.58)	6.6 (7.34)	12.4	—	—	C1
		7.4[d]	3.2[d]	3.2[d]	4.05(2.25)[d]	7.15(8.95)[d]	12.3[d]	—	—	C1
IX[b,e]	β-OAc	8.6	2.9	2.9	—	—	—	—	—	C1
XII[a,f]	β-F	1.5	—	—	1.35(1.25)	1.9 (1.96)	13.5	—	—	1C
XIII[b]	β-Cl	1.7	3.9	3.9	1.7 (1.64)	1.9 (1.93)	14.0	—	—	1C
IV[b]	β-Br	1.2	3.9	3.9	1.4 (1.34)	1.5 (1.53)	13.8	—	—	1C
XIV[a]	β-I	≈1.0	4.0	4.0	1.5 (1.44)	1.6 (1.63)	13.4	—	—	1C
XV[a]	β-OMe	2.5	3.8	3.8	2.8 (2.93)	2.1 (1.96)	13.0	—	—	1C
XVI[b,g]	β-OCH_2Ph	2.4	3.8	3.8	2.95(3.10)	2.5 (2.35)	13.25	—	—	1C
XVII[a,h]	α-F	3.3	3.3	2.9	5.3 (5.20)	10.75(10.87)	10.9	—	0.7	C1
XVIII[a]	α-Cl	4.4	3.3	3.3	5.1 (5.05)	10.7 (10.75)	10.9	0.4	1.0	C1
III[b]	α-Br	4.4	≈3.0	3.1	5.6 (5.26)	10.65(10.96)	10.8	—	0.9	C1
	R_5	$J_{4,5}$	$J_{3,4}$	$J_{2,3}$	$J_{1e,2}$	$J_{1a,2}$	$J_{1e,1a}$			
VII[a,i]	β-CH_2NHAc	10.1	2.8	2.6	5.6	10.5	—			C1

[a] Measured at 100 Mc/s.

[b] Measured at 60 Mc/s.

[c] Coupling Constants listed in parentheses after the 1st Order values were obtained by ABX analyses of the signals due to H_{5e} and H_{5a}.

[d] Measured in pyridine-d_5 solution.

[e] 1,2,3,4,6-Penta-O-acetyl-β-D-allopyranose.

[f] J_{H_1,F_1} = 49.2 c/s.

[g] J_{AB} (benzylic protons) = 12.2 c/s at +55° and +42°, and 12.0 c/s at -10° and -50°.

[h] J_{H_1,F_1} = 53.7 c/s; J_{H_2,F_1} = 25.1 c/s.

[i] 6-Acetamido-2,3,4-tri-O-acetyl-1,5-anhydro-6-deoxy-L-allitol, $J_{6,NH}$ = 5.6 c/s, the other coupling constants are arranged so as to correspond with those in the columns above.

14th February, 1966

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

Dear Professor Shapiro,

We would like to comment on the letter from Dr. Binsch in the 87th newsletter. It seems unecessary to introduce more terminology into the description of magnetic systems. The three terms symmetrical equivalence, chemical shift equivalence, and magnetic equivalence are each precisely defined and do not give rise to ambiguities in the description of spectra (for a discussion of these terms see reference 1 below). Magnetic non-equivalence we believe has been precisely defined[1,2] but perhaps what is needed is more discussion of its implications in the analysis of spectra.

Yours sincerely,

J.W. Emsley (University of Durham, England)
Jim Emsley.

J. Feeney (Varian Associates)
J. Feeney

L.H. Sutcliffe (University of Liverpool)

References.

1. "High Resolution Nuclear Magnetic Resonance Spectroscopy" Vol. 1. J.W. Emsley, J. Feeney and L.H. Sutcliffe. Pergamon 1965.

2. P.L. Corio, Chem. Rev. 66, 363 (1960).

הטכניון - מכון טכנולוגי לישראל

TECHNION - ISRAEL INSTITUTE OF TECHNOLOGY

הפקולטה לכימיה
DEPARTMENT OF CHEMISTRY

27 February 1966

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

Dear Professor Shapiro,

Erratum and addition to IITNMR 87-12

1. The shift values for Li^+ are zero and not -130 and +131 ppm as indicated (this is almost "self evident" since ~130 ppm at 16 Mc is ~ 2090 cps which is the modulation frequency of our integrator!).

2. The following values for Na^+ can be added to the table (from left to right) -(3-4)ppm; 10 cps; 0 ppm; 34 cps. Shifts are referred to NaCl.

Yours sincerely,

A. Loewenstein

A. Loewenstein

P.O.B. 4910 HAIFA CABLE ADDRESS KIRYAT HATECHNION TEL 58361 קרית הטכניון ת.ד. 4910 חיפה

90-16

Institut für physikalische Chemie
der Rhein.-Westf. Techn. Hochschule
Aachen, Direktor Prof. Dr. U. Franck

51 Aachen, den 3.3.1966
Klosterbongard 12
Fernruf 422 2154

Mr.
Dr. Bernard L. S h a p i r o
Illinois Institute of Technology

C H I C A G O , 60616

U S A

Third Nuclear Magnetic Resonance Workshop.

Dear Dr. S h a p i r o !

The third Workshop on high Resolution Proton Magnetic Resonance will take place at Aachen, Germany, on Monday (10:00 A.M) through Friday (5:00 P.M.) April 25 - 29, 1966. The Workshop will consist of several series of lectures, discussions, problem solving sessions, and laboratory demonstrations.

The first day is primarily reserved for those scientists without any knowledge on the matter. The participants will be introduced in the laboratory to the A-60 spectrometer by a serie of demonstrations which will include the determination of an unknown spectrum.

For the advanced participants there will be a demonstration of the Varian DA-60 spectrometer and the C-1024 Computer of Average Transients. If there will be any free time during the discussion sessions, one can examine problems submitted by the participants.

In addition, we will explain the Bruker-Spin-Echo-Spectrometer. Abstracts of the lections and of the problems will be handed to registrants.

With best wishes

R. Kosfeld

(Dr. R. Kosfeld)

Programm zum 3. Kolloquium über Kernresonanzspektroskopie.

Montag: 25.4.1966	10 s.t. - 12 Uhr:	Dr. Joop, Leverkusen Grundlagen der hochauflösenden KMR-Spektroskopie I.
	14.00 - 16.30 Uhr:	Dr. Joop, Leverkusen Grundlagen der hochauflösenden KMR-Spektroskopie II.
Dienstag: 26.4.1966	10.00 - 11.30 Uhr:	Dr. Scheidegger, Zürich Analyse von Kernresonanzspektren.
	14.00 - 15.00 Uhr:	Dr. Fluck, Heidelberg ^{31}P-Kernresonanzspektroskopie. (Theorie und Praxis).
	15.30 - 16.30 Uhr:	Übungen zur Deutung von KMR-Spektren.
Mittwoch: 27.4.1966	9.00 - 10.30 Uhr:	S. Wald, Aachen Einführung in die Berechnung von KMR-Spektren.
	10.45 - 12.00 Uhr:	Dr. Kosfeld, Aachen Anwendungen der Spin-Echo-Methode in der Chemie.
	14.00 - 15.00 Uhr:	Dr. Feeney, London Some Application of F-19 Resonance.
	15.30 - 16.30 Uhr:	Übungen zur Deutung von KMR-Spektren.
Donnerstag: 28.4.1966	9.00 - 10.30 Uhr:	Dr. Feeney, London Dynamic Processes studied by NMR. (Eine Einführung).
	10.30 - 12.00 Uhr:	Dr. Melera, Zürich Spezielle Arbeitsmethoden.
	14.00 - 15.00 Uhr:	Dr. v. Philipsborn, Zürich Doppel- und Mehrfachresonanz zur Spektreninterpretation.
	15.30 - 16.30 Uhr:	Übungen zur Deutung von KMR-Spektren.
Freitag: 29.4.1966	9.00 - 10.30 Uhr:	Dr. Sackmann, Göttingen Die Deutung von Spin-Spin-Kopplungskonstanten. (Eine Anwendung der MO-Theorie von Pople).
	10.30 - 12.00 Uhr:	Dr. Pettig, Jena Neuere Arbeiten zur Klärung von Molekülstrukturen.
	14.00 - 15.00 Uhr:	Dr. Brune, Karlsruhe Anwendungsmöglichkeiten der Protonenresonanz auf Probleme der Stereochemie. (Eine Einführung).
	15.30 - 16.30 Uhr:	Übungen zur Deutung der KMR-Spektren.

JET PROPULSION LABORATORY California Institute of Technology • 4800 Oak Grove Drive, Pasadena, California 91103

2 March 1966

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

Dear Barry:

One of the important analytical chemistry problems around our place is the determination of the nature and amount of hydroxyl groups in a number of materials. In the last few years I have had the occasion to try to develop some reliable n.m.r. methods for these analyses. I would like to describe a n.m.r. scheme for classification of hydroxyl compounds which has evolved and which in our hands has generally proved to be more reliable and informative than other recently described n.m.r. techniques.[1]

---

(1) See for example: a) O. L. Chapman and R. W. King, J. Am. Chem. Soc. 86, 1256 (1964); b) A. Mathias, Anal. Chim. Acta, 31, 598 (1964); c) V. W. Goodlett, Anal. Chem., 37, 431 (1965).

Because a number of functional groups can be acetylated, we initially considered that the acetate group might be a useful n.m.r. probe for classification purposes. Unfortunately, the differences in chemical shift between acetate groups of isomeric alcohols are only a few cps and provide no dependable scheme for classification. In addition many times the resonances of acetyl groups overlap the resonances of other types of protons in acetylated samples thus making quantitative estimation by electronic integration more difficult and much less reliable. The fact that ^{19}F chemical shifts are in general about an order of magnitude larger than ^{1}H chemical shifts for a given structural perturbation suggested to us that ^{19}F n.m.r. chemical shifts of the trifluoroacetyl derivatives of alcohols and perhaps amino, mercapto and phenolic functional groups might provide reliable classification schemes.

JET PROPULSION LABORATORY *California Institute of Technology • 4800 Oak Grove Drive, Pasadena, California 91103*

Although significant chemical shift concentration and solvent effect have been observed, study of the ^{19}F n.m.r. spectra of the trifluoroacetate (TFA) esters of a large number of alcohols revealed that the TFA group gives sharp ^{19}F signals and that the order of shielding is always primary < secondary < tertiary (See Figure 1). Comparison of the data in Figure 1 for the chemical shifts in ppm for the TFA's of cis-4-t-butylcyclohexanol (A) (75.09) and trans-4-t-butylcyclohexanol (B) (74.99) with those of 2-methyl-2-butanol (C) (74.99) and t-butyl alcohol (D) (75.05) would seem to refute this statement. However, this is an example of the concentration effects. In one case (Figure 1d) the solution was 5% in ester and in the other case (Figure 1a) 20% in ester. In a 20% ester mixture of DMSO (7% CCl_3F) A, B, C and D show chemical shifts of 74.57, 74.69, 75.00 and 75.06 ppm, respectively.

For a single unknown alcohol or a mixture of alcohols our operational procedure consists of TFA preparation, dissolution in a solvent if necessary, addition of a small amount of ethyl trifluoroacetate as an internal reference and recording of the spectrum. Ethyl trifluoroacetate is a reliable internal standard because at 56.4 Mc all other primary TFA's are downfield (2 — 17 cps), all phenol TFA's downfield (30 cps or more), all secondary TFA's upfield (3 — 15 cps) and all tertiary TFA's upfield (30 — 36 cps).

In collaboration with Mr. D. David Lawson and Mr. John D. Ingham of our Polymer Research Section some interesting new information concerning the structure of poly(propylene oxides) (PPO) has been obtained using this trifluoroacetylation-^{19}F n.m.r. technique. In every mixture of polymer TFA esters containing both primary (originating either from PPO's partially terminated with one or more ethylene oxide units or added polyethylene glycol) and secondary TFA groups, as might be expected, the primary TFA resonance always fall 10 — 17 cps (56.4 Mc) to lower field than the secondary. In the di-TFA esters of PPO materials (not terminated with ethylene oxide units) which we have studied thus far, we find no significant amounts of primary TFA groups (less than 0.5%). To the best of our knowledge all these latter polymers were prepared by the action of propylene glycol alkoxide on propylene oxide. In addition we find that the secondary TFA ester signals of all the liquid PPO materials are doublets of unequal intensity (Figure 2a) with a splitting of 1.9 — 2.5 cps (solvent dependence). The upfield member of the TFA doublet is most intense; the difference in intensity is most for low molecular weight PPO and just noticeable at molecular weight 4000. The doublet structure could arise either by a positional isomerization involving the end group diads or from the combinations of asymmetric carbon atoms involving the end group diads.

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We have distinguished between these two possibilities two ways. First, we prepared polymers of racemic PO initiated with sodium n-propoxide and obtained materials whose TFA esters gave two ^{19}F n.m.r. signals of equal intensities (See Figure 1b). Secondly, we polymerized with a solid potassium hydroxide catalyst a sample of d-propylene oxide to a crystalline polymer which yielded a di-TFA ester exhibiting a single secondary ^{19}F n.m.r. signal (Figure 1c) superimposible on admixture with the high-field member of the doublet of a racemic PPO-2000 di-TFA ester (Figure 1d). This proves that the doublet structure arises from the asymmetric centers in the polymer end group diads. From the inequality of the concentration of the two types of secondary hydroxyls, a certain degree of stereoselectivity must exist in the diol-alkoxide catalyzed polymerization of racemic PO.

I don't claim that the trifluoroacetylation-^{19}F n.m.r. technique is in every case the simplest and best means of characterizing hydroxyl groups. There will certainly be instances where other techniques are adequate. However with this method one is looking at the signal from three ^{19}F nuclei vs one ^{1}H nucleus (as in the case of several other recently described n.m.r. techniques) which can be a multiplet.[2] Thus,

---

(2) As can be seen in the spectra shown above and more readily in spectra recorded at slightly slower sweep rates, there exist small splitting (0.15 — 0.25 cps) of the CF_3- groups with the proton(s) five bonds removed.

---

at worst, a signal to noise increase of around 2.5 should be realizable. Because one observes the ^{19}F spectrum, signals from the other protons in the molecules of interest are far removed and the restrictions on the choice of solvent are essentially removed.

With best regards,

Stan

Stanley L. Manatt
Physics Section

SLM:jm

P. S. Title: Trifluoroacetylation-^{19}F n.m.r. Technique for the Classification of Hydroxyl Groups.

Figure 1. ^{19}F n.m.r. spectra of the trifluoroacetates of some hydroxyl compounds; chemical shifts in ppm (± 0.01) from 10% internal $CFCl_3$ given in parentheses; chemical shifts of overlapping signals determined from more highly resolved spectra of ester mixtures with fewer components; increasing field to right: a) 1. CH_3OH (74.21), 2. CH_3CH_2OH (74.43), 3. $CH_3CH_2CH_2OH$ (74.40), 4. $CH_3CH_2CH_2CH_2OH$ (74.39), 5. $(CH_3)_2CHCH_2OH$ (74.38), 6. $(CH_3)_3CCH_2OH$ (74.37), 7. $CH_3CHOHCH_3$ (74.68), 8. $CH_3CHOHCH_2CH_3$ (74.62), 9. $CH_3CH_2CHOHCH_2CH_3$ (74.52), 10. $(CH_3)_3COH$ (75.05), 11. $(CH_3)_2(CH_3CH_2)COH$ (74.99), 12. CF_3CO_2H (75.08) (20% ester mixture in dimethyl sulfoxide); b) 1. $CH{\equiv}CCH_2OH$ (74.95), 2. $C_6H_5CH_2OH$ (75.02), 3. $CH_2{=}CHCH_2OH$ (75.08), 4. $(CH_3)_3CCH_2OH$ (75.17), 5. $CH_3CH_2CH_2OH$ (75.20), 6. Lanosterol (75.35), 7. Cholesterol (75.41), 8. Cyclopentanol (75.43), 9. Cyclohexanol (75.44), 10. Cycloheptanol (75.45), 11. $CH_3CHOHCH_3$ (75.52) (15% ester mixture in methylene chloride); c) 1. C_6H_5OH (73.85), 2. CH_2OHCH_2OH (74.27), 3. $CH_2OHCH_2CH_2OH$ (74.30), 4. $CH_3CHOHCH_2\underline{OH}$ (74.33), 5. CHF_2CH_2OH (74.34), 6. CF_3CH_2OH (74.37), 7. CH_3CH_2OH (74.43), 8. $CH_3CH\underline{OH}CH_2OH$ (74.55), 9. $CH_3CHOHCH_2CH_3$ (74.62), 10. $CH_3CHOHCH_3$ (74.68) (20% ester mixture in dimethyl sulfoxide); d) From two different mixtures of 4-t-butylcyclohexanols; 1. <u>trans</u>-isomer (74.99), <u>cis</u>-isomer (75.09) (5% in dimethyl sulfoxide), 2. <u>cis</u>-isomer (76.28), <u>trans</u>-isomer (76.32) (5% in pentane).

Figure 2. ^{19}F n.m.r. spectra at 56.4 Mc of poly(propylene oxide) secondary trifluoroacetates; 20% by volume in 1,1,2,2-tetrafluoro-1,2-dibromoethane with 5% fluorotrichlormethane as an internal standard; sweep rate 0.4 cps/s and increasing field to right: a) Commercial racemic liquid polymer, P-2000; chemical shifts of doublet peaks 75.886 and 75.927 ppm upfield from internal $CFCl_3$; b) Polymer (mol. wt. 900) prepared by action of sodium <u>n</u>-propoxide on racemic propylene oxide; c) Crystalline polymer (mol. wt. 1690) prepared by action of solid sodium hydroxide on <u>d</u>-propylene oxide; d) Admixture of a) and c).

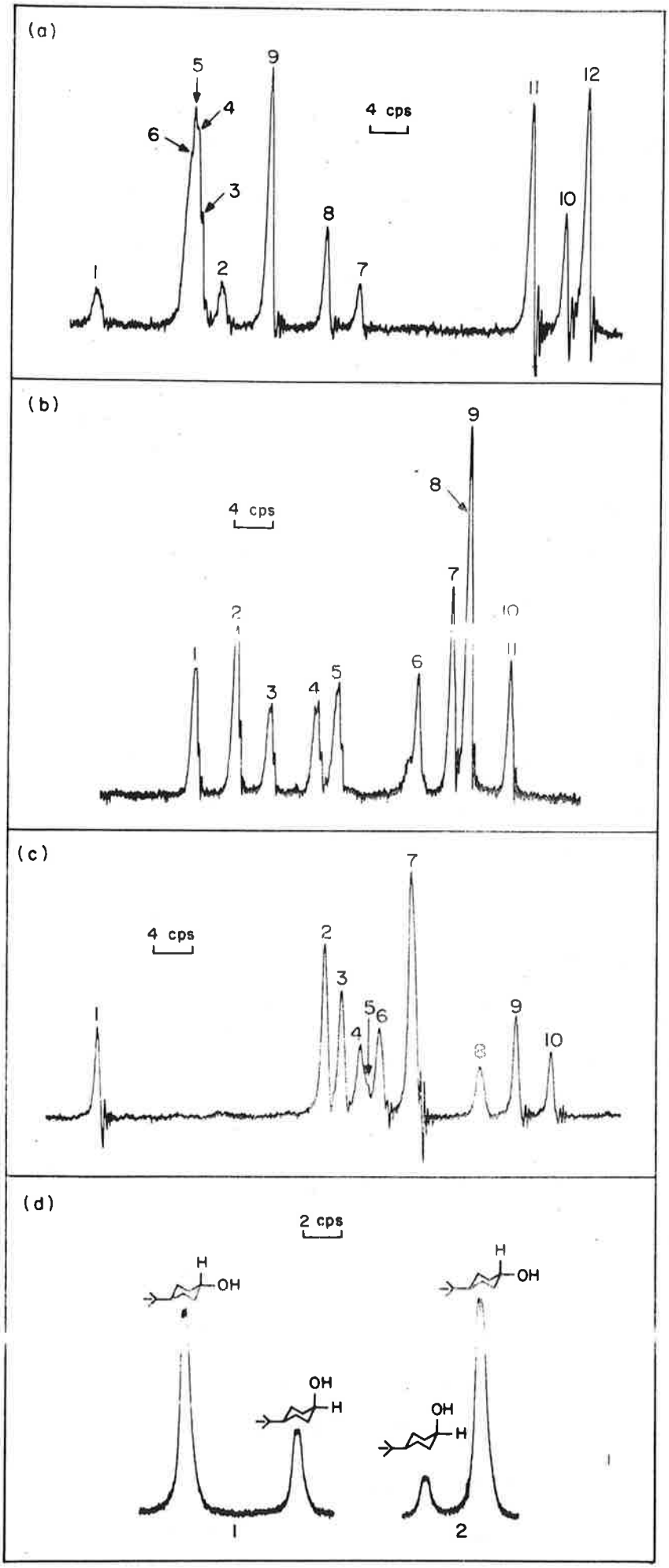


Figure 1

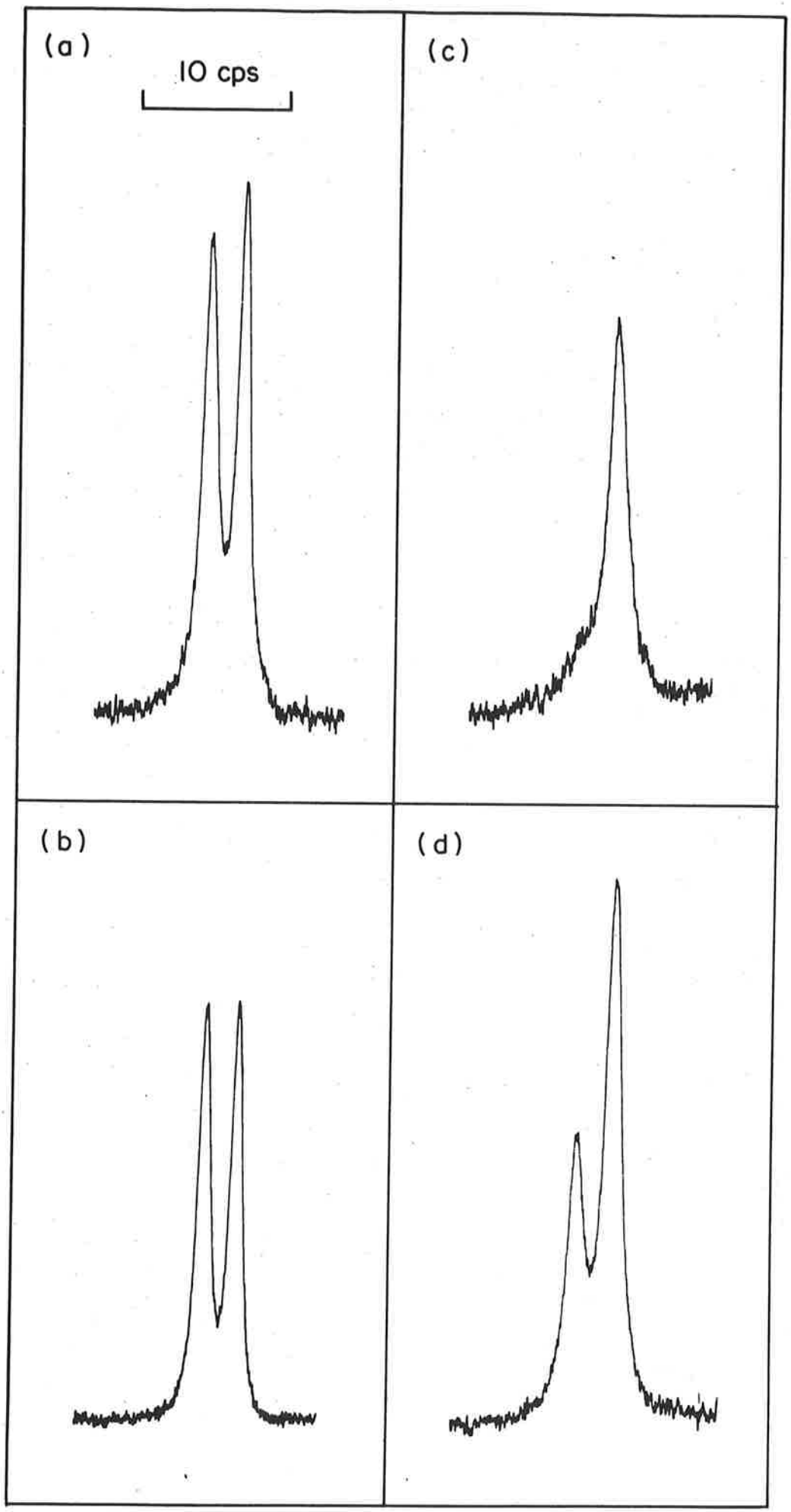


Figure 2

90-24

varian/611 hansen way/palo alto/california 94303/u.s.a./415/326-4000

7 March 1966

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

Dear Barry:

Cheap Rotary Spin Echoes

Since Ionel Solomon's original paper [Phys. Rev. Letters 2, 301 (1959)], little new work on rotary spin echoes seems to have found its way into the literature. Perhaps your readers would be interested in an adaptation of this ingenious experiment to the special case of high resolution work, particularly since the added instrumentation required is quite trivial. The idea was mentioned briefly in a talk on 'Selectivity in Pulsed NMR' at the 7th Experimental Conference on NMR in Pittsburgh last week.

We must first consider the transient nutation experiment of Torrey [Phys. Rev. 76, 1059 (1949)]. When a strong rf field H_1 is suddenly switched on and held at exact resonance, one observes a large oscillatory signal due to nutation of the magnetization vector at a frequency γH_1 radians/sec about the direction of H_1 in the rotating frame of reference. Owing to simultaneous spin-spin and spin-lattice relaxation, this transient signal would normally decay exponentially with a time constant T given by

$$\frac{1}{T} = \frac{1}{2}\left[\frac{1}{T_1} + \frac{1}{T_2}\right]$$

Provided that H_1 is strong compared with the inhomogeneities in H_o over the effective volume of the sample, the latter do not cause any appreciable fanning out of the individual magnetization vectors in the XY plane, and for this reason the effects of spin diffusion through magnetic field gradients may be neglected.

However in many cases a more rapid signal decay is observed, attributable to the dephasing effect of the spatial inhomogeneities in the radiofrequency field H_1, individual vectors fanning out in the vertical plane YZ, normal to the direction of H_1 (see figure). Most rf fields are sufficiently homogeneous to allow many cycles of oscillation to occur before the signal dies away. True coherence is not of course lost, and may be recovered by suddenly reversing the direction of the rf field H_1 in the rotating frame an arbitrary time τ after the initial application of H_1. Isochromatic magnetization vectors that have remained in the same region of the transmitter rf field will refocus at $t = 2\tau$ along the Z direction, and in passing through the XY plane will induce a new maximum amplitude of the oscillatory signal, a 'rotary echo'. Subsequent 180° phase reversals of H_1 at arbitrary intervals after the previous echo will generate a train of rotary echoes, and the envelope of the echo amplitudes yields the true decay time constant T.

In a good crossed-coil probe there is only a small spatial inhomogeneity in the rf field of the transmitter coils measured over the effective volume of the receiver coil, consequently spin diffusion effects are usually negligible, particularly when H_1 is weak or when several 180° phase reversals are made during the measurement.

varian

Professor B. L. Shapiro - Page 2
7 March 1966

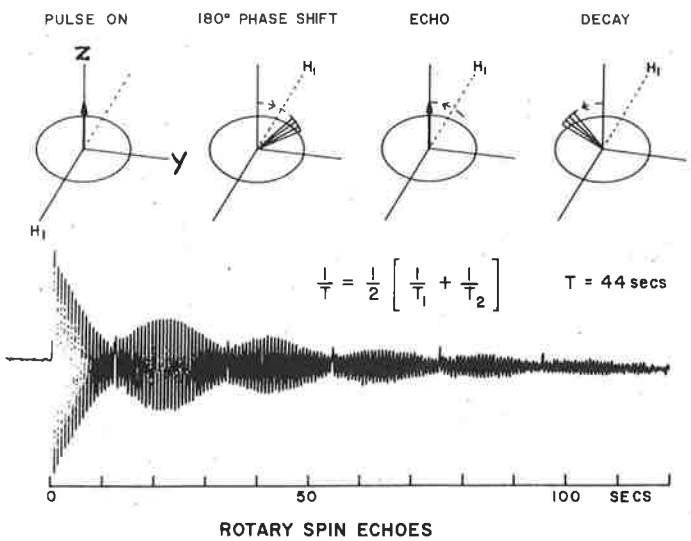
We have adapted this technique for high resolution samples with long T_1 and T_2, employing an rf field only just strong enough to overcome the effects of magnet field inhomogeneity, but still weak enough to single out a chosen line of the spectrum without appreciably perturbing the others. This is accomplished simply by the sudden application of magnetic field modulation at a frequency corresponding to exact sideband resonance for the chosen line (maintained by an internally locked field-frequency control). Pulsing on and phase reversal are achieved by manual operation of toggle switches--the only new equipment required.

Refocusing of isochromats by inversion of H_1 is shown schematically in the figure. The spectrometer detects the projection on the Y axis of the circular motion of the resultant of all magnetization vectors (the phase detector being adjusted for absorption mode) and many cycles of the oscillation occur between the phase reversals of H_1. We may measure the strength of H_1 from the nutation frequency ($\gamma H_1 \lambda$, where λ is the transition matrix element of the line in question), and in practice $\gamma H_1/2\pi$ was 1.3 Hz. The spatial inhomogeneity of H_1, measured by the decay time constant without phase reversals, was found to be less than 3% of H_1. This was for a Varian HR-60 spectrometer. The illustration shows the rotary spin echoes observed on the stronger line of the high-field doublet of the AB spectrum of 2,3 dibromothiophene; the decay of the echo envelope with T = 44 secs is in good agreement with T_1 and T_2 measured by selective pulse experiments on this same line.

Best regards,

Ray

Ray Freeman
Analytical Instrument Research



ROTARY SPIN ECHOES

90-26

PHYSIKALISCHES INSTITUT
DER UNIVERSITÄT BASEL
4056 BASEL, SCHWEIZ - KLINGELBERGSTR. 82
VORSTEHER: PROF. DR. P. HUBER

Prof. Dr. P. Diehl

Basel, March 7, 1966

Prof. B.L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago Ill. 60616
U.S.A.

Deceiving simplicity of spectrum (IITNMR 88, 12) is due to degeneration of subspectrum

Dear Barry,

A contribution of Mr. R.K. Kullnig in IITNMR Newsletter 88, page 12 provides an example of a deceiving simplicity in an NMR-spectrum which I discussed theoretically a few years ago (Helvetia Chimica Acta 47, 1, 1963). The explanation of this simplicity is straight-forward if we use subspectral arguments. In the paper mentioned above, deceiving simplicity is correlated with the degeneration of one or several subspectra into single resonances. In an ABX-case we have the following two effective chemical shiftdifferences of the ab-subspectra:

$$\delta_{ab} = \delta_{AB} \pm \tfrac{1}{2} (J_{BX} - J_{AX})$$

for $|\delta_{AB}| = |\tfrac{1}{2} (J_{BX} - J_{AX})|$ obviously one ab-spectrum must degenerate (Fig 1 b). This condition is exactly fulfilled in Mr. Kullnig's case.

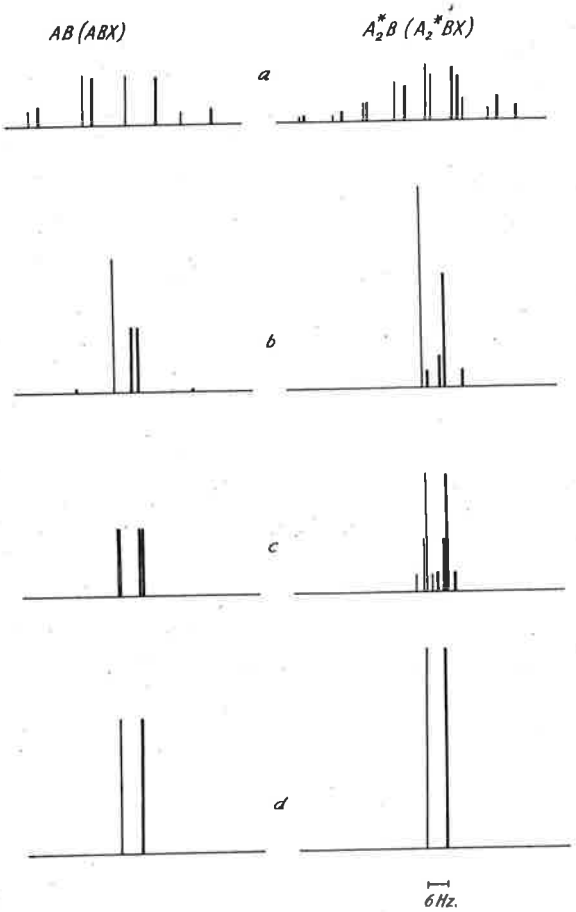
If all the subspectra degerate at the same time, we will observe the type of deceiving simplicity (Fig. 1 d) discussed by Abraham and Bernstein (Canad. J. Chem. 39, 216, 1961).

With best regards

Peter

Peter Diehl

Fig. 1



AB- und A_2^*B-Teile von ABX- und A_2^*BX-Spektren für:

a: $\delta_{AB} = 28$ Hz, $J_{AB} = 16$ Hz, $J_{AX} = 10$ Hz, $J_{BX} = 2$ Hz; $\delta_{AB} > 1/2(J_{AX} - J_{BX})$
b: $\delta_{AB} = 4$ Hz, $J_{AB} = 16$ Hz, $J_{AX} = 10$ Hz, $J_{BX} = 2$ Hz; $\delta_{AB} = 1/2(J_{AX} - J_{BX})$
c: $\delta_{AB} = 0$ Hz, $J_{AB} = 16$ Hz, $J_{AX} = 10$ Hz, $J_{BX} = 2$ Hz
d: $\delta_{AB} = 0$ Hz, $J_{AB} = 16$ Hz, $1/2(J_{AX} - J_{BX}) \ll J_{AB}$

90-28

ISOTOPE DEPARTMENT מחלקת איזוטופים

REHOVOTH · ISRAEL רחובות · ישראל

March 4, 1966

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

Dear Barry,

This year I am at the Weizmann Institute until July. Please be kind enough, however to credit this contribution to home base at the Division of Applied Chemistry, N.R.C. Ottawa.

Dr. Davidson of N.R.C., Dr. Fiat of the Weizmann Institute and I are investigating the temperature variation of line widths for both guest and host molecules in a variety of gas hydrates. Both high resolution and wide line techniques have been used. In the region where both methods could be used good agreement was found between them.

Two categories of gas hydrates are those in which the guest contains protons, and those in which the sole contribution to the observed line width comes from the host. Two examples of gas hydrates with non-proton containing guest molecules are shown in Figure 1. The activation energy for the process causing motional narrowing of the line width for SO_2 hydrate is 6.1 k.cal./mole.

A somewhat atypical example of the category where both guest and host contain proton is shown in Figure 2. By using deuterated water it is found that the guest line width is independent of temperature in the region studied. The rather odd temperature dependence of line width for ethylene oxide hydrate can be explained because the observed resonance line is a composite arising from both guest and host molecules. The observed line width will be determined primarily by the line width of the narrowest component. At high temperature this is due to host molecules, and at low temperatures, guest molecules. Support for this hypothesis comes from an analysis of the line shapes, which are Gaussian at the two temperature extremes, but deviate significantly in the region of maximum apparent line width.

There is a lot more data on structural effects of changing guest molecules and crystal lattices which we hope to publish in due course. However I hope this is enough to interest the readers and continue my subscription.

Yours truly,

S. Brownstein

SB/sa

CABLE ADDRESS: WEIZINST מען למברקים: · PHONE: 951721-7 טלפון:

FIGURE 1.

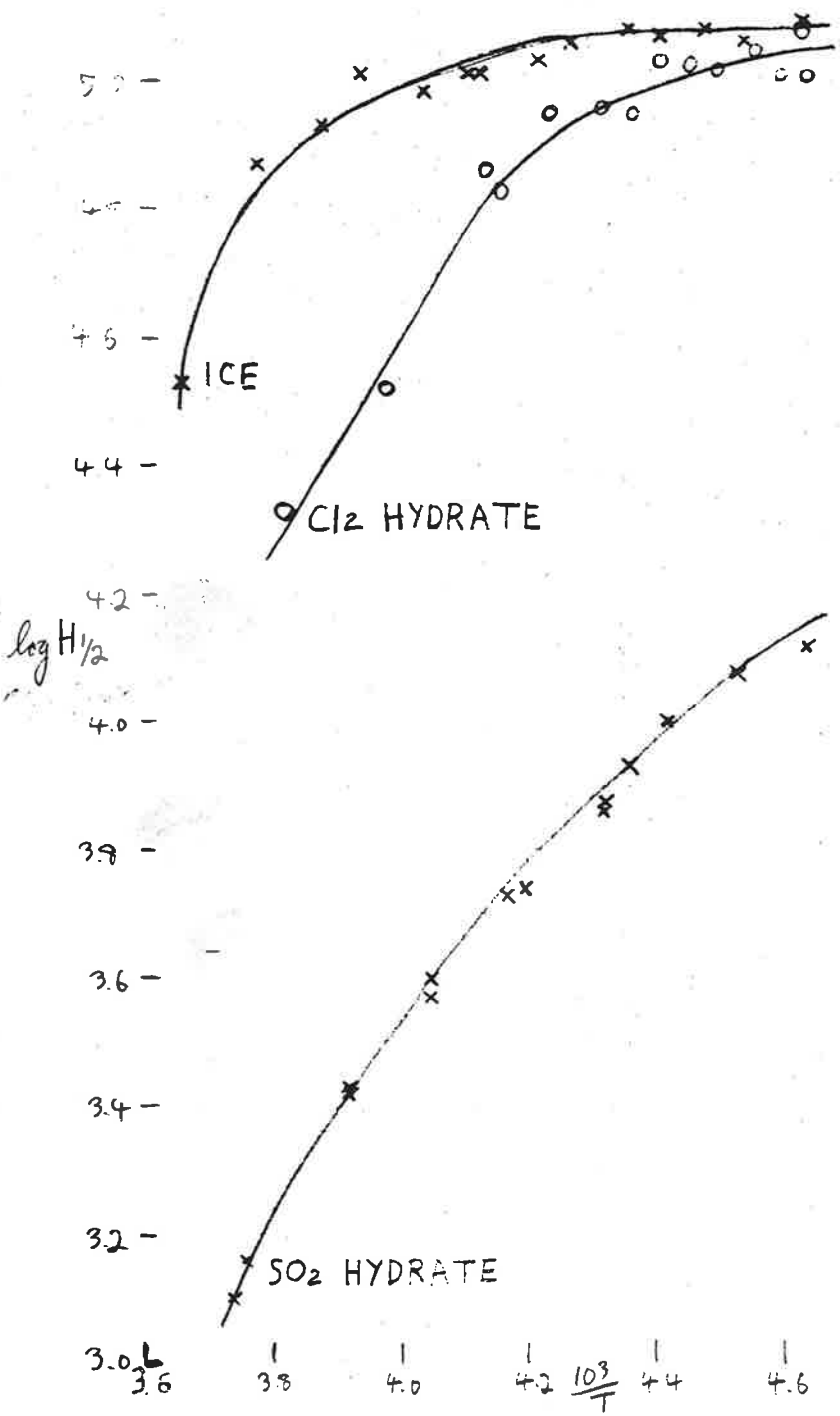
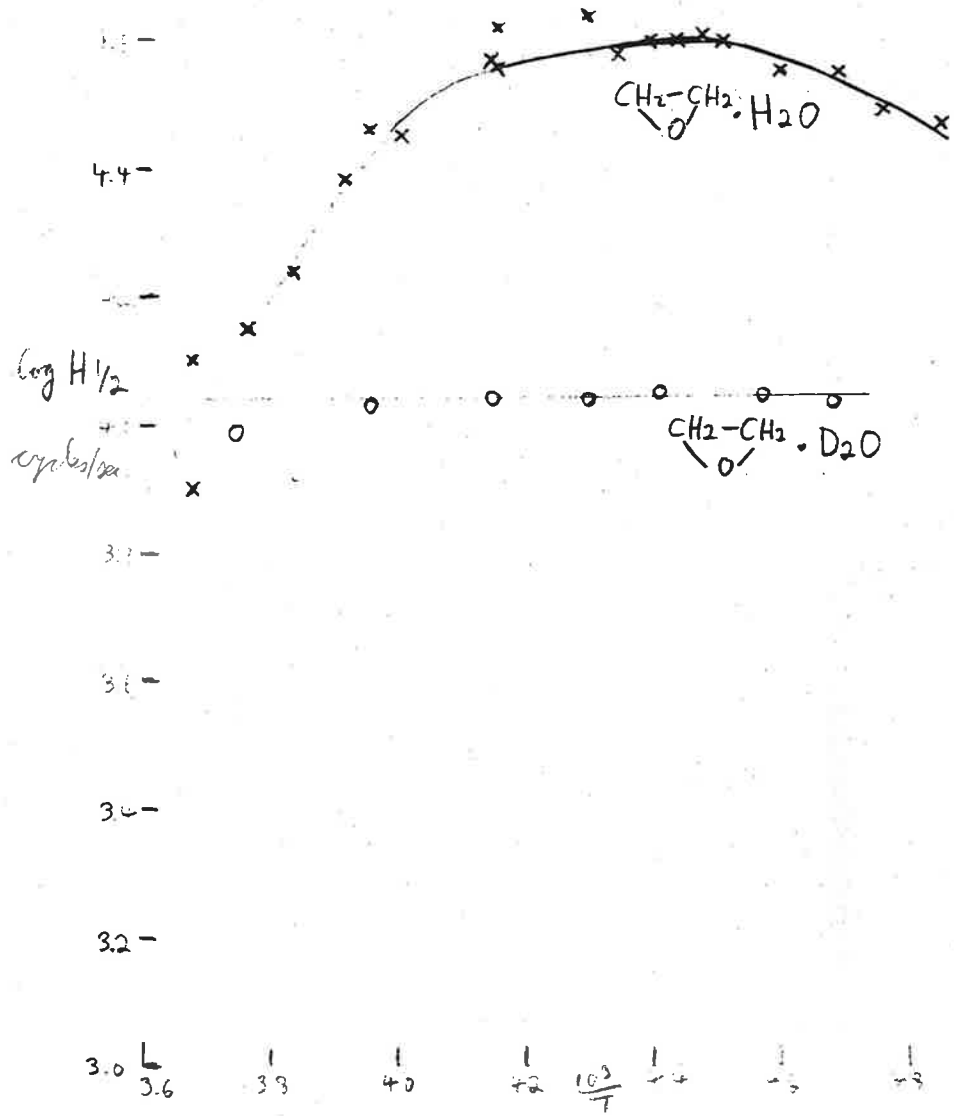


FIGURE 2



90-29

90-30

School of Chemical Sciences,
University of East Anglia,
Norwich, England.

Dear Dr. Shapiro,

Some N.M.R. work in Progress at East Anglia

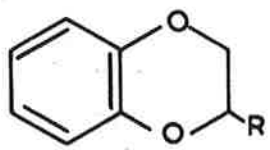
For this contribution we felt that it might be appropriate to summarise some of the N.M.R. topics that our own group is at present concerned with.

1. We are attempting to rationalise ortho effects by substituents on chemical shifts in polycyclic aromatic systems. It appears that the chemical shift difference is related to the ortho coupling constant J_{ab} in the corresponding unsubstituted compound by an equation of type:

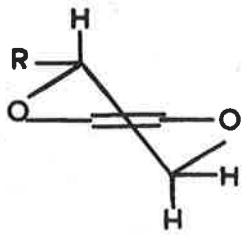
$$\Delta\tau = n_x J_{ab} + t_x$$

where n_x and t_x are constants for each substituent X (solvent being constant). (Mr. B. Ternai, Mr. G. J. T. Tiddy and Dr. P. R. Constantine).

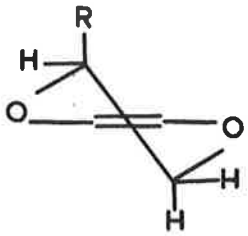
2. We are studying a series of 2-substituted benzodioxans (I) to try and determine the amounts of equatorial (II) and axial conformer (III) present. (Mr. M. J. Sewell).



I



II



III

3. We are examining a number of dihydronaphthalenes. The N.M.R. spectrum of the parent compound (Fig. 1) discloses an A_2B_2XY spectrum for the protons of the partly reduced ring (Fig. 2A) which is simplified to an A_2B_2 pattern of decoupling the olefinic proton (Fig. 2B). (Mr. B. Semple).

Yours sincerely,

P. R. Constantine

A. R. Katritzky

B. Semple

M. J. Sewell

B. Ternai

G. J. T. Tiddy

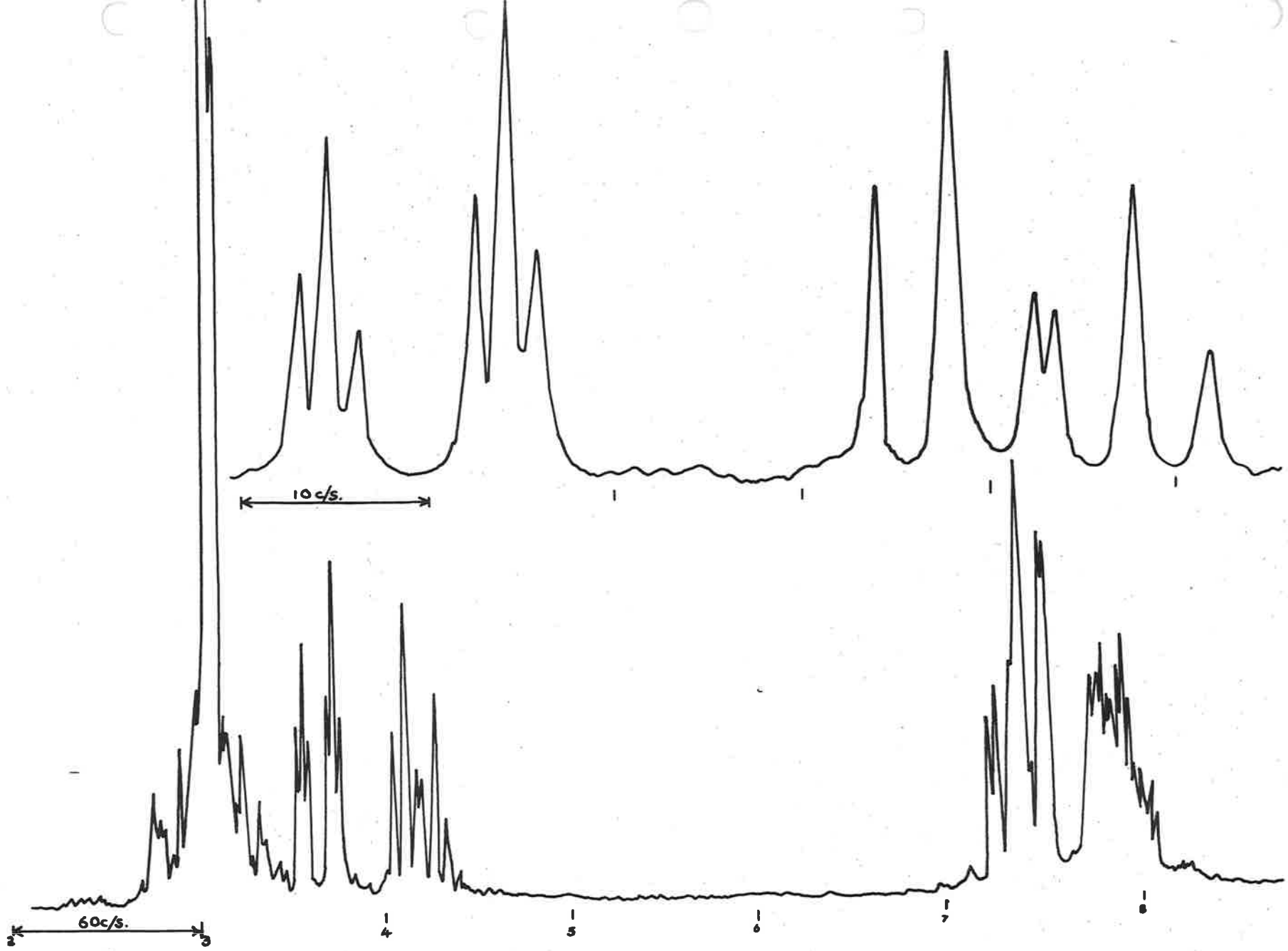


Fig. 1. N.M.R. spectra at 60 Mc/s of 1,2-dihydronaphthalene (τ scale), with (inset) expanded spectrum of the olefinic protons.

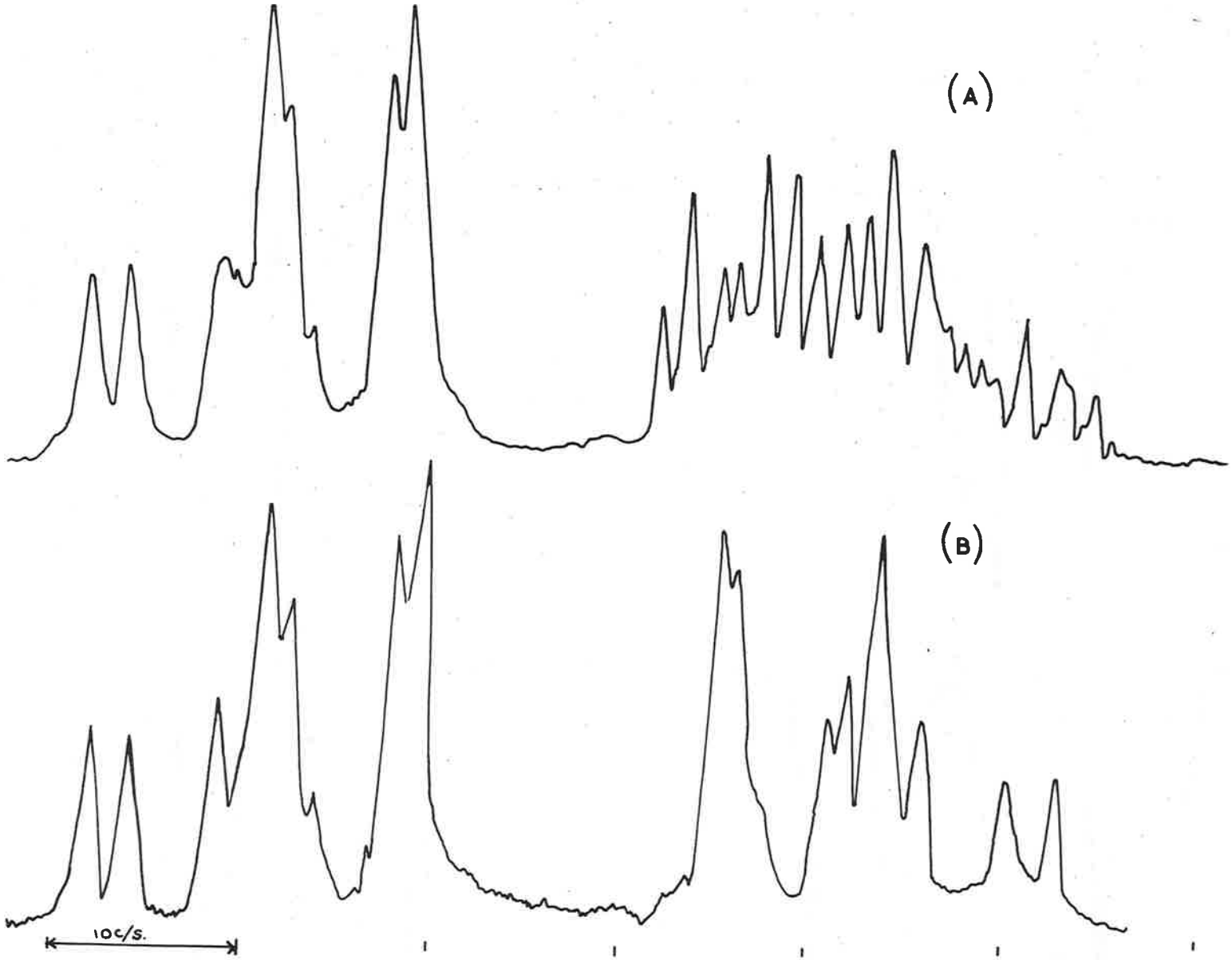


Fig. 2. Expanded N.M.R. spectra of CH_2 - CH_2 protons in 60 Mc/s N.M.R. spectra of 1,2-dihydronaphthalene (A) without decoupling and (B) with decoupling of the olefinic protons.

Abstracts of the 7th ENC

(7th Experimental NMR Conference - held at Mellon Institute, Pittsburgh, Pennsylvania, February 24-26, 1966)

Abstracts of papers presented at the 7th ENC, together with a copy of the program and the list of attendees, are available at a cost of $3.50 per set (post-paid to anywhere in the world). Orders must be accompanied by a check or money order (no purchase orders, requests for invoices, etc., please), made payable to "Experimental NMR Conferences", and should be sent to:

B. L. Shapiro
Secretary-Treasurer, ENC
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

3-17-66

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CONTINENTAL OIL COMPANY
RESEARCH AND DEVELOPMENT DEPARTMENT
PONCA CITY, OKLAHOMA

March 10, 1966

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

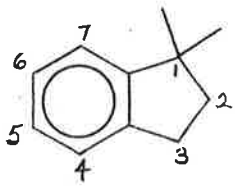
Dear Barry:

1.) ^{27}ALUMINOMALY

Recently we used an aqueous solution of $Al_2(SO_4)_3$ for aligning our HR-60 to study ^{27}Al resonances at 15.1 MHz. To our surprise, we observed two lines in the intensity ratio 6:1. The spacing was ~ 50 Hz. and the $\Delta\nu_{1/2}$'s 14 Hz. and 19 Hz. Adding H_2SO_4 intensified and broadened the less intense line at the expense of the more intense one. After consultation with L. O. Morgan, it appears the surprising thing is that we saw only two lines, considering the various possible aquo and sulfato complexes of Al^{+3}. This might be a way for someone else to study these complexes of Al^{+3}; we have no further interest.

2.) PMR OF METHYLINDANS

We have been studying the PMR of a series of methylindans prepared by Pete Eisenbraun's API group at Oklahoma State. The most interesting observation to date is the effect of aromatic methyl groups on the position of the gem-dimethyl resonance in 1,1-dimethylindans.



Aromatic methyl groups on the 4-,5-, or 6-positions cause an upfield shift of the 1,1-dimethyl resonance (0.01 ppm for the 4- and 6-positions; 0.04 ppm for the 5-position). A methyl group in the 7-position, however, causes the 1,1-dimethyl resonance to shift downfield 0.11 ppm. Thus the ortho-para shift (1) for these compounds is 0.15 ppm. This compares quite closely to the 0.13 ppm shift obtained by Dewhirst and Reilly[1] for the gem-dimethyl signals from 2-tolyl-2-methylbutanes. Since there can be no change in conformational preference in the indan series, we prefer to explain the observed shift on the basis of steric compression or van der Waals forces[2].

Sincerely,

Pat Flanagan

Pat W. Flanagan

PWF:SS

(1) K. C. Dewhirst and C. A. Reilly, J. Org. Chem. 30, 2870 (1965).

(2) W. A. Gibbons and V. M. S. Gil, Mol. Phys. 9, 163 (1965).

CARNEGIE INSTITUTE OF TECHNOLOGY
SCHENLEY PARK
PITTSBURGH, PENNSYLVANIA 15213

March 16, 1966

DEPARTMENT OF CHEMISTRY

TELEPHONE: 621-2600
AREA CODE 412

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

Dear Barry:

Given below is the abstract of D. G. Davis' Ph.D. thesis, summarizing the results of work we've been doing on the C^{13}-N.M.R. of some paramagnetic transition metal cyanide complexes.

The isotropic NMR shifts have been measured for C^{13} nuclei (in 1.1% natural abundance) in solutions, powdered solids, and single crystals of various paramagnetic iron group cyanides. The isotropic shifts (in ppm from the C^{13} resonance in benzene) are: 3.4×10^3, $Fe(CN)_6^{-3}$; 3.6×10^3, $Mn(CN)_6^{-4}$; 8.3×10^3, $Mn(CN)_6^{-3}$. Measurements on single crystals of $K_3Fe(CN)_6$ show twice the number of predicted NMR lines. This is taken as evidence for polytypism in this salt. From the single crystal data, the components of the hyperfine tensor for the axial and equatorial carbon atoms were found. For the axial pair: $A_z = -2A_x = -2A_y = 6.2$ Mcps; for the 2 equatorial pairs: $A_x = 7.5$ Mcps, $A_y = -3.4$ Mcps, $A_z = -4.2$ Mcps. From these anisotropic hyperfine constants and the isotropic contact term, the fraction of unpaired spin in the carbon atomic 2s and 2p is estimated. These are $f_{2p} \sim 0.045$; $f_{2s} \sim 0.005$. From NMR line width measurements, the electron correlation time is found to be approximately 10^{-12} sec.

The results above were obtained on a Varian DP-60 operating at 15.085 Mc/sec. We should also note that we could not observe a C^{13}-resonance for $K_3 Cr(CN)_6$ in either aqueous solution, polycrystalline or single crystal

continued--

samples, even though an extended search, under varying conditions, was made. Lowenstein et. al. (1) have also reported not being able to observe the C^{13} resonance in $Cr(CN)_6^{\equiv}$ in aqueous solution. Shulman (2) has suggested that the C^{13} line in $Cr(CN)_6^{\equiv}$ may be broader than in the other cyanides, in that the electron spin correlation time in $Cr(CN)_6^{\equiv}$ is longer. (Presumably, because of the symmetry of the A_{1g} ground state.)

We plan to carry out (1) single crystal studies on the $K_3Mn(CN)_6$ salt, although we have not yet been able to grow large enough crystals for this purpose; (2) variable temperature studies on the $K_3Fe(CN)_6$ single crystal; and (3) a further search, using signal averaging, for the $K_3Cr(CN)_6$ C^{13} resonance.

Sincerely yours,

Bob

Robert J. Kurland
Carnegie Institute of Technology

Donald G. Davis

Donald G. Davis
Mellon Institute

(1) M. Shporer, G. Ron, A. Loewenstein, G. Navon, Inorg. Chem. 4, 358 (1965)

(2) R. G. Shulman, Private Communication

RJK:kos

UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON 98105

Department of Chemistry

March 11, 1966

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

Dear Barry:

We have done a little work lately on some substituted azulenes from which one can draw a conclusion or two. The compounds were all tri-methyl substituted in the 4, 6 and 8 positions while varying the substituents at the 1 and 3 positions.

First, it appears that substitution on the five-membered ring does not appreciably effect the chemical shift of the substituents on the seven membered ring. On mono substituted compounds there is also no change in the coupling constant between H_2 and H_3 protons.

Although we have found coupling between H_2 and H_4, H_5 and H_6 in 1,3-dichloroazulene (the results of which we hope to report soon), no coupling is apparent in these tri-methyl substituted azulenes between H_2 and H_5 or H_7.

The compounds used were:

1) 1,3-dichloro-4, 6, 8-trimethyl azulene
2) 1,3-dibromo-4, 6, 8-trimethyl azulene
3) 4, 6, 8-trimethyl azulene
4) 1-Chloro-4, 6, 8-trimethyl azulene
5) 1, 4, 6, 8-Tetramethyl azulene
6) 1-Trifluoroacetyl-4, 6, 8-trimethyl azulene.

Compound No.

Position	1	2	3	4	5	6
1	- -	- -	2.82	- -	7.35	- -
2	2.81	2.52	2.48	2.76	2.65	2.01
3	- -	- -	2.82	3.08	2.88	3.08
4	7.13	6.99	7.45	7.31	7.20	7.28
5	3.5[illegible]	3.36	3.17	3.43	3.33	2.81
6	7.7[illegible]	7.63	7.58	7.62	7.62	7.52
7	3.5[illegible]	3.36	3.17	3.43	3.33	2.81
8	7.13	6.99	7.45	6.99	7.26	7.35

$J_{H_2,H_3} = 4.0$ cps.

Values are in ppm. with CCl_4 as solvent and TMS as reference. Concentrations were approximately 10%.

Sincerely,

Bernard J. Nist
Gary Hollander

PRINCETON UNIVERSITY
DEPARTMENT OF CHEMISTRY
PRINCETON, NEW JERSEY 08540

Frick Chemical Laboratory

March 15, 1966

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

Dear Professor Shapiro:

Re: The Determination of Optical Purity by n.m.r. Spectroscopy.

In a recent communication we pointed out the utility of n.m.r. spectroscopy for the determination of optical purity.[1] The method consists

---

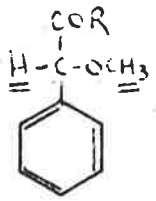
1. M. Raban and K. Mislow, Tetrahedron Letters No. 48, 4249 (1965).

---

of reacting the unknown mixture of enantiomers A and $\bar{A}$ with an optically pure chiral reagent B to produce a mixture of diastereomers AB and $\bar{A}$B. Since the ratio $\bar{A}$B/AB is equal to the ratio $\bar{A}$/A, the optical purity of A can be determined by integration of the n.m.r. signals of the diastereomers.

We have continued our investigations by searching for suitable B reagents and have had considerable success with p-toluenesulfinates and with esters and amides of O-methyl mandelic acid.

In Table I are collected the chemical shift differences for the O-methyl and methine hydrogens in some diastereomeric esters and amides of O-methyl mandelic acid.



R

Table I[a]

R	Δν (in op.s.) O-CH3 Benzene	O-CH3 Chloroform	-C-H Benzene	-C-H Chloroform
-O-CH(CH_3)CH_2CH_3	-	-	1.8	-
-NH-CH(CH_3)CH_2CH_3	0.8	0.7	0.6	-
-NH-CH(CH_3)C_6H_5	3.5	2.3	4.2	2.5
-O-Menthyl	0.5	0.4	4.2	2.5

[a]8% solutions, Varian A-60A, ambient temperature.

The spectrum of the mixture of diastereomeric p-toluenesulfinates of 2-propanol-1-d_3 (see Figure) illustrates the utility of n.m.r. for determining the ratio of diastereomers of compounds such as 2-propanol-1-d_3 which owe their chirality to dissymmetric deuterium substitution. The marked difference in the isopropyl methyl resonances in the two diastereomers (11 c.p.s.) is to be contrasted to the similarity in the other physical properties of the diastereomers, in particular gas chromatographic retention times. For these reasons the n.m.r. method will in our opinion be the method of choice for determining the optical purity of such compounds.

Sincerely yours,

Morton Raban

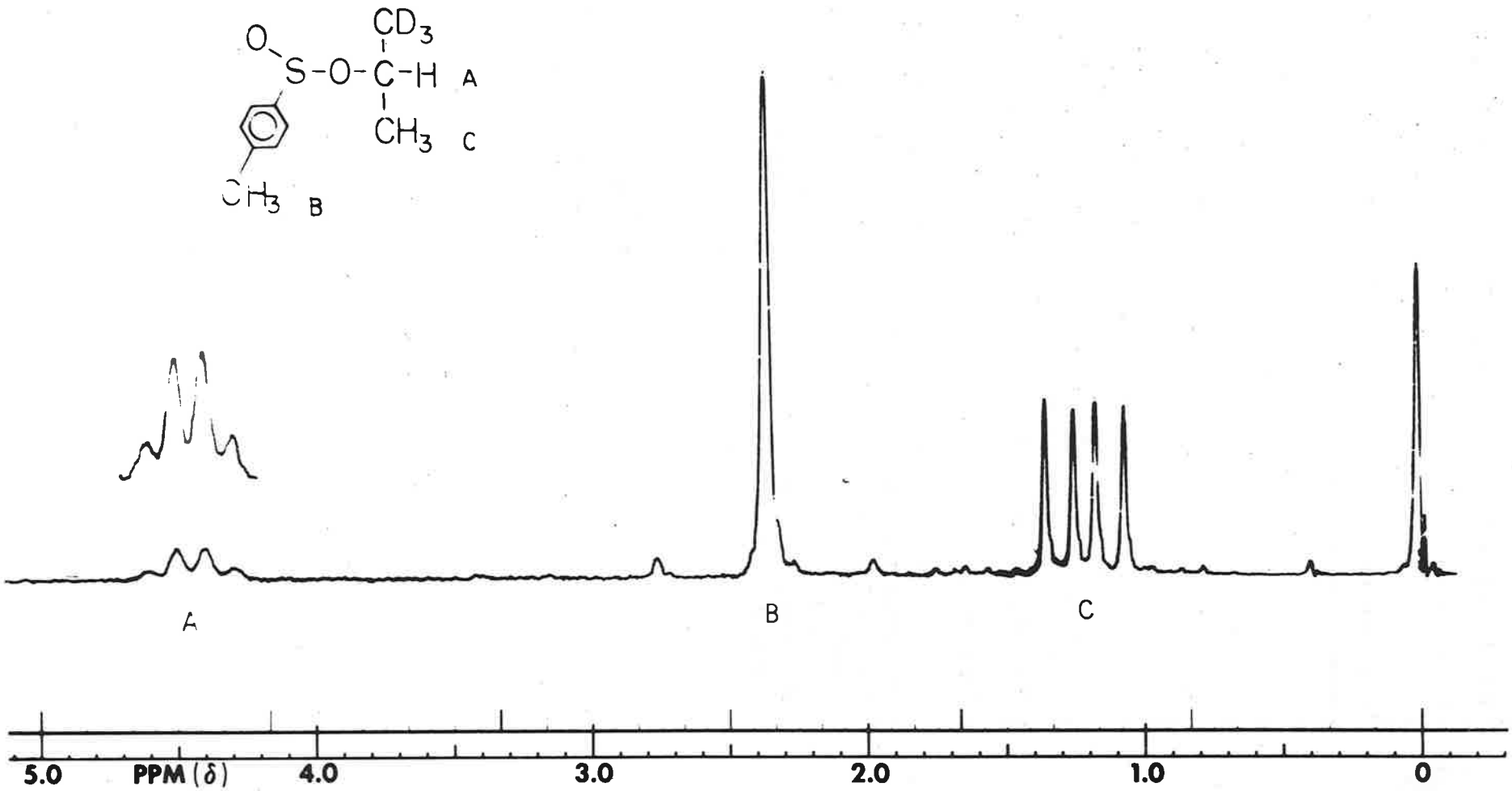
Morton Raban

Kurt Mislow

Kurt Mislow

Enc.

ec



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THE UNIVERSITY OF ARIZONA
TUCSON, ARIZONA 85721

COLLEGE OF LIBERAL ARTS
DEPARTMENT OF CHEMISTRY

March 12, 1966

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

Dear Barry:

There have been a number of discussions of the deuterium isotopic shift in proton magnetic resonance spectra, but there does not appear to have been any comment on the substituent dependence of these parameters. In the accompanying table are some representative values for substituted methanes. Within the halogen substituted compounds the magnitude of the shift is seen to be in the order F > Cl > Br > I.

Sincerely,

Mike Barfield

Mike Barfield
Assistant Professor

MB:ph

Geminal Proton-Deuterium Isotopic Shifts

Compound	$\delta(CH_2XY - CHDXY)$	Reference
1. CH_4	0.019 ± 0.001 ppm	A
2. CH_3CN	0.012 ± 0.001	B
3. CH_2FCN	0.016 ± 0.001	C
4. CH_2ClCN	0.011 ± 0.001	B
5. CH_2BrCN	0.010 ± 0.001	D
6. CH_2ICN	0.009 ± 0.001	B
7. $CH_2(CN)_2$	0.008 ± 0.003	C
8. CH_3CO_2H	0.012 ± 0.001	B
9. CH_2FCO_2H	0.019 ± 0.002	C
10. CH_2ClCO_2H	0.015 ± 0.001	D
11. CH_2BrCO_2H	0.012 ± 0.001	D
12. CH_2ICO_2H	0.008 ± 0.001	D

(A) R. A. Bernheim and B. J. Lavery, J. Chem. Phys. 42, 1464 (1965).

(B) M. Barfield, Ph.D. thesis, University of Utah, 1962.

(C) R. A. Powell and M. Barfield, unpublished results, 1965.

(D) R. A. Niedrich, M.S. Thesis, University of Utah, 1965.

UNIVERSITÉ DE LYON FACULTÉ DES SCIENCES

PHYSIQUE PROPEDEUTIQUE

V Réf. :

N Réf. : J. DELMAU - J. DUPLAN

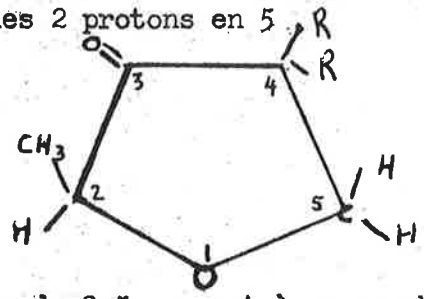
Villeurbanne, le 10 mars 1966

Couplages à distance .

Professor B.L. SHAPIRO
Department of Chemistry
Illinois Institute of Technology
Technology Center
CHICAGO , Illinois 60 616

Cher Professeur Shapiro ,

Le spectre d'un Méthyl-2 tétrahydrofurannone-3 disubstitué en 4 (1) fait apparaître un couplage à distance entre le proton en position 2 et l'un des 2 protons en 5 .

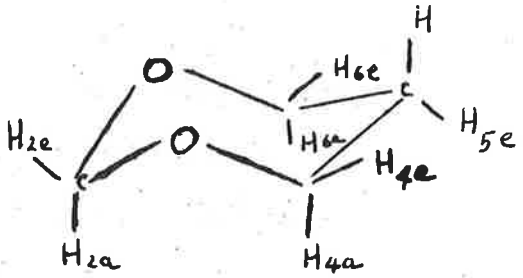


Ce couplage de 0,5 cps est à rapprocher de celui observé entre les protons H_{2e} et H_{4a} des dioxannes-1,3 pour lesquels on trouve : (2)

$|J_{2e - 4e}| = |J_{2e - 6e}| = 1$ cps

$|J_{2e - 4a}| = |J_{2e - 6a}| \simeq 0,45$ cps

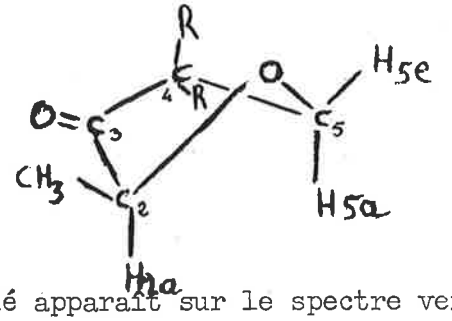
$|J_{2e - 5e}| = 0,9$ cps



Il semble plausible d'attribuer à ce tétrahydrofurannone une conformation du type enveloppe (3) dans laquelle C_2, C_3 , C_4 et C_5 seront approximativement dans le même plan.

Adresse : 43, boulevard de l'Hippodrome - Villeurbanne . Rhône
Téléphone : 52-07-04 . 52-07-05 . 52-07-20 . 52-07-49 . 52-07-52 . 52-07-55 . 52-07-73 . 52-07-80 . 52-07-92

Dans cette conformation le méthyl-2 se trouvant en position quasi équatoriale , le proton H_2 responsable du couplage avec l'un des protons H_5 est quasi axial .



Le proton H_5 couplé apparait sur le spectre vers les champs faibles . Diverses raisons nous amènent à penser qu'ils'agit là de H_{5e} :

a) <u>La valeur du couplage</u>

Le couplage étant voisin de celui observé dans les dioxannes , les protons qui interagissent doivent présenter même disposition relative que les protons H_{4a} et H_{2e} du dioxanne 1,3 . Dans le tétrahydrofurannone cette condition est effectivement réalisée pour H_{2a} et H_{5e} .

b) <u>Le déplacement chimique relatif de H_{5e} et H_{5a} : Système AB</u>

La différence entre ces déplacements chimiques , de valeur 8 cps, provient de l'anisotropie magnétique de la liaison C_2-O vis à vis des 2 protons H_{5e} et H_{5a} (les autres liaisons et en particulier C_3 - C_4 ont même orientation par rapport à ces 2 protons) . Etant donné l'orientation de la liaison C - O ,il faut s'attendre à trouver le proton H_{5e},qui voit sa constante d'écran diminuée , vers les champs faibles . C'est précisément le proton présentant un couplage à distance .

En conclusion le couplage trouvé chez les dioxannes-1,3 dans une conformation chaise entre H_{2e} et H_{4a} (distinct du couplage à distance classique du type M $|J_{2e-4e}| = 1$ cps) se retrouve dans des tétrahydrofurannones

présentant une conformation privilégiée du type enveloppe .

Croyez , cher Monsieur , à nos sentiments les meilleurs .

J. DELMAU et J. DUPLAN

Delmau Duplan

Références :

(1) DURAND : Résultats à paraître

(2) J. DELMAU , J. DUPLAN : Tetrahedron Letters N° 6 p. 559-565 (1966)

(3) E.L. ELIEL : Stereochemistry of Carbon Compounds
Mc Graw Hill , Series in Advanced Chemistry
N. Y. (1962)

90-47

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PETROCHEMICAL & POLYMER LABORATORY

P.O. Box 11, The Heath, Runcorn, Cheshire

Telephone: RUNCORN 3456 *Trunk Dialling:* OWA 853456 *Telegrams:* MONDIV. RUNCORN
Telex: 62655 ICIMONDIVHQ RCN

11th March, 1966

Your Ref:

Our Ref: JKB/MCMcI/PW

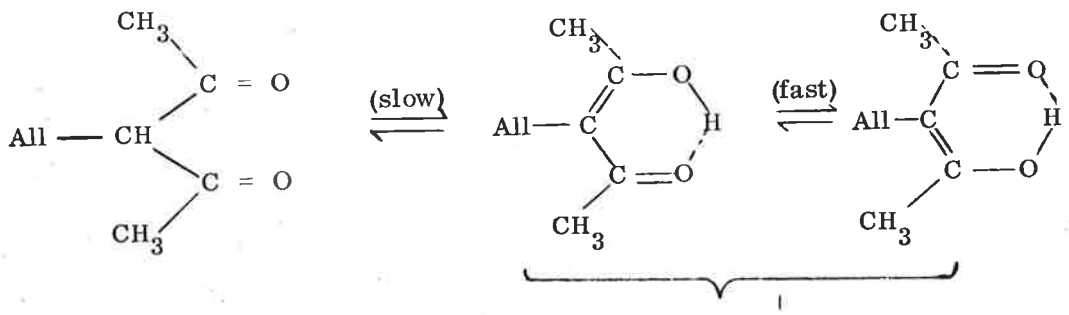
Associate Professor B.L. Shapiro,
Chemistry Department,
Illinois Institute of Technology,
Chicago,
Illinois 60616,
U.S.A.

Dear Professor Shapiro,

One of the undersigned (J.K.B.) has changed addresses from I.C.I. Dyestuffs Division, Manchester, to I.C.I. Petrochemical and Polymer Laboratory Runcorn. May we therefore ask to open a new "subscription" to I.I.T.N.M.R. Newsletter here in Runcorn. N.M.R. in the Manchester laboratory continues under Dr. Alan Mathias. As a first contribution from Runcorn, may we offer notes on two topics from our recent work.

Tautomerism in allylacetylacetone

The proton spectrum of neat allylacetylacetone, or of a 10% solution in CCl_4, at the normal operating temperature in our Perkin-Elmer R.10 spectrometer (32°C.) is deceptive, as it apparently shows a CH_3 doublet with a splitting of about 5 c/s. On looking further into this we found that these two peaks arise from the keto and enol tautomers (I) and (II) respectively:



(I) (II)

(All = CH_2=CH-CH_2-)

FROM: J.K. Becconsall and M.C. McIvor

TO: Associate Professor B.L. Shapiro

DATE: 11th March, 1966

Chemical shift assignments for neat allylacetylacetone are as follows. (δ-values in p.p.m. downfield from TMS internal reference):

	CH_3	$-CH_2-$	$>CH-$	OH	=CH-	$=CH_2$
keto (I)	2.14	2.54	3.84	-	ca.5.7	ca.5.0
enol (II)	2.06	3.01	-	16.85	ca.5.7	ca.5.0

In its tautomeric behaviour allylacetylacetone thus qualitatively resembles acetylacetone (L.W. Reeves, Canad. J. Chem., 35, 1351 (1957)), but the presence of the allyl group increases the proportion of the keto form. We are now studying the temperature-dependence of the equilibrium ratio in order to estimate the enthalpy of conversion.

A curious solvent effect in triphenylphosphine

The 60 Mc/s proton spectrum of triphenylphosphine, $(C_6H_5)_3P$, covers a range of only about 5 c/s at 60 Mc/s, showing that the chemical shift differences between ortho, meta and para positions are surprisingly small. Gordon Shaw, a Leeds University final-year undergraduate who worked with us recently, found that dilute solutions of triphenylphosphine give a doublet (splitting $3\frac{1}{2}$ c/s) in which the relative heights of the two peaks are concentration-dependent. In a 0.20 gm/ml. deuterochloroform solution the ratio is about 2:1, the upfield peak being the higher one. On further dilution the ratio changes steadily in favour of the downfield peak, and at 0.03 gm/ml the ratio is reversed to 1:2. We at first thought this was due to a chemical equilibrium involving two forms, but closer inspection showed that the peak widths too are concentration-dependent in an inverse sense, and the peak areas remain in the ratio 1:1 throughout, within the limits of accuracy of our measurements.

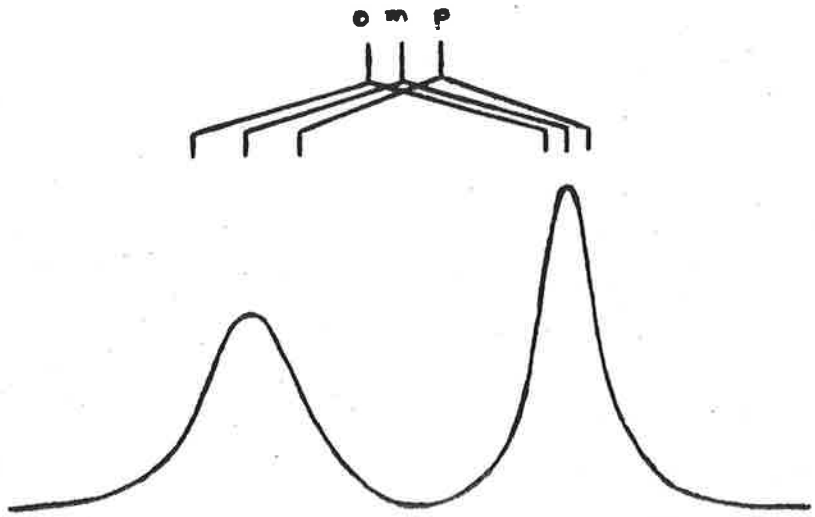
The explanation we propose is that the doublet splitting is due to proton-P^{31} coupling, and each peak contains the resonances of ortho, meta and para protons for one spin state of the P^{31} nucleus. The chemical shift differences are insufficient to be resolved, but they contribute appreciably to the peak widths. If the protons have different couplings to the P^{31} nucleus, this results in two peaks of equal areas but different widths (see sketch). The effect of varying the solution concentration is to change the relative chemical shifts, which in turn affects the peak widths.

FROM: J.K. Becconsall and M.C. McIvor

TO: Associate Professor B.L. Shapiro

CONTINUATION SHEET NO.: 3

DATE: 11th March, 1966



Evidence in support of this somewhat bizarre explanation is provided by proton-P^{31} spin decoupling experiments, which were kindly done by Ed Randall and Dereck Shaw at Queen Mary College, London. Irradiating the P^{31} resonance collapsed the doublet in each case to a single peak of less than 2 c/s $\frac{1}{2}$-intensity width.

Detailed results are being submitted for publication in Chemical Communications.

Yours sincerely,

J.K. Becconsall

M.C. McIvor

J.K. Becconsall
M.C. McIvor

0030A

90-50

UNIVERSITY OF COLORADO
BOULDER, COLORADO 80304

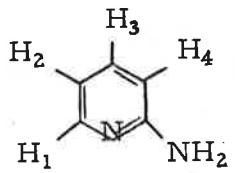
DEPARTMENT OF CHEMISTRY

March 15, 1966

Professor Barry Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry:

We have been carrying out an Analysis of the Proton Spectrum of 2-Aminopyridine (title) as a function of solvent and pH. Some preliminary data are given in Table 1 where the numbering system is shown below and chemical shifts are given relative to the shift of proton 1. Some data of Kowalewski and de Kowalewski[1] on 2-chloropyridine are given for comparison.



One should note that there is a solvent effect on the chemical shifts and on J_{23} and J_{34}. The smaller relative shifts in water are probably due to the upfield shift of proton 1 upon hydrogen bonding the lone pair on the pyridine nitrogen. We don't yet have an explanation for the effect on the coupling constants. A pH dependence study is currently being carried out.

The analyses were performed using the Reilly-Swalen program.

Sincerely yours,

James V. Mengenhauser

James V. Mengenhauser

Melvin W. Hanna

Melvin W. Hanna

MH;lu
encl.

[1] V.J. Kowalewski and D.G. de Kowalewski, J. Chem. Phys. 41, 2087 (1964).

Table I. NMR Data for 2- Pyridines.

	2-Aminopyridine		2-Chloropyridine(2)
Solvents	H_2O	CH_2Cl_2	none
Chemical Shifts (PPM)			
δ_{12}	1.207	1.625	1.135
δ_{13}	0.418	0.723	0.712
δ_{14}	1.280	1.763	1.035
Coupling Constants (cps)			
J_{12}	5.29	5.69	4.67
J_{13}	1.88	2.18	1.98
J_{14}	0.90	1.09	0.75
J_{23}	7.16	8.19	7.22
J_{24}	0.96	1.05	0.96
J_{34}	8.30	9.38	7.75
Average Deviations of Transition Frequencies (cps)			
	0.059	0.064	0.084

90-52

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Frick Chemical Laboratory

March 17, 1966

Dr. B.L. Shapiro
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Dear Barry,

We have a continuing interest in the detection of very weak hydrogen bonds by NMR. The small shifts involved can be easily masked by solvent effects, prompting us to take a closer look at the common NMR techniques used for study of relatively strong hydrogen bonds. These are:

1) dilution into an inert solvent (a test of self-association)
2) dilution into a proton acceptor
3) dilution into an aromatic solvent
4) temperature effects.

1. Dilution in inert solvents.

Although there is no doubt about the utility of this approach for strongly associated liquids (alcohols, phenols, water, etc.), the small shifts one observes for very weak proton donors are probably not indicative of hydrogen bonding (Table I).

Table I

$\Delta\tau^*$ (ppm)

	$CHCl_3$	CH_2Cl_2	CH_2I_2	MeI	Acetone
$\Delta\tau_{SA}$**	-.15	-.19	-.16	-.17	-.19
$\Delta\tau_{CCl_4}$	-.13	-.14	-.11	-.13	-.08

*We adopt the convention that: $\Delta\tau_X = \tau_{solute}$ in solvent X - τ_{solute} in cyclohexane.
**$\Delta\tau_{SA} = \tau_{neat\ liquid} - \tau$ in C_6H_{12}.

All samples were run on an A60-A, using TMS as an internal standard. τ's were measured with a side band technique. Concentrations were 1% by volume.

Notice that the dilution shifts do not distinguish between the compounds which are thought to be capable of hydrogen bond formation ($CHCl_3$, CH_2Cl_2, CH_2I_2) and those that are not. Secondly, the shifts in solute resonance dissolved in CCl_4 are quite comparable to the dilution shifts. We feel these effects are attributable, at least qualitatively, to the "polar effects" of the Buckingham,

Schneider and Schaefer theory (ref. 1) and give essentially no information about the hydrogen bonding ability of these compounds.

2. Proton Acceptor Solvents.

One frequently measures the proton donor ability of a compound by use of a "basic" solvent. Acetone and ether are compared in Table II.

Table II

$\Delta\tau$ in ppm.

	$CHCl_2CN$	$CHCl_3$	CH_2Cl_2	CH_3NO_2	Acetone
$\Delta\tau_{acetone}$	-1.14	-.90	-.47	-.53	-.09
$\Delta\tau_{Et_2O}$	- .97	-.69	-.28	-.18	-.05

This method provides a wide range of $\Delta\tau$'s whose order is at least qualitatively in keeping with our intuitions about proton donor abilities. Strongly polar compounds such as CH_3NO_2 show smaller shifts than very weak hydrogen bond formers such as CH_2Cl_2. Solvents such as Et_2O and Et_3N are particularly attractive because their polarizabilities, dipole moments and dielectric constants are quite low, minimizing solvent effects which influence the acetone data.

3. Dilution into aromatic solvents.

The magnetic anisotropy of aromatic solvents produces large (0.3 - 1.0 ppm) upfield shifts in the resonances of those solutes which interact with the π electrons of the ring system. Such shifts are characteristically observed in compounds which can form hydrogen bonds to the ring. However, all small polar molecules show such effects (Table III), so that "ring shifts" alone cannot suffice as criteria for proton-donating ability.

Table III

$\Delta\tau$ (in ppm)

	$CHCl_2CN$	$CHCl_3$	CH_2Cl_2	CH_3NO_2	CH_3CN	CH_3I	Acetone
$\Delta\tau_{C_6H_6}$	+1.47	+.91	+.79	+1.03	+1.07	+.55	+.37

4. Temperature effects.

Recent work (ref. 2) has indicated that temperature-induced resonance shifts of hydrogen-bonded protons reflect more than just a change in the bonded/non-bonded ratio. Thus, temperature data should be supplemented with other types of measurements for application to hydrogen-bonding problems.

In summary, weak hydrogen bonds can be characterized by NMR measurements, but some care is required. Proton donor ability is probably best measured in a solution of ether or triethyl amine. $\Delta\tau$'s of greater than -.2 ppm in these solvents are indicative of hydrogen bond formation.

Sincerely yours,

Irwin D. Kuntz
Assistant Professor

IDK/mb

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