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Newsletter

No. 129
JUNE, 1969

OVER

Deadline Dates: No. 130: 1 July 1969
No. 131: 4 August 1969

All Newsletter correspondence, etc., should be addressed to:

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

May 13, 1969

Dr. Barry Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas

Dear Barry:

Joe Ray, Al Colter and I have been studying charge delocalization in a series of para-substituted triphenylcarbonium ions by carbon-13 nmr shifts. Preliminary results for the unsubstituted compound (1) and for triphenylcyclopropenium cation (2) have been published elsewhere. A summary of the results for the substituted compounds is given in table I.

The shifts at a given position are given as the difference between those for triphenylcarbonium and the parent triphenylcarbinol. This difference should reflect only the charge delocalized from the central carbon if it is assumed that the shielding effects due to the para-substituent are the same in the carbonium ion and carbinol. By means of the empirically derived proportionality (160 ppm per electron) between carbon-13 nmr shifts and charge densities in aromatic systems (3,4) one can estimate the charges at the various positions.

Charge densities calculated by the HMO method correlate only qualitatively with the empirical charge densities. However, charge densities calculated by the CNDO method (5), correlate well, as shown in Table II, if a reasonable twist angle of the phenyl rings is assumed. A plot of the chemical shifts versus charge densities from the CNDO calculations (for an assumed twist angle of 30°) give a good linear correlation, with a slope of 210 ppm per electron. Also, charge densities at the central carbon, calculated from the difference between the central carbon shifts in the substituted triphenylcarbonium ion and trimethylcarbonium ion (6) correlate well with charge densities from HMO calculations and with the electronegativity of the substituent. Finally, the carbon-13 nmr shifts of

carbons alpha to the central carbon show a good linear correlation with σ_R reactivity parameters.

Sincerely,

Bob

Robert J. Kurland
Associate Professor

RJK:cr

(1) G. J. Ray, A. K. Colter, D. G. Davis, D. E. Wisnosky and R. J. Kurland, Chem. Comm., No. 597, 815 (1968)

(2) G. J. Ray, A. K. Colter and R. J. Kurland, Chemical Physics letters 2, 324 (1968)

(3) H. Spiesecki and W. G. Schneider, Tetrahedron Letters No. 14, 468 (1961)

(4) P. C. Lauterbur, Tetrahedron letters, No. 8, 274 (1961)

(5) P. G. Dobosh and J. A. Pople, private communication

(6) G. A. Olah, E. B. Baker and M. B. Comisarow, J. Am. Chem. Soc., 86, 1265 (1964)

SUGGESTED SHORT TITLE: Carbon-13 NMR Shifts and Charge Delocalization in Substituted Triphenylcarbonium Ions

RJK:cr

Notation for positions:

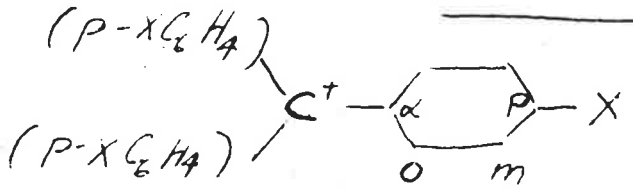


Table I

Carbon-13 Chemical shifts in $(p\text{-}XC_6H_4)_3C^+$

X	alpha(α)[a]	ortho(o)[a]	neta(m)[a]	para(p)[a]	central[b]
NO_2	8.0	-16.9	-2.7	-8.8	126.9
H	7.7	-15.0	-3.2	-17.0	129.0
Cl	8.8	-13.1	-3.6	-15.9	135.9
CH_3	8.7	-14.2	-3.2	-21.3	136.1
F	7.3	-16.2	-5.2	-11.3	136.9
OCH_3	8.9	-13.9	-4.2	-11.4	147.6
$N(CH_3)_2$	11.8	-13.6	-1.1	-6.4	163.9

(a) in ppm from the corresponding position m $(p\text{-}XC_6H_4)_3\text{-}COH$; a positive shift is upfield

(b) in ppm from the central carbon of $(CH_3)_3C^+$; see ref. 6.

Table II

Empirical Charge Densities and Charge Densities Calculated by the CNDO Method for Triphenylcarbonium Ion

Position	Charge Densities Calculated by		
	CNDO (60°)	CNDO (30°)	Empirical (carbon-13)
alpha	-0.003	-0.013	-0.048
ortho	+0.051	+0.071	+0.094
meta	+0.032	+0.015	+0.020
para	+0.051	+0.081	+0.106
central	+0.317	+0.249	+0.140

129-4

Technische Hogeschool Delft

Laboratorium voor Technische Natuurkunde

Prof.B.L. Shapiro
Texas A & M University
College of Science
College Station, Texas 77843
USA

Uw kenmerk	Uw brief van	Ons kenmerk	Delft, Nederland, Lorentzweg 1, tel. 01730-33222 toestel:
			6-5-1969
Onderwerp			

The influence of hydrogen bonding and of protonation on acetone

Dear Prof. Shapiro,

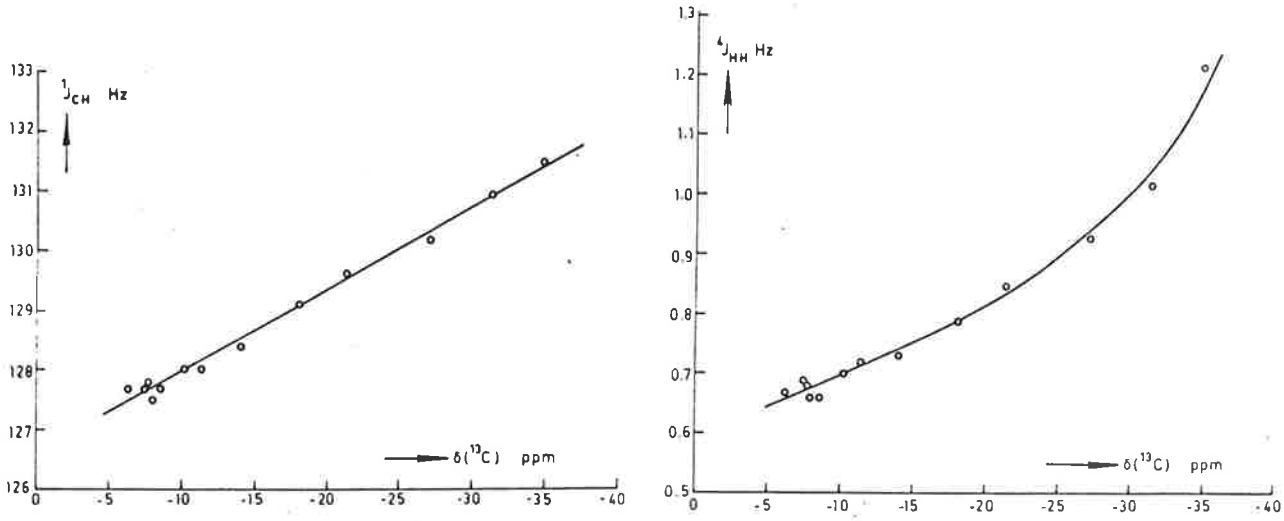
Besides the chemical shift $\delta(^1H)$ the coupling constants $^1J_{CH}$ and $^4J_{HH}$ can be obtained from the ^1H spectrum of acetone using ^{13}C satellites. From the ^{13}C spectrum we can get the chemical shifts $\delta(^{13}CH_3)$ and $\delta(^{13}CO)$. As is well known most of these parameters are highly solvent dependent (1,2). Some representative variations are given in the table. In this laboratory a systematic study has been carried out for 0.2 molar acetone in various solvents and for acetone at various concentrations in water. Furthermore the dependence of these parameters on the acidity is investigated for 0.2 molar acetone in sulfuric acid/water solutions. For this last case some interesting relations between the changes in $^1J_{CH}$, $^4J_{HH}$ and $\delta(^{13}CO)$ are shown in the figures.

An explanation for the variations can be found in H bonding and for the acidic solutions also in protonation of the carbonyl group. By the increased polarity of the carbonyl group the decreased screening of the carbonyl carbon can be explained qualitatively. The well-known increase of $^1J_{CH}$ in CH_3X with increasing electronegativity of X is also in agreement with this model. So a linear relation between these two quantities can be expected. For $^4J_{HH}$ a π electron contribution can be expected of about -0.6 Hz (3). As by now $^4J_{HH}$ is known to be positive (4,5) we have to postulate a positive contribution of about 1.2 Hz through the σ bonds and/or through space. Because of the complicated mechanisms for $^4J_{HH}$ there is no reason to expect a strictly linear relation between $^4J_{HH}$ and $\delta(^{13}CO)$ (see figure).

Extensive MO calculations have been carried out for acetone, the acetone/water complex and protonated acetone. Use is made of the Hückel-type method of Pople and

		pure acetone	0.2 molar acetone in water	0.2 molar acetone in sulfuric acid
$\delta(^{1}H)$	ppm	0	- 0.13	- 0.85
$^{1}J_{CH}$	Hz	126.8	127.6	131.5
$^{4}J_{HH}$	Hz	0.55	0.66	1.22
$\delta(^{13}CH_3)$	ppm	0	- 0.6	- 0.8
$\delta(^{13}CO)$	ppm	0	- 8.0	-35.0

Solvent effects on some NMR parameters of acetone (negative δ = lower field).



$^{1}J_{CH}$ and $^{4}J_{HH}$ versus $\delta(^{13}CO)$ for 0.2 molar acetone in sulfuric acid/water.

Santry, the extended Hückel method of Hoffmann (the last one also in iterative form) and of the CNDO method. The direction and sometimes also the order of magnitude of the changes are in general predicted reasonably well. The electron displacement in the direction of oxygen, which is found both for H bonding and for protonation, occurs mainly at the cost of the carbonyl carbon and the methyl hydrogens. The methyl carbon is hardly affected, which is in agreement with the near constancy of $\delta(^{13}CH_3)$.

For the reader interested in more details a copy of a Ph.D. thesis is available upon request. Please, credit this letter to Prof.Dr.J. Smidt.

Sincerely Yours,

W.H. de Jeu

G.P. Beneder

1 W.H. de Jeu, H. Angad Gaur & J. Smidt, Rec.Trav.Chim. 84, 1621 (1965)
2 G.E. Maciel & J.J. Natterstad, J.Chem.Phys. 42, 2752 (1965)
3 J.R. Holmes & D. Kivelson, J.Am.Chem.Soc. 83, 2959 (1961)
4 H. Dreeskamp, Z.Physik.Chem. 59, 321 (1968)
5 W.H. de Jeu & H. Angad Gaur, Molec.Phys. 16, 205 (1969)

NORTH CAROLINA STATE UNIVERSITY | AT RALEIGH

SCHOOL OF PHYSICAL SCIENCES AND APPLIED MATHEMATICS

DEPARTMENT OF CHEMISTRY
BOX 5247 ZIP 27607

May 7, 1969

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

Dear Barry:

Title: Nmr Line Shape Programs With Least Squares Fit

We have been studying the kinetics of redistribution reactions of the type

$$(CH_3)_3SbX_2 + (CH_3)_3SbY_2 \rightleftarrows 2(CH_3)_3SbXY$$

and have been measuring and calculating nmr line shapes for the different methyl proton resonances as a function of concentration and temperature. In order to obtain the best results we have modified our Fortran IV program for N sites and variable populations so that it will give a least square fit of the calculated line shape to experimental curve. The lifetime value for best fit is printed out and the curve is plotted along with the experimental points. (Figure 1).

We have used the program for two sites with unequal populations thus far but plan to use it on a three site case soon. It takes approximately 18 sec per 5 set of curves on the IBM 360 Model 75.

Anyone interested in obtaining a copy of this program can write directly to me. Dr. George Wahl, Jr. of our Department also has a similar program for an AB system and would be happy to supply it to anyone interested.

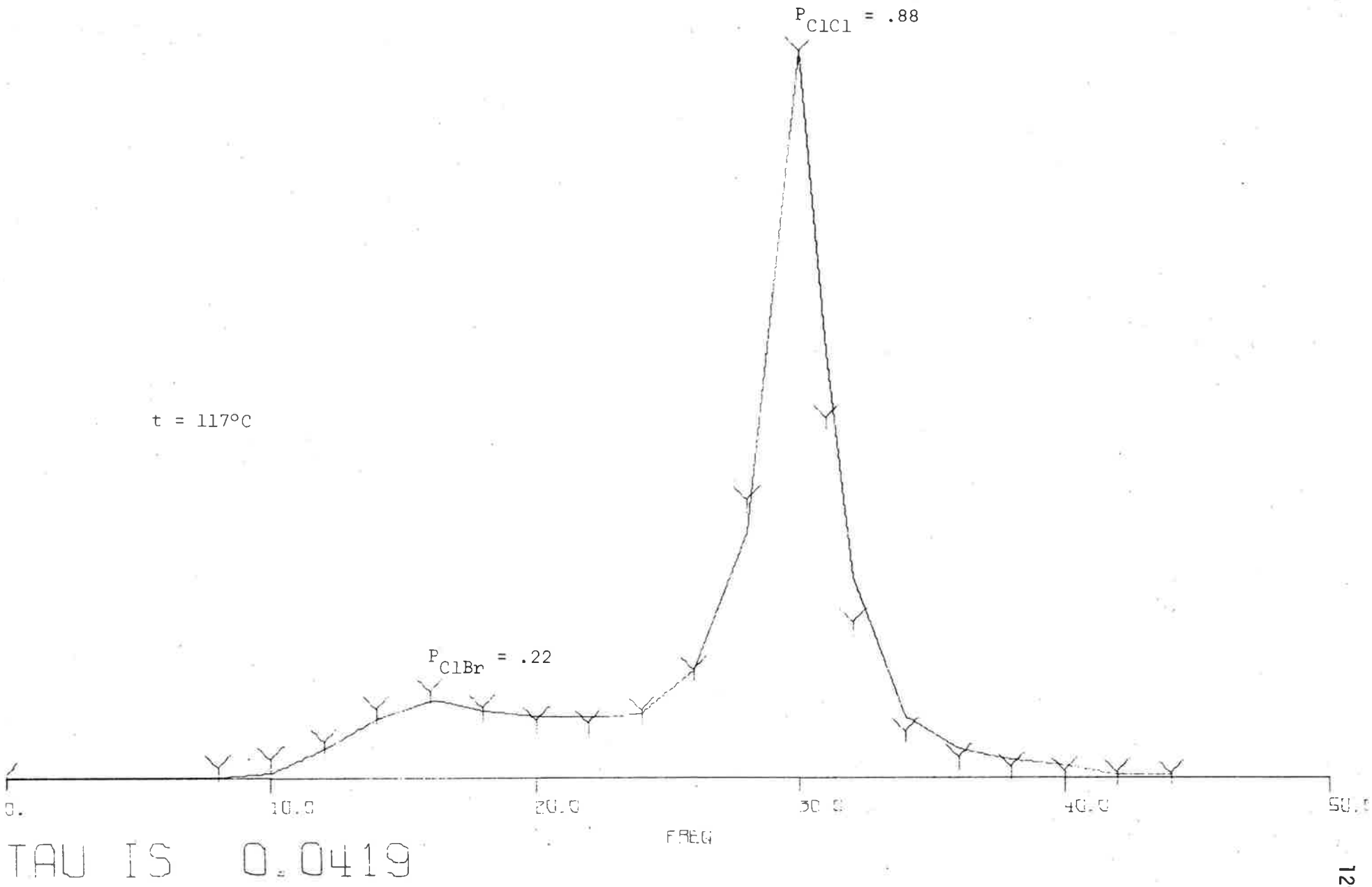
Sincerely,

Charlie

Charles G. Moreland

Robert Beam

Robert J. Beam


P_{ClCl} = .88
t = 117°C
P_{ClBr} = .22
0.
10.0
20.0
30.0
40.0
50.0
FREQ
TAU IS 0.0419

unilever research laboratorium

vlaardingen-nederland

POSTBUS 114 ▪ OLIVIER VAN NOORTLAAN 120 ▪ TELEX 23261 ▪ TELEFOON 010-353 000

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

U.S.A.

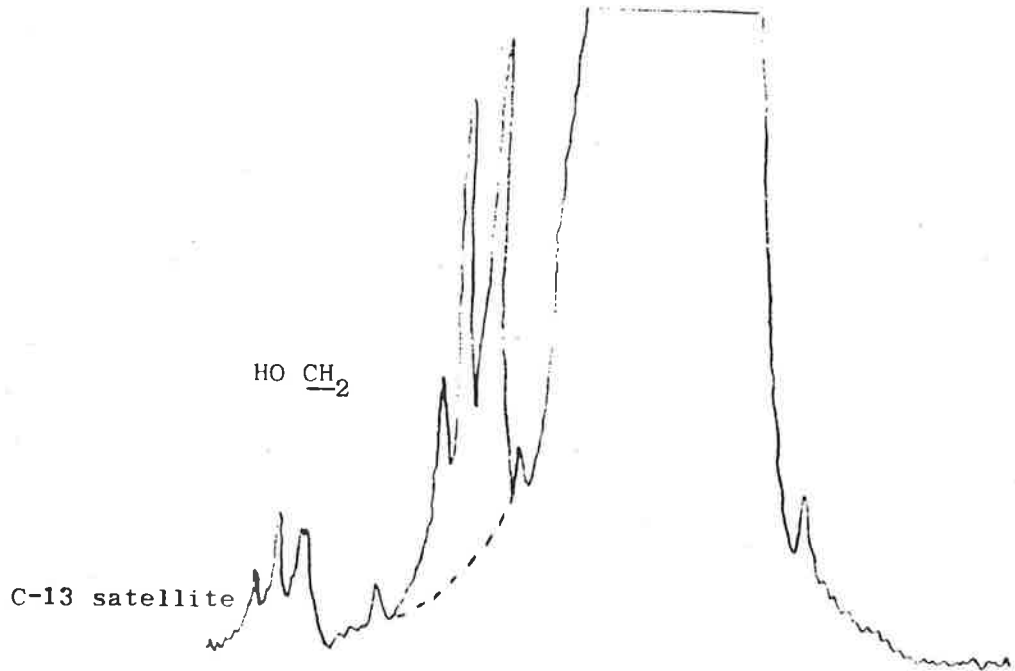
REF. CC/9235/as

VLAARDINGEN 22th April 1969

Dear Professor Shapiro,

Re: Polymer chain length measurements using C-13 satellites; copier for NMR spectra.

One NMR method of measuring average molecular weights of poly-ethylene glycols involves shifting the $\underline{CH_2}OH$ absorption clear of the internal $-(OCH_2CH_2)_n$ peak by complexing the terminal OH with an appropriate solvent. Page and Bresler (1) used pyridine and predicted the method's applicability up to MW 15-20,000, but we found this gave large discrepancies with other methods above MW 1000. However, a short search found a phenanthrene/quinoline solvent mixture to be more efficient in separating the peaks (ca 0.4 ppm), whilst we overcame the inherent problem of comparing the intensities of absorptions differing by orders of magnitude, by employing the downfield C-13 $(OCH_2CH_2)_n$ satellite as an internal quantitative reference. Use of a CAT is necessary (for an A60) to give the desired S/N, with intensities then being compared using a planimeter. The figure shows the result of 275 accumulation on a model sample of MW 2500.



AAN: Professor B.L. Shapiro,
Texas 77843.
U.S.A.

This technique has so far given accurate results for model samples up to values of MW 20,000. In the future we hope that our HA 100 plus forthcoming Fourier accessory linked to an IBM 1800 will be churning out the final answer after a few minutes operating time.

May I just chip into the discussion about spectra copiers some months back by mentioning the Van Der Grinten Océ 106 which we have been finding most economical and convenient to use. Any length of spectrum can be accomodated with a maximum width of 30 cm -and so far no accidents over several hundred copies.

Yours sincerely

UNILEVER RESEARCH LABORATORIUM
Vlaardingen

D.J. Frost

(1) T.F. Page and W.E. Bresler: Anal. Chem. 36, 1981 (1964).

129-10

THE UNIVERSITY OF NORTH CAROLINA
AT
CHAPEL HILL
27514

DEPARTMENT OF CHEMISTRY

May 14, 1969

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

Dear Barry:

Computer Program Questionnaire

The Task Group on Computer Applications of ASTM Subcommittee E-13.7 is compiling a list of computer programs which are useful in NMR research. This list will be generally available and will hopefully reduce some of the present duplication of effort.

We hope that your readers will use the attached questionnaire to inform us of their programs. We have no plans for a clearing house of programs at this time, but we strongly recommend that individuals make use of the existing exchanges, e.g., Quantum Chemistry Program Exchange (Indiana University, Bloomington, Indiana) and Program Exchange Library (Instrument Division, Perkin-Elmer Corp., Norwalk, Connecticut). The participants can simply list the appropriate exchange library as the program source on our questionnaire.

The questionnaire has been discussed with both Dr. E. Lustig and Professor R. K. Robin, who wrote about the need for such a list in previous issues of TAMUNN, and they have agreed to cooperate with our efforts.

Sincerely,

C. S. Johnson, Jr.
Chairman of the Task Group
on Computer Applications
of ASTM Committee E-13.7

CSJ:bkm

Attachment

TASK GROUP ON COMPUTER APPLICATIONS
ASTM SUB-COMMITTEE E-13.7

REQUEST FOR INFORMATION CONCERNING COMPUTER PROGRAMS OF INTEREST IN NMR RESEARCH

Name of Program (Code Designation):

Descriptive Title:

Author(s):

Address:

Source: (if different from author)

Computer:

Language:

Digits or Bits Per Word: Maximum Core Storage:

Input Form: Output Form:

Preferred Mode of Distribution:

Summary of Program:

Please return to: Charles S. Johnson, Jr.
Department of Chemistry
University of North Carolina
Chapel Hill, N. C. 27514

129-12

Imperial Chemical Industries Limited

DYESTUFFS DIVISION

P.O. Box 42, Hexagon House, Blackley, Manchester, 9

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

Your Ref:

Our Ref: A.R.S. B5

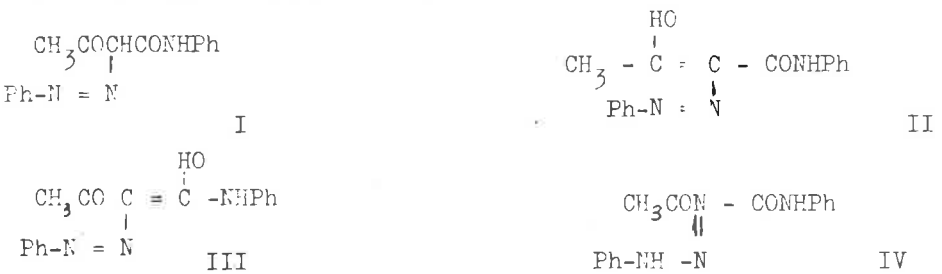
14th May, 1969

Dear Dr.Shapiro,

TAUTOMERISM STUDIES USING NITROGEN-14 NMR DATA

In previous communications (1,2) we have described the double resonance method which we use to obtain nitrogen-14 chemical shift data from proton NMR spectra. This method is limited to those nitrogen nuclei which show a detectable coupling to some proton in the molecule, but it largely overcomes the sensitivity problems associated with direct observation of nitrogen-14 signals.

1-phenylazo-acetoacetanilide, formally written as I, can exist in four possible tautomeric forms I - IV,

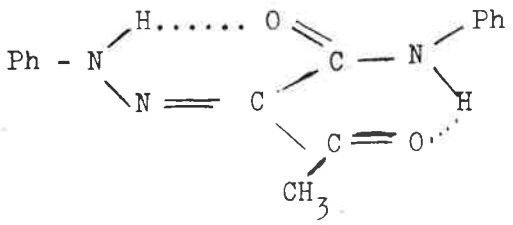


Three more forms are possible in theory if tautomerism of the amide NH proton is considered, but these are obviously less likely to occur. In addition, for each tautomer a variety of spacial arrangements is possible. In acetone solution, the NMR spectrum shows a CH_3 signal and a complex aromatic band proton due to ten protons. No CH signal is found, but two labile proton peaks can be seen at 11.4 and 14.7δ. Both these peaks are sharpened slightly when the sample is irradiated simultaneously at nitrogen-14 frequencies, thus showing that both protons are coupled to nitrogen nuclei and ruling out forms I, II and III above.

Nitrogen-14 chemical shifts were derived from the nitrogen frequencies causing the maximum sharpening of the labile proton peaks. The values obtained fully supported form IV. Thus the proton at 11.4δ is coupled to a nitrogen nucleus with a shift of 250 ± 15 ppm, a value typical of an amide nitrogen carrying a phenyl ring. The proton at 14.7δ is coupled to a nitrogen nucleus with a shift of 194 ± 15 ppm, a value indicative of the nitrogen atom alpha to the phenyl ring of a phenylhydrazone unit. The nitrogen-14 chemical shifts are referred to standard nitrate ion (1,2).

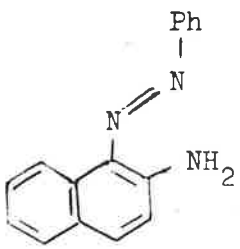
(Cont'd)

Finally the very lowfield positions of the two labile protons show that both these protons are strongly hydrogen-bonded and this last observation yields for the compound the full structure V,

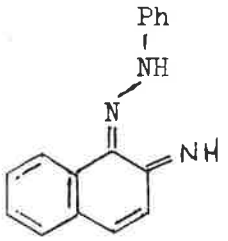


V

1-phenylazo-2-amino-naphthalene has also been examined. Here tautomerism involving forms VI and VII is possible



VI



VII

In acetone, a labile proton peak (area $\bar{=}$ 2) was found at 8.5 δ with coupling to a nitrogen nucleus of chemical shift 301 $\pm$ 3 ppm, a value typical of an aromatic amine. Thus in this compound there is no evidence for the phenylhydrazone form VII. The 2-methylamino derivative of VI behaved similarly and here coupling between the NH and CH_3 protons was also observed, providing further support for the amino/azo form of these compounds.

Yours sincerely,

P. Hampson A. Mathias.

P.HAMPSON. A.MATHIAS.

1. P.Hampson and A.Mathias. Molec Phys II, 541, 1966.

2. P.Hampson and A.Mathias. NMR Newsletter, 95, 1, 1966.

PH/LG.

129-14

PHYSIKALISCHES INSTITUT
DER UNIVERSITÄT BASEL
4056 BASEL, SCHWEIZ - KLINGELBERGSTR. 82
TEL. 43 04 22
VORSTEHER: PROF. DR. P. HUBER

NEUE NR.
061-44 22 00

Prof. Dr. P. Diehl

Basel, May 14, 1969

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

USA

Title: The influence of an electric field on the NMR spectra of molecules oriented in the nematic phase

Dear Barry,

We have investigated the NMR spectra of (cis) dichloroethylene, furan, thiophene and benzene oriented in the nematic phase of liquid crystals, with and without the application of an electric field applied in a direction perpendicular to the magnetic field and along the sample axis. The direct dipolar couplings and other anisotropic parameters have been found to change consistently to half their initial values with reversed signs at field strengths larger than 4 kV/cm. This has been attributed to a rotation of the liquid crystal optic axis by 90° by application of the electric field. This interpretation is further confirmed by the fact that the re-oriented sample permits sample-spinning without destruction of orientation.

An alternative arrangement of electrodes which allows to apply the electric field in a variable direction with respect to the magnetic field has also been constructed. It allows to vary the anisotropic parameters at will.

This definite and predictable variation can be used not only to simplify the analysis of the spectra but also to determine the various anisotropic parameters e.g. chemical shift anisotropy without referring to the shift in isotropic solution.

A typical spectrum of furan, with and without the application of an electric field is shown in the accompanying figure.

Yours sincerely,

Peter

(P. Diehl)

C.L. Khetrapal

(C.L. Khetrapal)

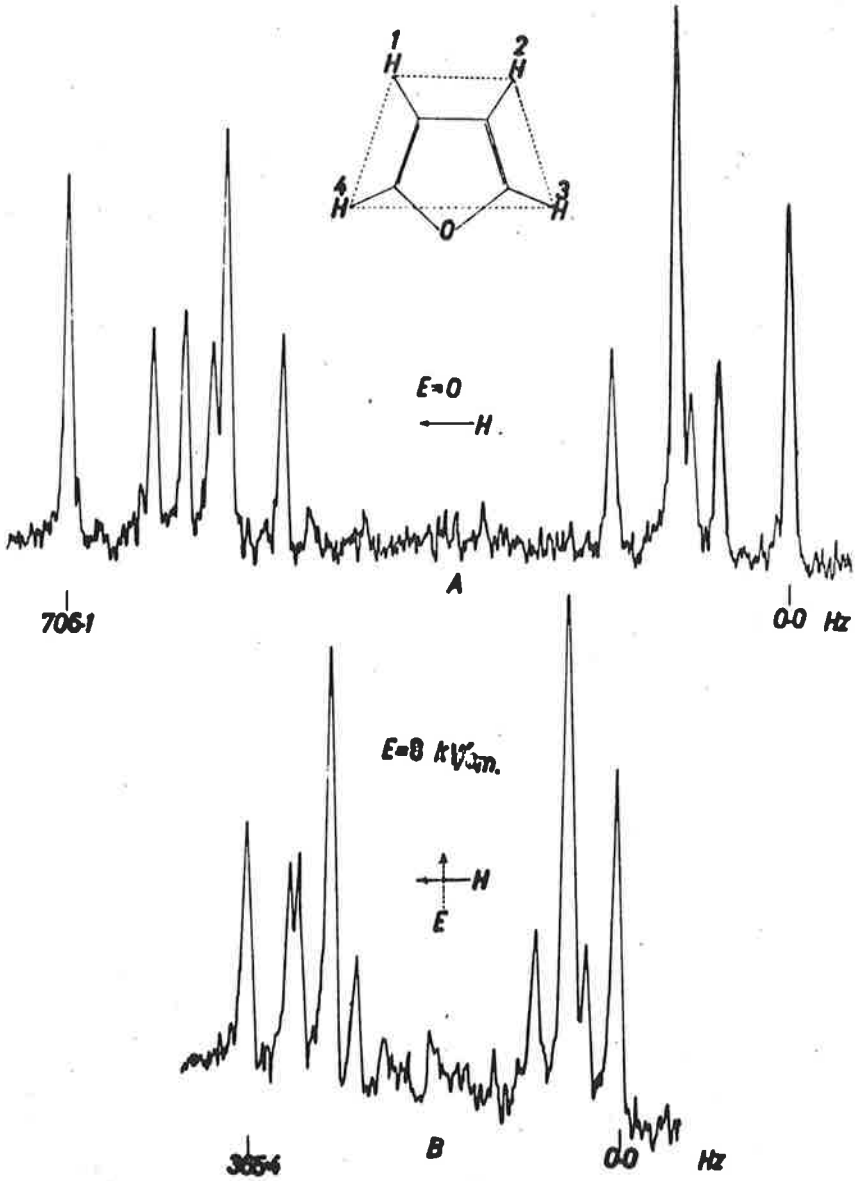


Figure caption

NMR spectra of furan in the nematic phase of 4-methoxy benzylidene-4-amino-α-methyl cinnamic acid-n-propyl ester. (A) without electric field, (B) with electric field (8 kV/cm). Concentration of furan ≈ 24 mole per cent; temperature 27° C.

129-16

FACULTÉ DES SCIENCES
DE MONTPELLIER

R. JACQUIER
Professeur

Place Eugène Bataillon
Tél. : (67) 72.29.44 — 72.16.00 — 72.28.58
Poste 803

Montpellier, le 16 Mai 1969

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

Titre : LAOCN 3 et IBM 360-40

Cher Professeur Shapiro,

Après la lecture de quelques lettres parues dans IIT NMR Newsletter (1,2), nous voudrions signaler que nous utilisons actuellement LAOCN 3 sur IBM 360-40.

Le programme initial de CASTELLANO et BOTHNER-BY (C et B-B)(3) a du être légèrement modifié, d'une part pour permettre l'utilisation de disques, d'autre part à cause de la place réservée aux variables indicées qui entraine un dépassement de capacité sur notre ordinateur (capacité effective : 64 - 10 = 54 K, 10 K étant la place retenue par l'assembleur).

Après modification et en calcul itératif, le nombre de spins maximum est 6, le nombre de transitions expérimentales 210 et le nombre de groupes indépendants de paramètres variables 15.

Nous avons testé le programme ainsi modifié en reprenant les calculs effectués par C et B-B (CASE 102 (4)) sur la pyridine (liquide pur) avec tous leurs paramètres expérimentaux.

La page 3 réunit les paramètres de départ, les paramètres finaux obtenus après 3 itérations (RMS ERROR et PROBABLE ERRORS OF PARAMETER SETS identiques dans les 2 cas) associés à une partie des transitions calculées à partir de ces paramètres (ceci sur 360 et sur 7040 (3)), ainsi que le même groupe de transitions calculées à partir des paramètres donnés par le calcul de C et B-B (toutefois, il faut noter que les paramètres utilisés après itération ont davantage de chiffres significatifs puisqu'ils sont pris en mémoire).

Si les résultats finaux peuvent être considérés comme identiques en ce qui concerne les constantes de couplage et les déplacements chimiques (ils sont meilleurs que ceux obtenus par BREMSER (2) sur un 360-30, notamment pour A(1,5)), par contre, certaines fréquences calculées diffèrent entre les deux calculs, la différence pouvant aller jusqu'à 5 milliherz (les différences de numérotation sont sans importance car elles sont dues à la dégénérescence de certains niveaux d'énergie). On remarque, par exemple, que le spectre calculé par C et B-B sur 7040 est plus condensé que les nôtres car lorsque notre calcul sur 360 fait apparaitre 2 transitions très voisines ou égales en énergie et d'intensités I_1 et I_2, celui de C et B-B donne une seule transition d'intensité $I_1 + I_2$.

Il est possible que pour des calculs faisant appel à des données expérimentales courantes, une erreur de l'ordre de 5 milliherz provenant du calculateur n'influence pas les résultats. Toutefois, cette erreur peut devenir inadmissible dans le cas de travaux expérimentaux très précis comme ceux décrits par FREEMAN et GESTBLOM (5).

Nous aimerions avoir l'avis de spécialistes de calcul numérique afin de savoir s'il existe des assembleurs pour 360 donnant une meilleure précision ou s'il est préférable de revoir certains tests de précision de LAOCN 3 ou d'en inclure de nouveaux en fonction de l'assembleur utilisé.

Veuillez croire, Cher Professeur Shapiro, à l'aasurance de nos sentiments les meilleurs,

R. JACQUIER.

J. ELGUERO.

A. FRUCHIER.

(1) E. LUSTIG, IITNMR, 1967, 107, 52.

(2) W. BREMSER, IITNMR, 1968, 118, 30.

(3) A. A. BOTHNER-BY et S. CASTELLANO, LAOCN 3, Mellon Institute, Pittsburg.

(4) Référence 3, p. 41.

(5) R. FREEMAN et B. GESTBLOM, IITNMR, 1968, 113, 43.

N°	Fréquences calculées	Intensités
209	419.220	1.143
207	419.225	0.043
186	420.224	0.560
166	420.226	0.065
190	420.258	0.063
170	420.260	0.552
182	420.964	0.051
184	420.969	1.369
136	421.985	0.464
145	421.986	0.253
66	422.069	0.258
75	422.070	0.472
201	423.944	0.188
156	423.945	0.410
205	423.978	0.416
160	423.979	0.192
79	424.938	1.268
138	425.703	0.063
142	425.706	0.715
68	425.787	0.705
72	425.790	0.061
28	426.862	1.581
120	427.272	2.324
87	427.281	0.544
134	427.350	0.574
178	427.891	2.554
6	429.059	1.854
55	429.144	1.889
64	431.814	2.186
147	431.832	2.226
2	432.975	2.675

Calcul direct

sur IBM 360-40

W(1)= 516.513
W(2)= 427.429
W(3)= 450.110
W(4)= 427.429
W(5)= 516.513
A(1,2)= 4.870
A(1,3)= 1.829
A(1,4)= 1.000
A(1,5)= -0.052
A(2,3)= 7.661
A(2,4)= 1.400
A(2,5)= 1.000
A(3,4)= 7.661
A(3,5)= 1.829
A(4,5)= 4.870

Après Itérations

sur IBM 360-40

N°	Fréquences expérimentales	Fréquences calculées	Intensités	Erreurs
207	419.205	419.224	1.184	-0.020
170	420.258	420.225	0.622	0.033
186	420.258	420.258	0.614	0.000
182	420.958	420.966	1.419	-0.009
136		421.983	0.644	
145	421.972	421.983	0.073	-0.012
66	421.972	422.067	0.074	-0.095
75		422.068	0.655	
205	423.970	423.945	0.055	0.025
160		423.945	0.542	
201		423.976	0.552	
156	423.970	423.976	0.056	-0.007
79	424.928	424.938	1.266	-0.010
138		425.703	0.777	
72		425.785	0.766	
28		426.859	1.581	
120	427.298	427.274	2.325	0.024
87		427.278	0.542	
134		427.347	0.575	
178	427.868	427.889	2.555	-0.021
6	429.128	429.058	1.853	0.070
55	429.128	429.145	1.890	-0.018
64	431.850	431.812	2.194	0.038
147	431.850	431.829	2.230	0.020
2	432.970	432.979	2.675	-0.009

W(1)= 516.516
W(2)= 427.430
W(3)= 450.111
W(4)= 427.430
W(5)= 516.516
A(1,2)= 4.870
A(1,3)= 1.829
A(1,4)= 1.000
A(1,5)= -0.053
A(2,3)= 7.661
A(2,4)= 1.400
A(2,5)= 1.000
A(3,4)= 7.661
A(3,5)= 1.829
A(4,5)= 4.870

Après Itérations

sur IBM 7040 (3)

W(1)= 515.000
W(2)= 427.300
W(3)= 450.600
W(4)= 427.300
W(5)= 515.000
A(1,2)= 5.500
A(1,3)= 1.900
A(1,4)= 0.900
A(1,5)= -0.400
A(2,3)= 7.500
A(2,4)= 1.600
A(2,5)= 0.900
A(3,4)= 7.500
A(3,5)= 1.900
A(4,5)= 5.500

N°	Fréquences expérimentales	Fréquences calculées	Intensités	Erreurs
207	419.205	419.219	1.186	-0.014
170	420.258	420.224	0.624	0.034
186	420.258	420.258	0.616	0.000
182	420.958	420.965	1.420	-0.007
145	421.972	421.986	0.716	-0.014
66	421.972	422.070	0.729	-0.098
205	423.970	423.945	0.597	0.025
156	423.970	423.977	0.607	-0.007
79	424.928	424.942	1.268	-0.014
138		425.707	0.778	
72		425.789	0.767	
28		426.858	1.581	
120	427.298	427.278	2.324	0.020
134		427.281	0.543	
87		427.349	0.575	
178	427.868	427.888	2.552	-0.020
15	429.128	429.061	1.853	0.067
46	429.128	429.144	1.888	-0.016
147	431.850	431.814	2.193	0.036
64	431.850	431.832	2.230	0.018
2	432.970	432.975	2.677	-0.005

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

May 16, 1969

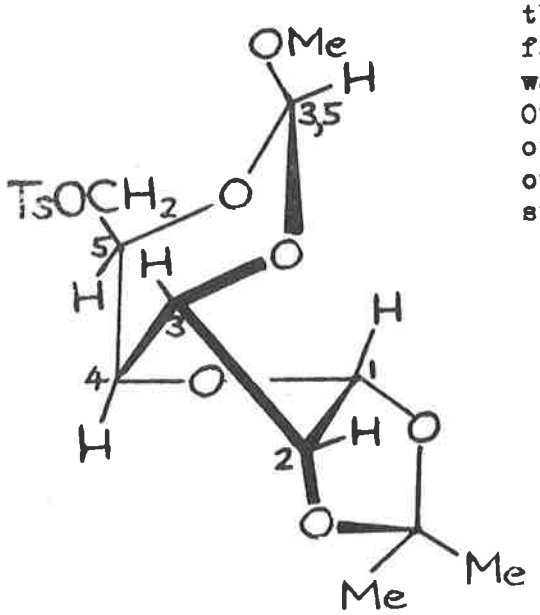
Professor B.L. Shapiro,
Department of Chemistry,
College of Science,
Texas A & M University,
College Station, Texas 77843.

IN REPLY REFER TO:
PMR Spectroscopy and Conformation of 1,2-O-isopropylidene-3,5-O-[(endo-methoxy)methylidene]-6-O-p-tolylsulfonyl-α-D-glucofuranose.

Dear Professor Shapiro,

We have recently investigated a pair of diastereomeric 1,2-O-isopropylidene-3,5-O-methoxymethylidene-6-O-p-tolylsulfonyl-α-D-glucofuranoses. The 100 MHz proton spectrum of one of these (2) was amenable to analysis as a 7-spin system using the LAOCOON 3 program. The observed spectrum and calculated spectrum after six iterations are shown in the Figure, and the corresponding refined parameters in the Table. A reduction in computation time was made by differentiating only the diagonal terms of the 35x35 matrix*. The methylidene proton (H-3,5) showed a small coupling (0.4 Hz) with H-4 (over five bonds), but since these protons were only weakly coupled, H-3,5 was excluded from the analysis so as to avoid having more than seven spins.

Consideration of the vicinal coupling constants and thermodynamic data from equilibration experiments indicated the configuration and conformation shown in the formula, in which the methoxyl oxygen atom and C-6 are syn-axial on the chair conformation of the m-dioxane ring. A strong "anomeric effect" evidently causes this diastereomer to be more stable than that in which the methoxyl group is equatorial. Evidence for the favored orientation of the methoxyl group shown was obtained from an intramolecular nuclear Overhauser effect. Irradiation of the methyl protons of the methoxyl group produced a 25% enhancement of the methylidene proton signal intensity, thus suggesting that these protons are in a cis arrangement.



Sincerely yours,

Bruce Coxon

Bruce Coxon, Research Chemist
Organic Chemistry Section,
Analytical Chemistry Division.

* By Courtesy of Dr. R.B. Johannesen.

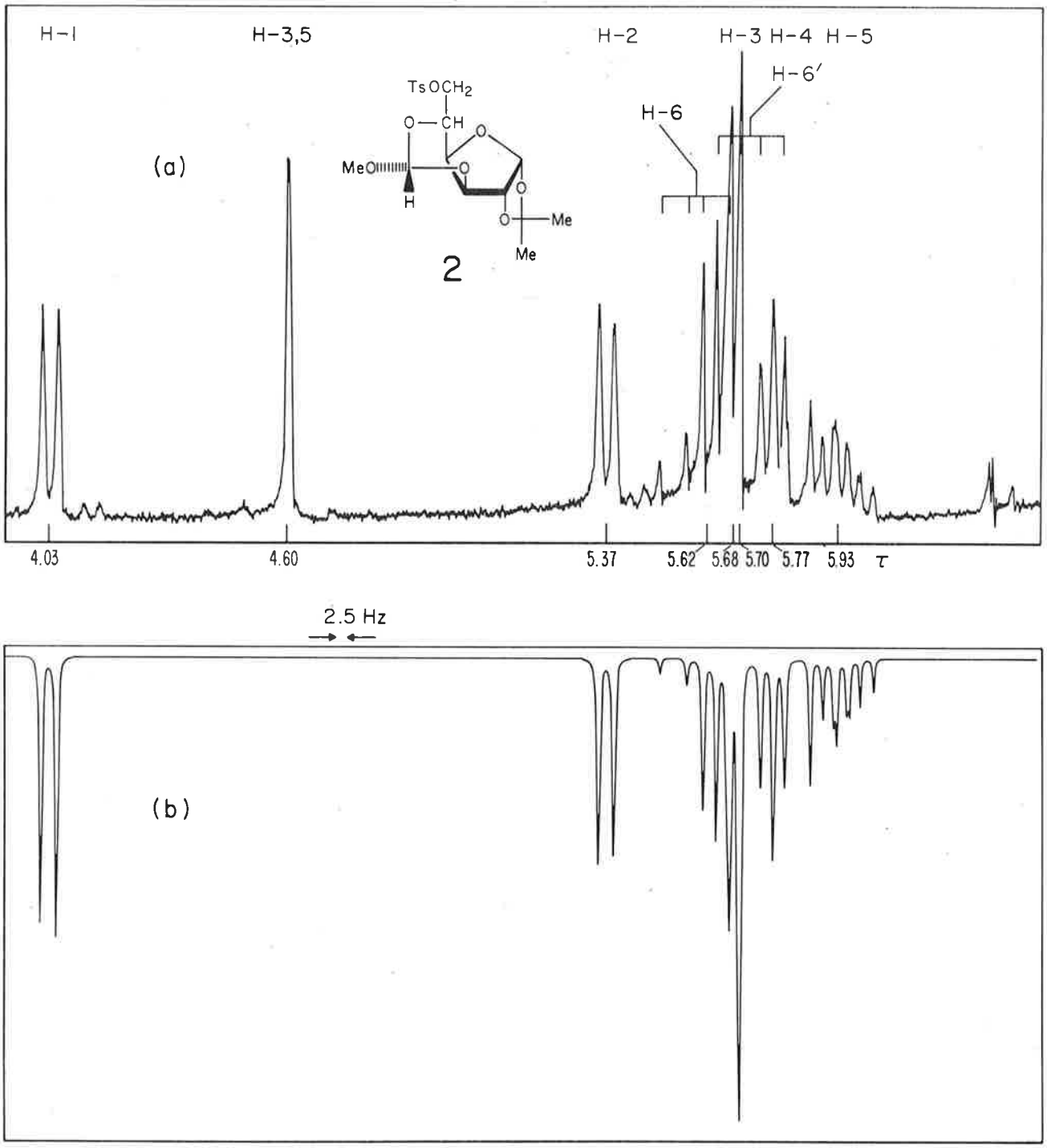

H-1
H-3,5
H-2
H-3 H-4 H-5
H-6′
H-6
(a)
TsOCH2
O—CH
MeO
H
Me
Me
2
4.03
4.60
5.37
5.62
5.68
5.70
5.77
5.93
τ
2.5 Hz
(b)

TABLE I

SPECTRAL PARAMETERS (Hz) OF 1,2-O-ISOPROPYLIDENE-3,5-O-[(ENDO-METHOXY)METHYLIDENE]-6-O-p-TOLYLSULFONYL-α-D-GLUCOFURANOSE (2) AT 100 MHz

Parameter	Initial	Refined (6 iterations)
ν_1	596.97	596.93 ± 0.01
ν_2	462.80	462.83 ± 0.02
ν_3	432.20	431.98 ± 0.02
ν_4	422.30	422.55 ± 0.02
ν_5	407.77	406.69 ± 0.01
ν_6	438.84	438.26 ± 0.02
$\nu_{6'}$	430.55	430.40 ± 0.03
$J_{1,2}$	3.75	3.69 ± 0.02
$J_{1,3}$	0	0.03 ± 0.02
$J_{1,4}$	0	-0.06 ± 0.02
$J_{1,5}$	0	-0.04 ± 0.02
$J_{1,6}$	0	-0.06 ± 0.03
$J_{1,6'}$	0	0.03 ± 0.03
$J_{2,3}$	0.30	0.39 ± 0.02
$J_{2,4}$	0	0.01 ± 0.02
$J_{2,5}$	0	-0.10 ± 0.02
$J_{2,6}$	0	0.38 ± 0.04
$J_{2,6'}$	0	-0.26 ± 0.05
$J_{3,4}$	2.95	2.87 ± 0.02
$J_{3,5}$	0	-0.06 ± 0.02
$J_{3,6}$	0	-0.02 ± 0.03
$J_{3,6'}$	0	0.16 ± 0.04
$J_{4,5}$	3.00	3.31 ± 0.02
$J_{4,6}$	0	0.21 ± 0.04
$J_{4,6'}$	0	0.23 ± 0.03
$J_{5,6}$	6.97	6.02 ± 0.02
$J_{5,6'}$	5.03	6.60 ± 0.03
$J_{6,6'}$	-10.50	-10.64 ± 0.02
$\nu_{3,5}$	539.6	
$J_{3,5:4}$	0.42	

129-22

UNIVERSITÉ D'OTTAWA
DÉPARTEMENT DE CHIMIE

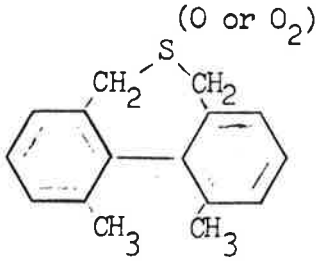
UNIVERSITY OF OTTAWA
DEPARTMENT OF CHEMISTRY

OTTAWA 2, CANADA

May 20, 1969.

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

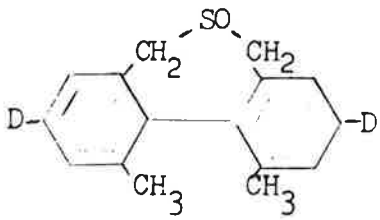
N.O.E.'s on a sulfoxide and a sulfone (I)



I

Dear Barry:

I thought that my experience in trying to obtain N.O.E.s on the sulfoxide I (TAMU #120) might be of some value in that others can profit by my mistakes. We wished to determine which proton of each AB pattern lay in the plane of its adjacent aromatic ring by observing an NOE for it but not for its geminal partner. We took the following steps: 1) Modified our HA-100 to avoid overload of its amplifier; 2) Since the aromatic ring gave an ABC pattern we made the dideutero derivative

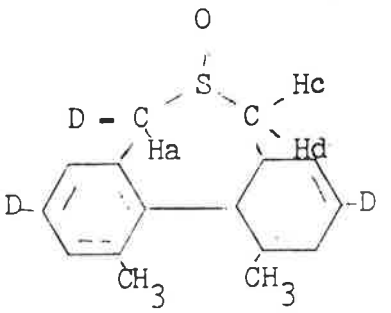


. Now the aromatic region appears as four broadened peaks. Two of these showed N.O.E's when the CH_3's were irradiated. But no N.O.E.'s between any benzylic and aromatic

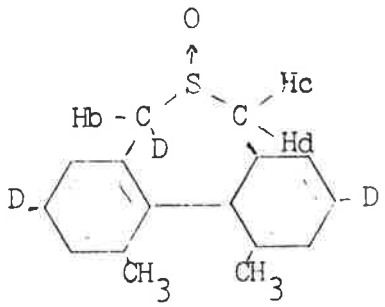
14 and 17%

...2

protons could be seen. 3) Since mutual geminal proton relaxation might be dominant we prepared the two trideutero compounds



and



but again no N.O.E's could be observed. 4) Finally we recalled the tendency of sulfoxides to dimerize. When we switched to D.M.S.O.-d_6 as solvent we observed a 27% N.O.E. for one of the above and a 3% N.O.E. for the other. The detection was repeated independently by a second operator.

Experiments with the corresponding sulfone have been much simpler. In fact when the low-field doublet of the AB pattern for the geminal methylenes was irradiated using two oscillators, one tuned to each line, a 10% increase in intensity for the aromatic region was observed (this is a 20% N.O.E. since all aromatics have the same shift.) Irradiation of the high-field doublet gave no N.O.E.

Finally we chemically inverted the S → O group of some partially exchanged sulfoxide (Chem. Comm. #8, 1969) to relate one AB pattern to the other. The results showed that the two lowest field doublets are assigned to protons in the plane of the adjacent ring. Oxidation of partially exchanged sulfoxide to sulfone confirmed the N.O.E. results.

The moral to us was a) always use DMSO-d_6 as the solvent for N.O.E. work on sulfoxides and b) as a general rule, always try a second solvent if no N.O.E. is found in the first attempt, for the absence of an N.O.E. is an inconclusive finding.

Best regards,

Robert R. Fraser.

RRF:mar

DEPARTMENT OF HYDROCARBON CHEMISTRY
FACULTY OF ENGINEERING
KYOTO UNIVERSITY
KYOTO, JAPAN

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

Dear Professor Shapiro:

^{13}C-^{14}N Spin Coupling Constant in Isonitrile

Recently in collaboration with Goto (JEOL Co., Tokyo) we have obtained ^{13}C-^{14}N spin coupling constants from proton-decoupled ^{13}C spectrum of t-butylisonitrile. In isonitrile the electronic symmetry about the nitrogen nucleleus is expected to be sufficient to give the small electric fild gradient necessary to avoid losing the ^{13}C-^{14}N fine strncure due to quadrupolar relaxation, as has been known for H-^{14}N coupling in isonitrile.

We have carried out proton-decoupled ^{13}C NMR experiment to wash out long-range ^{13}C-H coupling which broadens the ^{13}C signal. ^{13}C-{H} spectrum of t-butylisonitrile shows three carbon signals, lower two signals having triplet fine structure due to coupling with ^{14}N nuclens and the highest field one with singlet sharp line. The observed coupling constants are as follows:

	$\lvert J_{CN} \rvert$ (Hz)
$(CH_3)_3\ C\ \underline{N}\equiv\underline{C}$	4.1
$(CH_3)_3\ \underline{C}\ \underline{N}\equiv C$	5.1
$(\underline{C}H_3)_3\ C\ \underline{N}\equiv C$	0

It seems interesting to compare these values with those for corresponding nitrile molecule. Binsch et al. (J. Am. Chem. Soc., 86, 5564 (1964)) have obtained $^{13}C-^{15}N$ coupling constants for molecules containing various types of hybrid bonds. The $^{13}C-^{14}N$ coupling constants are available from these data by the relation $J\ ^{13}C-^{14}N = -0.713\ J\ ^{13}C-^{15}N$. They become as following:

	$\lvert J_{CN} \rvert$ (Hz)
$CH_3 - \underline{C}\equiv\underline{N}$	12.5
$C_6H_5 - \underline{C}=\underline{N}-CH_3$	4.9
$C_6H_5 - C=\underline{N}-\underline{C}H_3$	2

The substantial difference in the values of J_{CN} for $-N\equiv C$ and $-C\equiv N$ bonds implies that the hybridization in these bonds is different each other. A theoretical approach to explain these observations is now in progress.

Sincerely yours,

T. Yonezawa

T. Yonezawa

I. Morishima

I. Morishima

129-26

UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
4800 FORBES AVENUE
PITTSBURGH, PENNSYLVANIA 15213

May 21, 1969

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

Dear Barry:

PROTON MAGNETIC RESONANCE STUDIES OF COAL EXTRACTS

We have recently measured the hydrogen distribution in pyridine and carbon disulfide extracts of six coals ranging in rank from subbituminous A (76.3% maf carbon) to low volatile bituminous (90.4% maf carbon). The carbon atom distributions were estimated using only the ^{1}H NMR data, elemental analyses, and the equations of Brown and Ladner 1/. Results for the carbon disulfide extracts are summarized in figure 1.

BROADLINE ^{13}C NMR OF WHOLE COALS

We have observed ^{13}C magnetic resonance signals in cylinders of Pittsburgh bituminous coal and St. Nicholas anthracite. The absorption mode was employed. Although the lineshapes were distorted by passage effects, it was possible to estimate the linewidths to be less than four gauss for each coal. The resonance in the bituminous coal was 2-3 times as broad as that in the anthracite presumably due to the greater carbon-13--proton dipolar interactions. Signal-to-noise ratios were enhanced to 5-10 : 1 by spectral time-averaging.

Sincerely yours,

Herb Gus

H. L. Retcofsky R. A. Friedel

1/ J. K. Brown and W. R. Ladner, Fuel, 39, 87 (1960)

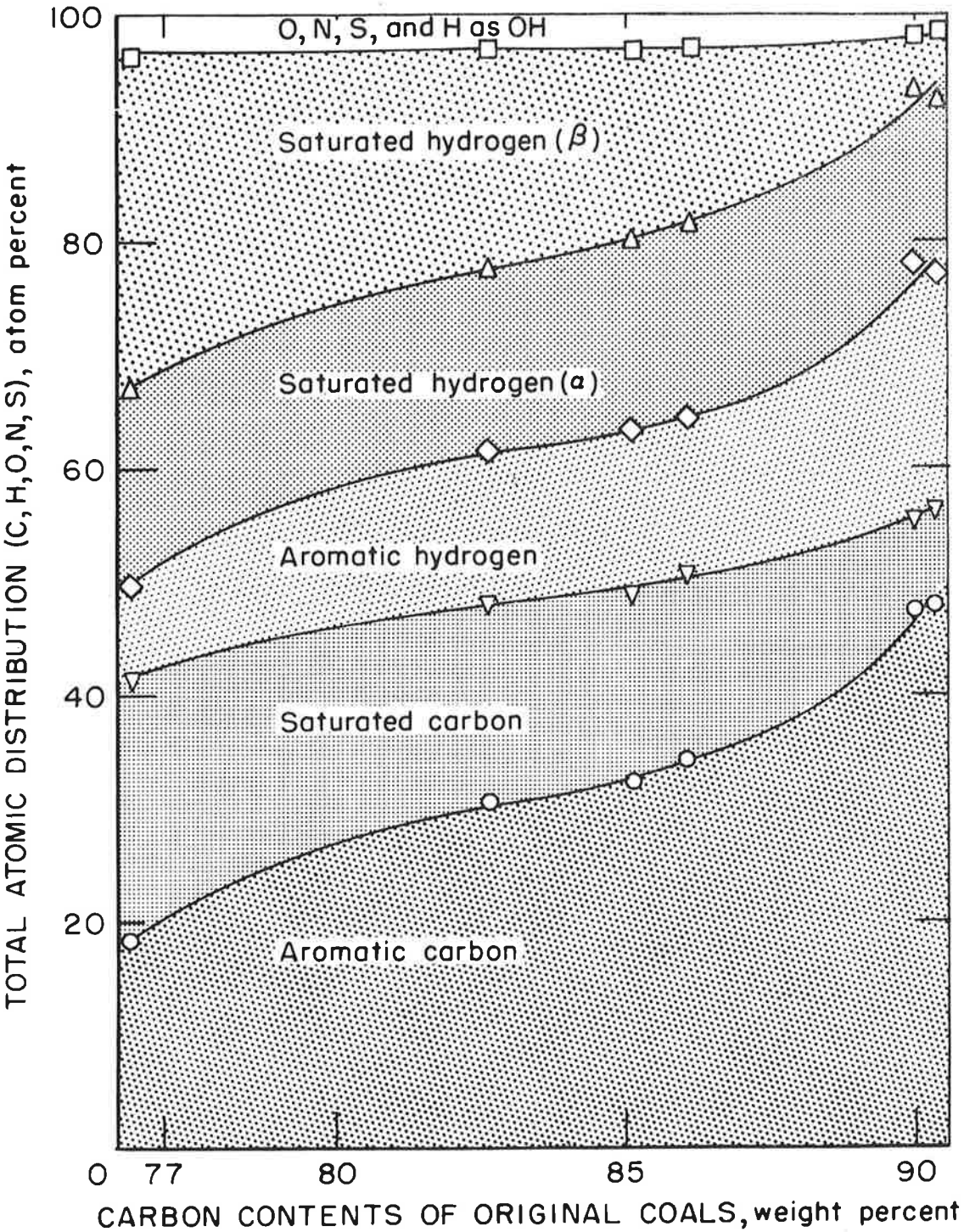


Fig. 1.- Atom distributions in carbon disulfide extracts of selected coals.

11-20-68 L-10912

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

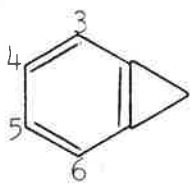
19 May 1969

Refer to: 328-MAC/SLM:sv

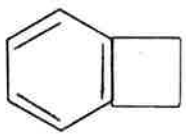
Professor B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Dear Barry:

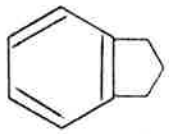
We have been studying the pmr spectra of some strained aromatic systems, e.g., benzocyclopropene, benzocyclobutene, in an effort to define the effect of strain on the aromatic couplings. Some sample results are given:



1



2



3

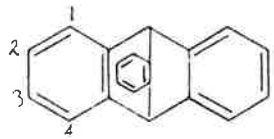
	δ_3	δ_4	J_{34}	J_{35}	J_{36}	J_{45}	RMS(LAOCN3)
1	7.15	7.19	6.04	0.33	1.85	7.63	0.037
2	6.76	6.91	7.36	1.00	1.03	7.79	0.026
3	7.00	7.07	7.59	1.17	0.48	7.20	0.035

The results are for $CDCl_3$ solution. In each case the adjacent methylene(s) were decoupled in the frequency sweep mode. Compound 1 was very kindly provided by Professor E. Vogel, Cologne, Germany.

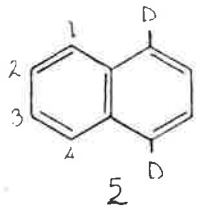
The only clear change is the increase of J_{36} with strain and the decrease of J_{35}. The interpretations of the changes in the ortho-couplings are nothing like so clear cut, and it is difficult to postulate bond fixation as the cause of these differences. At present this work is being (slowly) written up.

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

The use of NMRENIT, LAOCN3 or other iterative fitting programs is well established, particularly for non-explicit spectra, but there is one interesting point about application for explicit systems. This may be illustrated by reference to data for an AA′BB′ system in the literature. The usual "desk calculator" method of Dischler and Englert (Z. Naturforsch., 69, 1180, 1961) places unequal weightings on certain of the transitions. Thus experimental errors in the heavily weighted transitions may be reflected in the final parameters derived from the explicit formulas. This does not happen to the same extent in the complete computer solution. An example may make this clear. Ted Schaefer recently reported (Can. J. Chem., 45, 2155, 1967) the parameters for triptycene (4) shown in Column A. These were derived by a Dischler-Englert treatment. In Column B are the results derived with LAOCN3, using the same reported transition frequencies. There are significant differences in J_{12} and J_{13}.



4



5

	A	B
J_{12}	7.17	7.25
J_{13}	1.27	1.18
J_{14}	0.58	0.59
J_{23}	7.59	7.62

J_{12}	8.30
J_{13}	1.21
J_{14}	0.75
J_{23}	6.84

In connection with this work, we have run the spectra of 1,4-dideuterionaphthalene (5)(Fig. 1a), which gives a rather different set of spectral parameters than have been published for the unsubstituted compound (Fig. 1b).

Re-examining a number of other aromatics at 100 MHz yielded further parameters differing from literature values. Perhaps we will discuss this in our next contribution, hopefully before you get another chance to send us one of your blue letters.

With best regards,

M. Ashley Cooper

Stan

Stanley L. Manatt

Title: P.M.R. Spectra of Some Benzoid Aromatics

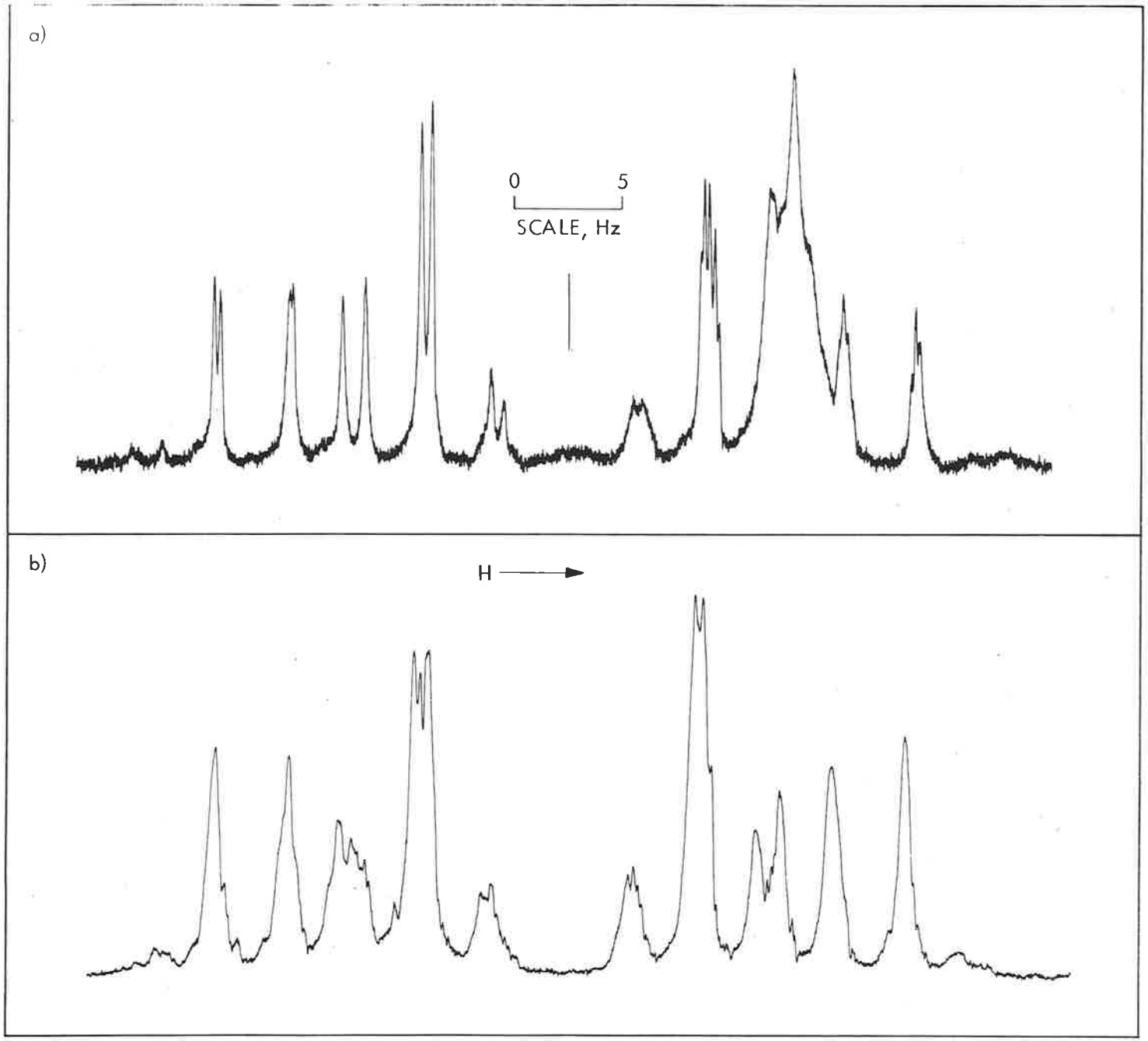


Fig. 1. 60 MHz Spectra of naphthalene. a) $C_{10}H_6D_2$ (1,4-dideuterio), b) $C_{10}H_8$.

THE CHEMICAL LABORATORY
UNIVERSITY OF COIMBRA
PORTUGAL

26th May, 1969

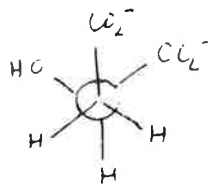
Professor B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843
U.S.A.

Dear Professor Shapiro,

Thank you very much for your reminder.

ON THE STRUCTURE OF THE 1:1 Zn (II) - MALATE COMPLEX.

Use has been made of the dependence of vicinal proton coupling constants upon the H-C-C-H dihedral angle and the nature and relative position of substituent groups in order to decide on the geometry of the ligand in the title complex. The observed values are 4.1 and 5.3 Hz, whereas the corresponding couplings for " free " malate ion are 3.2 and 9.5 Hz. The values for the complex show that the malate is then mainly in the following configuration



Yours sincerely,

Victor M.S. Gil

Victor M.S. Gil

J. S. Mariano

129-32

University of Strathclyde

Professor Patrick D. Ritchie
Professor Peter L. Pauson
Professor Alastair M. North
Professor Peter G. Perkins

Department of Pure and Applied Chemistry

Thomas Graham Building, Cathedral Street, Glasgow, C1
Telephone: Bell 4400 STD 041-552 4400

22nd May, 1969.

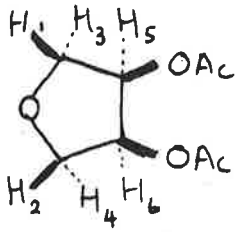
Professor B. L. Shapiro,
Department of Chemistry,
Texas A and M. University,
College Station,
Texas. 77843. U.S.A.

Spectra of Derivatives of cis 3,4-dihydroxytetrahydrofuran

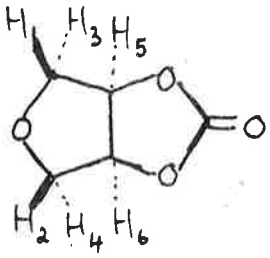
Dear Barry,

We have been looking at the spectra of some derivatives of anhydroerythritol (cis 3,4-dihydroxy-tetrahydrofuran) in which the hydroxyl groups are either normally esterified (e.g. di-acetate I, and dimesylate) or have been caused to participate in the formation of a cyclic derivative (ester or acetal) (e.g. carbonate II). Compounds of the second type include the cyclic sulphite (2 forms) and cyclic orthotrifluoroacetate[1]. Spectra of the two types are clearly distinguishable but analysis of the AA'BB'CC' spin systems has presented us with some headaches. We have been attempting to match experimental spectra with spectra computed with LAME[2], and have found that before a successful iterative calculation can be made, a good guess at the chemical shifts and coupling constants must have been made.

Taking the diacetate(I) and the carbonate as representative the results are as shown.



(I)



(II)

(I) in $CDCl_3$				(II) in $CDCl_3$			
δ_1	4.08	J_{15}	+ 6.3	δ_1	4.24	J_{15}	+ 0.1
δ_3	3.84	J_{16}	- 0.4	δ_3	3.61	J_{16}	+ 0.2
δ_5	5.36	J_{34}	- 0.1	δ_5	5.29	J_{34}	- 0.2
J_{12}	+ 0.1	J_{35}	+ 4.9	J_{12}	- 0.8	J_{35}	+ 4.2
J_{13}	-10.3	J_{36}	- 0.5	J_{13}	-12.3	J_{36}	- 0.8
J_{14}	$\pm$ 0.0	J_{56}	+ 5.7	J_{14}	- 0.8	J_{56}	+ 6.8

The small differences in chemical shifts between the two types are to be expected (and within each of the two types the major differences are seen in chemical shifts) but the differences of J's (particularly J_{15}) are responsible for the differences in the appearance of the spectra of the two types, and are indicative of greater rigidity in the bicyclic ring system (II).

Yours sincerely,

Peter Bladon.

Gordon Forrest.

References

1. Peter Bladon and G. C. Forrest, Chem. Comm., 1966, 481.

2. C. Haigh, TAMUNMR 121. 54. We are greatly indebted to Mr. Haigh for his generosity in supplying us with his program LAME

UNIVERSITÉ D'OTTAWA
DÉPARTEMENT DE CHIMIE

UNIVERSITY OF OTTAWA
DEPARTMENT OF CHEMISTRY

OTTAWA 2, CANADA

May 22, 1969

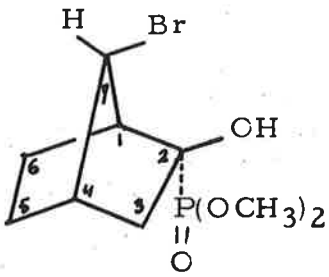
Professor B. L. Shapiro,
Department of Chemistry,
Texas A and M University,
College Station, Texas 77843,
U. S. A.

Dear Dr. Shapiro:

I would like to become a recipient for TAMUN-NMR letters. I understand that this implies a regular participation and I hope the following will serve to initiate my subscription.

Dr. C.E. Griffin has reported in TAMUN-NMR 127, 47 (1969) some cases of four-bonds ^{31}P, ^{1}H coupling (1.1 - 1.2 Hz) and a particularly high P-C-OH coupling (10.0 Hz).

In the course of an NMR study of organophosphorus compounds we have prepared some bicyclo-[2.2.1]-heptane and -heptene phosphonates:



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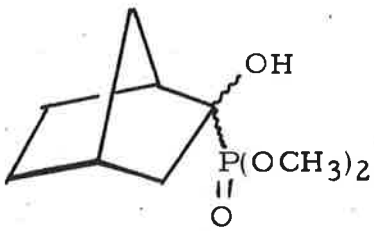
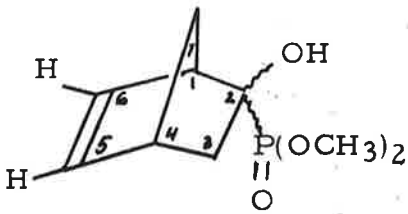


IIa-endo-P(O)(OCH$_3$)$_2$
IIb-exo- "



IIIa-endo-P(O)(OCH$_3$)$_2$
IIIb-exo- "

.....2

It is known that ^{31}P, ^{1}H vicinal coupling constants are a function of dihedral ^{31}P, ^{1}H angles in phosphonates[1]. Such a property and a complete interpretation of IIIb exo-NMR spectrum allow an unambiguous assignment of configuration of the carbon atom bearing the $-P(O)(OMe)_2$ group ($^{3}J_{PH} \sim 0$ for the endo-phosphonate). Among the many ^{31}P, ^{1}H couplings available from the spectra of I, II and III, particularly interesting were a 5Hz P-C_2-C_1-C_7-H coupling in compound I (paralleling the well-known W or M coupling) and a 3 Hz W coupling between P and H-6 in the IIIb-exo isomer. These are the largest $^{4}J_{PH}$ coupling constants ever reported as far as we know. Besides Dr. Griffin's results there is one reported case of $^{4}J_{PH}$ coupling in steroidal phosphonates[2] ($^{4}J_{PH} \sim 0.8$ Hz).

A P-C-OH coupling could be noted in the III-exo isomer and was absent in the endo isomer. The interpretation by Dr. Griffin for non-general P-C-OH coupling in α-hydroxyphosphonate by an intra molecular - P = O ... H-O- bond does not seem to completely account for the above results.

Those results and others (giving other examples of ^{31}P, ^{1}H spin-spin coupling dihedral angle dependence: J_{PH} (0°) ~ 16 Hz, J_{PH} (120°) ~ 6 Hz) will be presented at the C. I. C. Meeting to be held in Montreal in May 1969.

Sincerely yours,

Claude Benezra

Claude Benezra

CB:AE

(1) C. Benezra and G. Ourisson, Bull. soc. chim. France, p. 1825 (1966).

(2) J.A. Ross and M.D. Martz, J. Org. Chem., 34, 399 (1969).

Title: Long range ^{31}P, ^{1}H and P-C-OH coupling constants in some bicyclophosphonates.

I N S T I T U T E

FOR CHEMISTRY OF NATURAL PRODUCTS

ACADEMY OF SCIENCES OF THE U.S.S.R.

Ul. Vavilova, 32 Moscow, V-332

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

26 May 1969

Title: "The Use of the Sign of Long-Range Coupling Constant for Determine Molecular Structure."

Dear Barry,

From this date you can count me as a Muscovite. Just before leaving very hospitable Ottawa after completing the Postdoctorate Fellowship with Dr. S. Brownstein I would like to report some of the results, which was obtained some time ago in Moscow in collaboration with Dr. A.U. Stepanuants.

The configuration of the substituent in the 7-th position of the bicycloheptadiene (I) molecule may be determined by the sign of the long-range coupling constant ^4J of the protons $H_{(5)}$ and $H_{(7)}$. (It might be one of the first examples of application of the sign of protons long-range constant in conformational analysis.)

On the basis of the constants ^4J for a series of bicycloheptene derivatives, the empirical dependence of this coupling constant upon the dihedral angles of the fragment H-C-C-C-H was found [1,2] (Fig. 1). For example, for 1,2,3,4-tetrachlorobicyclo[2,2,1]heptadiene-2,5 during this study it was found that $^4J_{7\underline{syn}-5,6}$ = +0.64 cps and $^4J_{7\underline{anti}-5,6}$ = -0.15 cps [1,2].

The spectrum of bicycloheptadiene (I) (60 Mc/sec, $CHCl_3$ solution) corresponds to the AMX type for the protons in 4, 5 and 7 positions (Fig. 2a). By means of the straightforward spin-tickling and INDOR experiments (Fig.2 f-i) it was found that the long-range coupling constant in

. . . /2

this molecule has the opposite sign relative to the vicinal coupling constants. Assuming that the vicinal constants have, as usual, the positive sign, the results of these experiments can be represented as $^{3}J_{4-5}$ = +3.75 cps, $^{3}J_{4-7}$ = +1.95 cps and $^{4}J_{5-7}$ = -0.30 cps.

On the basis of the empirical correlation (Fig. 1) and the results for the molecule (II) it follows that because the long-range constant in the bicycloheptadiene I has the negative sign, the hydrogen atom in the 7-th position is in anti-orientation in respect to the chlorinated double bond. Without knowing the sign of the long-range constant ^{4}J it would be hard to choose amongst the syn- (|0.15| cps) and anti- (|0.60| cps) orientations. Thus the compound has the structure III.

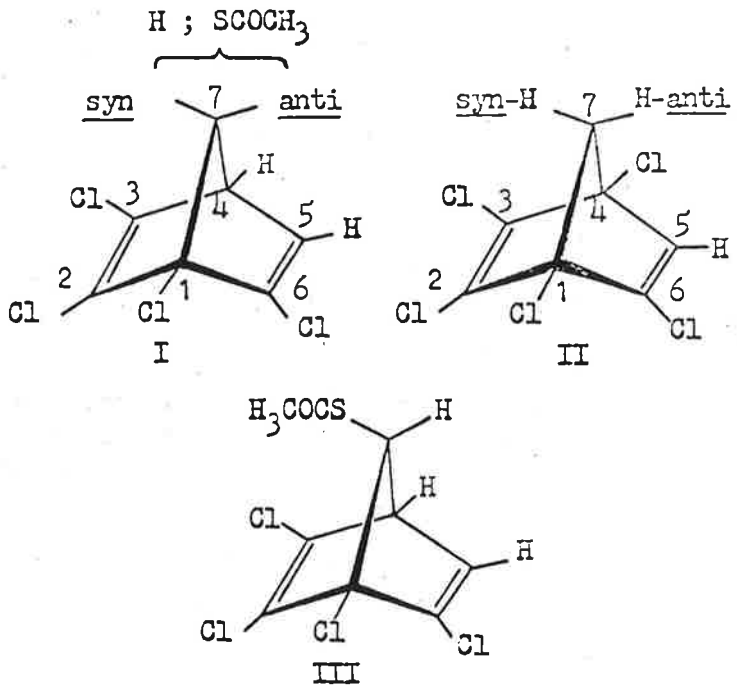
Sincerely yours,

Vladimir Bystrov

References:

[1] V.F.Bystrov and A.U.Stepanuants, Journal of Molecular Spectroscopy, 21, 241 (1966).

[2] V.F.Bystrov and A.U.Stepanuants, in "Radiospektroskopicheskie i Kvantovokhimicheskie Metody v Strukturnikh Issledovaniyakh" (Radiospectroscopical and Quantum Chemical Approaches to the Study of Structure), pp. 147-185; Izd. "Nauka", Moscow, 1967.



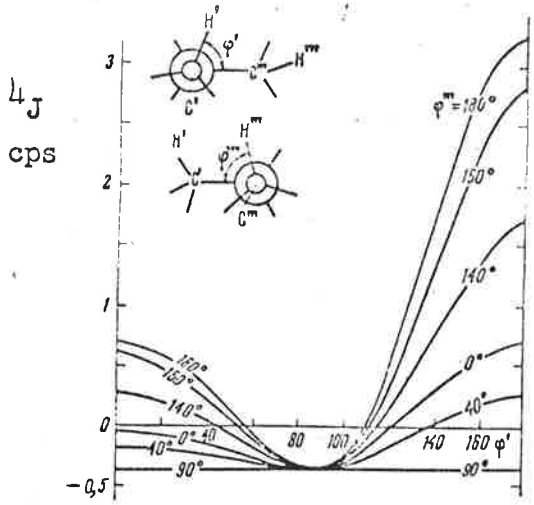


Fig.1. Dependence of the long-range spin-spin coupling constant ^4J (H'-C'-C'''-C'''-H''') on the dihedral angles φ' and φ'''.

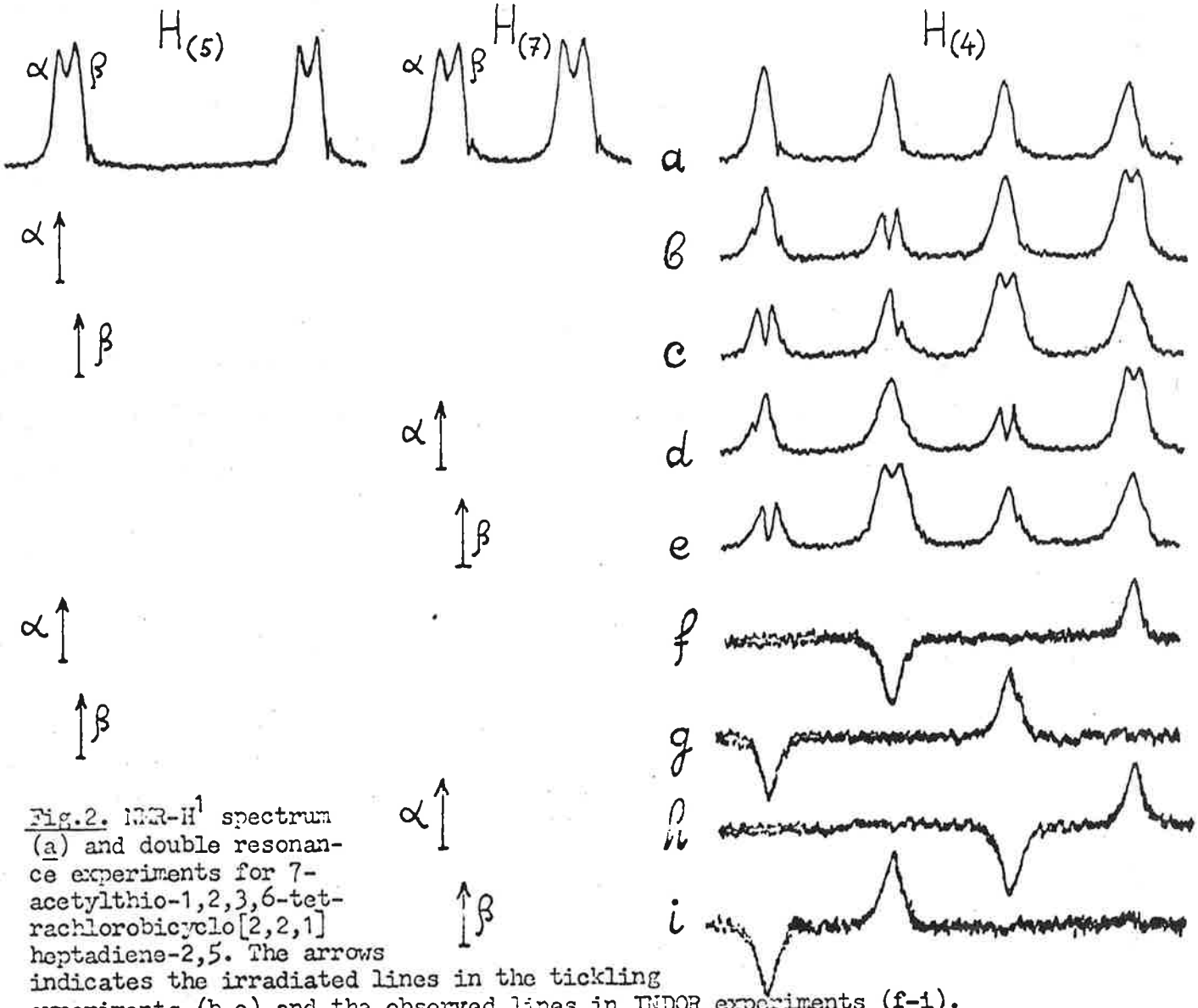


Fig.2. NMR-H^1 spectrum (a) and double resonance experiments for 7-acetylthio-1,2,3,6-tetrachlorobicyclo[2,2,1] heptadiene-2,5. The arrows indicates the irradiated lines in the tickling experiments (b-e) and the observed lines in INDOR experiments (f-i).

PHILIPS RESEARCH LABORATORIES
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Dr.JB/EdW

May 28, 1969

Prof. B.L. Shapiro
Department of Chemistry
Texas A & M University
COLLEGE STATION, Texas 77843
(U.S.A.)

Dear Dr. Shapiro,

Intensity comparison in ABX spectra simplified.

By courtesy of Mr. F.W. van Deursen of Philips Duphar, I am a regular reader of your TAMU Newsletter and I hope you will credit him for my modest contribution. Collection No. 120 contains a letter from Hoffman and Forsén, in which they discuss a simplification of ABX analysis. In my opinion, however, their method may be further improved by avoiding the rather cumbersome trigonometric function, used for the discussion of the intensities of the X part of the spectrum. It seems hardly to be realized, even in modern textbooks, how easily this function may be converted into an algebraic expression. This may be achieved in the following way:

$$\cos^2(\varphi_+ - \varphi_-) = \frac{1}{2}\left\{1 + \cos 2(\varphi_+ - \varphi_-)\right\}$$
$$= \frac{1}{2}\left\{1 + \sin 2\varphi_+ \sin 2\varphi_- + \cos 2\varphi_+ \cos 2\varphi_-\right\}$$
$$= \frac{1}{2}\left\{1 + \frac{J_{AB}^2 + \Delta_+\Delta_-}{4 D_+ D_-}\right\}$$

using the definitions for $\sin 2\varphi_+$ etc. given by Pople c.s.
The latter expression is readily computed with the values collected for the AB part of the spectrum. From the sign applied to $\Delta_+\Delta_-$ in order to obtain conformity between experimental and calculated relative intensities it is immediately obvious which of the possible two solutions is the correct one:

I $\nu_A - \nu_B > \frac{1}{2}|J_{AX} - J_{BX}|$ which is the case when $\Delta_+\Delta_- > 0$, or
II $\nu_A - \nu_B < \frac{1}{2}|J_{AX} - J_{BX}|$ appropriate when $\Delta_+\Delta_- < 0$.

My thanks are due to Mr. van Deursen for ample discussion of this topic.

Sincerely yours,

J. Bakker

Dr. J. Bakker

Universidad de Buenos Aires
Facultad de Ciencias Exactas
y Naturales

BUENOS AIRES, May 26, 1969.-

Prof. Bernard L. Shapiro
Texas A & M. University
College of Science
College Station, Texas 77843
USA

Title: Simple and effective Spinner Air Supply

Dear Prof. Shapiro:

I am very much affraid that this time my contribution to T.A.U.M.UN. will be rather poor, since I am in an "in between" stage, when some work was finished and is in press while the next one is in preparation. We are building some new electronic gadgets, and this takes time.

I would like to express my appreciation for contributions like P.O.E.M. (T.A.UM.U.N. Nr. 126, page 35). Having the burden of mantaining our instrument in operating conditions by ourselves, other peoples's experience is extremely valuable. It was e.g. very interesting to see how people progressively get rid of the cumbersone mercury batteries, replacing them with solid state devices. We did the same will amost all, except the one of the V-2100-B power supply. We just did not dare to. We now see that it is feasible, in spite of the limitations of the Zener diode.

I have been a bit surprised to see the pains which some people take to get an acceptable compressed air supply. We found that, indeed, it is important to have a good control over the spinner speed, and that once adjusted it should remain so. Our solution to this problem seems to us be much simpler than other we saw. We use a Reciprotor Electromagnetic air compressor. It is a small and simple device, working on the principle of mechanical resonance, which uses no oil (though a few drops can be used with advantage) is very clean (there is an in-put filter in which one can put a cotton wad) , noisless, and takes only a few watts (40). It can be simply controlled with a variable voltage autoransformer. We use the model 406-G for 220 V 50 Hz. (60 Hz models

//..

Universidad de Buenos Aires
Facultad de Ciencias Exactas
y Naturales

//..

are available).We found that this unit, even with only 110 V gives enough air for the spinner. It was a simple matter to instal a small Powestat transformer in a convenient place in the console to have a really fine control of the spinner.

The idea of using the Reciprotor pump is not really ours. It is being currently used (or at least, it was in 1964 when I was there) at Varian's in Zurich. It is manufactured by Reciprotor A.S. Krogshøjvej 47, Bagsverd, Copenhagen, Denmark. The price is about u$s 100.

Yours sincerely,

Valdemar J. Kowalewski

Battelle Memorial Institute · COLUMBUS LABORATORIES

505 KING AVENUE COLUMBUS, OHIO 43201 · AREA CODE 614, TELEPHONE 299-3151 · CABLE ADDRESS: BATMIN

May 29, 1969

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

Dear Barry:

Photochemical NMR

We have developed a technique to induce and to observe in situ photochemical reactions in the NMR spectrometer without affecting resolution. In addition to being inexpensive, the technique is also independent of NMR spectrometer geometry. Thus all spectrometers except possibly those incorporating superconducting magnets can probably be used with only dimension modifications of the apparatus.

Figure 1, shows the total optical path, the system components and their relationships. Light from a point source is condensed with a quartz condensing lens (focal length 25-mm). The condensed beam is focused beyond the aluminum front-surfaced mirror 45° to the incident beam, on to the top of the light pipe, which directs the light to the top of the NMR cell.

Two NMR cell designs which have worked well with the light-piping technique are shown in Figure 2, together with details of the light pipe configuration. Since Figure 2 was drawn we have found that a light pipe tapered to about 0.4 cm is a little better for cells like 2A. The cell shown in Figure 2A is a normal 5-mm high precision NMR tube into which is inserted a 3-mm quartz rod long enough to extend just below the surface of the liquid sample. The rod is shimmed with glass spacers to maintain concentricity. The cell in Figure 2B is a 5-mm OD quartz tube in which the lower 3-cm of the inside surface are abraded to provide a mechanism to scatter light piped in the tube wall into the sample. The optical bench is constructed of two separable parts (A and B) which, when assembled, are mounted together with dowel as indicated. Thus, movement of the probe, to exchange samples is unnecessary.

We have barely scratched the surface of Photochemical NMR. Results of our initial experiments, however, indicate that the technique could be a valuable tool and a new data source for both photochemists and NMR spectroscopists since NMR spectra of excited state species can be recorded.

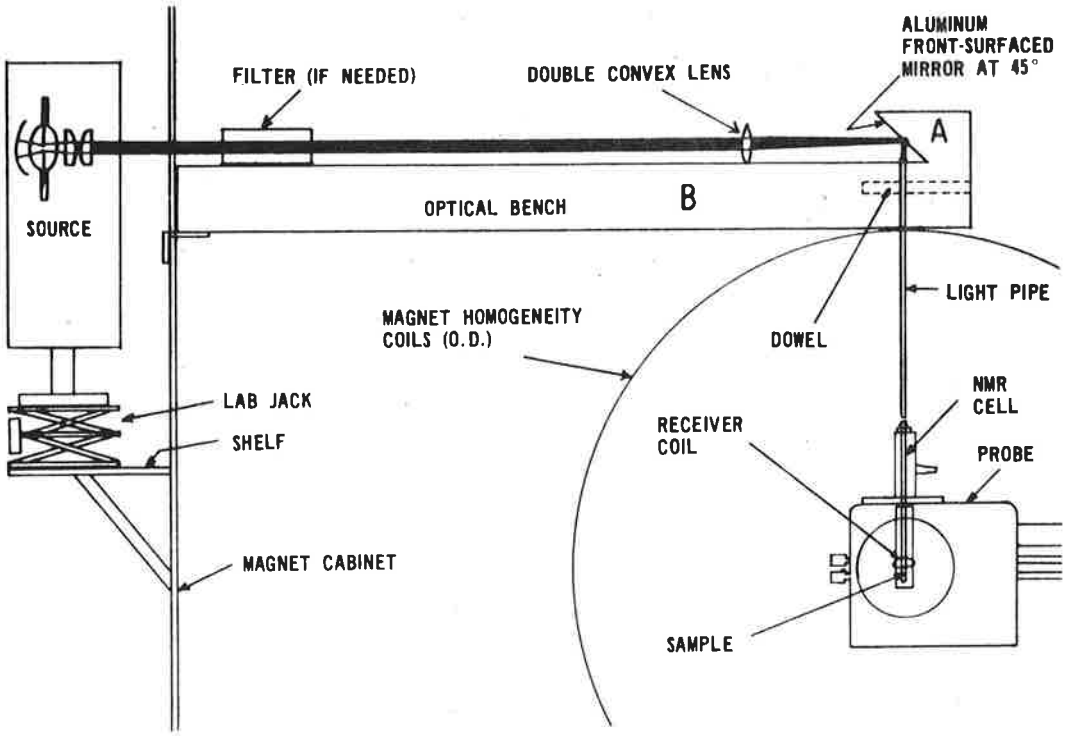


Figure 1. Total optical path

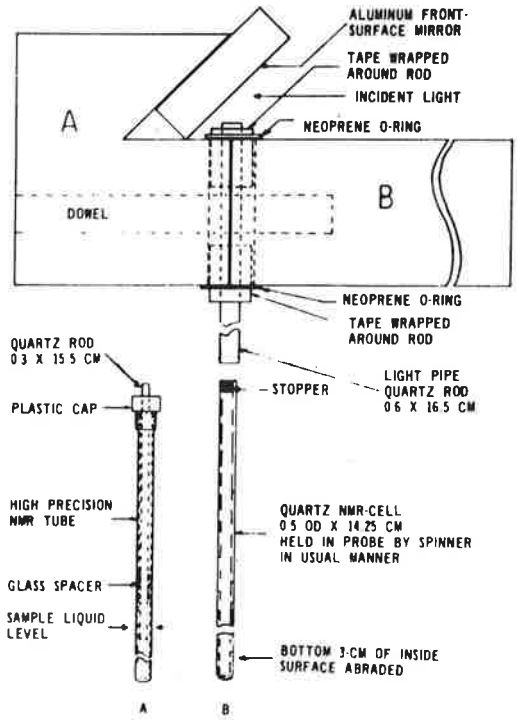


Figure 2. NMR Cell Design and Light Pipe Configuration

Brevity does not permit discussion in this letter of the reactions at which we have looked. However, I shall be glad to discuss what we have done with anyone who is interested. A communication which describes the apparatus and gives proof of methodology development has been submitted for publication. A limited number of preprints are available.

Vacation and reports notwithstanding I shall try to communicate a synopsis of some results with Photochemical NMR very soon.

Best personal regards.

Sincerely,

Tom

Thomas F. Page, Jr.
Senior Research Chemist
Organic and Polymer
Characterization Division

TFP:ejc

digital

May 30, 1969

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

Computer Program Available

Dear Professor Shapiro:

This communication is a notice of availability of a new computer program which is available at no charge. It was developed by D. F. Juers, R. J. Boettcher, V. J. Hull, and H. E. Zimmerman of the University of Wisconsin.

It calculates theoretical spectra for nucleii of spin 1/2. The calculated spectrum is displayed on an oscilloscope. Energies and intensities are printed on a teletype. Up to a six spin system can be handled. This is a small computer program.

The program is available through the Digital Equipment Corporation Users Library (DECUS), including tapes and instructions.

Sincerely,

Charles P. Spector

Charles P. Spector
PDP-8 Marketing

CPS/mlq

DIGITAL EQUIPMENT CORPORATION, 146 MAIN STREET, MAYNARD, MASSACHUSETTS 01754
(617)897-8821 TWX 710 347-0212 TELEX 94-8457

AUBURN UNIVERSITY

AUBURN ALABAMA

36830

SCHOOL OF ARTS AND SCIENCES

Department of Chemistry

Telephone 826-4043
Area Code 205

May 30, 1969

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

pK_a of Nitroethane from Catalyzed Ethanol Exchange

Dear Professor Shapiro:

As payment for our subscription to the TAMU NMR Newsletter you may be willing to accept this preliminary report of some work recently carried out, primarily by Curt Beeman, in our Department.

Ionization constants for nitroethane in water have been reported. However there do not appear to be corresponding measurements in other solvents where solvation effects might be considerably reduced. In this work Curt has utilized the acid catalyzed exchange of the hydroxyl proton of ethanol in nitroethane - ethanol- cycohexane mixtures to estimate the k_a of nitroethane in these systems. The technique was to prepare pure ethanol in which hydroxyl proton exchange was very slow (well resolved triplet). Nitroethane- ethanol- cyclohexane mixtures were prepared in which the ehtanol mole fraction was maintained constant (0.31 ± 0.02 mole fraction). A plot of $1/\tau$ versus mole fraction of the nitroethane was very linear and had a slope of 67.8 $sec^{-1}X^{-1}(EtNO_2)$. A similar set of measurements was carried out in which nitorethane was replaced with hydrogen chloride. The slope of the $1/\tau$ plot was 3.6×10^7 $sec^{-1}X^{-1}(HCl)$. The large slope indicates how sensitive this exchange is as a probe for hydrogen ion concentration. Meiboom has previously published $1/\tau$ values for pure ethanol acidified with HCl. The agreement between Curt's and Meiboom's measurements is very good. Assuming that HCl is behaving as a strong acid (X_{HCl} ca 10^{-7}) and that all hydroxyl proton exchange in the nitroethane system is due to proton catalysis a pK_a value for nitroethane in this solvent system of 11.24 is estimated.

The methylene quartet also under goes some interesting changes which we hope to interpret in terms of the nitroethane- aci-nitroethane equilibrium. However at present we are not ready to comment on this aspect.

Sincerely,

Charles B. Colburn, Head

R. H. Dinius

R. H. Dinius
Associate Professor

RHD:ls

129-48

May 29, 1969

(present address)
Chemistry Dept.
Univ. of Colo.
Boulder, Colo. 80302

(address after 1 August)
Analytical Research & Services
Central Research Laboratories
3M Center, P.O. Box 3221
St. Paul, Minn. 55101

Dear Barry:

I am moving to 3M (Minnesota Mining & Manufacturing Co) in the middle of the summer and would appreciate your counting this letter toward a renewal of the 3M subscription. George Tiers and I would be happy to accept any available back issues at 3M.

LAOCN3 (LAOCOON 3) MODIFICATION. In order to save the time and inconvenience of handling scratch tapes, we have modified the QCPE version (A. A. Bothner-By and S. Castellano, Quantum Chemistry Program Exchange, # 111, Chemistry Dept., Room 204; Indiana Univ.; Bloomington, Indiana 47401) of the program to store the eigenvectors in core. Subroutines CONDIT & NORMAL were revised to save 8000 storage locations, and our 7 spin modified version requires only 21,819 locations on a CDC 6400. Details, written in a "neutral" Fortran II or IV, are available.

PP COUPLING CONSTANTS: A. H. Cowley and W. D. White (J. Am. Chem. Soc., 91, 1913, 1917, 1922 (1969)) recently predicted that J(PP) is +217 Hz in the gauche rotamer and +707 Hz in the trans rotamer of F_2P-PF_2 using a parameterized LCAO-SCF MO theory including overlap. While Ralph Rudolph was at the Air Force Academy in Colorado (he is now at the Univ. of Michigan), he prepared some more P_2F_4 and we used a General Radio 1164 Frequency Synthesizer to perform heteronuclear tickling experiments to determine the signs of the coupling constants (see Table 1). We observed that J(PP) is -230 Hz, or opposite in sign to the calculated value. Internal lock spectra were run on an HA-100; we were able to resolve all 34 peaks in the AA'XX'X"X'" spectrum and determine the smaller vicinal J(FF). (Our enclosed spectrum can be compared to Johnson's, IITNMR 104-12, or J. Chem. Phys., 47, 5449 (1967).) We also observed a reasonable temperature variation of the vicinal J(FF) which we attribute to a change in the populations of the gauche & trans rotamers.

Dr. Rudolph and I have also observed a very interesting temperature variation of the geminal J(PSP) coupling in F_2P-S-PF_2 (see table 2). The geminal coupling changes by almost 100 Hz. We know of no other examples in which a geminal coupling changes by anywhere near this amount; further experiments and speculations on this result are in progress.

Sincerely yours,

Richard

Richard A. Newmark

Title: Another LAOCOON modification; PP Coupling Constants in P_2F_4 & PF_2SPF_2.

Table 1: F_2P-PF_2

	-1°C	-44°	-81°	-101°
J(PP)	-228.6	-229.16	-230.00	-230.31
J(PF)	-1194.1	-1192.9	-1191.4	-1191.1
J(PPF)	+65.79	65.37	64.30	63.96
J(FPPF)	+34.98	35.79	37.05	37.39
J(FPPF')	-1.71	-3.14	-5.27	-5.93

Table 2: $F_2P-S-PF_2$

	-1°C	-42°	-70°	-120°
J(PP)	+302.17	334.55	360.70	392.87
J(PF)	-1307.0	-1306.3	-1305.5	-1305.2
J(PPF)	+30.06	31.28	32.28	33.76
J(FPPF)	+8.86	9.45	9.70	10.48
J(FPPF')	+2.12	1.75	1.78	1.44

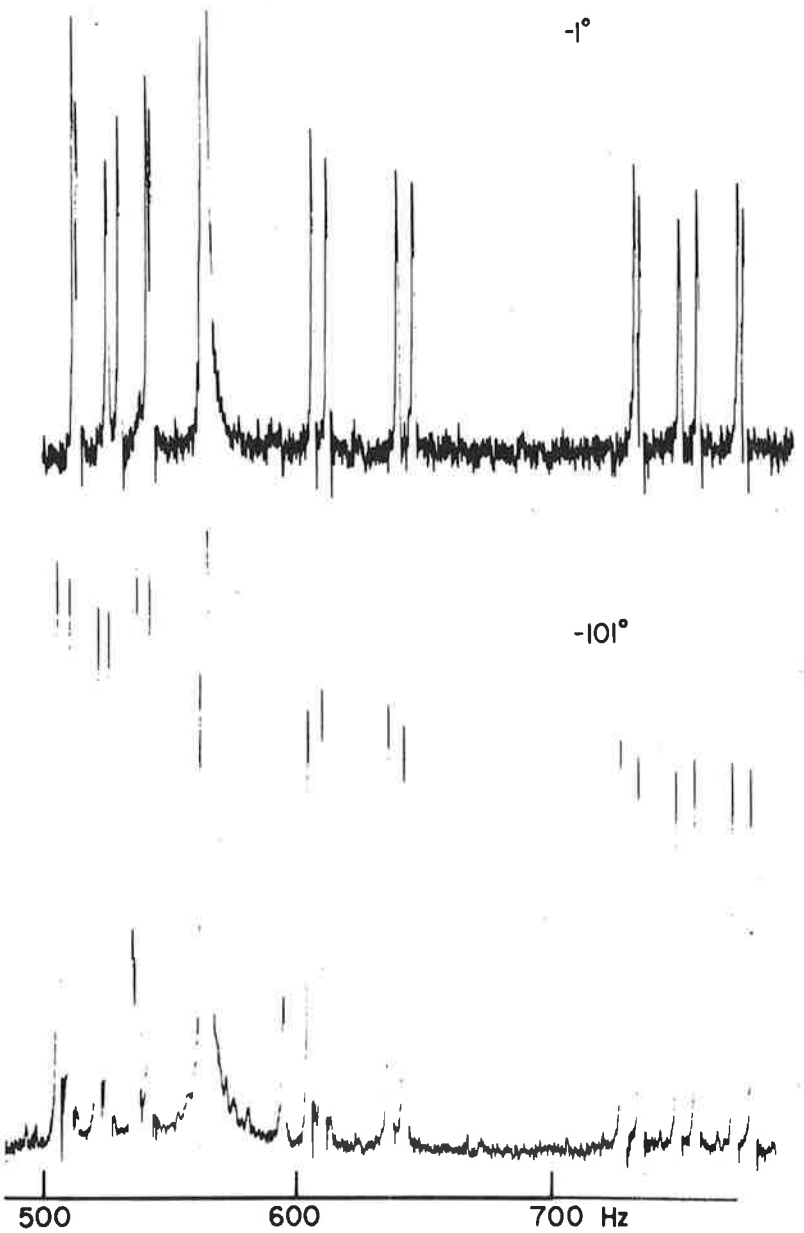
(The geminal J(FPF) was determined as +285 Hz, with a probable error of 13 Hz, from the frequencies of the outer lines in the P spectrum of P_2F_4 at -1°C. We assumed this coupling was +300 Hz in all the other spectra.)

The rms error between the observed & calculated transition frequencies in the upfield half spectrum was less than 0.1 Hz.

Figure:

Spectra of P_2F_4 at -1°C and -101°C.

The spectrum is symmetric, and only the up-field half spectrum is shown. The peak at 564 Hz comprises 50% of the intensity of the half spectrum. Spinning sidebands of this peak are evident in the -101° spectrum.



DEPARTMENT OF CHEMISTRY TUFTS UNIVERSITY MEDFORD, MASSACHUSETTS 02155

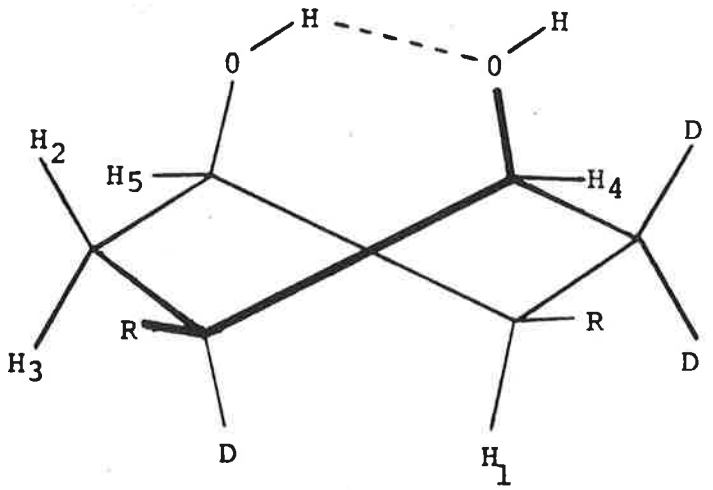
May 30, 1969

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

Can Cyclohexanols Give Negative Vicinal Couplings ($J_{HCCH} < 0$)?

Dear Barry:

We have encountered for an ABCXY system (I) difficulties in analysis similar to those reported in the Newsletter last month, "the hazards of assuming that an excellent match of calculated and experimental spectra signify that the correct NMR parameters have been found" (1). For cis,cis,cis-2,5-di-t-butyl-1,4-cyclohexanediol-2,6,6-d_3 (I), two sets of parameters were obtained which fit the observed spectral line positions equally well.



I

R = t-Butyl

Two Assignments for Diol I

Parameter	Assignment 1	Assignment 2
1	113.96	113.96
2	154.06	154.07
3	183.21	183.19
4	407.44	407.44
5	408.39	408.38
12	0.00	0.00
13	0.00	0.00
14	0.00	0.00
15	1.43	1.43
23	- 14.20	- 14.20
24	± 1.10	± 1.10
25	0.87	- 1.59
34	± 0.06	± 0.06
35	6.68	6.80
45	0.00	0.00
sum of squares of residuals	0.0065	0.0043
sum of square of energy level errors	0.0625	0.0633
average frequency deviation	0.061	0.060
largest frequency deviation	0.16	0.17

The spectrum of I was recorded in dimethyl sulfoxide-d_6 solution at 31° by use of our HA-100 with irradiation of deuterium. Rapid exchange of the hydroxyl hydrogens was observed. Triple resonance experiments in which deuterium and H_4 and H_5 were irradiated simultaneously gave a simple spectrum with a singlet for H_1 and a quartet for the geminal protons, H_2 and H_3.

To distinguish between the two assignments experimentally, a careful decomposition and fitting of intensities, or spin tickling experiments might suffice (1). Although the proper direct experiments have not been carried out to test it, we have concluded that assignment 1 is probably correct.

The only significant difference between assignments 1 and 2 is in the vicinal coupling constant, J_{25} = 0.87, and J_{25} = -1.59, respectively. If diol I can be considered to assume the twist conformation shown, as expected (2), then the dihedral angle Θ_{25}, between protons 2 and 5, would be ca. 88°, while Θ_{35} would be ca. 30°. Therefore, one would expect $J_{35} > J_{25}$, and the value of J_{25} should be essentially the minimum value of a Karplus-type relationship appropriate for diol I. Although we are not aware of any report of a negative vicinal coupling constant for a cyclohexanol derivative, few compounds with dihedral angles close to 90° are known, and a priori, there is no reason to exclude the possibility of a negative value for J_{25}.

However, for related cyclohexanols in chair conformations, the corresponding vicinal coupling constants between the C-1 proton and a proton trans

to it are as follows:

	Θ	J_{vic}	vicinal protons	hydroxyl group
ca.	64°	3.6 ± 0.5	ee	axial
ca.	172°	10.8 ± 0.2	aa	equatorial

Assuming a Karplus-type relationship (3),

$$J = A\cos^2\Theta - B\cos\Theta + C,$$

for which $J \approx C$ at ca. 88°, with C = -1.6 (J_{25}, assignment 2), solving simultaneously for Θ = 64° and Θ = 172° would give A = 17.2 and B = -4.4, but C = 0.9 (J_{25}, assignment 1), would give A = 11.4 and B = -1.2.

The nominal values one would expect (3,4) for A and B for cyclohexanols are $A \approx 10$ and $B \approx 1$. While assignment 2 leads to completely unreasonable values for A and B, assignment 1 gives fair agreement with the expected values. Therefore, we conclude that assignment 1, with a positive value for the vicinal coupling constant J_{25} for a dehedral angle of ca. 88°, is probably correct for diol I.

The long range coupling, J_{24} = 1.10 Hz, may be of interest since the $C\text{-}H_2$ and $C\text{-}H_4$ bonds do not lie in the same plane in the expected nonchair conformation of I shown above. Reversal of the sign of J_{24} had no effect upon the calculated line positions and intensities.

Sincerely yours,

Tony
Anthony Gallo

Bob
Robert Stolow

(1) B. F. Dowden and T. R. Lusebrink, TAMUNMR Newsletter, 128-1 (1969).
(2) R. D. Stolow and M. M. Bonaventura, J. Am. Chem. Soc., 85, 3636 (1963).
(3) C. Altona, H. R. Buys, H. J. Hageman, and E. Havinga, Tetrahedron, 23, 2265 (1967).
(4) R. D. Stolow, T. Groom, and M. Gerace, J. Am. Chem. Soc., 90, 3290 (1968).

DEPARTMENT OF CHEMISTRY

THE UNIVERSITY OF ALBERTA
EDMONTON, CANADA

28 May, 1969.

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

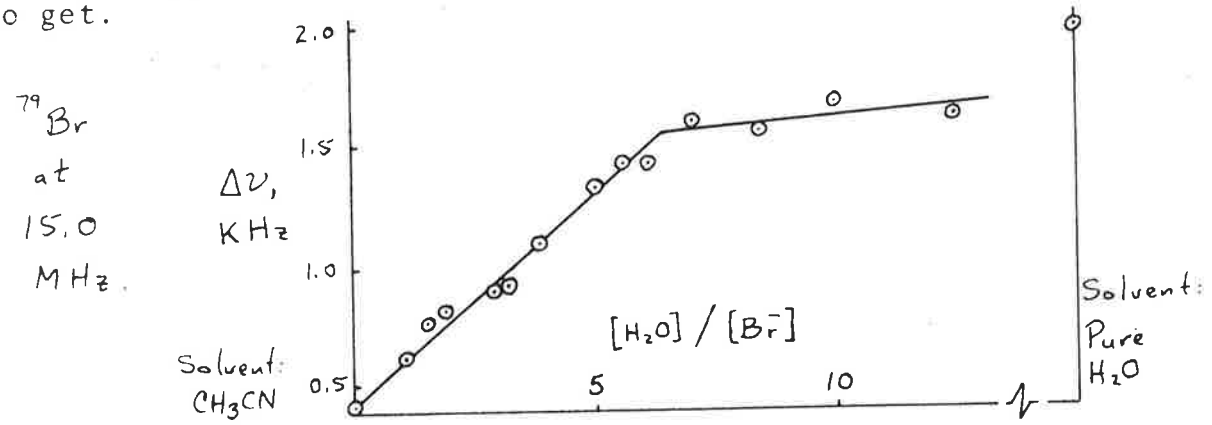
Title: BROMIDE HYDRATION NUMBER (?); POSTDOCTORAL APPOINTMENT AVAILABLE.

Dear Barry,

One of the more entertaining games a solvation chemist can play is to dissolve ions in a weakly-solvating medium, and then monitor some property of the solution as one adds a strongly-solvating solvent. If the property shows a singularity at [STRONG]/[ION] = N (one prefers that N be 4 or 6), one speculates that one has found a way to determine the solvation number of the ion(s) in the strong solvent.

Herewith an entry for bromide ion. Bob Green has measured the ^{79}Br linewidth of 0.2 M tetrabutylammonium bromide in acetonitrile as water is added, and finds a distinct break in the graph (see below) at [Water]/[Br^-] about 6 or 7. At the singularity in slope, [Water]/[CH_3CN] is about 0.06, whereas the linewidth, ca 1500 Hz, is 70% of the way from its value (430 Hz) in pure acetonitrile to its value (1980 Hz) in pure water. This suggests a strong, specific interaction, presumably $Br(H_2O)_n^-$, which saturates at n = 6 or 7.

The more obvious quadrupole relaxation models predict more complex behaviour than that observed, so for the moment we present this as a curiosity. It is interesting, in that halide ion hydration numbers are notoriously hard to get.



There is a postdoctoral position in the general field of ion-molecule interaction available in my laboratory, beginning next September.

Sincerely,

J. S. Martin

John S. Martin

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