Brian D. Sykes

Texas A & M University N-M-R Newsletter

No. 139
APRIL, 1970

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OVER

Deadline Dates: No. 140: 4 May 1970
No. 141: 1 June 1970

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

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

Universidad de Buenos Aires
Facultad de Ciencias Exactas
y Naturales

Physics Department

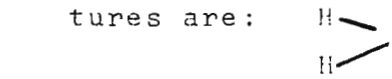
BUENOS AIRES, March 18, 1970.-

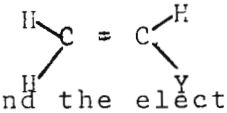
Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843
USA

ABX_3 spectra with $J_{AB} \sim nxJ_{AX}$ or nxJ_{BX} (n = 1,2)

Dear Professor Shapiro:

We have finished a study of ABX_3 spectra in which the A and B group of lines show a superposition of several transitions, which do not allow the relative signs of the J's to be determined.

It was possible to determine the magnitudes and signs of the J's in a series of substances whose structures are:  ; (Y = CN, COOH, OCH, C_6H_5, Br, $COOCH_3$ by using the selective decoupling and the Indor techniques.

Both methods indicate that, unlike what happens with compounds of the structure:  there seems to be no relation between the J's and the electronegativity of Y.

Yours sincerely,

Dr. Valdemar J. Kowalewski

Dra. Dora G. de Kowalewski

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February 9, 1970

Title: Comment on the F NMR spectrum of 1-methoxypentafluorocyclobutene.

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

Dear Barry:

In a recent issue Cavalli[1] reported the coupling constants in 1-methoxypentafluorocyclobutene. He suggested the vicinal and cross ring couplings to the vinylic fluorine are 20.0 and 7.9 Hz, respectively, based on assigning the upfield methylene fluorine resonance to the fluorines vicinal to the more electronegative vinylic substituent. I wish to suggest the opposite assignment of the difluoromethylene groups based on results in several similar 1-methoxy-2-halotetrafluorocyclobutenes.[1,2,3] Long range coupling to the methoxy group is observed from the low-field fluorines in the 2-fluoro, 2-chloro, and 2-bromo compounds. Since it is extremely unlikely that the stereochemistry of the long range coupling changes in these compounds, the lowfield resonances, must be assigned to the same fluorines in all four molecules. The rule[1] that the upfield resonance should be assigned to the fluorines vicinal to the more electronegative substituent appears to be inapplicable to this series.

The relative chemical shifts of the methylene fluorines have been calculated using electric field theory[4] with $B = 30 \times 10^{-18}$ e.s.u.[2] The calculated values reproduce the observed trend in the chemical shifts for the chloro, bromo, and iodo isomers and suggest that the upfield difluoromethylene group is vicinal to the more electronegative oxygen in these compounds. Admittedly, this type of calculation is very qualitative because it shows that the assignment of the methylene fluorines in the pentafluoro isomer should be opposite to that in the other three compounds. Also, the calculated chemical shift difference between the difluoromethylene groups in 1-chloropentafluorocyclobutene is 3.5 ppm, whereas the observed difference is only 0.6 ppm.[2]

In conclusion, the assignment of the fluorines in these cyclobutenes from chemical shift arguments remains very speculative. I favor the chemical shift assignment given in the table (which is opposite to Cavalli's assignment) primarily because this gives a vicinal $^3J_{FF}$ coupling, 7.9 Hz, which is more in line with the vicinal $^3J_{FF}$ couplings in 1,4,4-trifluorocyclobutene (3.8 Hz) and 1,4,4-trifluoro-2-chlorocyclobutene (4.9 Hz).[2]

Sincerely yours,

Richard A. Newmark

Richard A. Newmark
Analytical Research & Services

RAN:jz

1. L. Cavalli, TAMUNMR Newsletter, 134-32
2. R. A. Newmark, G. R. Apai, and R. O. Michael, J. Magnetic Resonance, 1, 418 (1969); R. A. Newmark, unpublished results.
3. S. F. Campbell and E. F. Mooney, unpublished results quoted in E. F. Mooney, Annual Review of NMR Spectroscopy, 1, 261 (Academic Press, 1968).
4. J. Feeney, L. H. Sutcliffe and S. M. Walker, Mol. Phys., 11, 129, 137 (1966).

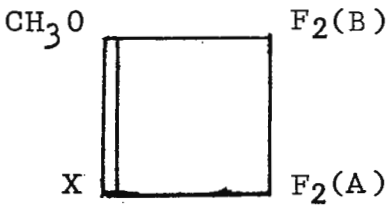

Table. Observed and calculated (see text) chemical shifts in 1-methoxy-2-halotetrafluorocyclobutenes. The calculated values are given relative to the chemical shifts of the chloro compound. The assignment of the observed chemical shifts is uncertain; the long range coupling to the methoxy is from the lowfield fluorine resonance.

X	observed chem shifts (ppm)		$J(F_A,OCH_3)$ (Hz)	calculated chem shifts (ppm)		reference
	A	B		A	B	
F	117.1	119.7	0.47	121.4	119.0	1
Cl	117.2	118.5	0.51	117.2	118.5	2
Br	115.8	118.1	0.46	116.0	118.3	2
I	113.7	117.2		114.5	118.0	3

N.V. **PHILIPS-DUPHAR**

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TELEGRAMS:
VITAMINE - WEESP

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

Uw ref./Your ref.	Onze ref./Our ref.	Afd./Dept.	Datum/Date
	FvD/BZ/47	56630	March 9, 1970

Hindered rotation of a dichlorophenylmethane.

Dear Dr. Shapiro,

We would like to present an example of hindered rotation due to steric interaction by chlorine atoms. At room temperature the NMR spectrum of 3,5-bis (dichloromethyl)-2,4,6-trichloronitrobenzene (Fig. 1) in $CDCl_3$ shows a broad hump (Fig. 2), which sharpens to a singlet at higher temperatures. At the lower temperature limit (-30°C) the spectrum consists of four singlets. Inspection of Newman projections (Fig. 3) reveals that each methylene chloride group in this molecule can have six orientations, of which the exchanges between 1a and 1b, respectivily between 3a and 3b, can expected to be fast, while the probability of 2a and 2b is low. Consequently each methylene chloride group would have two main orientations, 1ab and 3ab, between which the exchange is slow. Combined with the other, equivalent methylene chloride group in the molecule this compound may exhibit three configurations, two symmetrical ones, giving rise to one singlet each, and an asymmetrical one, giving rise to two singlets. From the low temperature spectrum it appears that the abundance of each of the three configurations is appreciable and therefore the energy differences between them must be small.

Yours sincerely,

F.W. van Deursen
G. Breman

N.V. PHILIPS-DUPHAR
Research Laboratories,
Dept. 30

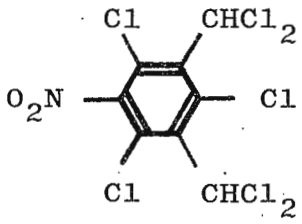


Figure 1.

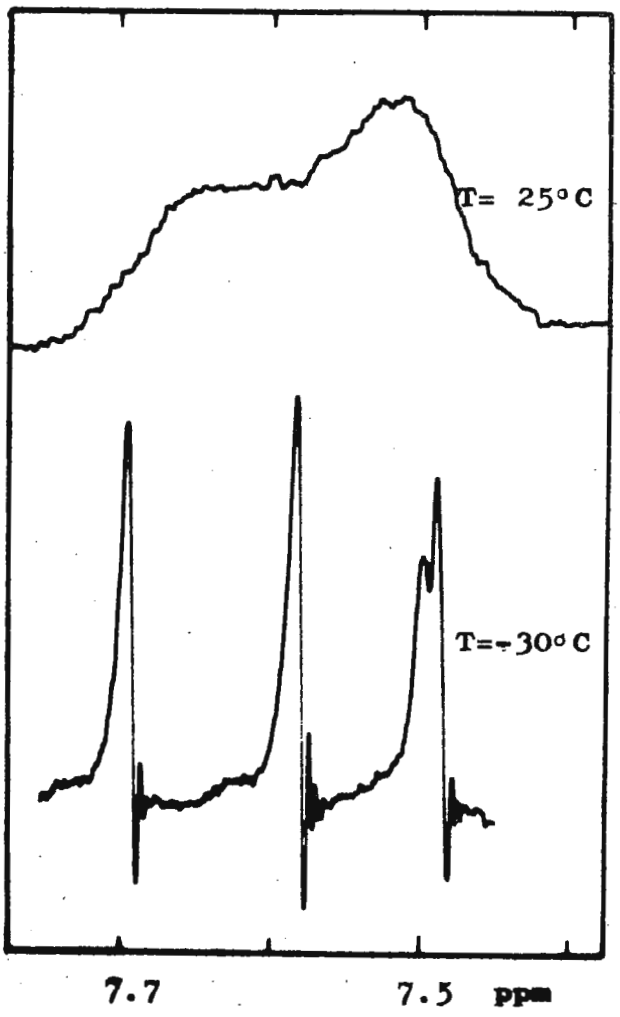


Figure 2.

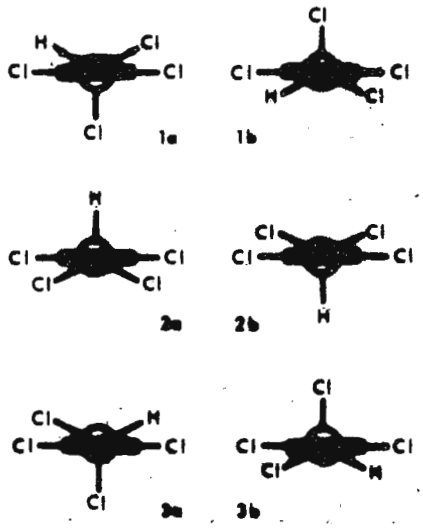


Figure 3.

THE UNIVERSITY OF UTAH

SALT LAKE CITY 84112

DEPARTMENT OF CHEMISTRY
CHEMISTRY BUILDING

March 11, 1970

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

Liquid Nitrogen Trap-Coil Assembly for Low Temperature NMR

Dear Dr. Shapiro:

The cooling coils provided with current varible temperature probes are generally too efficient. Nitrogen often condenses inside the coils, and plugs of liquid nitrogen are carried into the probe. The obvious result is poor temperature regulation.

We have solved the problem of condensation while still maintaining efficient cooling by using the trap-coil assembly shown in the accompanying diagram. The apparatus consists of two sets of coils and a trapping chamber. The nitrogen flow is routed through a set of coils inside the chamber, to the outer coils, which are surrounded by liquid nitrogen. Any liquefication which occurs in the outer coils is trapped when the cold nitrogen stream empties into the chamber. The chilled gas exits from the top of the trap. The trap can be used for extended periods of continuous operation because the warm inner coils evaporate any condensate which collects in the bottom of the chamber.

Our traps were constructed by the department glassblower out of common Pyrex stock items. Except for periodic reannealing, they have provided trouble free cooling for low temperature work.

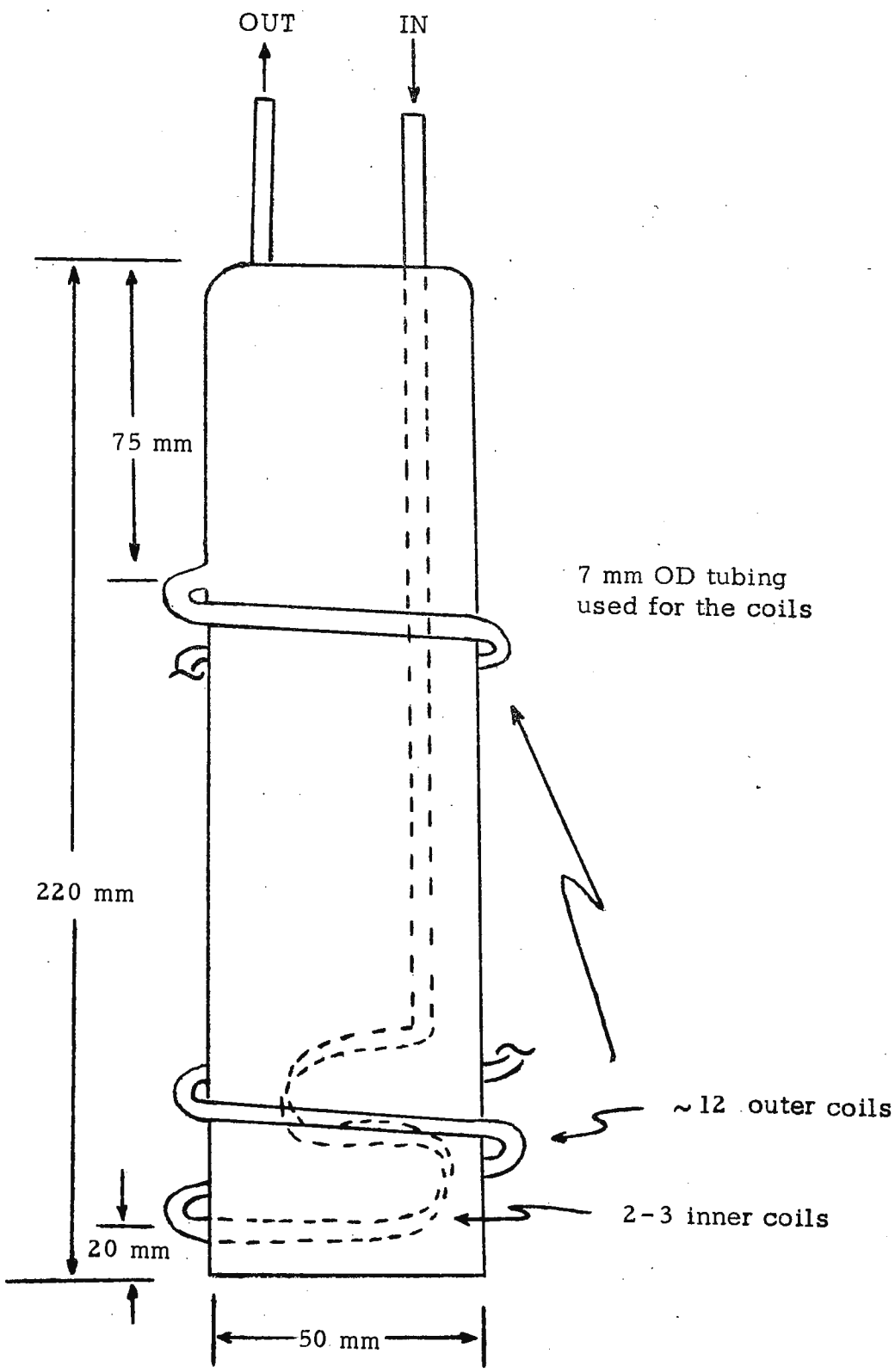
Please count this contribution toward Dr. Grant's subscription.

Very truly yours,

C. Dale Poulter

C. Dale Poulter
Assistant Professor

CDP:bjh


OUT
IN
75 mm
220 mm
20 mm
50 mm
7 mm OD tubing
used for the coils
~12 outer coils
2-3 inner coils

THE UNIVERSITY OF MANITOBA

DEPARTMENT OF CHEMISTRY WINNIPEG, CANADA

March 12, 1970

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

Dear Barry,

Short title: A bit of doggerel looking for a good tune.
or Excerpts from the waist land.

You bother me with letters blue,[1)]
Imply that I will come to rue
My tardiness in writing you
About our doings fine and new.

You try to wake my cogitation!
Remembering that T_1 relaxation
Depends on robust stimulation
Of Schaefer, sunk in dissipation?

Before your final letter red
Comes to say that you are fed
Up with such a slug-a-bed,
Here is my missive to be read:

We did offer methyl nitrate
To other molecules as bait
To see if we could separate
Effects of friction [2)] on the fate
Of azote's [3)] level-jumping rate
From other causes [4)] known to date.

Our line-shape fits[5)] are going well,
But 'tis too early sure to tell
If Binsch's way of fitting many
Is better than Anet's uncanny
Peaking of the Gaussian bell.

If halogens nasty present their derrieres[6)]
Single bonds and their rotational barriers
Cannot be found via M.O. carriers.
It behooves us therefore to play with a function
Which allows us to fit with empirical unction
The experimental to the calculational junction.
We have played this game with some success:
With halogen-toluenes we managed to guess
The stable conformers with some finesse.

When amino protons are hydrogen bonded
To neighbouring groups which are properly ronded,
They don't do what we thought they do
But hop between atoms with much ado [7)]
It seems they shouldn't
And we wish they couldn't
But wait pro tem
It's in Can. J. Chem.

Christine and Helen, Rod and Fred
Brian and Jim and Mark have led
In doing the work to earn their bread.

Notes

1) My admiration knows no bounds
For editors and other hounds
Who dutifully do their rounds
With prods and threats and other sounds.

2) Aye, there's the rub
For Scholar Lehn and sub
Have partly scooped us from this tub.

3) This word is used in comprehension
That firm and constant use-abstention
Of simple words is a convention.

4) Causes have effects
And effects causes
But poetry elects
To have these clauses.

5) If you want the elocution
Of the compounds' appelution,
See our recent contribution
To this journal's page pollution.

6) My apologies to French Canadians
Whose amour propre is here invadians.

7) About nothing, of course.

Yours hopefully,

Ted Schaefer
Professor ?

TS/lg

P.S. Has anybody a 12 inch current stabilized magnet on offer? A nice old fashioned high impedance Varian magnet would do nicely.

University of East Anglia

From Dr. R.K. Harris.

School of Chemical Sciences
University Plain
Norwich NOR ~~88X~~ 88C, ENGLAND
Telephone Norwich ~~XXXX~~ 56161.

23 March 1970.

Dear Barry,

SENIOR RESEARCH ASSOCIATE WANTED

I would like to use the pages of TAMUNMR to advertise a position available here for work in NMR. The post is at Senior Research Associate level (salary scale £1240 - 1585 per annum, with starting rate depending on qualifications) and is held in conjunction with the Science Research Council Atlas computer at Didcot, Berks. The object is to co-ordinate and develop work on computer applications to NMR. In particular this involves establishing a library of FORTRAN routines for use on Atlas. We already have eight such programs in the library. Some updating is necessary, but most of the work consists of modifying programs obtained from other sources or writing new programs. Development work is usually done using the University of East Anglia computer (I.C.L. 1905 E). Some opportunities will be available for application work, and the School anticipate having an 8000 word computer on-line to our HA100 instrument in ca. 9 months' time. The Atlas computer at Didcot is available to all U.K. universities, and the successful applicant for the post will be expected to maintain contact with other British NMR spectroscopists.

The post is for a period of two years, and I would expect the man appointed to stay the full time. The appointment starts for preference on 1 July 1970. F.S.S.U. benefits are paid. Applicants should get in touch with me directly, and should give details of their academic career (particularly with regard to experience in theoretical chemistry, NMR spectroscopy, mathematics and computing). They should themselves ask two referees to write to me in support of the application.

Best wishes,

Robin

R.K. Harris.

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

RKH/MAC.

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March 18, 1970

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

Dear Prof. Shapiro:

^{35}Cl NMR of Zinc Complexes

We are continuing a study of Zn^{2+} complexes by ^{35}Cl NMR and have recently studied a number of smaller zinc chelates ranging in size from Zn (glycinate) to the Zn (iminodiacetate) complex. We describe the amount of ^{35}Cl relaxation produced in 0.5M NaCl by a given complex in terms of its molar relaxivity parameter, $\bar{\nu}$. In these systems $\bar{\nu} \propto P \times q^2 \times \tau$ where P, represents the probability of Cl^- binding, q, the electric field gradient experienced by a bound ^{35}Cl and τ, the tumbling time for the complex. Values of $\bar{\nu}$ are obtained from an analysis of pH vs. ^{35}Cl NMR line width titrations of 0.5M NaCl solutions containing Zn^{2+} and a chelating molecule. Below we summarize some of our observations.

(1) When Zn^{2+} (aq) is complexed by a bidentate ligand, $\bar{\nu}$ usually increases due to an increase in q and or τ. When one chelating atom is sulfur, there appears to be a particularly large increase in q.

(2) Chelation by tridentate ligands may either increase or decrease $\bar{\nu}$ relative to its aqueous value. There are clearly opposing factors operating. A decreased accessibility of the metal ion in this type of complex is often compensated for by an increase in the q experienced by bound chloride.

(3) The formation of 1:2 complexes usually reduces the accessibility of the Zn^{2+} ion to zero. There are exceptions, however. For example, the formation of Zn (Glycinate)$_2$ does not reduce ^{35}Cl relaxation by Zn^{2+} to zero. Because the two glycine ligands use only four coordination sites and because each ligand contributes only one negatively charged atom for chelation, the Zn^{2+} remains available for chloride binding.

Sincerely yours,

James Happe

James Happe
Raymond Ward (subscription credit)
Bert Holder
Al Maddux

JH:ob

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 18 Mars 1970

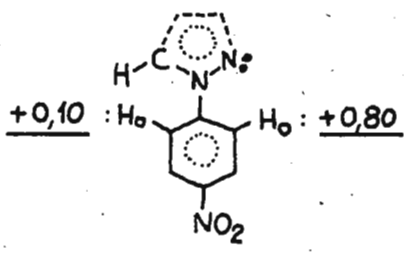
Professeur B.L. Shapiro
Department of Chemistry
Texas A and M University
College Station
TEXAS 77843 U. S. A.

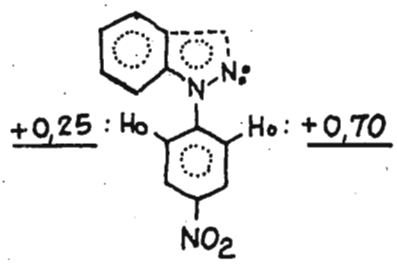
Titre : ATROPOISOMERIE DES N-ARYL AZOLES.

Cher Professeur Shapiro,

La RMN nous a permis de déterminer l'atropoisomérie des (dinitro-2',4' phényl)-1 azoles et benzazoles en solution dans le $CDCl_3$.

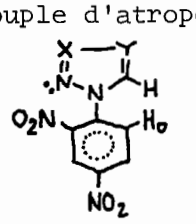
Partant de la valeur δ = 7,27 pour les protons du benzène et d'un effet de + 0,23 ppm pour un groupement nitro en meta [Van Meurs, Rec. Trav. Chim. Pays Bas, 87, 145 (1968)] nous avons calculé pour les p-nitrophényl azoles et benzazoles les increments suivants:

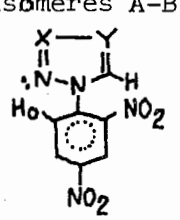


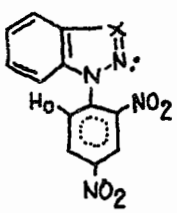


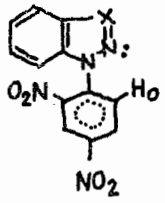
p-Nitrophényl-1	δ_o exp	δ_o calc [7,27 + 0,23 = 7,50]
Pyrrole	7,58	7,50 + 0,10 = 7,60
Imidazole	7,59	
Triazole-1,3,4	7,62	
Pyrazole	7,90	7,50 + (0,10+0,80)/2 = 7,95
Triazole-1,2,3	7,99	
Triazole-1,2,4	7,92	
Tétrazole-1,2,3,4	7,98	
Triazole-1,2,5	8,30	7,50 + 0,80 = 8,30
Indazole	7,98	7,50 + (0,70+0,25)/2 = 7,97
Carbazole	7,73	7,50 + 0,25 = 7,75

Avec ces incréments nous avons calculé le déplacement chimique du proton H_o des dérivés N-dinitro-2,4 phénylés pour chaque couple d'atropoisomères A-B et C-D.


A

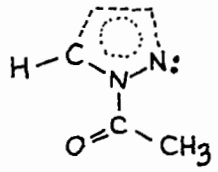

B


C


D

(Dinitro-2',4' phényl)-1	δ_o exp	δ_o calc [7,27+0,46 = 7,73]		Atropoisomère predominant :
		A,C	B,D	
Pyrazole	7,84	7,83	8,53	A
Triazole-1,2,3	7,92			
Triazole-1,2,4	7,91			
Indazole	8,02	7,98	8,43	C
Benzotriazole	8,02			

Nous avons aussi essayé de déterminer la configuration de N-acétyl azoles par une méthode analogue : la cohérence est moins bonne, mais il apparait que la configuration privilégiée est celle réprésentée par E :


E

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

R. JACQUIER.-

J. ELGUERO.-

SCHEIKUNDIG LABORATORIUM
DER VRIJE UNIVERSITEIT
AMSTERDAM-Z.

De Lairessestraat 174 - Telefoon 71 74 51

AMSTERDAM, March 24, 1970.

Uw ref.:

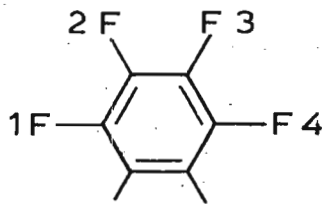
Onze ref.:

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

The chemical shift anisotropies in 1,2-dibromotetrafluorobenzene

Dear Professor Shapiro,

We would like to report our measurements of the NMR spectra of 1,2-dibromotetrafluorobenzene, both in CCl_4 and in nematic solvents.



The analysis of the spectrum in CCl_4 was quite simple, 1,2-dibromotetrafluorobenzene being an AA'XX' spin system. Subspectral analysis of the spectrum yielded values for the indirect couplings which agree with the values recently published by Cooper (1).

From the analysis of the spectra in nematic solvents the following parameters have been obtained

$$J_{12} = -21.5 \text{ Hz}$$
$$J_{13} = 2.9$$
$$J_{14} = 8.2$$
$$J_{23} = -19.7$$

exp. 1 (t = 42° C)	exp. 2 (t = 47° C)
D_{12} = - 1247.7 ± 0.4 Hz	D_{12} = - 1008.0 ± 0.9 Hz
D_{13} = - 246.2 ± 0.4	D_{13} = - 198.5 ± 1.0
D_{14} = - 178.4 ± 0.5	D_{14} = - 144.1 ± 0.9
D_{23} = - 1345.9 ± 0.5	D_{23} = - 1091.9 ± 1.0
$\sigma(1)$ = 2610.5 ± 0.3	$\sigma(1)$ = 2777.1 ± 0.6
$\sigma(2)$ = 3786.0 ± 0.3	$\sigma(2)$ = 4037.9 ± 0.6
Chemical shifts have been measured with respect to an internal reference (CF_4) at a frequency of 56.4 MHz.	

We are interested in the change of the chemical shift due only to the orientation. Hence corrections on the measured change in the chemical shift have to be made for the influence of the temperature difference and for the solvent effect which accompanies the transition from the isotropic to the nematic phase (2).

By extrapolating the isotropic chemical shifts, measured at 58°, 67° and 75° C, the isotropic chemical shifts at 42° and 47° C were found :

	exp. 1	exp. 2
$\sigma(1)$ =	3554.5 Hz	3553.1 Hz
$\sigma(2)$ =	5180.2	5179.7

By subtracting these values from the corresponding values in the table a downfield change in the chemical shifts is obtained

	exp. 1	exp. 2
$\Delta\sigma(1)$ =	944.0 Hz	776.0 Hz
$\Delta\sigma(2)$ =	1394.2	1141.8

The correction for the influence of the isotropic to nematic transition on the reference molecule CF_4 has been inferred from experiment 2, where signals from molecules dissolved in nematic and isotropic layers were obtained simultaneously. A downfield shift of 23.5 Hz was found by going from the isotropic to the nematic phase. Applying this correction gives

	exp. 1	exp. 2
$\Delta\sigma(1)$ =	967.5 Hz	799.5 Hz
$\Delta\sigma(2)$ =	1417.7	1165.3

To estimate the influence of the isotropic to nematic transition on the molecules under study ($C_6F_4Br_2$), the following approach is proposed. By comparing the D-values in the two experiments, it strikes that the D-values in experiment 1 are 1.235 times the corresponding D-values in experiment 2. This means that the motional constants (as defined by Snyder (3)) obey the following relations:

a $(C_{3z^2-r^2}/C_{x^2-y^2})_{exp.1} = (C_{3z^2-r^2}/C_{x^2-y^2})_{exp.2}$

b $(C_{3z^2-r^2})_{exp.1} = 1.235\ (C_{3z^2-r^2})_{exp.2}$

In consequence the change in the chemical shift ($\Delta\sigma$) in experiment 1 should be 1.235 times the corresponding change in experiment 2. By taking the correction due to the influence of the transition of the isotropic into the nematic phase on $C_6F_4Br_2$ equal in the two experiments, one can easily calculate this correction and the true $\Delta\sigma$'s. The results are

	exp. 1	exp. 2	correction
(1) =	883 Hz	715 Hz	85 Hz
(2) =	1326	1074	91

The true $\Delta\sigma$'s thus obtained are changes in σ due solely to the influence of orientation. The separate components of the shielding tensor can be evaluated if additional $\Delta\sigma$ values are available from measurements with largely differing ratio of motional constants.

Yours sincerely,

(J. Gerritsen) (G. Koopmans) (C. MacLean)

1. M.A. Cooper, Org. Magn. Res. 1, 363 (1969).
2. A.D. Buckingham, E.E. Burnell, C.A. de Lange, J. Am. Chem. Soc. 90, 2972 (1968).
3. L.C. Snyder, J. Chem. Phys. 43, 4041 (1965).

OAKLAND UNIVERSITY
Rochester, Michigan 48063
Affiliated with Michigan State University
Area 313 377-2000
DEPARTMENT OF CHEMISTRY

6 April 1970

Professor Bernard L. Shapiro
Department ofChemistry
Texas A and M University
College Station, Texas 77843

Dear Dr. Shapiro:

METHANOL NMR THERMOMETER.
THERMISTOR THERMOMETER.

In a previous letter (TAMUNN, 122, 20, November 1968), we reported the redetermination of the chemical shift of methanol and ethylene glycol.

While the shift of glycol has been confirmed, the shift given for methanol is too high at temperatures below 255°K. The cold nitrogen gas cools the sweep coils of the Varian A-60 slightly, even though a vacuum dewar insert was used, and the calibration of the sweep width changes.

To avoid the problem, the field was modulated at 100 Hz, and the resulting sidebands were used for calibration. The new calibration curve for methanol has been reported (1).

We have now extended the measurements down to the freezing point of methanol, and the calibration curve is given on the next page. Details are being published (2). Somewhat surprisingly, the quadratic equation describing the calibration is the same as the previous one (1) within 0.8°K at any temperature.

The temperatures were measured with a thermistor probe (3), and the reproducibility was 0.2°K. Temperatures can be read directly on a calibrated meter, and the measurement is faster and more accurate than measurement of the chemical shift. The probe will be manufactured at a modest price if enough can be sold. Please write to me if you are at all interested. A scribble on a reprint request card will do.

I would like to be put on the mailing list for TAMUNN.

Sincerely yours,

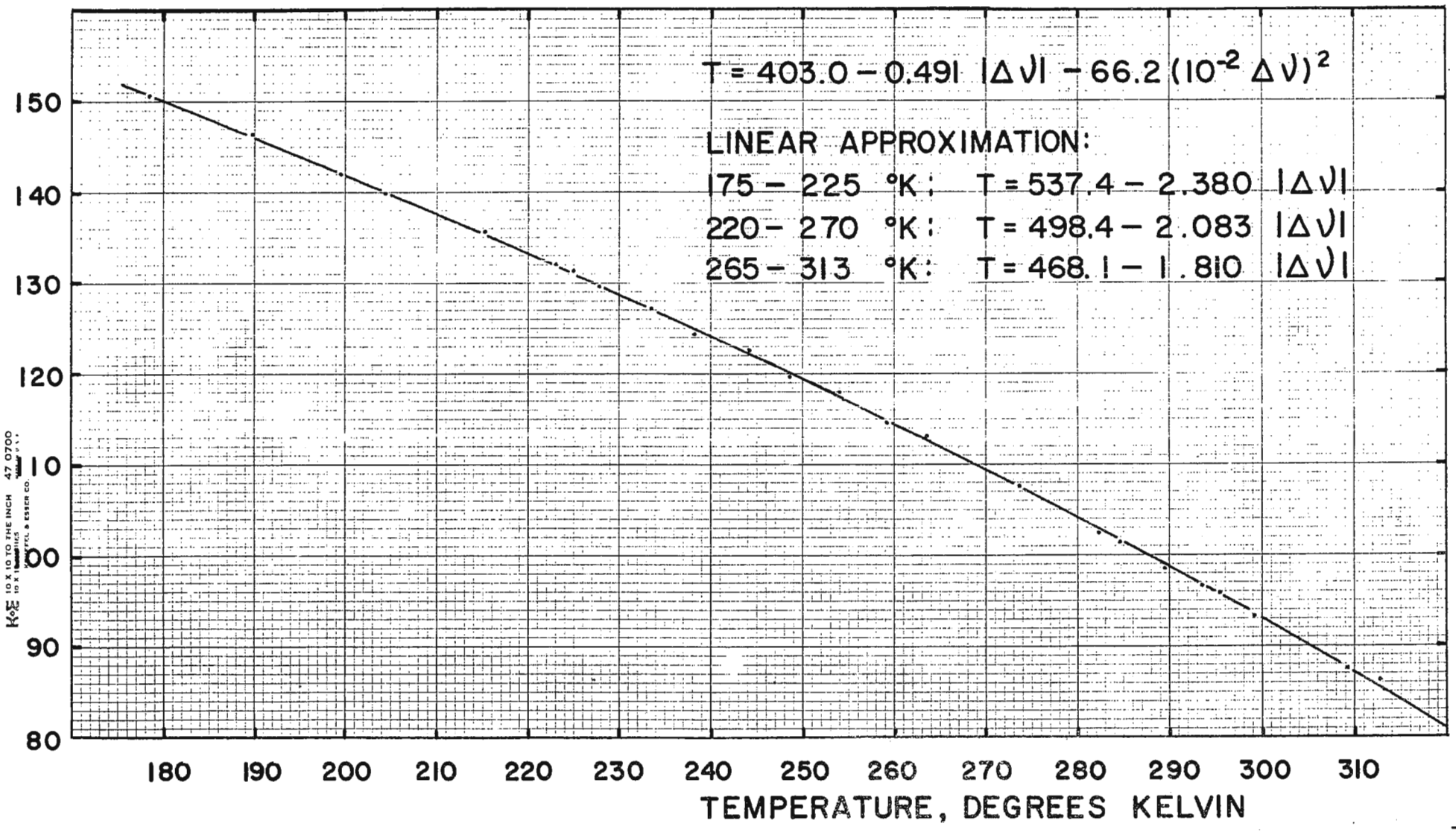
Anthony L. Van Geet

Anthony L. Van Geet
Associate Professor

ALV/smm

(1) A. L. Van Geet, 10th Experimental NMR Conference, Pittsburgh, Pa., February 1969.
(2) A. L. Van Geet, Anal. Chem., 42, May 1970 (Correspondence).
(3) A. L. Van Geet, Anal. Chem., 40, 2227 (1968).

OU 10 *In Observance of the University's First Ten Years*


CHEMICAL SHIFT OF METHANOL, HERTZ
T = 403.0 − 0.491 |Δν| − 66.2 (10⁻² Δν)²
LINEAR APPROXIMATION:
175 − 225 °K: T = 537.4 − 2.380 |Δν|
220 − 270 °K: T = 498.4 − 2.083 |Δν|
265 − 313 °K: T = 468.1 − 1.810 |Δν|
150
140
130
120
110
100
90
80
180
190
200
210
220
230
240
250
260
270
280
290
300
310
TEMPERATURE, DEGREES KELVIN

INSTITUT FÜR ORGANISCHE CHEMIE
DER UNIVERSITÄT KÖLN
Doz.Dr.H.Günther

5 KÖLN, ZÜLPICHER STRASSE 47
TELEFON: 470 3283

March 23, 1970

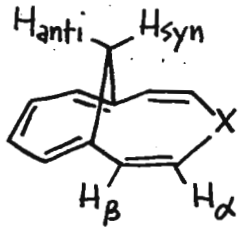
Prof.Dr.B.L.Shapiro
Texas A+M University
Department of Chemistry
College of Science
College Station, Texas

Large Deshielding Effect of Sulfur

Dear Barry,

since some time I had the feeling that a contribution to TAMU-NMR-Newsletter from our group was due and the arrival of your blue letter left no doubt that I was right. Thanks for the reminder.

Recently, we have looked at the spectra of some new systems of the bridged variety of annulenes, synthesized by E. Vogel and his group. The details of the spectral analyses will be reported by us in a full paper. The aim of this letter is to call attention to the dramatic change found for the chemical shifts of the methylene protons in the thiophene-analogue III as compared to the resonance frequencies of these protons in the hydrocarbon I and the oxepine-analogue II:



	X	τ_α	τ_β	τ_{syn}	τ_{anti}	$^2J_{H_{syn},H_{anti}}$
I	CH_2	5.22	3.72	6.28	9.79	11.59 Hz
II	O	4.52	4.29	5.48	9.37	10.35 "
III	S	5.22	3.54	3.73	8.76	11.47 "

In III H_{syn} is deshielded 2.55 ppm and H_{anti} by 1.03 ppm as com- to the data of I. For II, the effect is similar, but less pronounced. As far as the resonance frequencies of the ringprotons H_α and H_β are concerned, oxygen shows the stronger influence on their chemical shifts. In addition, the change observed for the geminal coupling constant of the bridge protons indicates some change in geometry for compound II, which seems reasonable on the basis of the van der Waals radii of the X-group in I-III.

The observed effect of sulfur is in accord with reports in the literature[1]. Its cause is at present investigated.

Sincerely yours,

D. Cremer K. Müllen H. Günther

[1] E. Campaigne et al., J.Org.Chem. 27, 135 (1962); M. Tomoeda et al., Tetrahedron Letters 1964, 1233.

HARVARD UNIVERSITY

DEPARTMENT OF CHEMISTRY

12 Oxford Street
Cambridge, Massachusetts 02138
U.S.A.

April 2, 1970

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

Dear Barry:

Recently Sykes, Schmidt and Stark (1) estimated the rotational correlation time of the succinate-inorganic phosphate-aspartate transcarbamylase complex from the measured relaxation times for succinate undergoing rapid chemical exchange with ATCase. We have recently made a similar estimate for the acetylsalicylic acid-human serum albumin complex from the measured relaxation times for the acetyl protons of acetylsalicylic acid. The values obtained are:

ATCase (MW $\simeq$ 100,000) $\tau_c = 1 \times 10^{-8}$ secs
HSA (MW $\simeq$ 70,000) $\tau_c = 4 \times 10^{-8}$ secs

These are close to the values determined from other methods; i.e., fluorescence depolarization (2). The details of these measurements and calculations will be published shortly.

Yours sincerely,

Brian

Brian D. Sykes

(1) B.D. Sykes, P.G. Schmidt and G.R. Stark, J. Biol. Chem. 245, 1180 (1970).

(2) G.E. Churchick, Biochem. Biophys. Acta. 147 511 (1967)

Short Title: NMR Estimates of Rotational Correlation Times of Biological Macromolecules

RUTGERS UNIVERSITY *The State University of New Jersey*

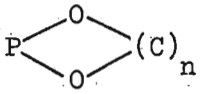
SCHOOL OF CHEMISTRY
Ralph G. Wright Laboratory
New Brunswick, New Jersey 08903

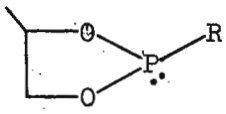
April 7, 1970

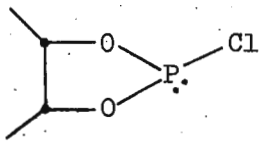
Dr. B. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843

Phosphorus Chemical Shifts of Cyclic cis-trans-isomers

Dear Dr. Shapiro:

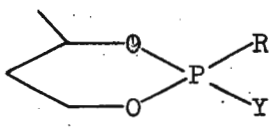
Several investigators have pointed out that geometrically isomeric cyclic organophosphorus compounds of skeletal type  (n = 2 or 3) can have different ^{31}P chemical shifts.[1-7] These differences of chemical shifts range from less than 1 ppm to 15 ppm. We would like to report values for some additional isomeric pairs.

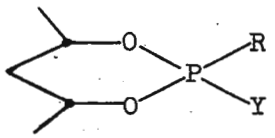




	R	
1	OC_2H_5	-140.5*, -142
2	OC_6H_5	-134*, -137
3	C_6H_5	-168*, -170
4	$N(CH_3)_2$	-145.5*, - 150.5

	$\delta^{31}P$
5	-164.5*, -171

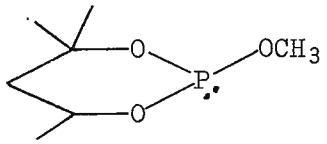




	Y	R	$\delta^{31}P$
6	-	CH_3	-163* -189
7	O	OCH_3	+6.5 +5.4

	Y	R	$\delta^{31}P$
12	-	OCH_3	-129* - 135
13	O	$C(C_6H_5)_3$	-20 -25

8	O	$OCH_2C(CH_3)_3$	+7.8	+5.4
9	O	CH_3	-22	-29
10	O	C_6H_5	-12	-19
11	S	OCH_3	-64.7	-66.4



14 $\delta^{31}P$ = -133.5*, -134.2

Chemical shifts are relative to external 85% H_3PO_4 and were obtained with a Varian Model HA-100 operating at 40.5 MHz.

*Major component of apparent equilibrium mixture

It appears that the difference in chemical shifts for the two isomers of 6 is exceptionally large and further work on similar systems is warranted. Interestingly, in what are believed to be equilibrium mixtures[2,8](1-6, 12 and 14) the more stable isomer absorbs at higher field. The chemical shifts for the isomers of 11 differ considerably from those reported by Mikołajczyk[5] (-141.4 and -148.6 ppm relative to external 80% H_3PO_4) but are similar to those for many acyclic thiophosphates (-40 to -75ppm)[9] and other six-membered cyclic thiophosphates (-63.0 and -64.8ppm)?

Sincerely,

The Rutgers Phosphorus Group

1. Denney, D.B. and Jones, D.H., J. Amer. Chem. Soc., 91, 5821 (1969).

2. Denney, D.Z., Chen, G. Y. and Denney, D.B., J. Amer. Chem. Soc.,91, 6838 (1969).

3. Ramirez, F., Patwardhan, A.V., Desai,N.B. and Heller, S.R., J. Amer. Chem. Soc., 87, 549 (1965).

4. Hall, L. D. and Malcolm, R.B., Chem. and Ind. (London), 92 (1968).

5. Mikołajczyk, M., Angew. Chem., Int. Ed., Engl., 8 (7), 511 (1969).

6. Mikołajczyk, M. and Schiebel, H.M., Angew. Chem., Int. Ed. Engl., 8 (7) 511 (1969).

7. Majoral, J. P. and Navech, J., C. R. Acad. Sci, Paris, Ser. C, 268, 2117 (1969).

8. Denney, D.Z. and Denney, D.B., J. Amer. Chem. Soc., 88, 1830(1966).

9. Mark, V., Dungan, C.H., Crutchfield, M.M., and Van Wazer, Jr., Topics in Phosphorus Chemistry, 5, 227 (1967).

THE UNIVERSITY OF TOLEDO
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COLLEGE OF ARTS AND SCIENCES
DEPARTMENT OF CHEMISTRY

April 8, 1970

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

Conformational Free Energies of Phosphate Substituents

Dear Barry:

Conformational free energies have been determined for a wide range of substituents in mono-substituted cyclohexanes, but no investigation of phosphorus-containing substituents have been reported. We have recently prepared and examined the spectra of a series of C_6H_{11}-O-P and C_6H_{11}-P compounds. In the cyclohexyl phosphates, C_6H_{11}-$OP(O)(OC_6H_5)_2$ (1) and C_6H_{11}-$OP(O)(OCH_3)_2$ (2), methine resonances were well separated and $-\Delta G$ values of 0.54 [$OP(O)(OC_6H_5)_2$] and 0.60 kcal/mole [$OP(O)(OCH_3)_2$] were obtained. The chemical shift method (cis- and trans-4-t-butylcyclohexyl phosphates as references) was employed; methine chemical shifts were determined with the aid of ^{31}P double resonance and ring deuteration. Applications of the peak area method have thus far proved to be unsuccessful; the methine resonances of 1 and 2 show only viscosity broadening at -50°. The ΔG values are unremarkable, falling in the ranges observed for other -OR substituents, e.g. $-OCOCH_3$ (0.70), $-OSO_2CH_3$ (0.56).

Studies of cyclohexanes possessing phosphorus substituents directly bonded to the ring are in progress, but, to date, the chemical shift approach has been unsuccessful. The deshielding effects of substituents such as $-P(O)(OCH_3)_2$, $-P(C_6H_5)_2$ and $-P(O)(C_6H_5)_2$ are too weak to lead to clear separation of the methine resonance from the ring proton envelope. The chemical shift approach may be applicable to $-P(CH_3)(C_6H_5)_2^+$.

Best regards,

Clay

Claibourne E. Griffin

CEG:mr

139-28

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH
BETHESDA, MARYLAND 20014

April 9, 1970

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

Title: Computer-Assisted Analysis of 220 MHz PMR Data of Protein Imidazole Resonances.

Dear Barry:

We have been engaged in detailed computer-assisted PMR studies at 220 MHz of the downfield region of several small proteins. Principally we are interested in the imidazole C2-H resonances in this region. Because of the low signal strengths (even after extensive time-averaging) the crossing of peaks when the pH is changed, and the presence of other resonances in this region of the spectrum, ambiguities occur which may make identification of these resonances equivocal.

The time-averaged spectra have been fitted to Lorentzian curves with a least squares program (MODELAIDE) (1) using an IBM 360/50 computer and an on-line IBM 2250 display. This allows determination of peak areas, widths and chemical shifts where there is overlap. The values of chemical shift as a function of pH have also been fitted to the theoretical relationship, a rearrangement of the well-known Henderson-Hasselbach equation (2). This allows a more objective analysis of the data, including the precise determination of pK values and of continuity where the titration curves cross.

Examples of the results of curve-fitting of data obtained for Staphylococcal nuclease (Nase) are shown in the accompanying figures. This is an interesting case because of the previous interpretation of data at 100 MHz to indicate a slow, local conformational equilibrium involving one of the imidazole groups[3]. This interpretation required (i) that two peaks have partial proton areas and sum to unity relative to the other discrete C2-H resonances, and (ii) that the titration curves of these peaks be related by the exchange phenomenon, with neither being described by a single Henderson-Hasselbach relationship. We believe, however, that the higher resolution at 220 MHz, together with the computer-assisted analysis of the data, has yielded a more complete understanding of this region of the PMR spectrum, which makes the conformational equilibrium hypothesis for Nase unlikely.

 April 9, 1970

This work is being prepared for publication (4).

Best regards,

Jack Cohen

Jack Cohen
Physical Sciences Laboratory
Division of Computer Research
and Technology

1. R.I. Shrager, Computer Graphics (SIGGRAPH-ACM) No. 3, p. 17 (1969), J. Assoc. Comp. Mach., in press.
2. Edsall, J.T., and Wyman, J., 'Biophysical Chemistry', Vol. I, Chapter 8 (AP, N.Y., 1958).
3. J.L. Markley, M. Williams, and O. Jardetzky, Proc. Natl. Acad. Sci., 65, 645 (1970).
4. J.S. Cohen, A.N. Schechter, R.I. Shrager and M. McNeel, in preparation.

Fig. 1 - A 220 MHz spectrum of S. nuclease in 0.1 M NaCl - D_2O at pH 5.11 fitted with Lorentzian curves. This is a CALCOMP plot; 0 = observed, * = calculated, ———— = components. The base-line is a large Lorentzian peak upfield from these resonances.

Fig. 2 - Titration curves of the imidazole C2-H resonances of nuclease in 0.3 M NaCl - D_2O. Circles are observed points; triangles are calculated points for the best fit to the theoretical equation. The lines connect the calculated points (Fig. traced from CALCOMP plots).

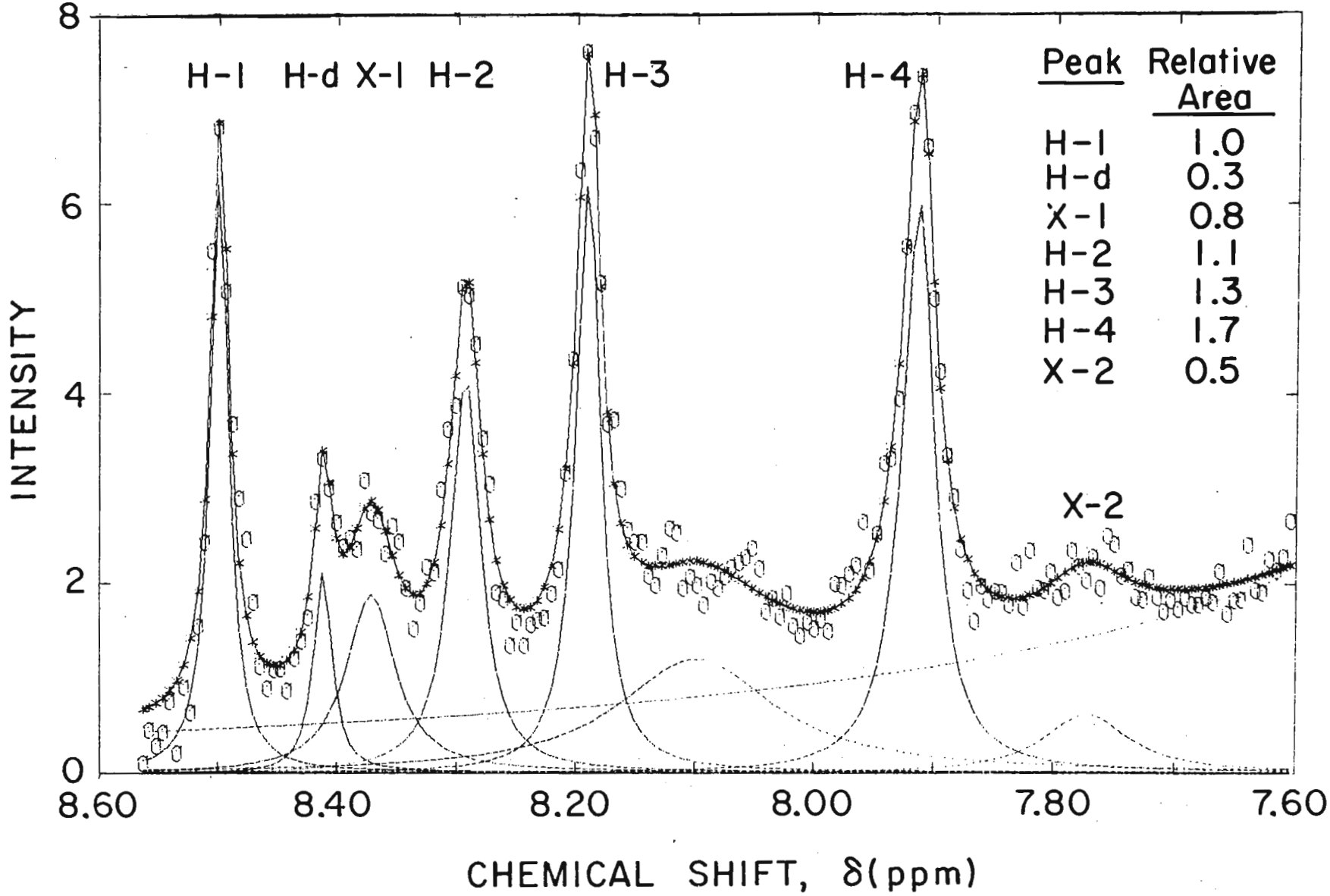
H-1
H-d
X-1
H-2
H-3
H-4
X-2
Peak
Relative Area
H-1 1.0
H-d 0.3
X-1 0.8
H-2 1.1
H-3 1.3
H-4 1.7
X-2 0.5
INTENSITY
0
2
4
6
8
8.60
8.40
8.20
8.00
7.80
7.60
CHEMICAL SHIFT, δ(ppm)

FIGURE 1

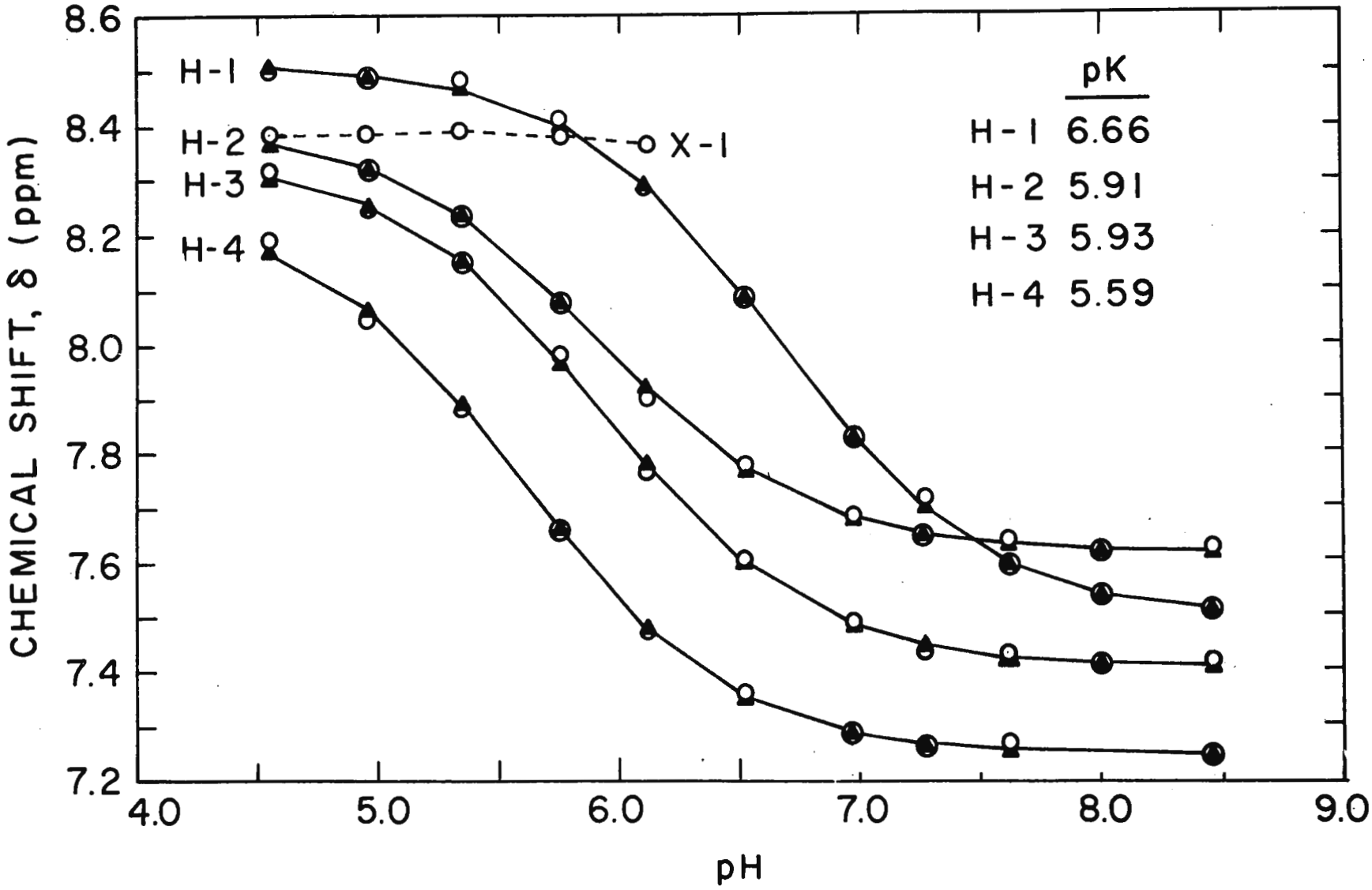
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
CHEMICAL SHIFT, δ (ppm)
4.0
5.0
6.0
7.0
8.0
9.0
pH
H-1
H-2
H-3
H-4
X-1
pK
H-1 6.66
H-2 5.91
H-3 5.93
H-4 5.59

FIGURE 2

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TAMU NMR Newsletter

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