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Newsletter

No. 154

JULY, 1971

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A monthly collection of informal private letters from Laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication". Reference to the TAMU NMR Newsletter by name in the open literature is strictly forbidden.

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Deadline Dates: No. 155: 2 August 1971
No. 156: 6 September 1971

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

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

GORLAEUS LABORATORIA
DER RIJKSUNIVERSITEIT

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Tst.

LEIDEN, June 29 1971

Professor B.L. Shapiro,
Department of Chemistry,
Texas A & M University,
COLLEGE STATION, TEXAS 77843.
U.S.A.

Dear Professor Shapiro,
Magnetic Non-equivalence of the Ethoxy-groups of Diethyl- α -bromobenzylphosphonate
Magnetic non-equivalence of the methylene protons in an ethoxy group of dissymmetric molecules is a well-known phenomenon. Recently we stuck to a molecule with two ethoxy-groups which appeared to be non-equivalent too i.e. diethyl- α -bromobenzylphosphonate. (Fig. 1).

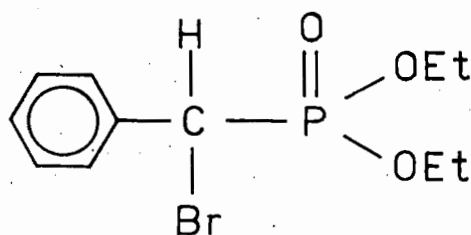


Figure 1

The 100 Mhz spectrum of the ethoxy-groups (Fig. 2) consists of two triplets for the methyl-groups, of a multiplet for one of the methylene-groups and of two quartets for the other methylene-group.

The multiplet was analysed by the computer program LAME as an A_3MX system (X stands for phosphorus), the KM part of which consists of 8 quartets.

The resonances of the other ethyl-group were analysed as an A_3M_2X system, giving rise to two quartets for the M_2 part. The results are presented in Table I.

The following conclusions appear from Table I:

1. The two ethoxy-groups are magnetically non-equivalent.
2. In one of the ethoxy-groups the methylene protons are magnetically non-equivalent, whereas in the other they are isochronous.
3. The P-H coupling constants are different for all different methylene protons.

VERVOLGBLAD:

This non-equivalence is a reflection for the asymmetry of the molecule. In our case the compound is a d,l pair. When the d,l mixture is solved in an optically active solvent (say for instance a D-form) two solvates can be formed, a D,d and a D,l form, which have in principle different NMR spectra¹.

1) W.H. Pirkle, S.D. Beare; J.Am. Chem. Soc. 91, 5150 (1969).

Table I

A ₃ KMX system			
100 Mc/s in CCl ₄		220 Mc/s in CDCl ₃	
$\nu_A = 112.07(0.03)$	$\nu_K = 390.21(0.04)$	$\nu_A = 235.04(0.02)$	$\nu_K = 908.03(0.03)$
$\nu_M = 410.75(0.04)$	$\nu_X = 9999$	$\nu_M = 948.04(0.03)$	$\nu_X = 9999$
$J_{AK} = 7.31(0.02)$	$J_{KX} = 9.16(0.07)$	$J_{AK} = 7.21(0.02)$	$J_{KX} = 8.52(0.05)$
$J_{AM} = 7.31(0.02)$	$J_{MX} = 7.63(0.07)$	$J_{AM} = 7.21(0.02)$	$J_{MX} = 7.25(0.05)$
$J_{KM} = 10.62(0.05)$		$J_{KM} = 10.22(0.03)$	
A ₃ M ₂ X system at 100 Mc/s in CCl ₄			
$\nu_A = 136.0(0.05)$	$\nu_M = 435.4(0.05)$	$\nu_X = 9999$	
$J_{AM} = 6.94(0.04)$		$J_{MX} = 8.14(0.1)$	

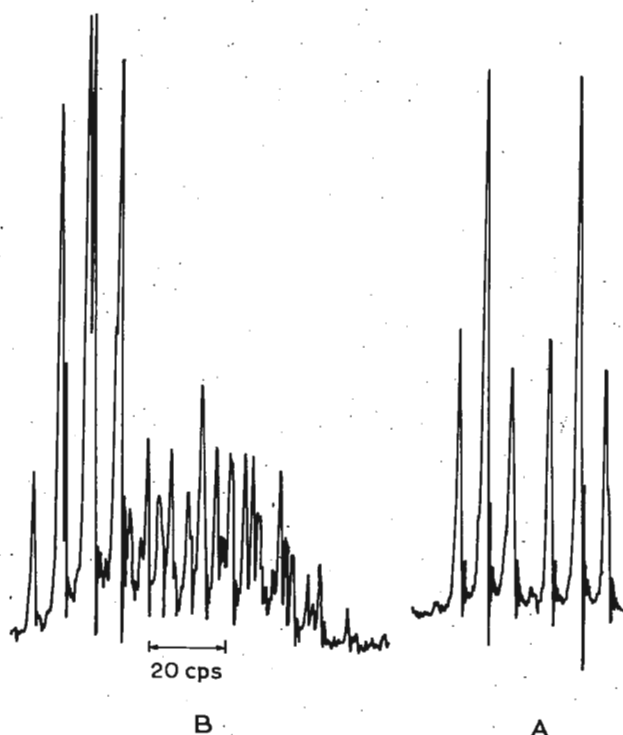
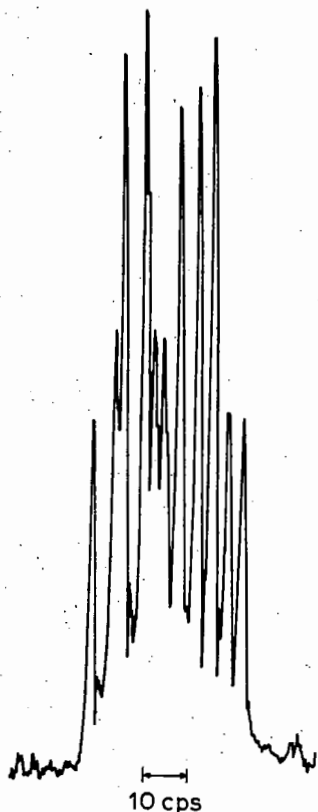


Figure 2

A: Methyl groups

B: Methylene groups

VERVOLGBLAD:

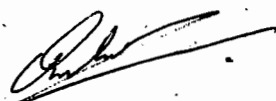
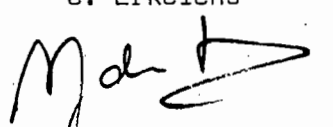



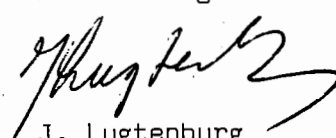
Indeed the NMR spectrum of a mixture of equimolar amounts of d,1-diethyl- α -bromobenzylphosphonate and 1-1,1, 1-trifluoro-2-hydroxy-2-phenylethane in CDCl_3 shows four triplets of about equal intensity in the methyl region (Fig.3) indicating four magnetically non-equivalent methyl-groups.

The 220 Mc/s NMR spectrum was run on the Varian HR-220 of the TNO Research Institute in Delft, the 100 Mc/s NMR spectra were recorded on our JEOL-PS-100.

Figure 3

sincerely yours,


C. Erkelens

A.J. de Hoog


P.W. Henniger

J. Lugtenburg



M. P. O. BOX 8, NIAGARA FALLS, NEW YORK 14302
PHONE (716) 773-2345

June 8, 1971

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

Dear Barry:

I find myself in the embarrassing position of needing a contribution to the Newsletter with little of a scientific nature in hand to report. In view of the fact that we have had our T-60 in operation for about 1 1/2 years, I thought a few comments about the instrument and its operation might be in order for anyone contemplating purchase of a small routine spectrometer.

Our instrument is equipped with the Perma-Lock, spin decoupling, and variable temperature accessories. In addition, we have the battery stand-by and air compressor unit supplied by Varian. These latter components are well worth the money in added convenience especially for spectrometer placement (i.e. with the air supply you have a self-contained unit needing only 110 V power). Our instrument has been in continuous operation for 1 1/2 years with many different chemists and technicians operating the spectrometer which speaks well for the instrument. In general, the instrument is tuned once a week by a capable operator and only requires fine Y adjustment thereafter. It seems to be an exceptional instrument for routine operation and is capable of quite good performance. In buying an instrument of this type, as you well know, one should very carefully evaluate how it is to be used and purchase the appropriate accessories. For this specific instrument, I can make the following comments about this point.

We have found in our particular situation where this is a second instrument (we have a well equipped HA-100) it receives its major use in routine operation (i.e. a non locked mode). For cases like this I believe the basic spectrometer with the possible addition of the spin decoupling module

would be most adequate. The Perma lock works quite well but is an added inconvenience for most of the chemists. However, there are a few "must" circumstances. Because of bad drift problems it is absolutely necessary to have the Perma lock if the variable temperature accessory is purchased. Secondly, to make full use of the Perma lock one should also have the digital readout system. It is just not possible to obtain accurate chemical shifts on expanded spectra in locked operation because of uncertainty in the position of the lock which is particularly annoying. As far as the variable temperature accessory goes I believe it is the most annoying feature on the instrument especially since we had become accustomed to room temperature operations first. For instance, the sample eject is no longer operable; one places one's finger over a hole leading to the probe to eject the sample which seems rather "Mickey Mouse" to me. Secondly, with the variable temperature probe it is necessary to balance each sample, a minor annoyance especially to chemists unfamiliar with NMR spectrometers. Finally, the operation of the variable temperature unit itself is a nuisance. It is not possible to calibrate the temperature readout device so it is essentially useless. To obtain a particular temperature you dial a voltage which is equated to temperature by a graph, balance a galvanometer and read the temperature on the dial. Since this can't be calibrated, it can easily be off 4-5°C even when new and the temperature has to be measured by some other technique anyway.

In general, we are quite pleased with the overall performance of the instrument but I thought these comments might be useful for anyone contemplating purchasing a routine spectrometer.

Sincerely,



Dave Marr
Group Leader-Research

DM/mr

TITLE: COMMENTS ON THE T-60



U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

June 9, 1971

AIRMAIL

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

Dear Barry:

Quantitative Analysis of Sugars.

We have certainly found the improved sensitivity of the new generation of spectrometers useful for quantitative measurements of minor components of mixtures. In the Figure, are shown proton spectra (CW, 16 scans at 90 MHz using a Bruker HFX-11) of the anomeric-hydroxyl proton region of solutions of various \underline{D} -glucose samples in methyl sulfoxide- \underline{d}_6 . (a) crystalline α - \underline{D} -glucose, (b) crystalline β - \underline{D} -glucose, (c) melted α - \underline{D} -glucose, and (d) melted β - \underline{D} -glucose. By integration of spectrum (a) within a Fabritek 1074 instrument computer we determined that the crystalline α - \underline{D} -glucose (NBS Standard Reference Material 917 for clinical analysis) contains 0.9% of the β -anomer, and from spectrum (b) that crystalline β - \underline{D} -glucose (Nutritional Biochemicals Corporation) contains 1.0% of the α -anomer.

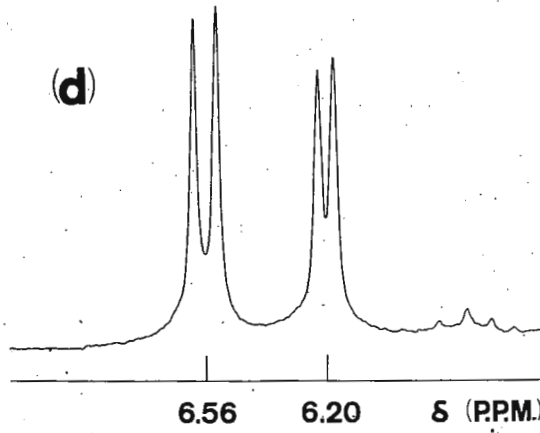
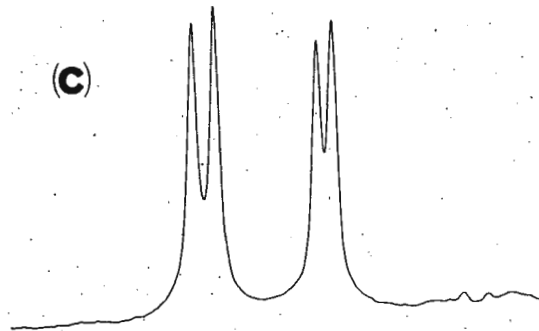
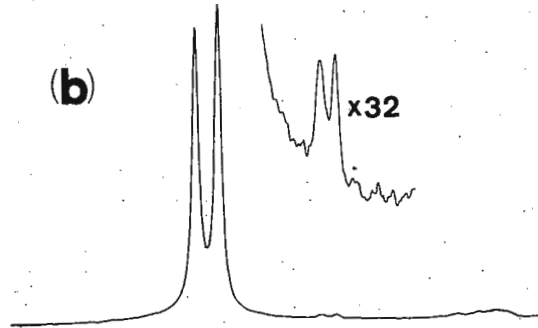
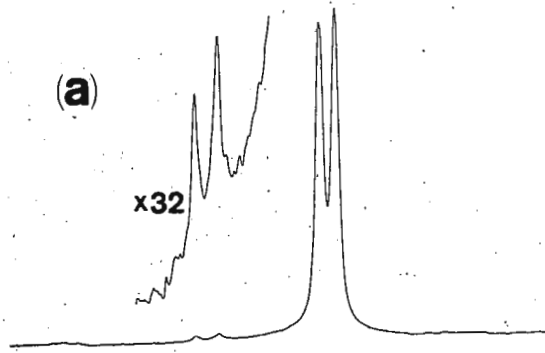
Integration of spectra (c) and (d) showed that melted α - \underline{D} -glucose contains 47.4% of the α -anomer, and that melted β - \underline{D} -glucose contains 47.9% of the α -anomer.

These results, and others, indicate that crystalline α - and β - \underline{D} -glucose both anomerize rapidly during melting to give the same equilibrated mixture of anomers.

Sincerely yours,

Bruce Coxon

Bruce Coxon
Research Chemist
Organic Chemistry Section
Analytical Chemistry Division



THE UPJOHN COMPANY

KALAMAZOO, MICHIGAN 49001
TELEPHONE (616) 382-4000

June 16, 1971

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

Dear Barry:

Re: Analysis of an AA^{*}BB^{*} SpectrumFor my subscription renewal I would like to describe the results of an AA^{*}BB^{*} analysis using LAOCN-3.

The observed 100 MHz NMR spectrum for the AA^{*}BB^{*} portion of diethylene-triamine in d₅-pyridine solution is shown in Figure 1. Not shown in the spectrum is an amine-hydrogen singlet at δ 1.43. Because of the overlaps it was not immediately clear to me which lines were the required two doublets (lines 1, 3 and 2, 4) and the two doublets-of-doublets (5, 6; 7, 8 and 9, 10; 11, 12). Searching through the collections of Wiberg and Nist, Bovey and Grant et al did not turn up any similarities; hence, spectra were computed from what seemed a reasonable set of parameters. After several modifications, guided by the excellent analyses by Grant, et al, a spectrum was obtained which furnished line numbers for iteration with LAOCN-3. The spectrum was fitted to 20 lines (4 lines were undetected) with an RMS error of 0.057, Figure 2.

The parameters were:

δ_A	=	2.76351	$\nu_0 \delta$	=	14.441
δ_B	=	2.61910	K	=	$J_{AA^*} + J_{BB^*} = -20.836$
J_{AA^*}	=	-9.918	M	=	$J_{AA^*} - J_{BB^*} = 1.000$
J_{BB^*}	=	-10.918	N	=	$J_{AB} + J_{AB^*} = 11.928$
J_{AB}	=	6.716	L	=	$J_{AB} - J_{AB^*} = 1.504$
J_{AB^*}	=	5.212			

Professor B. L. Shapiro

Page 2

June 16, 1971

Since K was large in magnitude and L was small in magnitude the value of K and the two geminal coupling constants which it measures was not determined accurately.

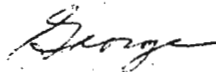
The solution is not unique. Other values of K, within bounds, gave the same spectrum after adjustment of the other parameters, accordingly (using the iterating options of LAOCN-3).

The values of the gem couplings are in approximate agreement with those for the ABX system recorded in the Varian catalog for a similar compound, 1-amino-2-decanol ($J = \text{ca. } -12$).

The rotationally averaged vic couplings are in approximate agreement with those found by Hirst and Grant for 2-bromoethanol ($J_{AB} = 6.45$, $J_{AB'} = 5.05$).

Since the spectrum is symmetrical, assignments cannot be made for nuclei A or B; i.e., switching values of $J_{AA'}$ and $J_{BB'}$ and/or switching values of J_{AB} and $J_{AB'}$ made no change in the spectrum but only renumbered the lines. The assignments were, therefore, made according to previous experience.

Sincerely,



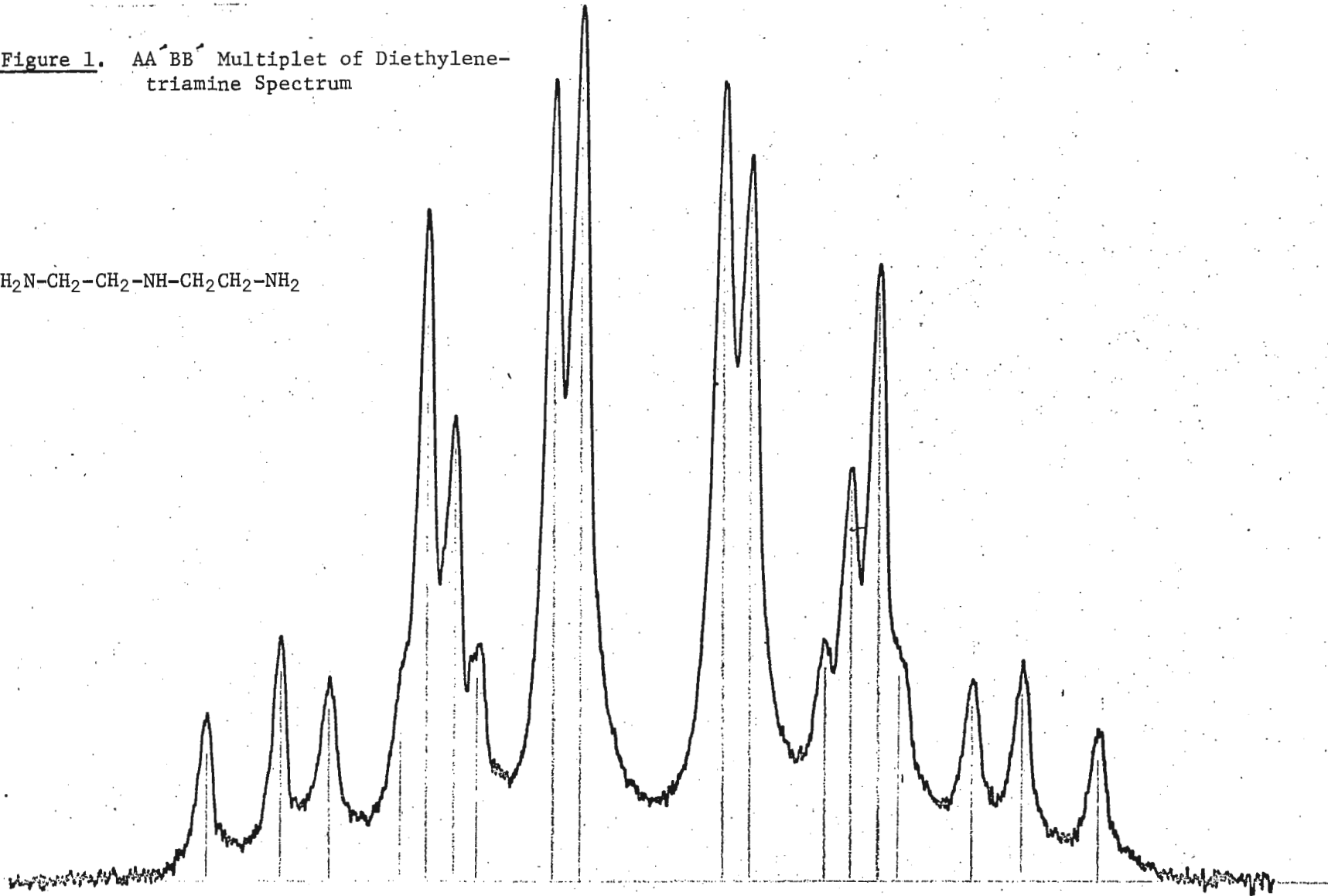
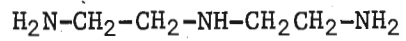
George Slomp
Physical and Analytical Chemistry

GS/ejw

References:

1. K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, 1962, Chapter 5.
2. F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, 1969, Appendix D.
3. D. M. Grant and R. C. Hirst, J. Chem. Phys., 38, 470 (1963).
4. R. C. Hirst and D. M. Grant, J. Chem. Phys., 40, 1909 (1964).

Figure 1. AA'BB' Multiplet of Diethylene-
triamine Spectrum



290

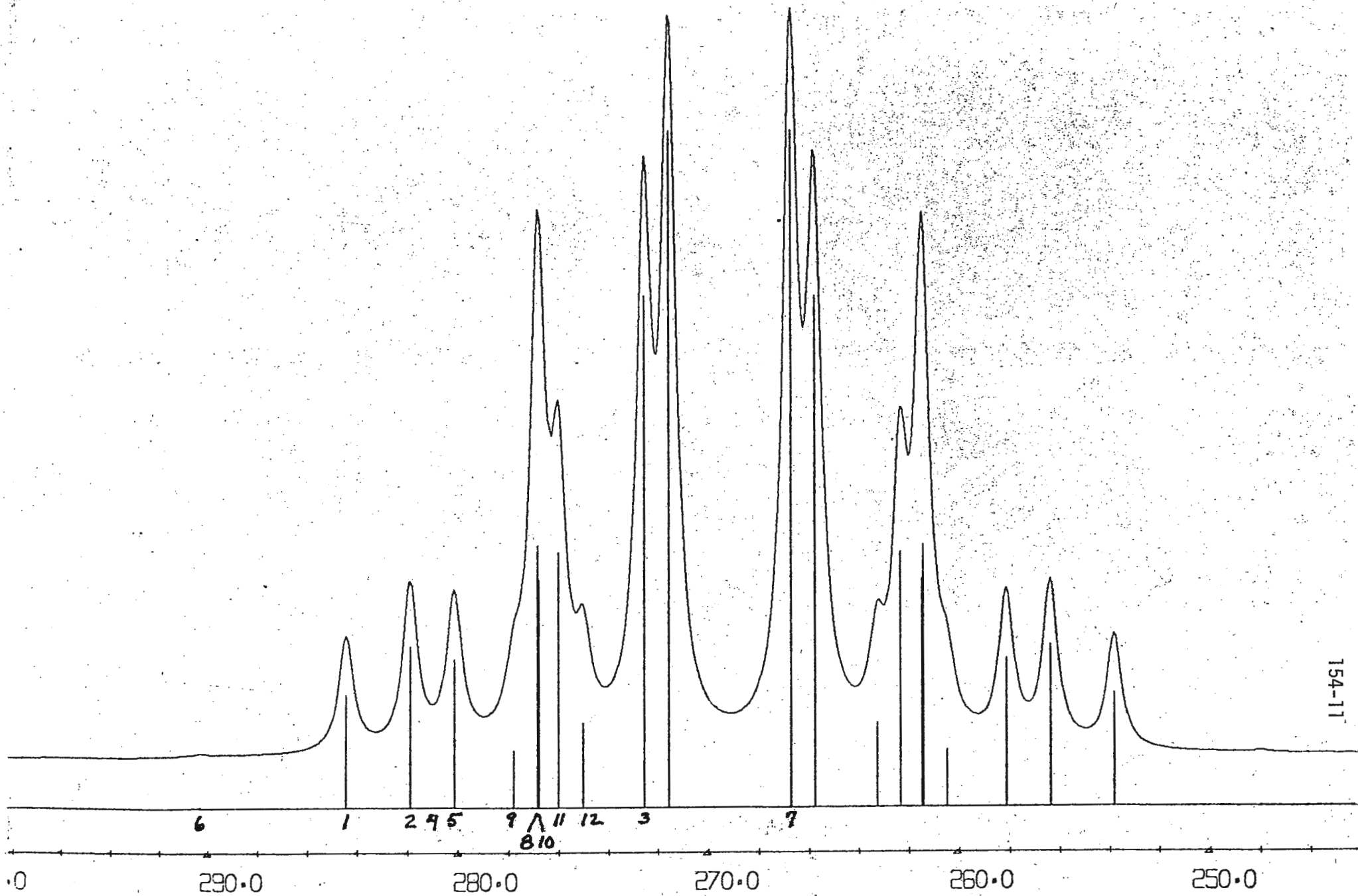
280

270

260

250

Figure 2. Computed Spectrum for AA'BB' Multiplet

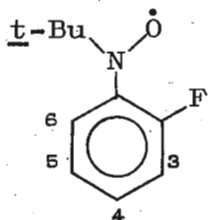


Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
COLLEGE STATION, Texas 77843
USA

^1H and ^{19}F NMR Contact Shifts in Aromatic t-Butyl Nitroxide Radicals

Dear Professor Shapiro,

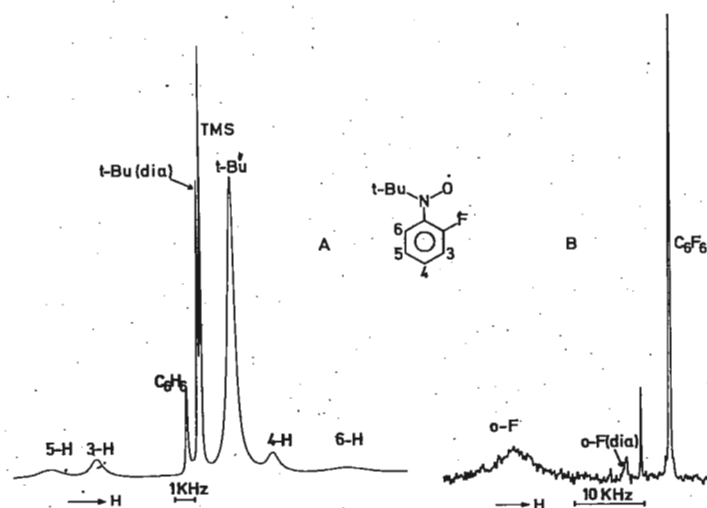
We have recorded ^{19}F NMR and ESR spectra of some fluorinated aromatic nitroxides and found a good agreement between the ^{19}F splitting constants obtained by the two methods. The absolute sign of the ^{19}F splittings is opposite to that of the proton in the same position. From this, conclusion can be drawn about the mechanism of spintransmission. I enclose one of our spectra and data for one of the radicals.



	a_3	a_4	a_5	a_6	a_{F}	$a_{\text{t-Bu}}$
NMR	+0.59	-0.56	+0.89	-1.03	+1.37	-0.23
ESR	0.58	0.56	0.90	1.04	1.35	0.25

A: ^1H spectrum

B: ^{19}F " "



Sincerely yours,
Kurt Torssell
Kurt Torssell
Professor, fil.dr.

Please, credit this contribution to the subscription of

DEPARTMENT OF THE AIR FORCE
AIR FORCE MATERIALS LABORATORY (AFSC)
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433



REPLY TO
ATTN OF:

AFML/LPH (R.E. Rondeau)

23 June 1971

SUBJECT:

PROGRAM EDREM

TO: Professor Bernard L. Shapiro
Texas A & M University
College of Science
College Station, Texas 77843

Dear Dr. Shapiro:

Although spectral parameters of complicated spectra are now usually obtained through the use of iterative computer techniques, spectra analyses are still far from being routine. The task of assigning individual experimental peaks to the computed frequencies remains. In making these assignments, as large a number of experimental lines must be measured with as high an accuracy as possible.

By using an analog-to-digital converter to digitize the pmr spectra and by formulating a computer program to edit and manipulate the digitized data, we've not only eliminated the time and tedium of hand measurements, but also significantly increased the accuracy of these measurements.

The technique is described in a paper to be published in Anal. Chem. Preprints are available as well as a listing of the program (EDREM) used to process the digitized data. It's too late now, but I've just learned that EDREM is a French non-non if spelled backward.

Sincerely,

Roger E. Rondeau
Roger E. Rondeau



UNIVERSITY OF SASKATCHEWAN REGINA CAMPUS

DEPARTMENT OF CHEMISTRY

REGINA SASKATCHEWAN

June 24, 1971

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

Re: Complete Analysis of Cis- and Trans-Butene-2 PMR spectra.

Dear Dr. Shapiro:

We have recently finished a rather extensive analysis of the proton spectra of cis- and trans-butene. The results are as follows

	S_{CH_3}	$S=CH$	$^3J_{olef.}$	$^3J_{vic}$	$^4J_{allyl}$	$^5J_{homoallyl}$
cis-butene	1.559	5.403	10.795	6.755	-1.854	1.198
trans-butene	1.582	5.381	14.992	6.444	-1.724	1.592

Coupling constants are accurate to ± 0.01 Hz except for the olefinic coupling (± 0.02 Hz). All lines were measured by precise audio side band techniques on a Varian A-60A. (neat liquid, ambient t) The computer program TWOSUM (1), which is based on NMRIT and NMREN, was employed utilizing all the subspectra (i.e. $aa'bb'$, $aa'b_3b'$ and $aa'b_3b_3'$). For trans-butene-2 262 out of 420 theoretical transitions were assigned, and similarly 251 out of 450 for cis-butene-2. Our results are fairly close to those of Harris and Howes (2). The major point of difference is that the greatly improved accuracy of our data allows us to unequivocally state that the transoid allylic coupling (in the cis-isomer) is more negative than the cisoid allylic coupling, contrary

cont'd-2

Dr. B. L. Shapiro

-2-

June 24, 1971

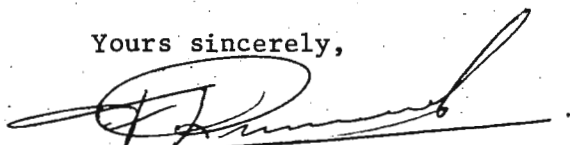
to theoretical predictions (3), but in line with previous findings for 1,2 dialkylated olefins (4). Following the discussion in ref 4, it appears that steric repulsion followed by rehybridization of the sp^2 carbons is still the dominating factor. For instance the $^3J_{cis} = 10.8$ is still larger than the $^3J_{cis} = 10.1$ for mono alkylated olefins, although smaller than the range 11.5-12.0 for cis-olefins with bulkier alkyl groups. (less steric hindrance) Also, the $sp^2 - sp^3$ vicinal coupling is larger for the cis isomer; again the lesser sterical hindrance reduces this difference to 0.31 Hz as compared to 0.6 - 1.0 Hz normally found. The more negative value for the transoid allylic coupling (-0.13 Hz difference with the cisoid allylic coupling) can be explained in the same way including the fact that this difference is only half of what is normally found.

This all looks very satisfactory were it not that at present we are getting rather incomprehensible results for cis- and trans-(t-Bu)CH = CH-(iPr) (but that can wait until the next blue note).



L. W. Kaslander

Yours sincerely,



F.H.A. Rummens

FHAR/js

1. G. De Maté, A Quirt, J.S. Martin; U of Alberta.
2. R.K. Harris, B. R. Howes; J. Mol. Spectrosc. 28, 191 (1968).
3. M Barfield; J Chem Phys 41, 3825 (1964); J.A.C.S. 93, 1066 (1971).
4. F.H.A. Rummens, J.W. de Haan; Org. Magn. Res. 2 351 (1970).

DWJ/CMC

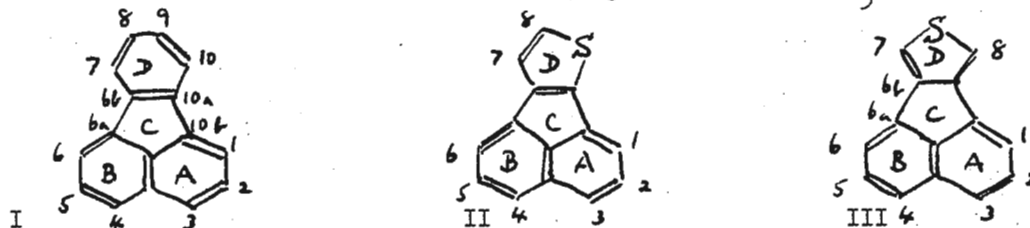
22nd June, 1971.

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

Dear Professor Shapiro,

Close ABC Systems in Acenaphtho [1,2-b]thiophene

Drs. K. D. Bartle (University of Leeds) and R. S. Matthews (University of Durham) and D. W. J. have recently assigned two rather closely overlapped ABC systems in acenaphtho [1,2-b]thiophene(II). This π -electronic isomer of fluoranthene(I) was prepared by Drs. A. Birch and D. A. Crombie of the Polytechnic, Huddersfield. The 100 MHz ^1H spectrum (Fig.1) of II in CDCl_3 also shows at highest



field an AB quartet; common line widths (as well as the HMO calculated ortho bond orders along H(6)...H(7)) suggest negligible inter-ring coupling. In the H(1-3) and H(4-6) ABC systems, H(2) and H(5) are so close as to give a single quartet, but application of ABC spacing rules to the four quartets from the other four protons led to assignments (AMX limit) for the four groups; iterations on a version of Mr. C. W. Haigh's LAME yielded four sets of ABC parameters (Hz downfield from TMS):

	(a)	(b)	(c)	(d)
ν_A	761.48 ± 0.07	760.96 ± 0.11	760.88 ± 0.10	761.62 ± 0.10
ν_B	744.07 ± 0.06	744.13 ± 0.09	744.09 ± 0.08	744.11 ± 0.07
ν_C	764.63 ± 0.06	763.51 ± 0.10	764.67 ± 0.08	763.41 ± 0.09
J_{AB}	6.91 ± 0.09	6.87 ± 0.15	6.91 ± 0.12	6.78 ± 0.14
J_{AC}	0.60 ± 0.08	0.53 ± 0.12	0.54 ± 0.11	0.60 ± 0.09
J_{BC}	8.10 ± 0.08	8.09 ± 0.13	8.06 ± 0.11	8.21 ± 0.13

Root-mean-square
error(Hz) 0.067

0.102

0.092

0.079

The observed spectrum could be obtained by (a) + (b) or by (c) + (d); of these, (c) + (d) gave much the better agreement between calculated and observed frequencies for ABC combination lines:

calculated	(a) and (b)	745.76	746.24	739.06 (intensity 0.09)	739.54 (intensity 0.13)
calculated	(c) and (d)	745.21	746.79	738.54 (intensity 0.06)	740.09 (intensity 0.22)
experimental		745.3	746.6	740.3	

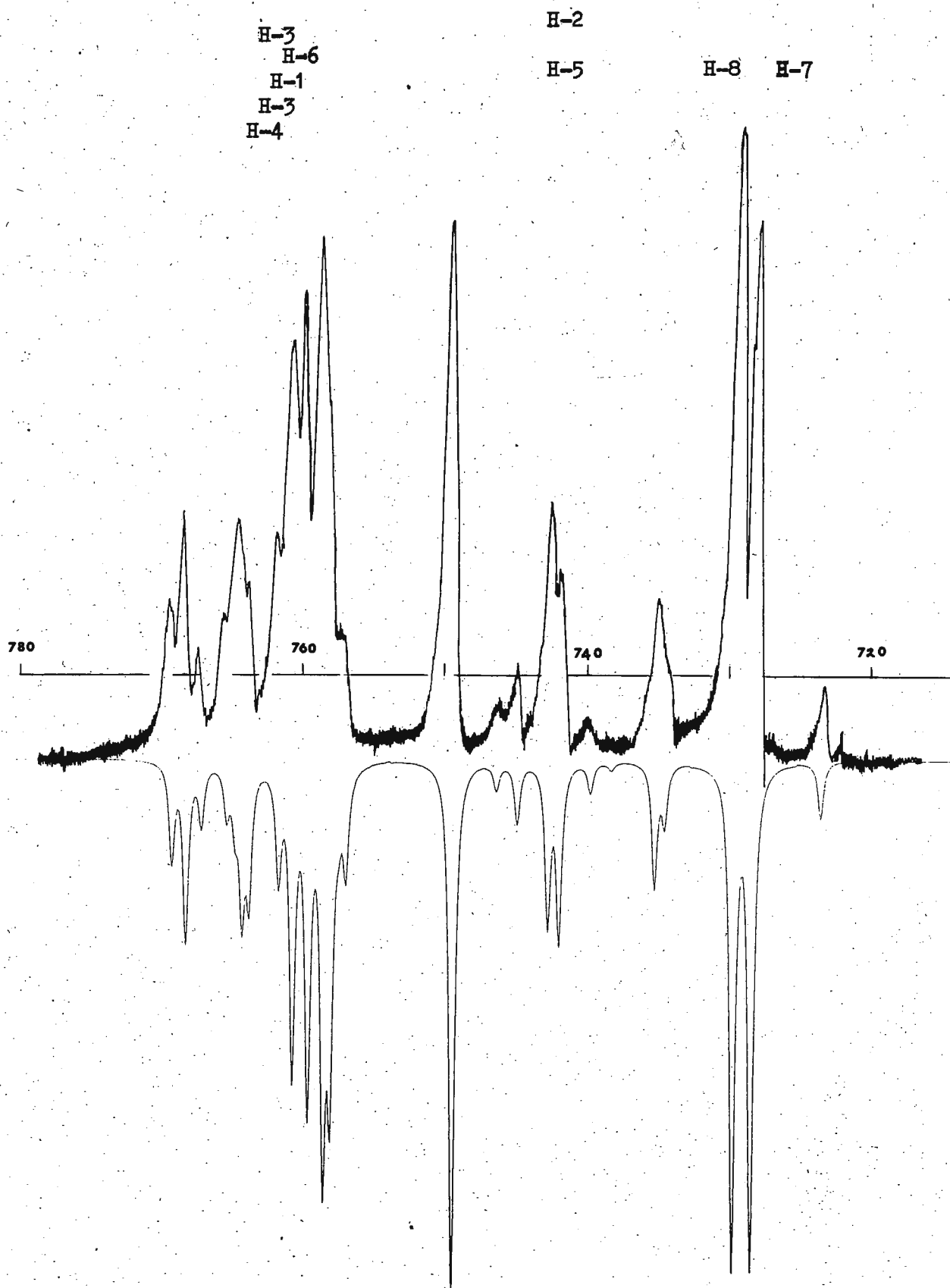


Fig.1. Experimental (upper) and calculated (lower) 100 MHz ^1H spectrum of acenaphtho[1,2-b]thiophene in CDCl_3 solution.

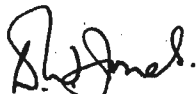
Magnitudes of ortho couplings establish ν_B 's as H(2), H(5). In III (with equivalent ABC's), $J_{23} > J_{12}$; combined with HMO bond-order calculations, this gives downfield shift $\delta_3 > \delta_1$. For II, sets (c) and (d) must be associated with rings A and B or B and A, i.e. $\delta_1 = 7.60_9$ or 7.61_6 ; $\delta_3 = 7.64_7$ or 7.63_4 ; $\delta_6 = 7.61_6$ or 7.60_9 ; $\delta_4 = 7.63_4$ or 7.64_7 p.p.m. Relations between δ and MO-calculated charge densities, ρ^+ , yielded $\delta_6 > \delta_1$ and $\delta_4 > \delta_3$, i.e. one inequality supporting each assignment. Acceptance of $\delta_4 > \delta_3$ [H(3,4) are further from C-S than H(1,6)] led to association of (d) with H(1-3) and (c) with H(4-6).

Replacement of 304 TL Tubes in Varian V-2100 B Magnet Power Supply

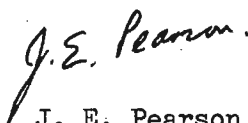
Following Professor R. Kaiser's problem (TAMUNMR, 146, 12) about replacing 304 TL pass tubes in the 12" Varian magnet power supply V-2100 B by transistors, J.E.P. would like to point out the advantage of paralleled transistors as described in Rev. Sci. Instrum 42, 713 (May, 1971). Availability of high-voltage power transistors (e.g. DTS-702) makes this arrangement feasible; greater reliability (and lower power consumption) can be achieved at no greater cost (for the components) than a new set of 304 TL's.

Dr. R. S. Matthews is now at Department of Chemistry, University of Durham, England.

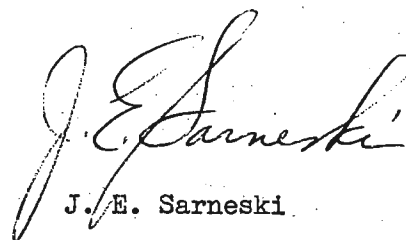
Yours sincerely,



D. W. Jones



J. E. Pearson



J. E. Sarneski

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FACULTY OF SCIENCE

OUR REF.

28th June, 1971.

YOUR REF.

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

Dear Barry,

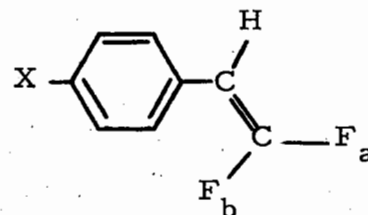
N. M. R. Studies on p-substituted $\beta\beta$ -difluorostyrenes

We have been looking at the effects of para-substituents of varying electron donating and withdrawing power on the fluorine-fluorine and fluorine-proton coupling constants of a series of $\beta\beta$ -difluorostyrenes.

The analogous pure proton system has been studied by Stothers' group who reported an approximately linear correlation between σ_X and J_{HHgem} values.

To date we have studied five para-substituted $\beta\beta$ -difluorostyrenes, the J_{FF} values for each substituent being

p-X	J_{FF} (Hz)	σ_X
CH ₃ O	38.1	-0.268
CH ₃	35.2	-0.069
H	33.4	0.000
F	34.2	+0.062
CN	22.5	+0.660



These values yield an approximately linear plot, analogous to that described for styrenes. Also, as in the styrene series, the values of J_{HF} (cis and trans) do not correlate well with σ values.

In the spectrum of the p-fluorine substituted olefin, we observed long-range fluorine-fluorine couplings of 2.1 c. p. s. to F_b and 4.4 c. p. s. to F_a . A few other cases are known to us from the literature but we plan to try some structural variations before we are through.

Please credit this contribution to the Monash subscription.

Lindsay

Lindsay K. Smith

Yours sincerely,

Ian

Ian D. Rae.

EMORY UNIVERSITY
ATLANTA, GEORGIA 30322

DEPARTMENT OF CHEMISTRY

June 29, 1971

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

Dear Barry:

Additivity of Substituent Effects on Long-Range ^{13}C -H Coupling Constants

Since obtaining our new-generation instrument, the Bruker HFX-90, some two years ago, we have been pushing its time-averaging carbon-13 capability in the direction of complete high-resolution ^{13}C spectral analysis. In this manner we have systematically determined under uniform conditions a large number of long-range ^{13}C -H coupling constants, particularly for substituted benzenes. This has alleviated somewhat the previous scarcity of this type of data.

Very recently we have completed the high-resolution ^{13}C analyses of the six-spin monohalobenzenes. By consideration of the ^{13}C -H coupling constants from these analyses along with the ^{13}C -H coupling constants in benzene (1), the halogen substituent effects on the long-range couplings can be readily determined. Assuming additivity of these substituent effects, we have calculated additivity values for sixty-three long-range ^{13}C -H coupling constants in ortho- and meta-dihalobenzenes for which experimental coupling constants are available (2,3). These additivity calculated values and the experimental values are compared in Figure 1. For all sixty-three long-range ^{13}C -H coupling constants the average deviation from exact correspondence (represented by the 45° line) between calculated and observed is only 0.20 Hz.

Additivity of substituent effects accounts quite satisfactorily, then, for most of the observed ^{13}C -H couplings in these dihalobenzenes. There are several deviations from additivity, however, which are clearly experimentally significant, and these will be discussed elsewhere. Complete high-resolution ^{13}C analysis from spectra taken on new-generation spectrometers now seems to be sufficiently reliable to be used effectively in systematic aromatic substituent effect studies.

A. R. Tarpley, Jr.
A. R. Tarpley, Jr.

Sincerely yours,

J. H. Goldstein
J. H. Goldstein
Professor of Chemistry

- 2 -

1. F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2967 (1967).
2. A. R. Tarpley, Jr. and J. H. Goldstein, *J. Mol. Spectrosc.*, **37**, 432 (1971).
3. A. R. Tarpley, Jr. and J. H. Goldstein, *J. Mol. Spectrosc.*, in press.

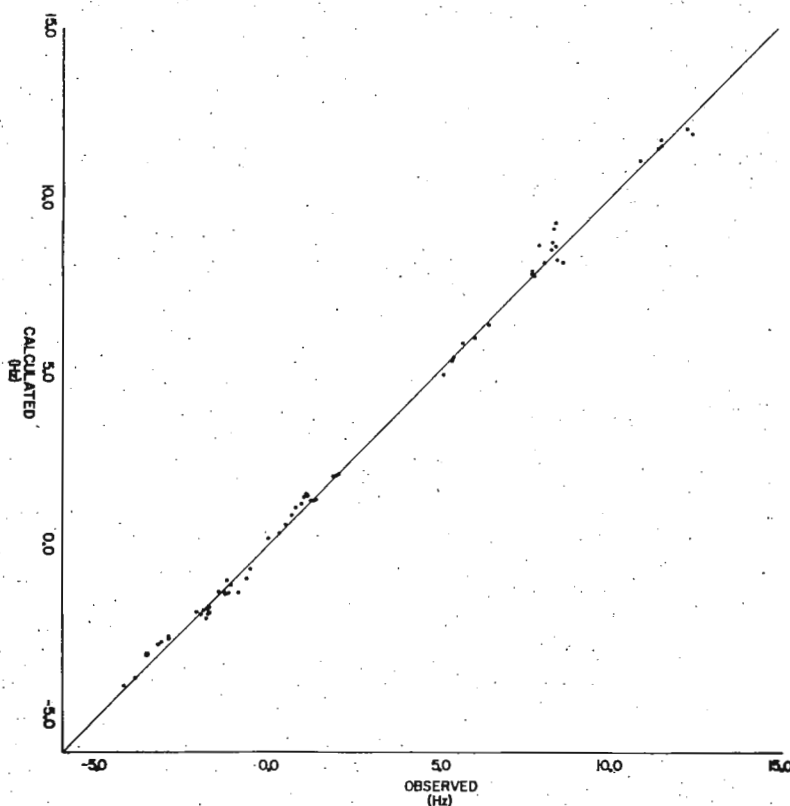
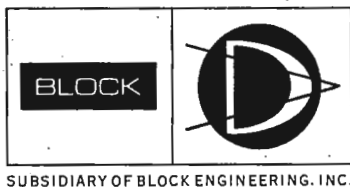


Figure 1. The long-range ^{13}C -H coupling constants calculated by additivity of substituent effects versus those observed in ortho- and meta-dihalobenzenes.



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B. L. SHAPIRO

June 29, 1971

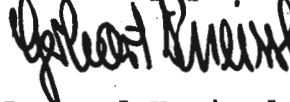
Professor B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

"A-60 and HA-100 Probes wanted"

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Prof. Bernard L. Shapiro
Dept. of Chemistry
Texas A & M University
COLLEGE STATION
TEXAS - 77843

N.M.R. Spectra of Some Cyclobutanes: The sign of 4J and their correlation with the Stereochemistry

Dear Professor Shapiro,

we have analysed the 1H n.m.r. spectra of two series of isomeric ring-fused disubstituted cyclobutanes, in order to obtain the sign of cross-ring four-bond coupling constants, and to study their correlation with the stereochemistry (1).

Since there are still disagreement about the most important mechanism which governs the long-range couplings in saturated systems, the availability of experimental data (including their signs) would be furthermore valuable.

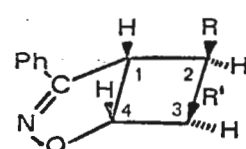
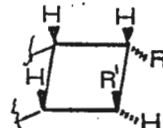
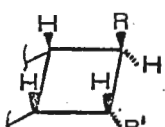
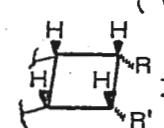
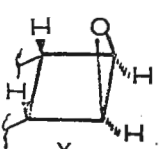
As concerning the problem of stereochemistry in cyclobutanes, the cis and trans orientation of protons on the ring is normally determined on the basis of vicinal coupling evidences only. Since the three-bond couplings are strongly depending by substituents, dihedral angles, and by even slightly distortions of the ring, very often J_{trans} are found to be greater than J_{cis} ; then in these conditions the configuration of protons cannot be obtained at all.

On the contrary the four bond couplings show a very interesting relationship with the cis-trans orientation of the interacting protons, as it is evidenced by our results (Table 1) and by the scattered data collected from the litterature (1).

4J are found to be positive, when the two interacting protons are cis, negative when they are trans; and their sign seems much more sensitive to the cis-trans orientation of protons, than to the effect of substituents or to the distortion of the ring. For that reason 4J seem much more suitable for studying the stereochemistry of cyclobutanes than the usual vicinal couplings, which show strong variation with small distortion, and ambiguity between the cis and trans values.

The analysis of the spectra in many solvents and at different temperatures was performed by using the LAOCN3 program;

Table 1

Long-range couplings		${}^4J_{1,3}$	${}^4J_{2,4}$	${}^4J_{1,3}$	${}^4J_{2,4}$
CDCl ₃		trans	trans	cis	cis
	I	R = R' = Cl	-1.66	-0.68	
	II	R = R' = Br	-1.77	-0.73	
	III	R = R' = COOMe	-1.44	-0.94	
	IV	R = R' = Cl	-1.49		+1.23
	V	R = R' = Br	-1.38		+1.21
	VI	R = Cl, R' = OH	-1.55		+1.42
	VII	R = R' = Cl		-0.91	+2.42
	VIII	R = R' = Br		-0.61	+2.48
	IX	R = R' = Cl (*)		+2.98	+2.13
	X		-0.57	-0.73	
	XI		all J are positive		

(*) acetone-d₆

the signs of all coupling constants were determined by tickling experiments and again deduced from the analysis (2). In table 2 are reported the data of the four chloro stereoisomers in one solvent only.

The values of long-range couplings are qualitatively in agreement with the theoretical prediction of Barfield (3). The agreement lies only on that ${}^4J_{cis}$ are higher than ${}^4J_{trans}$, and the arrangement of cis protons is more close than the trans to the "zig-zag" path. The four bonds in the cis configuration are not coplanar, and the ϕ and ϕ' angles are well below 180°, even with a distortion of the cyclobutane ring. On the other hand the trans interactions are more negative than theoretically expected. Of course agreement with theory in these couplings would have been surprising, because Barfield's angular calculation are based only on the "indirect" contribution

Table II

		ABCX						
I	J_{AB}	2.87	J_{BC}	6.89	ν_A	446.8	ν_C	477.4
	J_{AC}	-1.66	J_{BX}	-0.68	ν_B	472.3	ν_X	533.1
	J_{AX}	8.59	J_{CX}	4.06				
		ABCD						
IV	J_{AB}	6.71	J_{BC}	8.30	ν_A	439.8	ν_C	478.6
	J_{AC}	-1.48	J_{BD}	1.23	ν_B	460.0	ν_D	509.0
	J_{AD}	3.68	J_{CD}	7.75				
		ABMX						
VII	J_{AB}	3.93	J_{BM}	5.05	ν_A	430.5	ν_M	471.0
	J_{AM}	2.42	J_{BX}	-0.91	ν_B	435.4	ν_X	548.9
	J_{AX}	7.67	J_{MX}	6.00				
		ABCD						
IX	J_{AB}	2.98	J_{BC}	7.63	ν_A	502.8	ν_C	537.8
	J_{AC}	7.05	J_{BD}	5.12	ν_B	524.4	ν_D	539.6
	J_{AD}	6.79	J_{CD}	2.13				

to coupling, in the absence of any quantitative information about the "direct" contribution. Thus in these small rings, many factors can be important, such as the number of coupling paths, the relative orientation of substituents, as well as the probable increasing contribution of a direct mechanism, even in not highly strained molecules.

- (1) A short note will appear very soon on Tetrahedron Letters.
- (2) All the data will be published in Organic Magnetic Resonance.
- (3) M. Barfield and B. Chakrabarti, Chem. Rev. 69, 757 (1969); M. Barfield, J. Chem. Phys. 41, 3825 (1964); M. Barfield and M. Karplus J. Am. Chem. Soc. 91, 1 (1969).

Very sincerely yours

Rosario Mondelli 'R. Mondelli



Technische Hogeschool Delft

Laboratorium voor Technische Natuurkunde

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

Uw kenmerk Uw brief van Ons kenmerk Delft, Nederland, Lorentzweg 1, tel. 01730-33222
June 30, 1971 toestel:

Onderwerp

Dear Professor Shapiro,

In addition to our letter of 8.12.1970 entitled: Free precession decay for a two spin ($\frac{1}{2}$)-system, that appeared in the NMR Newsletter Nr. 148 of January 1971, we wish to inform you that the calculation of this free precession decay has already been given by Look, Lowe and Northby, J. Chem. Phys. 44 (1966) 3441, an article that until recently has escaped from our attention.

However, our work was not entirely a duplicate because firstly, we were able to take into account more precisely the interaction between the spin pairs, and secondly, we extended the calculations by considering the influence of the amplitude of the modulation field and of saturation of the spin system on the decay in the case, that the Fourier Transform of the lock-in signal is used. About this and the measurements mentioned in our letter, a lecture will be given at the Fourth International Symposium on Magnetic Resonance, to be held in Israël in September this year.

Sincerely yours,

R.A. Wind.:

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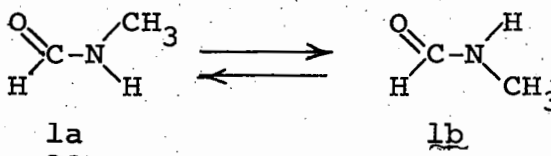
July 1, 1971

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

Title: Hindered Rotation in a Monosubstituted Amide

Dear Barry:

We have completed a relatively difficult kinetic study on rotation about the C-N bond in N-methylformamide (1).



This system was chosen because the minor isomer 1b was present in sufficient concentration for these studies to be carried out.

The rotational free energies of activation differ by an amount almost equal to the ΔF° value for isomer equilibrium. The frequency factors are relatively normal. The activation parameters are comparable to those for DMF but somewhat different than those for formamide.

We shall be reporting the data in the near future.

Sincerely yours,

Bob

Robert C. Neuman, Jr.
 Associate Professor of Chemistry

RCN:mmm

UNIVERSITY OF COLORADO

BOULDER, COLORADO 80302

DEPARTMENT OF CHEMISTRY

July 2, 1971

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

Dear Barry:

Proton Magnetic Relaxation Studies of Water Coordination in Vanadyl(IV) Fluoro Complexes. Position Available.

We have used pulsed NMR to measure T_1 and high resolution NMR to measure T_2 of aqueous vanadyl solutions containing added fluoride ion. In vanadyl complexes the proton exchange rate, τ_H , is approximately equal to T_{2B} , the transverse relaxation time of waters bound in the first coordination sphere of VO^{2+} . $T_{1B} > \tau_H$ however. Thus, τ_H can be obtained from a T_2 study. Using the stability constants of Ahrland and Noren¹, one can then calculate the exchange rate of each fluoro substituted complex. Leaving out the lengthy details of the analysis we find the following exchange rate constants:

<u>COMPLEX</u>	<u>SPECIFIC RATE CONSTANT (sec⁻¹)</u>
$VO(H_2O)_5$	5.25×10^3
$VOF(H_2O)_3$	1.9×10^4
$VOF_2(H_2O)_2$	3.7×10^4
$VOF_3(H_2O)$	4.9×10^5

The fact that the rate constants increase with fluorine substitution is significant since it has previously been shown that the mechanism for proton exchange involve protolytic dissociation rather than whole water exchange^{2,3}. Since it is difficult to envisage how fluoride ligands increase the rate of proton dissociation it appears that addition of one or more fluoride ligands increases the rate of whole water exchange so as to make this the dominant mechanism.

References

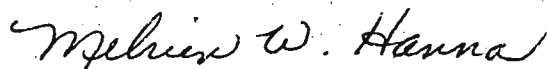
1. S. Ahrland and B. Noren, Acta Chem. Scand. 12, 1595 (1958).
2. T. J. Swift, T. A. Stephenson and G. R. Stein, J. Am. Chem. Soc. 89, 1611 (1967).
3. J. Reuben and D. Fiat, Inorg. Chem. 6, 579 (1967); K. Wuthrich and R. C. Connick, ibid., 683 (1967).

-2-

We have need of a technician with training equivalent to a B.S. in Chemistry to be involved with a new FT-NMR system which we will be getting in September. NMR experience would be helpful as would a desire to learn electronics and the inner workings of NMR spectrometers. A new B.S. would be considered as would older people with the proper experience. Salary to be negotiated but around \$8,000-\$9,000. Suggested candidates or applications should be sent to me.

I hope this serves to reinstate my subscription after a long absence.

Sincerely yours,



Melvin W. Hanna
Professor of Chemistry

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