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Texas A & M University N-M-R Newsletter

No. 234

March, 1978

TAMU NMR NEWSLETTER - ADVERTISERS

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    We welcome two new additions to the list of CONTRIBUTORS.

    ┌───┐
    │ DEADLINE DATES: No. 235: 3 April 1978   │
    │   No. 236: 1 May 1978   │
    └───┘
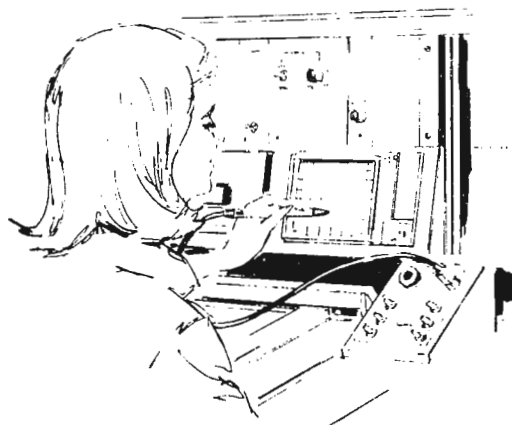

    All Newsletter Correspondence, Etc. Should Be Addressed To:

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

THE PROCTER & GAMBLE COMPANY

MIAMI VALLEY LABORATORIES

P. O. BOX 39175
CINCINNATI, OHIO 45247

February 7, 1978

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

Dear Barry:

High-Resolution NMR of Solids in Colloidal Solution

We have been interested in the NMR of surface-adsorbed species on calcium hydroxyapatite, $Ca_5(OH)(PO_4)_3$, which is the prime mineral constituent of bone and tooth enamel. However, the broad lines encountered with the solid present problems. For example, the ^{31}P NMR (on our Bruker HX-90) of hydroxy-apatite solid is about 2kHz broad due to a combination of P-P and P-H dipolar interactions and possibly a small chemical shift anisotropy. In order to narrow the resonances to observe the ^{31}P NMR of surface-adsorbed species, we decided to look at suspended colloidal particles whose rotational correlation time would be short enough to average the broadening interactions.

Therefore, hydroxyapatite was prepared with a high specific surface area ($80m^2/g$, the average particle size from electron microscopy being about 150X150X500 Å), and suspended in D_2O (600 mg/2 ml). In order to form a stable colloidal suspension, a "peptizing agent" (a diphosphonate such as EHDP – see Figure) was added which adsorbed to the surface and whose negative charge caused interparticle repulsion. In addition, prolonged ultrasonication of the suspension was necessary to obtain a significant amount of solid in colloidal solution.

The ^{31}P NMR of a typical colloidal solution is shown in the Figure. The EHDP signal at -19 ppm (downfield from H_3PO_4) is due to adsorbed EHDP, since addition of further EHDP results in a sharper peak superimposed at the same chemical shift. The solution phosphate peak arising from dissolved hydroxy-apatite is identified by its shift upfield at lower pH, whereas the solid hydroxyapatite peak is insensitive to pH (and can be removed by ultracentri-fugation). The resonance of the hydroxyapatite has indeed sharpened from 2kHz to about 100 Hz, a factor of 20. The residual breadth is due to factors other than field inhomogeneity, as evidenced by the sharpness of the solution phosphate peak.

This approach to high-resolution NMR in solids has several interesting aspects. One is that the isotropic ^{31}P chemical shift of hydroxyapatite can be measured accurately to be -2.6 ppm (downfield from H_3PO_4); this differs both from protonated phosphate groups in other solids and from PO_4^{-3} in solution. Secondly, the ^{31}P NMR of surface-adsorbed species such as diphosphonates can

THE PROCTER & GAMBLE COMPANY

Dr. Bernard L. Shapiro
February 7, 1978

be observed as sharpened peaks. We have looked at both ^{31}P T_1's and the ^1H NMR of this system to try to further characterize the adsorption.

This technique offers a means of obtaining high-resolution NMR in solids with conventional high-resolution NMR equipment. I hope that this example will suggest other applications.

Sincerely yours,

THE PROCTER & GAMBLE COMPANY
Research and Development Department

James Yesinowski
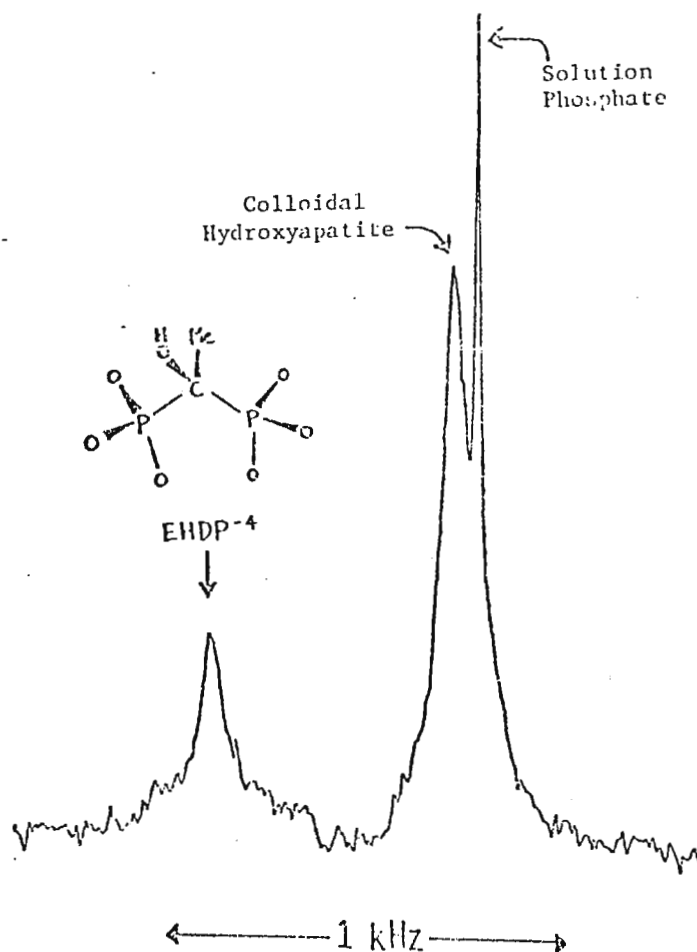
James P. Yesinowski

psm

Figure: ^{31}P Spectrum of Colloidal Hydroxy-apatite + EHDP

THE UNIVERSITY OF NEW ENGLAND

ARMIDALE, N.S.W. 2351

Department of Organic Chemistry

14th February, 1978

Dear Professor Shapiro,

Subject: **Field-Dependent AB Coupling Patterns**

I have only recently received the November, 1977, Newsletter and, by this time, you may already have received other letters on the present subject. I am not aware of any published detailed treatment, so here goes.

Gareth and Sandra Eaton's "expressions" for the field positions of the four AB lines at constant frequency ν_0 (TAMUNMR 230-33) are correct as far as they go, but they are in fact equations that may be solved exactly to give the following explicit expressions (the spins here being labelled A and B):

$$H_1 = (h/2g_A g_B \beta)[(g_A + g_B)(\nu_0 - J/2)] - C_-$$

$$H_2 = (h/2g_A g_B \beta)[(g_A + g_B)(\nu_0 + J/2)] - C_+$$

$$H_3 = (h/2g_A g_B \beta)[(g_A + g_B)(\nu_0 - J/2)] + C_-$$

$$H_4 = (h/2g_A g_B \beta)[(g_A + g_B)(\nu_0 + J/2)] + C_+$$

where $C_\pm = (h/2g_A g_B \beta)[(g_A - g_B)^2(\nu_0 \pm J/2)^2 + g_A g_B J^2]^{\frac{1}{2}}$

I am not sure what the Eatons are saying in the statement that follows their equations, but probably it is related to the present result that the field splitting of the A lines, $(H_2 - H_1)$, is less than that of the B lines, $(H_4 - H_3)$. The difference is, however, likely to be very small. The field values may be put into frequency units (Hz) by multiplying by $2g_A g_B \beta / h(g_A + g_B)$. The _mean_ splitting is then equal to J, and the difference between the A and B splittings is $2(C_+ - C_-)$ (in Hz). Put $g_A = g(1 + d/2)$ and $g_B = g(1 - d/2)$, where d is the fractional chemical shift. Then $g_A + g_B = 2g$, $g_A - g_B = gd$, $g_A g_B = g^2(1 - d^2/4)$, and

$$C_\pm \text{ (in Hz)} = \tfrac{1}{2}(d^2\nu_0^2 \pm d^2\nu_0 J + J^2)^{\frac{1}{2}}$$

For any practically useful field in n.m.r., $\nu_0 \gg J$, so $d^2\nu_0^2 \gg d^2\nu_0 J$, but J^2 may be comparable with $d^2\nu_0^2$. In close approximation, therefore,

$$C_\pm \text{ (in Hz)} = \tfrac{1}{2}[(d^2\nu_0^2 + J^2)^{\frac{1}{2}} \pm d^2\nu_0 J/2(d^2\nu_0^2 + J^2)^{\frac{1}{2}}]$$

The difference in splittings is then

$$D = 2(C_+ - C_-) \text{ (in Hz)} = d^2\nu_0 J/(d^2\nu_0^2 + J^2)^{\frac{1}{2}} = dJ/(1 + J^2/d^2\nu_0^2)^{\frac{1}{2}}$$

The maximum value of D is therefore dJ, and the fractional difference, D/J, decreases as $J/d\nu_0$ increases (_e.g._, for a chemical shift of 100 ppm and J = 100 Hz, D_{max} = 0.01 Hz. $D/J = 10^{-4}$ at 100 MHz, and decreases to 7.07×10^{-5} at 1 MHz).

Similarly, relative intensities in a field-swept n.m.r. spectrum differ little from those in the frequency-swept spectrum, and the differences are unlikely to be detected experimentally.

Yours sincerely,

N. V. Riggs

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DEPARTMENT OF CHEMISTRY / 303·753-2436

February 28, 1978

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

Dear Barry: Field Dependent AB Coupling Patterns Cont'd.

Thank you for sending us a copy of N. V. Riggs' contribution commenting on our TAMUNMR 230-33. We gave the expressions for the positions of the four lines in the AB quartet in a form which we thought clearly exhibited the field dependence of the transitions at constant frequency. The expressions can be rearranged so that the field values do not occur on the right hand side. Riggs' provides one such form. We have used a slightly different form in a paper submitted to J. Mag. Res. discussing the field dependence of AB patterns in EPR. Our point in the statements following the equations for $H_1, \ldots, H_4$ was simply that the expressions for the AB quartet are usually given at constant field, not constant frequency. Usually the difference is ignored, and Riggs provides numerical values which justify the usual approximations. However, if you consider an "extreme" magnetic resonance case of X-band EPR $\nu_0 \approx 9.5 \times 10^9$ Hz, $g_1 = 2.0059$, $g_2 = 2.0924$, and J = 300 MHz (~107G) the four lines of the AB quartet occur at 3175.1, 3278.0, 3348.0, and 3454.4 Gauss. The spacings H_4-H_3 and H_2-H_1 differ in this case by 3.5 Gauss. In Riggs' notation D/J = .033.

Although we cannot cite as dramatic an example from NMR, maybe some Newsletter reader can provide one.

Sincerely,

Gareth R. Eaton
Associate Professor of Chemistry

Sandra S. Eaton
Assistant Professor of Chemistry

copy: N. V. Riggs

GRE:SSE:ms

NICOLET TECHNOLOGY CORPORATION

145 East Dana Street
Mountain View, California 94041

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

February 20, 1978

H$_2$O and HOD in CDCl$_3$

Dear Barry:

The other day, I had occa-
in CDCl$_3$ for use in sensitivity
opened a newly received bottle
made up the 0.1% ethylbenzene
gas through it. The proton
excellent signal-to-noise, a
frequency side of it three
these little peaks are assign-
and the J$_{H,D}$ of 1.01 - 1.05 Hz
1.1 Hz values reported by

This is the first time
slow exchange of water protons

sion to make up a sample of 0.1% ethylbenzene
tests of a 20 mm NT-150 proton probehead. I
of 99.8% CDCl$_3$ (Aldrich, lot no. 051877 EB),
solution, and then bubbled a little nitrogen
spectrum of this solution showed, apart from
rather large water peak and just to the low-
little "impurity" peaks. Much to my surprise,
able to HOD. The isotope shift of 0.031 ppm
are in good agreement with the 0.030 ppm and
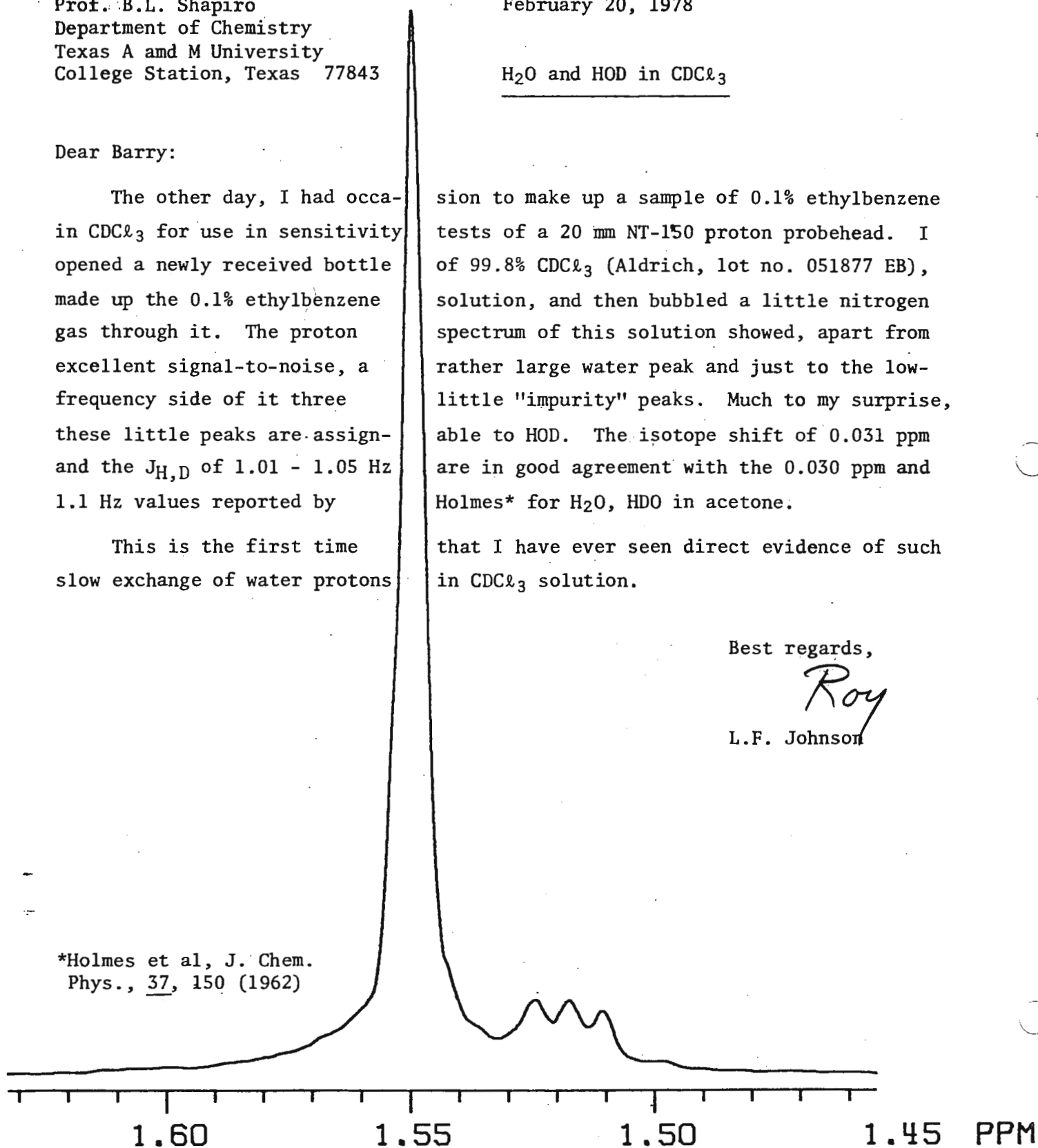Holmes* for H$_2$O, HDO in acetone.

that I have ever seen direct evidence of such
in CDCl$_3$ solution.

Best regards,

Roy

L.F. Johnson

*Holmes et al, J. Chem.
Phys., 37, 150 (1962)

1.60   1.55   1.50   1.45 PPM

Department of Chemistry   **The Florida State University**
Tallahassee, Florida 32306

VARIABLE FREQUENCY ^{13}C RELAXATION *continued*

February 17, 1978

Dear Barry:

In our recent communication[1] we noted that neat 1,2 decanediol at 54°C (well above its melting point of 26°C-28°C) shows a pronounced field dependence for all of its ^{13}C spin-lattice relaxation times. The T_1's ranged from 0.55 for C-1 to 5.3 sec for C-10 at 67.9 MHz but from 0.27 to 3.4 sec for C-1 to C-10 at 22.6 MHz (see Table). Data was also given for neat 1-decanol, n-heptane and n-ecosane showing <u>no</u> field dependences.

Studies of 1,2-decanediol and related compounds have been continued. At all temperatures completed (30-65°C) for neat 1,2 decanediol a field dependence <u>is present</u>. These field dependences are attributed to the presence of a non-exponential autocorrelation function $G(\tau)$ describing molecular reorientation. (Equivalently, this requires a distribution of correlation times rather than a single defined τ_{eff}.) This effect is presumed to result from complexities of the glycol "solvation", or perhaps "micelle" formation. An interesting feature of these relaxation data is the propagation of the field dependence through the ten carbon chain, in opposition to predictions of earlier theories, which decouple CH_2 carbon segments formally removed from a site of restriction. We were able to quantitatively predict the observed behavior with a new theoretical treatment[2] combining a non-exponential $G(\tau)$ and existing treatment of multiple internal motions. Recently, London and Avitabile[3] stated that modification of the simple independent rotation model can also bring about a field dependence along hydrocarbon chains. In modifying the previous theory, London and Avitabile assumed that the carbon-carbon bonds are in either a <u>trans</u> or <u>gauche</u> configuration and that any transitions between states is allowed except the $g^+ \rightleftarrows g^-$. Adjacent g^+g^- states are allowed also. Since there are restrictions on states of the system, the carbon-carbon bond rotations should be correlated to their neighbor's. This modified theory applies well to polymers and lecithin-type systems, but the 1,2 decanediol data cannot really be classified in these areas. The 1,2-decanediol data is not explained by any of these theories including this recent modification by London and Avitabile.[3]

Furthermore, our more recent (and still preliminary!!) data indicate further complexities. For solutions of 1,2-decanediol one might expect reduced solvation complexities (or might one?) especially at higher temperatures where thermal motion increases. As shown in the Table below, at lower observation temperatures there is no significant field dependence observed for 2 Molar 1,2-decanediol in benzene, while the ten carbon field dependence reasserts itself at higher temperatures. Similar preliminary data are available for lower concentrations.

We are currently expanding these studies to gain some understanding of the complex motional behavior apparently inherent to these systems. Included will be solvent effects (to induce and inhibit micelle and other "structure" formation) as well as measurements on other straight chain alcohols and glycols.

We also plan to utilize correlated chain conformations in an improved calculation scheme to better define theoretical approaches to understand alkyl chain dynamics.

Table: 1,2 DECANEDIOL $HOCH_2CH(OH)CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
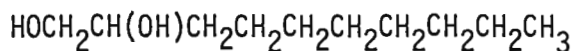
| | | 1 | 2 | | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
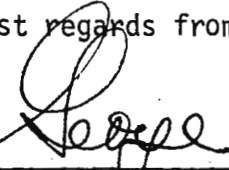
67.9 MHz

Carbon #	1	2	3	4	5-7	8	9	10
neat 54°	.50	.80	.60	.65	.9	1.8	2.7	5.3
2M 33°C	.30	.55	.46	.58	.79-.91	1.6	2.4	3.7
2M 45°C	.72	1.1	.83	1.0	1.2-1.8	2.9	4.2	5.2
.5M 65°C	3.1	3.5	3.1	3.4	3.7-5.0	6.7	7.8	8.2

22.6 MHz

	1	2	3	4	5-7	8	9	10
neat 54°C	.27	.41	.30	.35	.50	.95	1.5	3.4
2M 34°C	.39	.65	.50	.60	1.1	1.7	2.2	3.3
2M 45°C	.42	.86	.54	.64	1.2-1.1	1.9	2.4	3.5
.5M 65°C	1.8	2.8	2.0	2.2	3.4	---	7.2	⌐ 7.0

Best regards from sunny Florida,

George C. Levy
Professor

Mary P. Cordes
Research Assistant

David E. Axelson
Postdoctoral Fellow

(1) G.C. Levy, M.P. Cordes, J.S. Lewis and D.E. Axelson, J. Am. Chem. Soc., 99, 5492 (1977).

(2) G.C. Levy, D.E. Axelson, R.L. Schwartz and J. Hochmann, J. Am. Chem. Soc., 100, 410 (1978).

(3) R.E. London and J. Avitabile, J. Am. Chem. Soc., 99, 7765 (1977).

INSTITUT FÜR PHYSIK DER UNIVERSITÄT BASEL   CH - 4056 Basel (Schweiz) February 23, 78

EXPERIMENTELLE PHYSIK DER KONDENSIERTEN MATERIE

Klingelbergstrasse 82, Telefon 061 - 4420xx442280

Prof.Dr.P.Diehl

Prof. B.L. Shapiro
Texas A and M University
Department of Chemistry
College Station
Texas 77843   USA

Title: Proton chemical shift anisotropy of benzene

Dear Barry,

We have lately been studying spectra of oriented benzene in various liquid crystal solvents. As a by-product of this study we made a new determination of the proton chemical shift anisotropy of benzene which I would like to report in this letter:

We used the smectic liquid crystal HAB as a solvent and measured the chemical shift difference, with the optic axis at 0° and 90° with respect to the magnetic field. Methane was added as an internal reference in order to eliminate suszeptibility anisotropy and local contributions. The result for the shift anisotropy is

$$\Delta\sigma = -2.59\pm0.04 \text{ ppm}$$

This disagrees slightly with earlier results, $\Delta\sigma = -2.9\pm02$ ppm (1) measured by nematic-isotropic phase transition, $\Delta\sigma = -3.45\pm0.7$ ppm (2) measured with T-variation and internal TMS reference and $\Delta\sigma = -3.05\pm0.35$ ppm (2) with external TMS reference. The new measurement deviates considerably from an early theoretical prediction based on the ring current exclusively, $\Delta\sigma = -4.4$ ppm (3), but is closer to a later prediction (4) of $\Delta\sigma = -2.16$ ppm.

Yours sincerely

P. Diehl   H. Zimmermann

Literature:

(1) A. Saupe and G. Englert, Phys. Rev. Lett. 11, 462 (1963).
     G. Englert and A. Saupe, Z. Naturforsch. A19, 172 (1964).
     A. Saupe. Z. Naturforsch. A20, 572 (1965).

(2) J. Lindon and B.P. Beiley, Mol. Phys. 19, 285 (1970).

(3) B.P. Beiley, J. Chem. Phys. 41, 2304 (1964).

(4) H.G. FI. Roberts. Chem. Phys. Lett. 11, 259 (1971).

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**Laboratorium
für anorganische Chemie**
Eidg. Technische Hochschule
Zürich

8006 Zürich, February 14, 1978
Universitätstrasse 6

Post doctoral Position Available

I should like to make your readers aware that a postdoctoral research position in our group is now available. The research will concern itself with ^{31}P and ^{195}Pt NMR studies of catalytically active metal complexes. The position is initially available for one year with the possibility of an extension to a second year. Salary ≂ $ 17,500/year. Interested readers should write to me directly at the address shown above.

Yours sincerely

Dr. P. S. Pregosin

БЪЛГАРСКА
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Sofia 13, Bulgarien

Sofia, den 8 February 19 78

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

^{13}C NMR Spectra of Some Dihydrocoumarins

Dear Professor Shapiro,

Here is our reply to the blue reminder (and the pink one which is probably under way).

For some time we are studying the ^{13}C spectra of various cyclic and acyclic diastereomers in relation to their configuration and conformation. For a series of 4-alkyl-3-phenyl-3,4-dihydrocoumarins, a configurational dependence of the chemical shift was observed for the first carbon atoms of the substituents (3' and 4'). The δ-values (TMS = 0) are listed below.
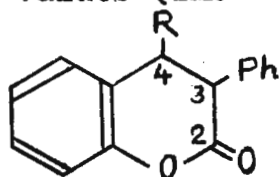
R =	Et		i-Pr		t-Bu		CH$_2$Ph	
	cis	trans	cis	trans	cis	trans	cis	trans
C-3'	134.7	136.2	134.7	136.8	136.2	137.6	134.5	135.9
C-4'	22.1	28.2	27.2	33.6	35.6	35.0	35.6	42.4

The upfield shifts observed for the cis-compounds are in accord with the "δ-effect" since the ^{1}H data indicate strong predominance of the conformer with pseudoaxial substituents in the case of trans-compounds.[1] It is interesting that for the t-Bu compound the difference in steric interactions for both isomers appears to be small. There is practically no configurational effect upon the C-2, C-3 and C-4 shifts.
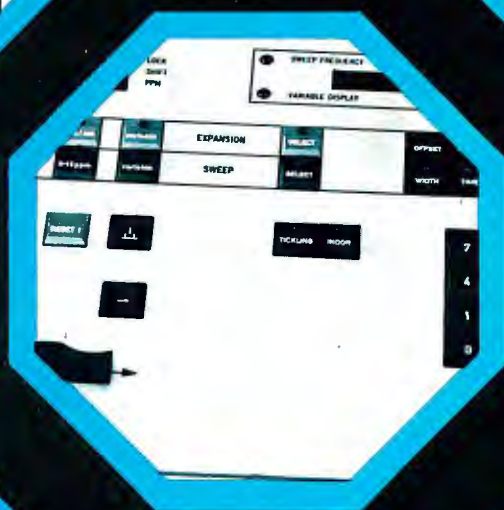
Sincerely yours,

Stefan

Stefan L. Spassov

[1] S.L.Spassov, A.G.Bojilova and C.Ivanov, C.r.Acad.bulg.Sci. 28, 1383 (1975).

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Dr. Bernard L. Shapiro
Department of Chemistry
Texas A. & M. University

COLLEGE STATION, TX 77843

USA

February 2, 1978

Dear Sir,

For a junior Ph.D. a <u>postdoctoral position</u> for NMR. work
is immediately available (for 1-2 years) at the University
of Lausanne. He could be a physical chemist or a chemist
with sufficient knowledge of apparatus (Bruker HX; WP 80
CW; WP 60 FT and, hopefully, CPX 270). He would be expec-
ted to do semi-independent research with one of the insti-
tute's research groups, preferentially on O-17. Salary :
from Frs. 41'000/year upward, depending upon experience
and family status.

Candidates should write to me adding a brief curriculum
vitae and names of referees.

Sincerely

(Prof. H. Dahn)

Department of Energy
Laramie Energy Research Center
P.O. Box 3395, University Station
Laramie, Wyoming 82071

February 23, 1978

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

Dear Dr. Shapiro:

A Signal Averager Interface for Multiple-pulse Sequences

In making T_2 measurements on biological systems we ran into a familiar problem. If the echoes are milliseconds wide but the complete train of echoes many seconds long, the signal averager or transient recorder must be adjusted to place a very limited number of acquisition points on each echo. Most of the data points are just baseline. This is a hopeless situation if the averager is not synchronized to the pulse generator of the spectrometer, as in our Bruker BKR-322S and Nicolet 1074 system. But even if the averager is synchronized to place an acquisition point at the top of each echo, the data taking procedure is not yet optimized.

A higher signal to noise ratio can be achieved by digital means or by eyeball if more points are taken on the echo. In addition, seeing all of each echo on the display scope may aid in tuning up. The scheme is shown in the figure, where the interface waits a time t_d after a π-pulse and runs the averager for a time t_r. On our system, providing for this scheme was not significantly more difficult than providing for a single point on each echo.

The Bruker BKR-322S has a "calib" output which provides a variable, synchronized clock for the interface. In the absence of this feature a divider network, to be fed by the spectrometer's master clock, could be added to the interface by duplicating one of the dividers in our design. No modifications were made to the Bruker or the Nicolet. This will be true for most spectrometers to which a signal averager has been added. At worst, the pulse gating and clock circuitry of the spectrometer might have to be tapped and brought out to BNCs. Any signal averager with external address advance will work.

The interface is very simple to build, using integrated digital circuitry. It costs one man-day and about $75, including power supply and cabinet. We settled on particular ratios of t_d and t_r to the clock period, but making these variable would be easy for any good technician armed with a rotary switch. In this case, the interface could also be set to give a single point on each echo. We included an extra switch which allows the same sort of observation of the signals from a triplet sequence. The schematic, logic diagram and more details are available on request.

Dr. Shapiro   February 23, 1978

     By the way, if there are any other lost souls out there with a
Nicolet FFT system based on a 4K PDP-8, we have a flexible monitor
and relaxation data software system which fits into the nooks and
crannies of the PDP-8 not used by the FFT program. Paper tape and
documentation available on request.
     Please credit this report to Dr. Netzel's account.

Sincerely,

Dale McKay

Dale McKay
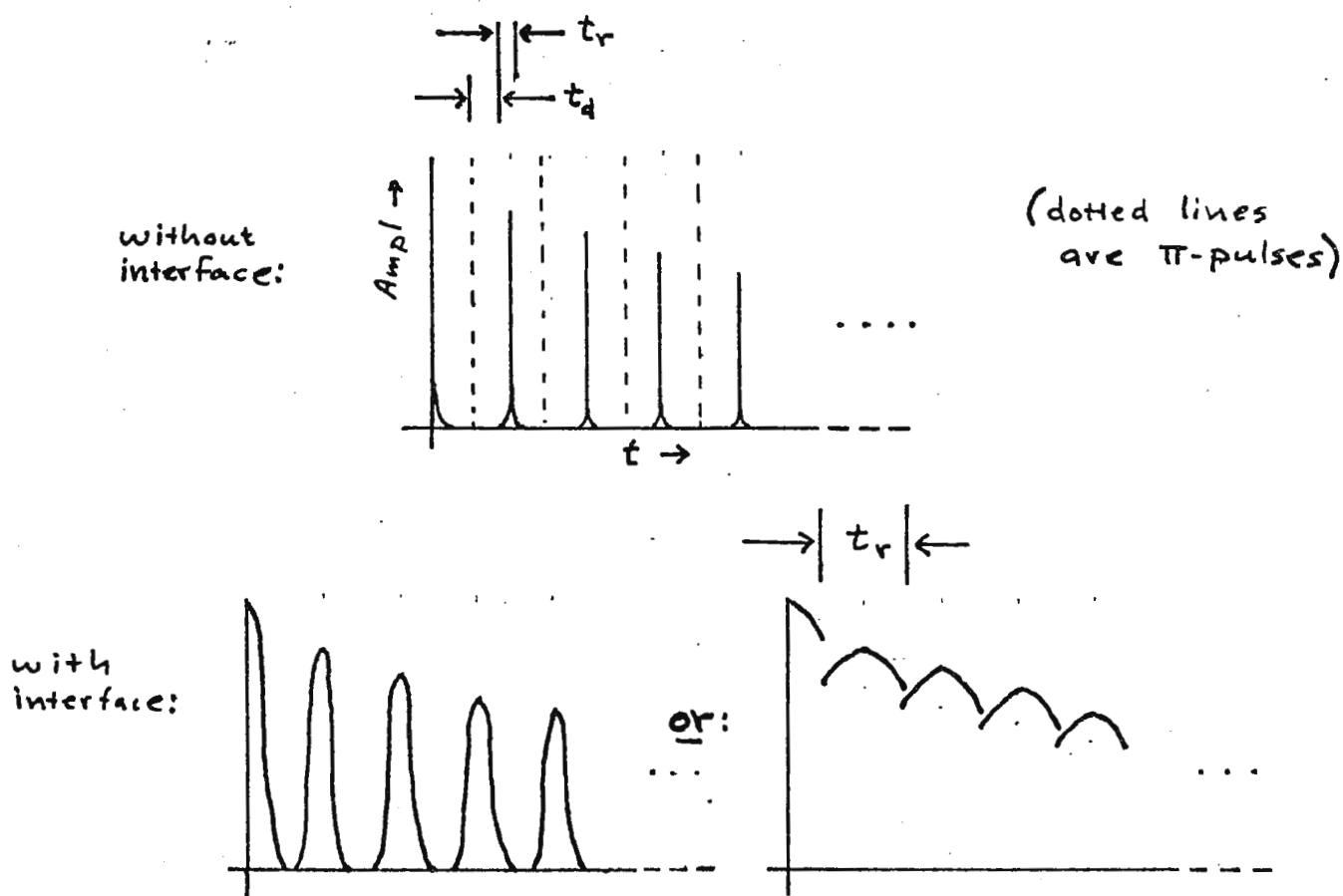
Universität Regensburg

FACHBEREICH CHEMIE UND PHARMAZIE
Institut für Chemie

G. Becher
A. Mannschreck

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

THE (E)/(Z) ISOMERS OF A HIGHLY METHYL SUBSTITUTED BUTADIENE

Dear Professor Shapiro,

a mixture of (E,Z), (E,E) and (Z,Z) isomers of dimethyl
2,3,4,5-tetramethyl-2,4-hexadienedioate was obtained by photo-
merization of (E,Z) which was known[1]. Pure (E,E) and (Z,Z) were
isolated by a combination of thicklayer and vapour phase chromato-

(E,E)   (E,Z)   (Z,Z)
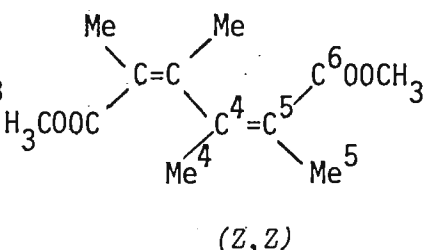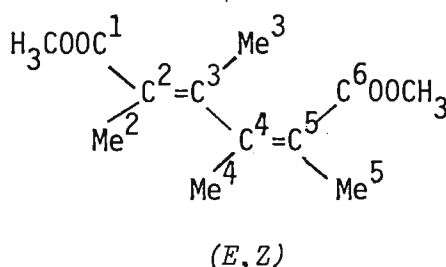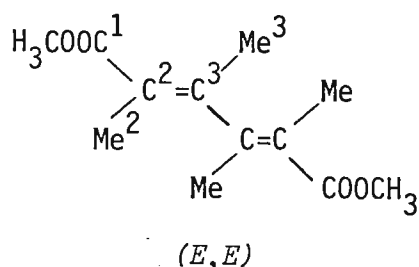
graphy and the configurations assigned by means of $^5J_{HH}$ (Table 1).
We have confirmed the validity of the rule[2] $^5J_{HH}(E) > {}^5J_{HH}(Z)$
by looking at the ^{13}C satellites of the CH_3 signals for dimethyl
(E)-2,3-dimethylbutenedioate ($^5J_{HH}$ = 1.57 Hz) and dimethyl
(Z)-2,3-dimethylbutenedioate ($^5J_{HH}$ = 1.17 Hz). Surprisingly, the
^1H nmr signals of Me^2 and Me^3 in (E,Z) are shifted *downfield*
by benzene (Table 1). We do not know yet the conformation of the
carbonyl groups relative to the C=C bonds, i.e., whether the
arrangement is *s-cis* or *s-trans* or both. Therefore, the above
unusual ASIS cannot yet be compared to known downfield shifts
in some enones (cf. ref. 3). Comments are welcome.

Since highly substituted dienes are twisted around the
central single bond[5], the above butadienes should be chiral.
In this respect, the usefulness of (+)-tris(3-heptafluorobutyryl-
D-campherato)-europium(III), (+)-Eu(hfbc)$_3$, was proven[6]. It
may generate additional splittings in the ^1H nmr spectrum as
far as the enantiomerization, i.e. partial rotation around the

Table 1. ^{1}H Nmr Data (+34°C)

		$^5J_{HH}$[Hz]	$\delta(C_6D_6)$	$\delta(CCL_4)-\delta(C_6D_6)$
(E,E)	Me^2	1.5	1.72	0.00
	Me^3	1.5	2.04	+0.01
(E,Z)	Me^2	1.5	1.80[a]	-0.17
	Me^3	1.5	2.30[a]	-0.25
	Me^4	1.0	1.51[a,b]	+0.36
	Me^5	1.0	1.77[a,b]	+0.10
(Z,Z)	Me^4	0.9	1.83	0.00
	Me^5	0.9	1.89	-0.06

[a] Assignment corresponding to ref. 4.

[b] Assignment according to $\delta(CCl_4)-\delta(C_6D_6)$; cf. ref. 3.

central single bond via the *s-trans* transition state, is slow.
In fact, around -20°C several signals of *(E,Z)*, *(E,E)*, and
(Z,Z) show such splittings which coalesce at higher temperatures.
For each diene, at least one of these signals was suitable for
lineshape analysis[7]. In $CCl_4/CFCl_3$ (2:1), using [(+)-Eu(hfbc)$_3$]:
[diene] = 0.4 to 0.8, the following barriers to partial rotation,
$\Delta G^{\ddagger}$, were obtained:

$$(E,E): \quad 75.5 \pm 1.5 \text{ kJ/mol} \quad (\quad +20°C)$$
$$(E,Z): \quad 66.7 \pm 0.8 \text{ kJ/mol} \quad (\quad +26°C)$$
$$(Z,Z): \sim 60 \quad\quad\quad \text{kJ/mol} \quad (\sim -10°C).$$

The order of barrier heights *(E,E)* > *(E,Z)* > *(Z,Z)* is a resonable
one: In the crowded transition state for *(Z,Z)* the $COOCH_3$ groups
can be turned out of planarity, thus minimizing non-bonded inter-
actions. In contrast, the transition state for *(E,E)* suffers
from CH_3/CH_3 interactions which are more difficult to diminish.

Table 2. ^{13}C Nmr δ-Values in ppm from (CDCl$_3$, +30°C)

	C^1	C^6	C^2	C^5	C^3	C^4	Me^2	Me^3	Me^4	Me^5
(E,E)	169.2		122.0		148.6		15.9[a]	18.8[a]		
(E,Z)[b]	169.2	168.4	122.8	120.0	148.0	151.1	16.2	18.7	19.8	14.7
(Z,Z)		168.7		120.4		151.0			19.9[a]	14.8[a]

[a] Assignment is uncertain.

[b] Assignments *within* the different groups of carbons are tentative.

The ^{13}C spectrum of *(E,Z)* seems to be a superposition of the *(E,E)* and *(Z,Z)* spectra (Table 2). This is in agreement with the above mentioned twist about the C^3-C^4 bond, i.e., with a low π interaction between the two C=C units. The greatest difference (Δδ = 2.4 ppm) between *(E,E)* and *(Z,Z)* was found for C^3/C^4 which are connected by the formal single bond. However, the origin of this difference is not understood.

Moreover, nmr work on non-planar ketones[8], chiral diaziridines[9], chiral donor/acceptor interaction[10], and ion association in iminium salts[11], is going on in our group.

Sincerely yours,

Georg Becher

Albrecht Mannschreck

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11) F.Lefèvre.

WAYNE STATE UNIVERSITY

COLLEGE OF LIBERAL ARTS   DETROIT, MICHIGAN 48202

February 23, 1978

DEPARTMENT OF CHEMISTRY

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

Chelation of Alkali Metal Cations by Diacetamide

Dear Barry,

We have recently described an nmr method for studying chelation of alkali
metals by acetylacetonate anion (acac) [J. Am. Chem. Soc., 99, 6527 (1977)].
We have now extended this study to the neutral isoelectronic analog diacetamide
(DA). While diacetamide exists exclusively in the E, Z configuration in non-polar
solvents, [J. Am. Chem. Soc., 97, 5811 (1975)] both E, Z and Z, Z forms can be
observed in methanol solutions in a ratio E, Z:Z, Z of ca. 2:1. The ratio of configu-
rational isomers was determined by integration of the low temperature (ca. -100°C)

(eq. 1)

E, Z   Z, Z   Z, Z·M+
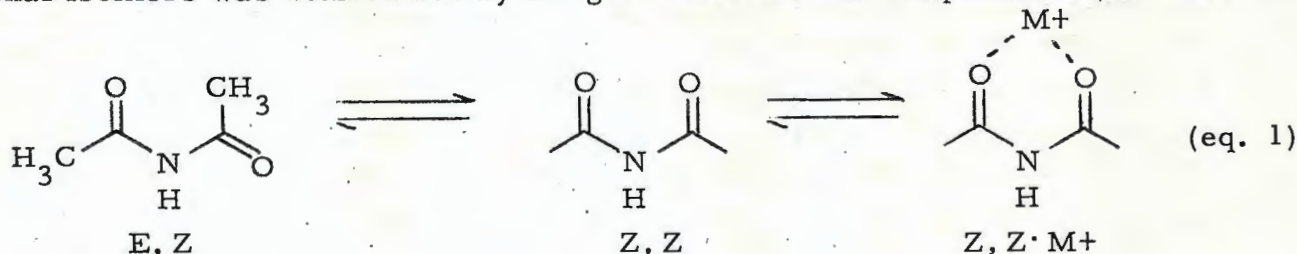
proton nmr spectra. The increased stability of the Z, Z form in methanol solution
can be understood by noting that the calculated dipole moments for the corresponding
configurational isomers of diformamide are: Z, Z 6.46D and E, Z 3.53D. Thus the
more polar configuration is observed only in the more polar solvent.

When alkali metal salts are added, the equilibrium is further shifted to the Z, Z
configuration as the result of chelation and consequent stabilization of the Z, Z
configuration. In similar experiments with acac the magnitude of the shift critically
depends on which metal ion is used, $Li^+ > Na^+ > K^+$. In the present case a different
order is observed. Addition of one mole of potassium or sodium ion shifts the
configurational ratio from 34% to 61% or 62% respectively of the Z, Z form while a
mole of lithium ion causes a shift only to 48%. Thus, in this case, the order is
$Na^+ \sim K^+ > Li^+$. Further work is underway to elucidate the reasons for this change
in ion specificity on going from the charged to the neutral ligand.

Richard A. Keintz

Morton Raban

THE UNIVERSITY OF WINNIPEG

WINNIPEG, CANADA   R3B 2E9

February 21, 1978

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

Dear Barry,

Hindered Rotation in Heptachloro-o-xylene. The Use of Covariance to

Determine Uncertainty in $\Delta G^{\neq}$.

We have recently completed a study of the hindered rotation of the dichloromethyl groups in $\alpha,\alpha,\alpha',\alpha',3,4,6$-heptachloro-ortho-xylene(HCOX) using DNMR line shape analysis, supplemented with a homonuclear double resonance saturation transfer technique. The rate process in HCOX involves a coupled rotation of the two substituted methyl groups and the non-mutual exchange of the three pairs of protons between two equally populated conformers. The data was treated in the usual way with the errors obtained from Binsch's program

ACTPAR (1): E_a = 15.3±0.3 kcal/mole, $\Delta H^{\neq}$ = 14.6±0.3 kcal/mole, $\Delta S^{\neq}$ = -8.8±0.8 cal/deg/mole, and $\Delta G^{\neq}$ = 17.22±0.07 kcal/mole at 25°C. For $\Delta G^{\neq}$, which is "known" to be the most reliable transition state parameter for comparing data, we

determined the uncertainty σ ($\Delta G^{\neq}$) from the equation (2,3):

$$\sigma^2(\Delta G^{\neq}) = \sigma^2(\Delta H^{\neq}) + T^2\sigma^2(\Delta S^{\neq}) - 2T\rho\ \sigma(\Delta H^{\neq})\ \sigma(\Delta S^{\neq})$$

The last term in this equation represents the covariance between $\Delta H^{\neq}$, $\Delta S^{\neq}$ where ρ is the correlation coefficient from the data used to determine $\Delta H^{\neq}$, $\Delta S^{\neq}$ (i.e. the plot of $\ln(k/T)$ vs. T^{-1} where k is the experimentally determined rate constant); $\sigma(\Delta H^{\neq})$, $\sigma(\Delta S^{\neq})$ are uncertainties in $\Delta H^{\neq}$, $\Delta S^{\neq}$. We compared the uncertainties in $\Delta G^{\neq}$ using the covariance term with the values reported for similar chloro-substituted toluenes determined in Ted Schaefer's lab. The inclusion of the covariance term would indicate that the values of $\Delta G^{\neq}$ should be more accurate than previously reported. Please credit this to Rod Wasylishen's account.

Sincerely,

H. M. Hutton
Department of Chemistry

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