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No. 40

Author Index

DEADLINE FOR NEXT ISSUE

FEBRUARY 26, 1962

UNION CARBIDE CHEMICALS COMPANY

DIVISION OF UNION CARBIDE CORPORATION

SOUTH CHARLESTON 3, W. VA.

RESEARCH AND DEVELOPMENT DEPARTMENT   November 16, 1961

Dr. Aksel A. Bothner-By
Director of Research and Editor,
  The Mellon Choly
Mellon Institute
4400 5th Avenue
Pittsburgh 13, Pennsylvania

Dear A_2B_2:

　　　　Brevity being allegedly golden, I dare not consume much space to
thank you for the binders for your individualistically punched Mello-N-M-R
issues. They work very nicely, however..... Say, is black the only color
you have? My taste is more for pastel greys and greens, so if the Holiday
Spirit should sieze you uncontrollably in the coming weeks.......

　　　　Perhaps your other Broadline reader will be interested in some
Super Low Resolution F^{19} work carried out here in recent months on fluoro-
carbon polymer samples. The prettiest results have been obtained with oriented
(i.e.,stretched) fiber samples of polytetrafluoroethylene (PTFE). Room
temperature absorption derivative spectra at 40 Mc for oriented PTFE fibers
are shown in the attached Figure 1 for the cases when the fiber axes are
oriented (a) parallel or (b) perpendicular to the applied static magnetic
field, H_O. The measured spectra are clearly unsymmetrical, a fact at first
puzzling but later (and I believe correctly) attributed to the magnetic aniso-
tropy of the C-F bonds. Based on studies at both 40 Mc and 56.4 Mc, the
magnetic anisotropy, $\Delta\sigma \equiv |\sigma_{xx} - \sigma_{zz}|$, in PTFE is found to be about 216 ± 6 ppm.

　　　　An indirect consequence of this work is to obtain the estimate that
the unshielded F^{19} nuclear reconance position — the hypothetically isolated
F^- ion position — should be about 272 ± 6 ppm upfield from $CFCl_3$, or about
703 ± 6 ppm upfield from the F_2 molecule position. Comment on these numbers is
invited.

　　　　For impatient souls, skeptics, and those without enough to read
otherwise, preprints of two papers submitted for publication in the Journal of
Polymer Science are available on request. These are entitled: "Magnetic Aniso-
tropy Effects in Broadline N-M-R Spectra of Polytetrafluoroethylene" and
"Observation of Chemical Shifts in a Bulk Crystalline Polymer". Prompt
delivery. Satisfaction guaranteed or your money back. They will be sent to
you in a plain wrapper. No one will call.

　　　　　　　　　　　Yours truly,

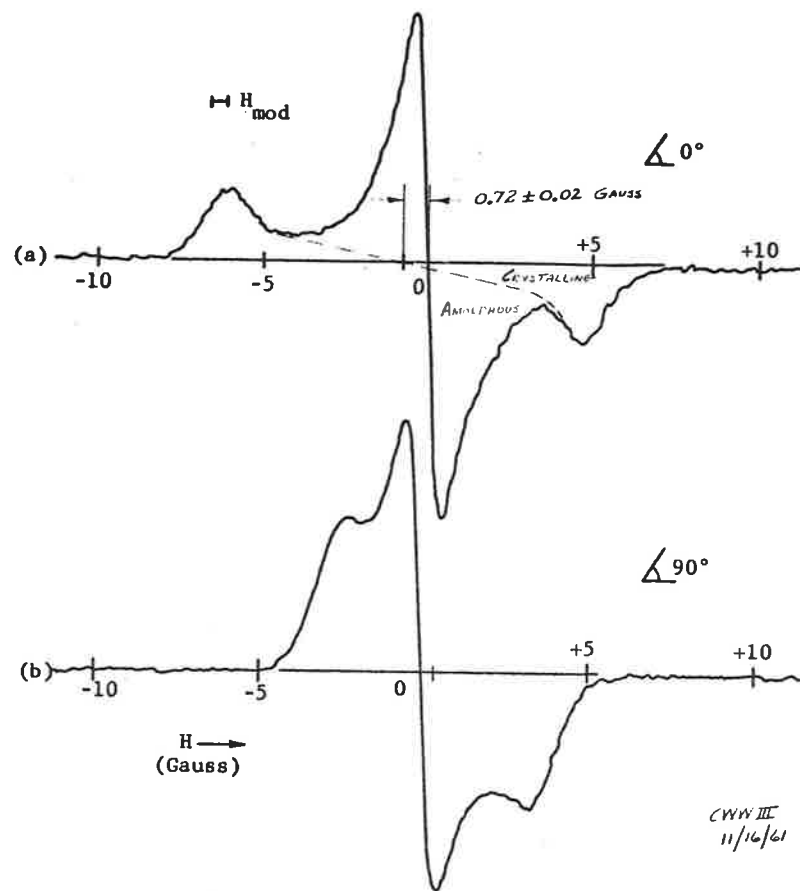　　　　　　　　　　　Crusty Charlie

　　　　　　　　　　　Chas. W. Wilson, III

CWW/dtf

Figure 1:　F^{19} N-M-R Derivative Spectra of Oriented PTFE Fibers
at 26°C and 40.0 Mc. (a) Fiber Axes Parallel to H_O.
(b) Fiber Axes Perpendicular to H_O.

VARIAN
associates

(Ray Freeman)

PROTON SPIN DECOUPLING

Our interest in the application of this technique to the determination of relative signs of spin coupling constants (Mellon Newsletter No. 33) led Dr. Whiffen and I to enquire a little more closely into the mechanism of multiplet collapse in double irradiation experiments. The theory follows the general lines of the treatment of Bloom and Shoolery (Phys. Rev. $\underline{97}$, 1261, (1955)) but there are some special features which appear when the nuclei are all of the same species, and we find that they are most conveniently represented graphically. We shall consider here only the simplest case, an AX type proton spectrum where X is subjected to an rf field H_2 at frequency v_2 while A is investigated by means of a very weak rf field H_1 at frequency v_1. Observation of a resonance transition implies a relation between v_1 and H_0 (the static field) so that with v_1 as ordinate and H_0 as abscissa we have represented the positions of the four possible A transitions by the four branches of the curves in Fig. 1. Numbers inside the circles indicate the trend of intensities expressed as percentages of the intensity of one of the lines of the doublet observed when $H_2 = 0$. The origin has been taken to be the cross-over point so that strictly the ordinate is $\Delta' = v_1 - v_2 - \delta_{AX}$ and the abscissa $\Delta = \gamma_X H_0/2\pi - v_2$.

At this point we must distinguish two ways of investigating the spectrum. Experimental simplicity is the great merit of the 'field sweep' method where v_1 and v_2 are constant and H_0 is varied. These spectra may be predicted by laying a ruler horizontally on one of the figures at a height appropriate to Δ' and by reading off positions and intensities. The second method we may call the 'frequency sweep' method for now H_0 and v_2 are held constant while v_1 is swept over the A spectrum. Theoretical patterns are then given by drawing a vertical line on the figure at the appropriate value of Δ. In the figures Δ, Δ' and $\gamma H_2/2\pi$ have all been expressed as multiples of J_{AX}.

Dichloroacetaldehyde is a good example of an AX system and Fig. 2 shows a comparison of the experimentally obtained spectra of this substance with the patterns predicted by Fig. 1. The 'frequency sweep' spectra have been obtained by means of a field stabilization system of the type described by Professor Primas (Mellon Newsletter No. 33).

Some general rules can be deduced by consideration of Figs. 1 and 2. First, an 'exact resonance' spectrum ($\Delta' = 0$) of a 'field sweep' experiment contains only a single line, for the satellites have moved right out and gone down to zero intensity. Otherwise 'field sweep' experiments give three line spectra that are not symmetrical about their centres, and which do not obey an intensity sum rule. On the other hand 'frequency sweep' spectra are always symmetrical and the total intensity equals that of the unperturbed spectrum. Careful inspection of the figures shows that it is easier to discriminate between 'exact resonance' and a small offset of v_2 in a 'field sweep' experiment than in a 'frequency sweep', a property that is essential for accurate measurement of chemical shifts by spin decoupling, and very desirable in the determination of relative signs of spin coupling constants.

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associates

We have found these and similar curves almost indispensible in under-standing various double irradiation experiments. If anyone is interested in a more complete description, this work has been submitted for publication in Proc. Phys. Soc.

Yours sincerely,

Ray Freeman

R. Freeman
Instrument Division

Field-Sweep
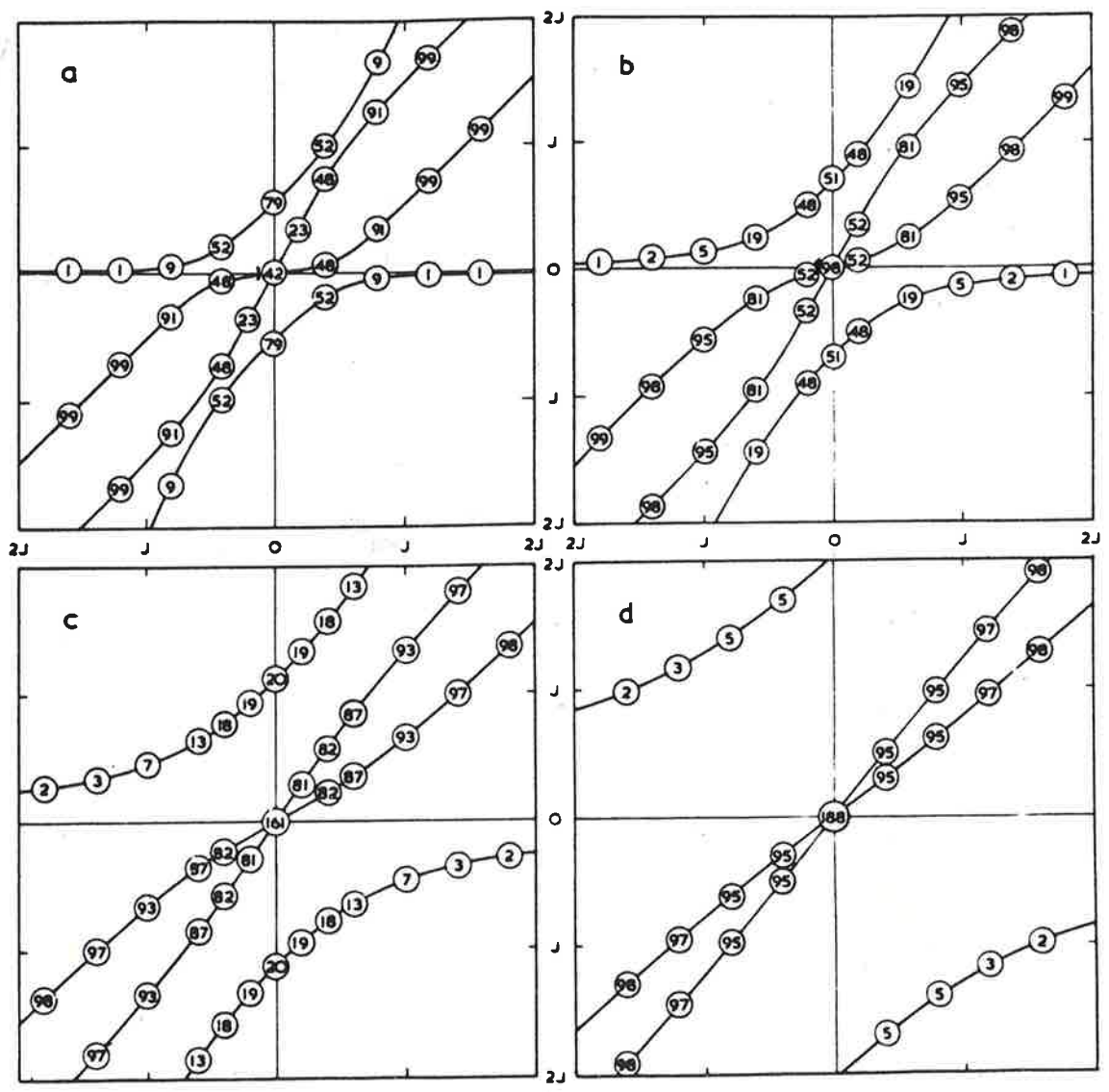
A SCHEMATIC REPRESENTATION OF THE LINES OBSERVED IN THE 'A' PART OF AN 'AX' SPECTRUM WHEN A SECOND RADIOFREQUENCY H_2 IS APPLIED NEAR THE X RESONANCE. THE VERTICAL AXIS REPRESENTS THE DIFFERENCE IN FREQUENCY BETWEEN THE TWO R F FIELDS MINUS THE AX CHEMICAL SHIFT. THE HORIZONTAL AXIS IS THE DIFFERENCE BETWEEN THE APPLIED MAGNETIC FIELD AND THE FIELD THAT WOULD BE REQUIRED TO CENTRE H_2 ON THE X DOUBLET. BOTH AXES ARE EXPRESSED IN UNITS OF J_{AX}. CURVES HAVE BEEN CALCULATED FOR FOUR DIFFERENT RADIOFREQUENCY LEVELS (a) $\gamma H_2/2\pi = J/4$ (b) $\gamma H_2/2\pi = J/2$ (c) $\gamma H_2/2\pi = J$ (d) $\gamma H_2/2\pi = 2J$

Figure 1
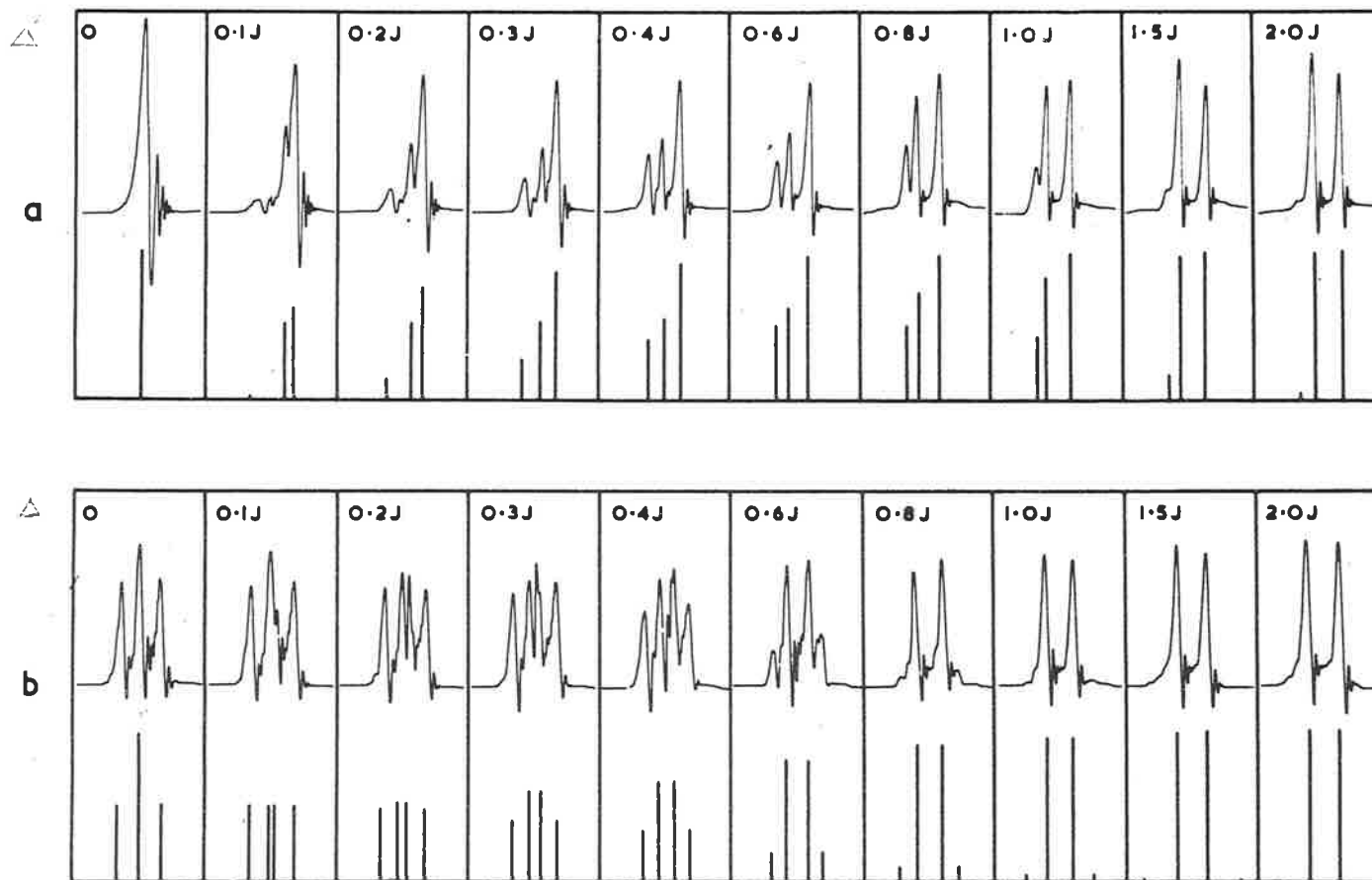
THE A RESONANCE OF AN AX SPECTRUM (DICHLOROACETALDEHYDE) WHEN A SECOND R-F
FIELD ($\gamma H_2/2\pi = J/2$) IS APPLIED NEAR THE X RESONANCE. H_2 HAS BEEN
INTENTIONALLY OFFSET FROM THE CENTRE OF THE X DOUBLET BY A QUANTITY Δ
EXPRESSED IN UNITS OF J_{AX}. (a) THE FIELD SWEEP METHOD, FOR VARIOUS VALUES
OF $\acute{\Delta} = \nu_1 - \nu_2 - \delta$. (b) THE FREQUENCY SWEEP METHOD FOR VARIOUS VALUES OF
$\Delta = \gamma_X H_0/2\pi - \nu_2$. THEORETICAL PATTERNS WERE OBTAINED FROM FIGURE 1(b).

40-4

5th Jan., 1962

Dr. J. Lee

Dr. A. A. Bothner-By,
Mellon Institute,
4400, Fifth Avenue,
Pittsburgh, 13,
Pennsylvania,
U.S.A.

Dear Dr. Bothner-By,

In our investigations of internal motion kinetics, by observations on absorption spectra arising from nuclei exchanging between <u>two</u> equally-populated environments of near equal relaxation times, we have found the enclosed graphs more useful than those published previously. Whereas the custom has been to plot such spectral parameters as $\delta\omega_e/\delta\omega$, $\delta\omega_{\frac{1}{2}}/\delta\omega$ and I_{min}/I_{max} against $k/\delta\omega$ (or its inverse) for various selected values of $T_2\delta\omega$, where

$\delta\omega_e$ = separation of maxima before coalescence,

$\delta\omega$ = chemical shift,

$\delta\omega_{\frac{1}{2}}$ = band width at half height after coalescence,

I_{min}, I_{max} = central minimum and maximum intensities before coalescence,

k = kinetic rate constant (= $1/\gamma$ where

γ = mean lifetime in either environment),

T_2 = transverse relaxation time,

we would prefer to replace the $\delta\omega$ by $\delta\omega_\infty$, the separation of band maxima at infinitely slow exchange (k = 0), since this is the directly measurable quantity (when the temperature is much less than the coalescence value).

The relevant algebraic expressions (some of which have been presented before [1]) are:

(a) $\underline{T_2 = \infty}$

(i) $\delta\omega/\delta\omega_\infty = 1$

(ii) $\delta\omega_e/\delta\omega = (1 - 8r^2)^{1/2}$

(iii) At coalescence, $r = 1/2\sqrt{2}$

(iv) $I_{min}/I_{max} = 16r^2 - 64r^4$

(v) $\delta\omega_{\frac{1}{2}}/\delta\omega = \left[1 - 8r^2 + (64r^4 - 16r^2 + 2)^{1/2}\right]^{1/2}$

(b) $\underline{T_2 \neq \infty}$

(i) $\delta\omega/\delta\omega_\infty = \left\{\frac{1}{3} - \frac{4}{3(T_2\delta\omega_\infty)^2} + \frac{2}{3}\left[1 + \frac{4}{(T_2\delta\omega_\infty)^2} + \frac{16}{(T_2\delta\omega_\infty)^4}\right]^{1/2}\right\}^{1/2}$

(ii) $\delta\omega_e/\delta\omega = 2\left[-2\left(\frac{1}{q} + \frac{1}{2q^2r} + \frac{1}{8r}\right)(r + 2qr^2) + \left(\frac{1}{q} + \frac{1}{2q^2r} + \frac{1}{8r}\right)^{1/2}(2q^2r^3 + 4qr^2 + 2r)^{1/2}\right]^{1/2}$

(iii) At coalescence,

$\frac{1}{r^3}\left(\frac{3}{q} - \frac{4}{q^3}\right) + \frac{1}{r^2}\left(4 - \frac{24}{q^2}\right) - \frac{1}{r}\cdot\frac{48}{q} - 32 = 0$

(iv)

$I_{min}/I_{max} = \dfrac{(1 + \frac{1}{2qr})\left[p^2 + \frac{1}{4}\left(\delta\omega_e/\delta\omega\right)^2\left(1 + \frac{1}{qr}\right)^2\right]}{s\left[(1 + \frac{1}{2qr})p + \frac{1}{8r}\left(\delta\omega_e/\delta\omega\right)^2\left(1 + \frac{1}{qr}\right)\right]}$

(v) $\delta\omega_{\frac{1}{2}}/\delta\omega = 2\left\{4sr\cdot\frac{\frac{1}{r} + q}{\frac{1}{r} + 2q} - 2r^2\left(1 + \frac{1}{qr}\right)^2 + 2\left[r^4\left(1 + \frac{1}{qr}\right)^4\right.\right.$
$\left.\left. - 4sr^3\left(1 + \frac{1}{qr}\right)^2\cdot\frac{\frac{1}{r} + q}{\frac{1}{r} + 2q} + 4s^2r^2\frac{\left(\frac{1}{r} + q\right)^2}{\left(\frac{1}{r} + 2q\right)^2} + s^2r^2\right]^{1/2}\right\}^{1/2}$

where

$r = k/\delta\omega$

$q = T_2\delta\omega$ $\qquad\left[= \frac{2}{q}\text{ when } k = \infty\right]$

$p = \frac{1}{2r}\left[\frac{1}{q^2} - \frac{1}{4}\left(\delta\omega_e/\delta\omega\right)^2 + \frac{1}{4}\right] + \frac{1}{q}$

$s = \frac{1}{q} + \frac{1}{2q^2r} + \frac{1}{8r}$

We should like to thank you very much for sending MELLONMR, which we find useful and interesting. Please accept my apologies for the delay in sending my contribution.

Yours sincerely,

J. Lee

[1] See for example, Gutowsky and Holm, J. Chem. Phys., 1956, <u>25</u>, 1228
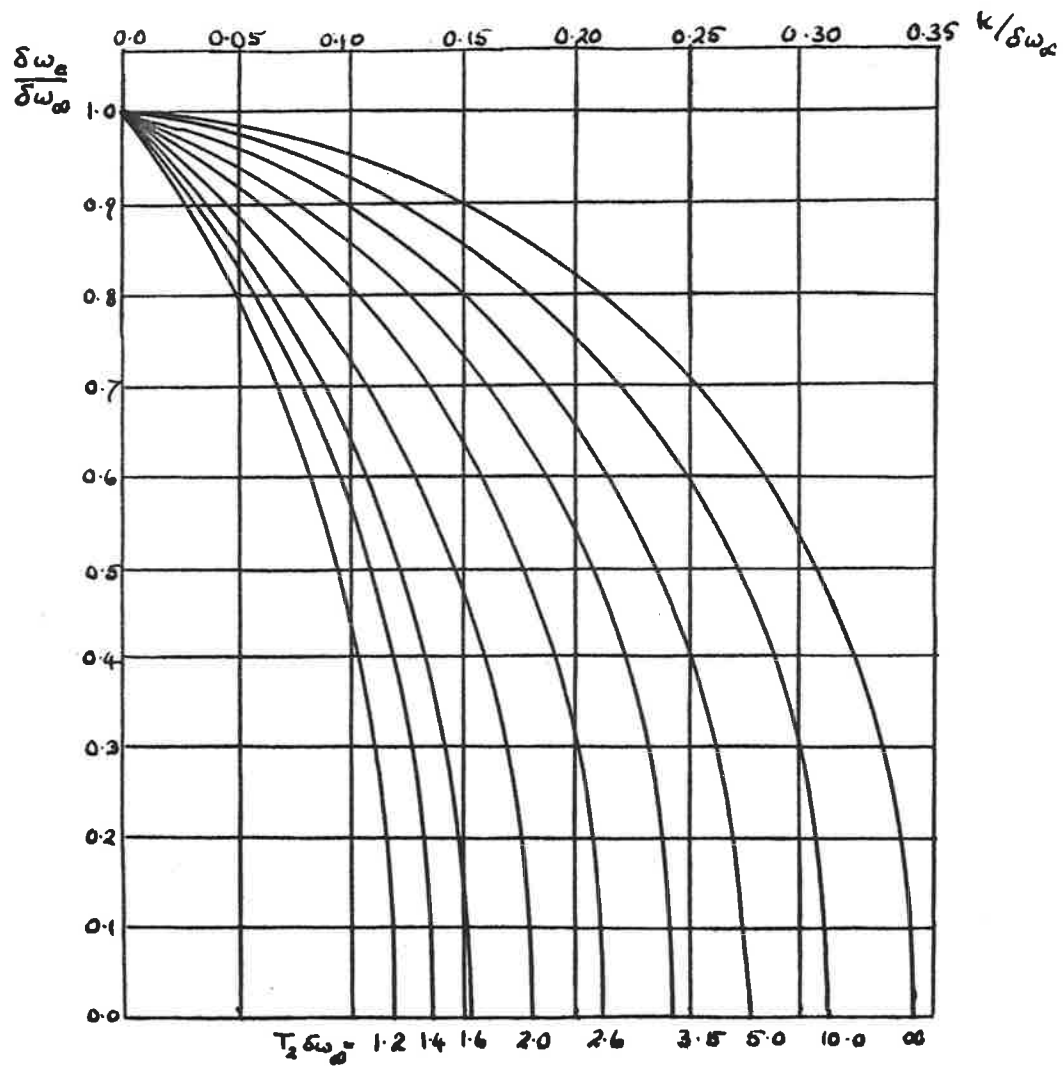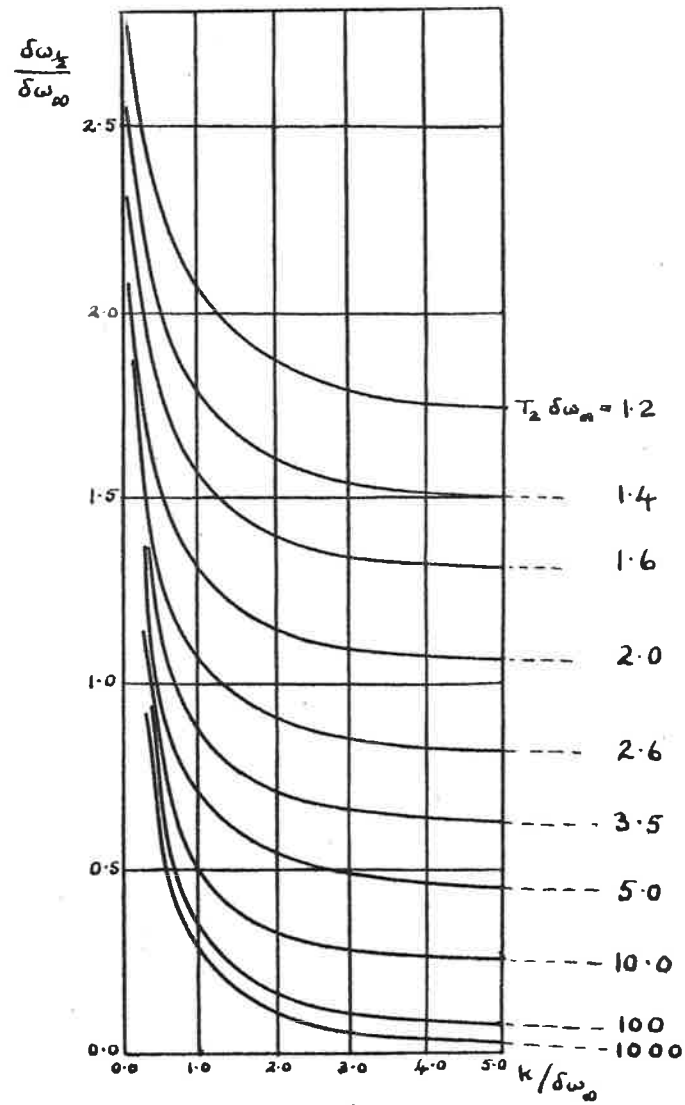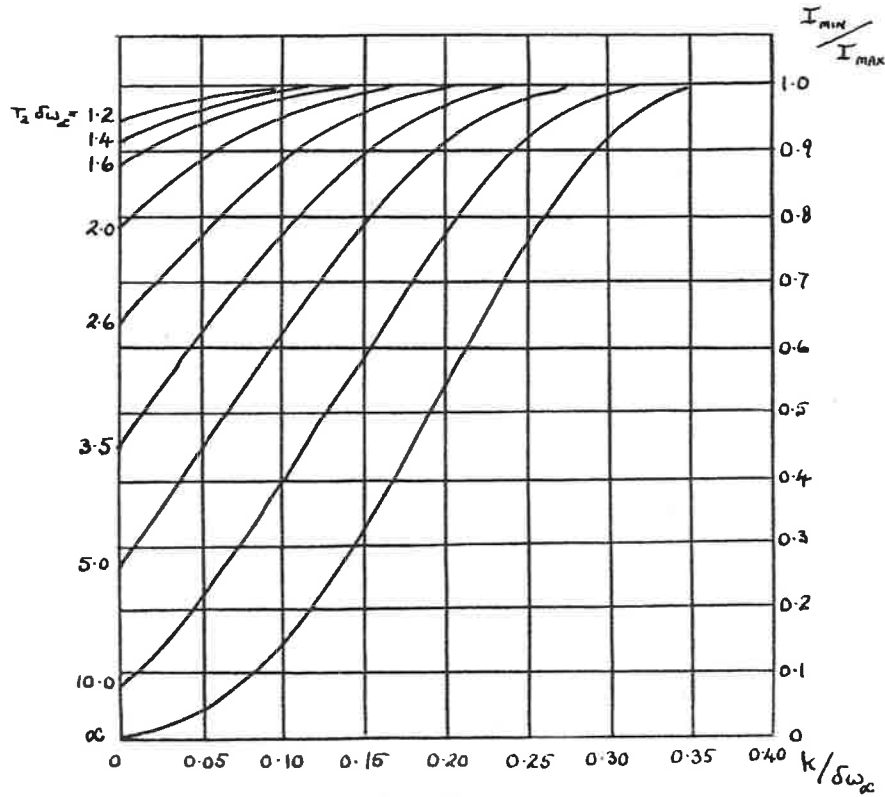
FIG. 1

FIG. 2

(J. Lee)

40-6

(J. Lee)

January 11, 1962

Dr. A. A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Bothner-By:

Sorry to be so slow in sending this note to you.
This period at the end of the semester is always miserable
as far as getting anything done.

Recently, we have been interested in investigating
the potential energy as a function of angle of rotation
in some halogen substituted ethanes by NMR methods. The
only compound which we have treated completely is CFClBr-
CFClBr. Actually, there are two isomers of this compound,
a meso form and a d-l form.

We have investigated the F spectrum, at 56.4
megacycles, of a mixture of these two isomers as a
function of temperature from room temperature down to
-100°C. At room temperature, where free rotation is
taking place, the two isomers each have only one kind of
fluorine atom, and hence the spectrum consists of a pair
of lines, with a separation of 48.4 cps. The high field
peak contains 52.8% of the total integrated area.

At -100°C, the spectrum is a superposition of the
spectrum of the three rotamers of each of the two isomers.

FIG. 3
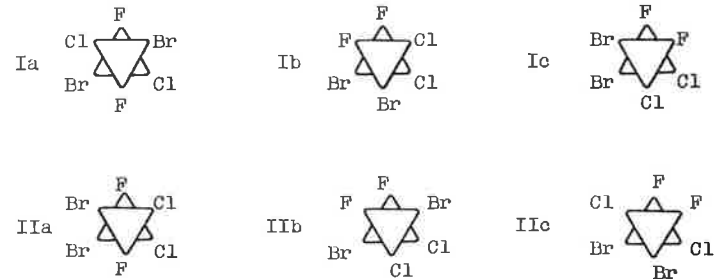
Rotamers Ia, IIa, IIb, and IIc should yield single lines. Rotamers Ib and Ic are mirror images of each other, and hence have identical spectra. They should yield a pair of doublets. This is precisely the spectrum observed at -96°C, as shown in Fig. 1. Chemical shifts and integrated areas of the several lines are tabulated below. By fairly straight forward reasoning, it is possible to make the following assignments of the low temperature peaks.

Line	Chemical Shift (cps)	% of Total Integrated Area	Assignment
A	0.0	23.7	IIb
B	94.9 ⎫		
C	116.0 ⎭	10.0	Ib and Ic
D	205.3 ⎫		Ia
E	214.2 ⎭	50.4	IIa
F	264.5 ⎫		
G	286.2 ⎭	9.3	Ib and Ic
H	368.1	6.6	IIc

It is immediately apparent that the coupling constant between the fluorine atoms which are gauche to each other in rotamers Ib and Ic is 21-1/2 cps.

From the low temperature areas, the relative energies of the three potential minima can be calculated, and are tabulated below. Using the Eyring equation for estimating rate constants of interconversion between the three rotamers as a function of barrier heights, an IBM program was written to calculate the observed spectra as a function of temperature, using the low temperature data and assuming various barriers to rotation.

One finds that all of the barrier heights do not affect the calculated spectra. The calculated spectra depend only upon the following three parameters:

1. The height of the lowest barrier in isomer I.
2. The height of the barrier between configurations IIa and IIb.
3. The height of the lower of the other two barriers in isomer II.

In the enclosed figures, the calculated spectra are compared with the observed. The following values of the above tabulated parameters were chosen as the best fit values.

Parameter	194°K	207°K	233°K	Best value
1	10.0 kcal	10.0 kcal	10.5 kcal	10.2 kcal
2	9.5	10.0	9.5	9.7
3	10.0	10.5	10.0	10.2

Potential energy as a function of rotation configuration.

Isomer I		Isomer II	
Configuration	Energy	Configuration	Energy
Ia	0 cal	IIa	119 cal
Iab	⩾10.2 kcal ‡	IIab	9.7 kcal
Ib	438 cal	IIb	0 cal
Ibc	⩾10.2 kcal ‡	IIbc	⩾10.2 kcal *
Ic	438 cal	IIc	450 cal
Ica	⩾10.2 kcal ‡	IIca	⩾10.2 kcal *

‡ The energies of configurations Iab and Iac are equal. The energy of either Iab or Ibc is equal to 10.2 kcal.
* The energy of IIbc or IIac is equal to 10.2 kcal.

From the low temperature data, one can draw some conclusions about the chemical shift of a fluorine atom as a function of the relative orientation of the other end of the molecule. A fluorine atom gauche to a fluorine and a chlorine atom is to the highest field; a fluorine atom gauche to a fluorine and a bromine atom is to lowest field; and a fluorine

atom gauche to a bromine and a chlorine atom is at intermediate field. In order of high field shifting ability, this implies Cl > F > Br. Such an order is somewhat surprising.

   At the present time, we are continuing this work on other halogen substituted ethanes. It is hoped that after we have investigated a few more such compounds, it will be possible to at least put the steric part of the potential energy on a sound, empirical basis.
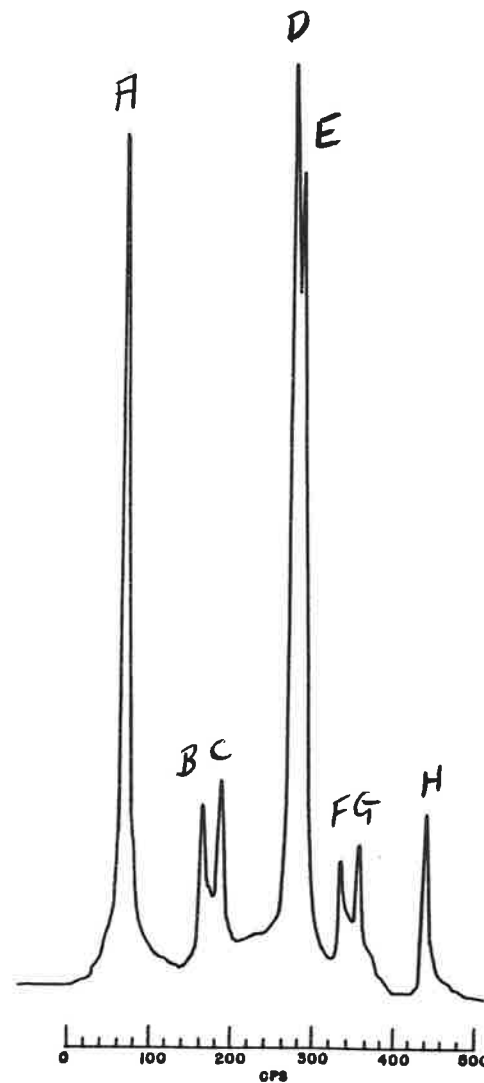
Sincerely,

C. H. Sederholm

C. H. Sederholm

Douglas Thompson by S. ng
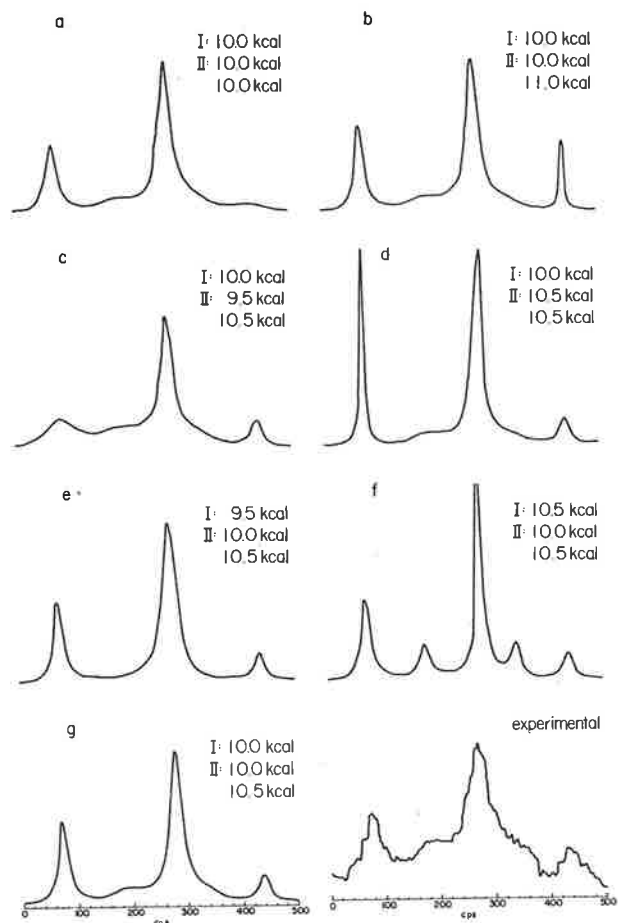
Douglas Thompson

Richard Newmark

Richard Newmark

F^{19} Spectrum of CFClBr — CFClBr at -96°C.

MU-24685

a
I: 10.0 kcal
II: 10.0 kcal
10.0 kcal

b
I: 10.0 kcal
II: 10.0 kcal
11.0 kcal

c
I: 10.0 kcal
II: 9.5 kcal
10.5 kcal

d
I: 10.0 kcal
II: 10.5 kcal
10.5 kcal

e
I: 9.5 kcal
II: 10.0 kcal
10.5 kcal

f
I: 10.5 kcal
II: 10.0 kcal
10.5 kcal

g
I: 10.0 kcal
II: 10.0 kcal
10.5 kcal

experimental

Experimental and calculated spectra of CFClBr – CFClBr at 207°K

a
I: 10.0 kcal
II: 9.5 kcal
10.5 kcal

b
I: 10.0 kcal
II: 9.5 kcal
9.5 kcal

c
I: 10.0 kcal
II: 10.0 kcal
10.0 kcal

d
I: 10.0 kcal
II: 9.0 kcal
10.0 kcal

e
I: 9.5 kcal
II: 9.5 kcal
10.0 kcal

f
I: 10.5 kcal
II: 9.5 kcal
10.0 kcal

g
I: 10.0 kcal
II: 9.5 kcal
10.0 kcal

experimental

Experimental and calculated spectra of CFClBr – CFClBr at 194°K

a

I 10.5 kcal
II 9.5 kcal
9.5 kcal

b

I 10.5 kcal
II 9.5 kcal
10.5 kcal

c

I 10.5 kcal
II 9.0 kcal
10.0 kcal

d

I 10.5 kcal
II 10.0 kcal
10.0 kcal

e

I 10.0 kcal
II 9.5 kcal
10.0 kcal

f

I 11.0 kcal
II 9.5 kcal
10.0 kcal

g

I 10.5 kcal
II 9.5 kcal
10.0 kcal
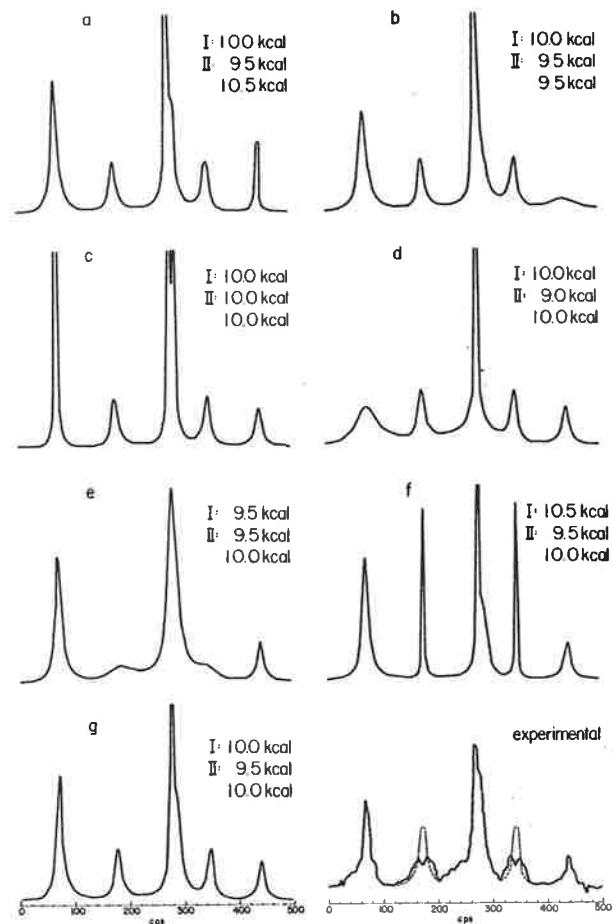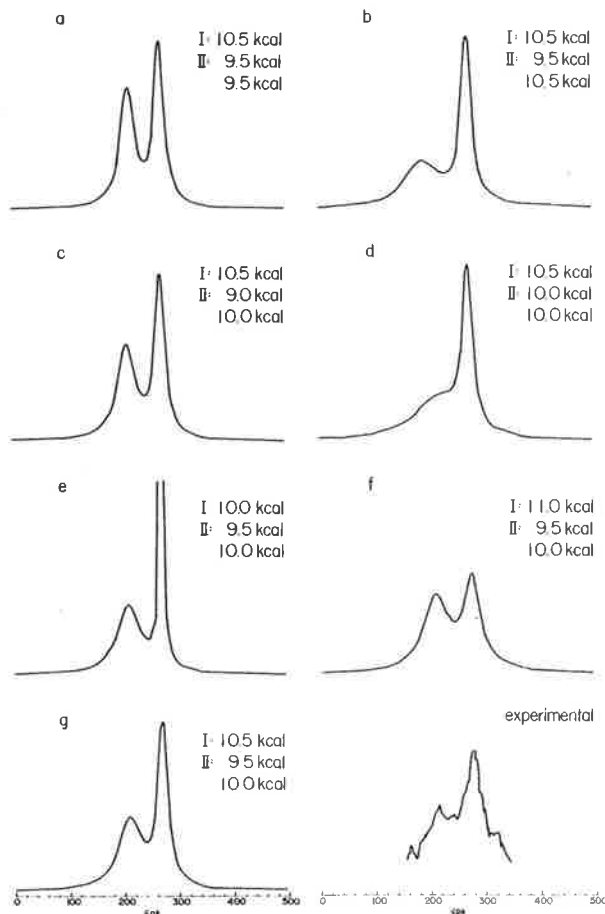
experimental

Experimental and calculated spectra
of CFClBr - CFClBr at 233°K

Department of Chemistry,
Imperial College,
London, S.W.7.

19th January, 1962.

Dr. A. A. Bothner-By,
Mellon Institute,
4400 Fifth Avenue,
Pittsburgh 13, Pa.

Dear Dr. Bothner-By,

Although my name does not appear on your mailing list, Professor Wilkinson suggested I send the following results as a contribution from the Inorganic Chemistry section of the Department.

I have been applying the recently developed double irradiation method for the determination of relative signs of spin coupling constants[1,2,3] to F-F and H-F coupling constants in fluorocarbons, and some results obtained for trifluoroethylene derivatives are given below.

$$CF_2=CFCl \quad J_{12} = J_{gem}^{FF} \pm ; \quad J_{13} = J_{cis}^{FF} \pm ; \quad J_{23} = J_{trans}^{FF} \mp .$$

$$CF_2=CFH \quad J_{12} = J_{gem}^{FF} \pm ; \quad J_{13} = J_{cis}^{FF} \pm ; \quad J_{23} = J_{trans}^{FF} \mp ;$$

$$J_{34} = J_{gem}^{HF} \pm ; \quad J_{24} = J_{cis}^{HF} \mp ; \quad J_{14} = J_{trans}^{HF} \pm .$$

$$CF_2=CFCF_3 \quad J_{12} = J_{gem}^{FF} \pm ; \quad J_{13} = J_{cis}^{FF} \pm ; \quad J_{23} = J_{trans}^{FF} \mp ;$$

$$J_{34} = J_{gem}^{FF_3} \mp ; \quad J_{24} = J_{cis}^{FF_3} \pm ; \quad J_{14} = J_{trans}^{FF_3} \pm .$$

The double irradiation apparatus constructed by Turner[4] was used. Since all the spectra are, to a very good approximation, first-order at 56.4 Mcs., the interpretation of the decoupling experiments was straightforward. In the majority of cases, the measurements were carried out in pairs (e.g. group 1 was irradiated while group 2 was measured, and vice versa) and hence a knowledge of the decoupling frequencies was not normally required, although it provides a useful check.

Yours sincerely,

D.F. Evans

D. F. Evans

[1] Maher and Evans, Proc. Chem. Soc., 208 (1961).
[2] Freeman and Whiffen, Mol. Phys., 4, 321 (1961).
[3] Freeman, Mol. Phys., 4, 385 (1961).
[4] Turner, J. Chem. Soc. (in the press).

COMPOUND 8

CHCl₃

TMS

$\tau=0$

$\tau=5$

$\tau=10$

$\tau=15$

THE JOHNS HOPKINS UNIVERSITY · BALTIMORE 18, MARYLAND

DEPARTMENT OF CHEMISTRY

January 9, 1962

Dr. Aksel A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Bothner-By:

We have continued our work on the high resolution nmr spectra of porphyrins and have recently examined rather carefully peaks in the high-field (τ = 11.4 - 16.3) side of the spectrum. These peaks are now generally agreed to result from protons bonded to the nitrogens at the center of the ring and their high-field position is due to ring current effects. Becker, Bradley and Watson[1] have also studied the nmr spectra of porphyrins, and in all compounds that they have studied, the N-H peak is single and fairly sharp. They concluded that there is a rapid tautomerism of the NH protons making all four pyrrole rings equivalent on a time average basis. We have observed that the NH peak in many of these compounds is single within limits of our resolution; however, we have also observed that if one varies the electro-negativity of the groups substituted on the periphery of the molecule, the NH peak is often broadened, presumably due to unresolved multiplets and/or N^{14} quadrupole interactions. In one case, however, 2, 4-bis (2-carboxycyclopropyl) deutero deuteroporphyrin IX Me₄, the NH peak is clearly a doublet with τ = 14.15 and 14.36. The spectrum is shown in Fig. 1. In this case, at least, it appears that if tautomerism exists between the N-H hydrogens, it is slow.

Very truly yours,

Walter S. Koski

WSK/kal

[1] E. D. Becker, R. B. Bradley and C. J. Watson, J.A.C.S., 83, 3743 (1961).

THE UNIVERSITY OF LIVERPOOL

TELEPHONE: ROYAL 6022
Extension 356

DEPARTMENT OF
INORGANIC AND PHYSICAL CHEMISTRY
VINE STREET, LIVERPOOL, 7

THE NMR SPECTRA OF SOME PERFLUOROALKYL HALIDES

by N. Boden, J. W. Emsley, J. Feeney and L. H. Sutcliffe,

Donnan Laboratories, Liverpool University, England.

Our programme on fluorine resonance spectra has been furthered by the examination of several fully fluorinated alkyl halides some of which are new compounds[1,2]. The spectra were obtained by means of a Varian 4300 B spectrometer operating at 56.4 Mc sec^{-1}. Below are listed the chemical shifts (ppm) of the neat liquids measured from the external reference trifluoro acetic acid: positive shifts are to high fields of the reference

$(CF_3)_2CFBr$ $\delta_{CF_3} = 1.15$ $\delta_{CF} = 66.9$

$(CF_3)_2CFI$ $\delta_{CF_3} = -2.00$ $\delta_{CF} = 70.4$

$CF_3CF_2CF_2I$ $\delta_{CF_3} = 2.25$ $\delta_{CF_2} = 40.6$ $\delta_{CF_2I} = -17.2$

$CF_3CFI\,CF_2Cl$ $\delta_{CF_3} = -5.65$ $\delta_{CF_A} = -15.8$ $\delta_{CF_B} = -12.5$ $\delta_{CFI} = 38.7$

$\begin{array}{cc} CF_3 & CF_3 \\ CF.CF & \\ CF_2Cl & CF_2Cl \end{array}$ $\delta_{CF_3} = -8.87$ $\delta_{CF_2} = -20.6$ $\delta_{CF} = 84.5$

$(CF_3)_2CF.CF(CF_3)_2$ $\delta_{CF_3} = -5.54$ $\delta_{CF} = 103.3$

A dilution experiment was conducted on $(CF_3)_2CFI$ with $CFCl_3$ as solvent which also served as an internal reference. The high field band recorded above occurred at the same chemical shift while the low field band was slightly affected (for a 50% solution, $\delta_{CF_3} = -2.51$ ppm from external CF_3COOH; $\delta_{CF_3} = 76.0$ ppm from internal $CFCl_3$). Because of the small effect the remaining compounds were examined as neat liquids.

Several interesting points emerge from the data given above. Firstly, the isopropyl bromide and iodide have CF group shifts showing large magnetic anisotropic effects[3]. Secondly, the replacement of a fluorine atom by a chlorine atom in CF_3CFICF_2Cl has an enormous effect on the shielding of the CF group. (Being of the $C_s - C_1$ type[4] this molecule has magnetically non-equivalent F atoms in the CF_2 group, irrespective of the rate of internal rotation.) A similar large effect is observed in the chemical shifts of the CF groups of $(CF_3)_2CF.CF(CF_3)_2$ and $\begin{array}{cc} CF_3 & CF_3 \\ CF.CF & \\ CF_2Cl & CF_2Cl \end{array}$

Fluorine-Fluorine Spin-spin Interactions

The coupling constants derived from a first order analysis of the spectra are listed below in the units cycles sec^{-1}.

$(CF_3)_2CFBr$ $J_{CF_3-CF} = 8.9 \pm 0.5$

$(CF_3)_2CFI$ $J_{CF_3-CF} = 12.5 \pm 0.1$

$CF_3CF_2CF_2I$

$$\begin{cases} J_{CF_3-CF_2} = 0.8 \pm 0.1, J_{CF_3-CF_2I} = 9.4 \pm 0.2 \\ J_{CF_2-CF_2I} = 4.7 \pm 0.2 \end{cases}$$

CF_3CFICF_2Cl

$$\begin{cases} J_{CF_3-CF} = 11.8 \pm 0.1, J_{CF_3-CF_A} = 9.4 \pm 0.1 \\ J_{CF_3-CF_B} = 11.8 \pm 0.1, J_{CF-CF_A} = 18.8 \pm 0.5 \\ J_{CF-CF_B} = 18.1 \pm 0.5, J_{CF_A-CF_B} = 116 \pm 2 \end{cases}$$

$(CF_3)_2CF.CF(CF_3)_2$ $J_{CF_3-CF} = 9.0 \pm 0.1$

The high resolution spectrum of $\begin{smallmatrix} CF_3 & & CF_3 \\ & CF.CF & \\ CF_2Cl & & CF_2Cl \end{smallmatrix}$ is complicated

and has not yet been fully analysed. In the spectrum of $(CF_3)_2CF.CF(CF_3)_2$ there is evidence for more than one coupling constant suggesting the presence of F-F coupling between atoms four bonds removed. The wide variation of the magnitude of the J values with change in the number of bonds separating the interacting nuclei in $CF_3CF_2CF_2I$ probably indicates that the coupling constants are not all of the same sign. If the coupling constants are all of the same sign in CF_3CFICF_2Cl then the molecule most likely exists as an interconverting mixture of the two rotational isomers shown.

It is intended to study the effect of temperature on the spectra of the above derivatives which can exhibit rotational isomerism.

The F-F coupling constant having the value 0.8 cycles sec^{-1} appears to be the smallest reported to date and the absorption bands of $CF_3CF_2CF_2I$ in which this coupling constant features will clearly be useful for checking the resolution of a spectrometer for ^{19}F resonance.

1. R.D. Chambers, W.K.R. Musgrave and J. Savory,
      Proc. Chem. Soc., 113, 1961 .

2. R.D. Chambers, W.K.R. Musgrave and J. Savory,
      J. Chem. Soc., 3779, 1961 .

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4. J. Lee and L.H. Sutcliffe,
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Chemical Shifts of Some Organo-Silicon Compounds

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As part of a general program on the NMR properties of organo-silicon compounds, an assortment of proton chemical shifts have been measured and tabulated. In general, we have been interested in the methyl resonance in series of $Me_aX_{3-a}Si$, where X = -Cl, -OSi, -Ph, and -OR. This sharp, distinct methyl resonance has proven most useful in NMR analysis.

Spectra were recorded by standard techniques on a Varian Associates Dual-Purpose Spectrometer operating at 40 mcps. All shifts were measured with respect to C_6H_{12} or $(CH_3)_4Si$, TMS, 5% by volume in CCl_4, using double side-band techniques. Each measurement was the average of 5 up-field and 5 down-field sweeps through the sample reference and TMS side-bands located at ca. +5 cps on each side of the sample resonance. Sidebands were injected through magnetic field modulation and sideband frequencies were measured to +0.1 cps. Shift measurements were made at 3 or 4 sample concentrations of 1-20% by volume and the reported value is the infinite dilution value obtained by extrapolation. The combination of the double side-band measurements, averaging, and extrapolation results in chemical shifts which can be considered reliable to at least $\Delta\nu = +0.1$ cps or $\Delta\delta = +0.0025$. The quite small variations in shifts among some silicon series makes this degree of precision essential for analytical purposes.

Table I lists the measured shifts of a variety of silicon compounds. The nomenclature used for the methyl siloxanes is consistent with Rochow[1]:

1. E.G. Rochow, Chemistry of the Silicones (John Wiley and Sons, New York, 1961).

$M = (CH_3)_2Si-\phi-$, $D = -\phi-Si(CH_3)_2-\phi-$, and $T = -\phi-Si(Me)\overset{-\phi}{\underset{-\phi}{<}}$. The shifts are reported as cps from internal TMS at 40 mcps and are shifts to low field in all cases. For shifts of <10 cps, measurements were made with respect to internal C_6H_{12} and corrected by ν (C_6H_{12}) $-\nu$(TMS) = 57.9 cps. In the mixed methyl-phenyl systems, the sharp methyl resonance has proven most useful; the natural widths of the phenyl resonances are considerably larger than the shift differences in some series. However, the frequency of the dominant peak of the phenyl resonance was measured to less precision and is reported for comparison.

Aside from general analytical implications, the most interesting feature of this data is the effect of substitution of electronegative groups and its comparison with analogous carbon series. Figure 1 shows the effect of chlorine substitution on the Me*Si resonance which smoothly shifts to low field, consistent with general concepts of chlorine vs. methyl electronegativities. The similar results of Webster[2] on H*Si resonances are shown for comparison. However, oxygen substitution effects only minor

2. D.E. Webster, J. Chem. Soc., 5132 (1960).

shifts as shown for $Me*SiMe_x(OEt)_{3-x}$. The first ethoxy effects only a 3.1 cps shift to low field; the second and third ethoxy groups each shift the Me*Si resonance by 1.0 cps upfield. This is probably not unreasonable when considering that the β-protons in ethers are only shifted by a slight amount. Likewise, the small shift associated with -O-Si substitution is shown in the siloxane series $MeSiMe_x(-O-Si-)_{3-x}$. Further a small chain-length effect can be seen. This chain-length effect makes it possible to clearly resolve the various M and D units for molecular weights up to 500-600.

There is a small ring-size effect in the cyclic methyl siloxanes, probably associated with ring strain in the smaller units. The series appears to level off at D_5 to a value in good agreement with the central D units in the linear series. It is unprofitable to speculate about the significance of the one datum for the MeT compound.

The Me*Si resonances are particularly useful for identifying structural isomers in the methyl-phenyl systems as typified by the data for cis- and trans-cyclic trimers. This sensitivity to stereo or structural configurations on the adjacent Si atoms has proven to be of significant analytical interest.

This data will be incorporated in a publication to be submitted to Analytical Chemistry.
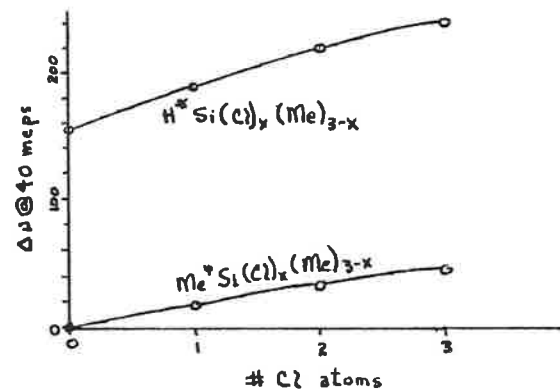
TABLE I

Methyl chloro silanes

Me*Si(Me)$_3$	(0)
Me*Si(Me)$_2$Cl	17.5
Me*Si(Me)Cl$_2$	32.5
Me*SiCl$_3$	46.5

Methyl ethoxy silanes

Me*Si(Me)$_3$	(0)
Me*Si(Me)$_2$(OEt)	3.1
Me*Si(Me)(OEt)$_2$	2.1
Me*Si(OEt)$_3$	1.1

Phenyl chloro silanes

Ph*SiCl$_3$	302[a].
Ph*Si(Ph)Cl$_2$	300[a].
Ph*Si(Ph)$_2$Cl	297[a].

Cyclic permethyl siloxanes

D$_3$	5.5
D$_4$	3.6
D$_5$	3.0
D$_7$	2.9

Linear permethyl siloxanes

M*-M	2.5	M-D*-M	0.8
M*-DM	3.9	M-D*-DM	1.6
M*-D$_2$M	4.0	M-D*-D$_2$M	2.0
M*-D$_3$M	4.0	M-D*-D$_3$M	1.9
M*-D$_4$M	4.0	MD-D*-DM	2.9
		MD-D*-D$_2$M	2.9

Cyclic methyl-phenyl siloxanes	Me	Ph
[(Me)Si(Ph)-O]$_3$, "cis"	20.4	290[a]
[(Me)Si(Ph)-O]$_3$, "trans"	17.5(2x) 15.0(1x)	293[a]
[Si(Ph)$_2$-O]$_4$		290[a]
[Si(Me*)(EtCN)-O]$_4$	5.6 $\pm$ 0.2	
(no evidence for cis-trans shift)		
[Me*T]$_{12}$	4.7	