July 62

Mailed: 27 June 1962

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No. 45

DEADLINE FOR NEXT ISSUE
July 25, 1962

Mellon Institute

4400 Fifth Avenue
Pittsburgh 13, Pa.

25 June 1962

Practical Matters

1. Until further notice, all contributions to M.E.L.L.O.N.M.R. should
   be sent to the attention of B. L. Shapiro, since A. A. Bothner-By
   is about to depart for a sabbatical year abroad. (Address for
   period 1 Sept. 1962 - 1 June 1963, Institut der Organischen
   Chemie, Universität München, West Zone, Germany).

2. Participants who are able to send in copies of their contributions
   are reminded that due to our increased circulation, they are re-
   quested to send 200 copies. All pages should be 8-1/2" x 11" and
   have at least 1/2" margin on the left hand side.

3. Since photo-copies of various kinds do not reproduce too well,
   contributors are urged to submit their originals to us, and we
   will be happy to return these if requested.

ESSO RESEARCH AND ENGINEERING COMPANY

(FORMERLY STANDARD OIL DEVELOPMENT COMPANY)

P. O. BOX 45, LINDEN, N. J.

CENTRAL BASIC RESEARCH LABORATORY

J P LONGWELL
    DIRECTOR

P V SMITH, JR
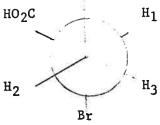   ASST DIRECTOR

TELEPHONE: WABASH 5-1600

May 29, 1962

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

Dear Dr. Bothner-By:

We have been engaged in a study of magnetic non-equivalence of methyl and methylene groups in the past few months. Some of our results are as follows.

1. 2,3-Dibromopropionic acid. - In agreement with the results of double-resonance experiments (Freeman, no. 41) and of the double-quantum spectrum (McLaughlan, no. 43), we have found the vicinal and germinal coupling constants to be of opposite sign by analysis of the 60 mc. spectrum in various solvents. In every case the transition intensities, particularly of some combination lines, calculated for the set containing couplings of opposite sign were in better agreement with observed intensities than were those calculated for the set with couplings of the same sign. Although the assignment,

was made by Freeman, our data contraindicate his basis for doing so, viz., "...J_{AX} and J_{BX} (J_{13} and J_{12}) vary with solvent because the statistical weights of the three rotational isomers change, but J_{AB} (J_{23}) remains constant and can therefore be assigned with confidence to the geminal coupling." Our analyses indicate all coupling constants have the same order of solvent dependence; if valid, these results have some interesting corollaries.

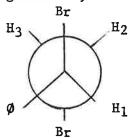2. (1,2-Dibromoethyl)benzene. - From the dibromides prepared from α-deuterostyrene and trans-β-deuterostyrene,

TABLE OF SPECTRAL PARAMETERS

$CH_2BrCHBRCO_2H$

1	2	3	12	13	23	Solvent
8.57	39.63	66.16	10.92	4.53	-9.91	Benzene
8.70	43.62	57.03	11.31	4.38	-10.11	Chloroform
8.43	49.40	54.16	11.36	4.06	-10.22	Acetonetrile
8.44	49.33	54.61	11.0	4.5	-9.8	Acetone

$CH_2BrCHBrC_6H_5$ — Solvent

1	2	3	12	13	23	Solvent
8.55	72.00	75.76	5.24	10.86 (10.96)*	-10.08	Carbon tetrachloride
8.59	71.83	75.90	4.28	11.76	9.99	Carbon tetrachloride
8.45	80.28	78.22	5.59	10.25 (10.46)*	-10.54	Acetone
8.44	79.92	78.60	6.33	9.49	10.45	
8.60	72.63	75.89	5.58	10.60 (10.80)*	-10.27	Chloroform

	$(CH_3)_2CBrCHBrC_6H_5$	$(CH_3)_2CBrCHBrCO_2H$	$(CH_3)_2CHCHC_6H_5$ $9H$	Solvent
Chem. shift of methyls	5.1	16.5	13.1	Benzene
	5.9	6.0	12.3	Chloroform
	7.1		11.0	Carbon tetrachloride

* Value measured from spectrum of
dibromide from trans- β -deuterostyrene.

one can make an unambiguous spectral assignment to the (1,2-dibromo-ethyl)benzene spectrum, assuming only that bromine adds _trans_ to the double bond. This assignment is,

Spectral analyses using Swalen's iterative scheme and/or an empirical scheme devised for three-spin systems afford the parameters listed. Although sets containing both positive and negative J_{23}'s are present, satisfactory agreement between observed and calculated spectra with the set containing couplings of the same sign was <u>never</u> obtained. Continued iteration by either scheme resulted in an almost constant rate of change of J_{12} and J_{13}, <u>i.e.</u>, the iterative procedure was, at best, converging very slowly. The consistently better agreement between J_{13} in the set containing $J_{23} < 0$ and the observed coupling constant in the dibromide from trans- β-deutero-styrene gives further support to this assignment. Again, J_{23} is quite solvent dependent. Because $\nu_3 - \nu_2 > 0$ in benzene, chloroform, and carbon tetrachloride but $\nu_3 - \nu_2 < 0$ in acetone (and also pyridine), one might find a binary solvent mixture with acetone where the chemical shift between the two methylenes vanishes although they will remain non-equivalent by virtue of their different 1,2- and 1,3- couplings.

3. Non-equivalent methyl groups - A table of chemical shifts summarizes our observations. Each of the methyl resonances of A $[C_6H_5CHBrCBr(CH_3)_2]$ and B $[(CH_3)_2CBrCBrHCO_2H]$ are quite broad, but no fine structure was resolved. (The half-width of internal TMS was ~0.3 cps., that of the methyls~1.1 cps.) Since long-range coupling has been observed in

$$CH_2Br \quad \overset{\overset{\displaystyle CH_3}{|}}{CHBr} \quad CO_2H \quad ,$$

and its ester, and in <u>erythro</u>-$CH_3CHBrCHBrCO_2H$, a lack of such coupling in B would be surprising. The temperature-dependence of the spectrum might be illuminating.

Finally, if chemical shift differences were a valid criterion of non-equivalence, and if non-equivalence arose from differences in conformational population, then the larger chemical shift of the non-equivalent methyls in A than that of the non-equivalent methylenes in (1,2-dibromoethyl)benzene would imply larger differences in conformational populations in A than in the substituted benzene. This seems unreasonable; chemical shifts are probably poor criteria of non-equivalence.

To make an obvious suggestion to Moore's "problem" (no. 43), deuterate one of the methyls stereospecifically. We've been thinking of doing this for A or B.

Sincerely,

Eugene I. Snyder

EIS/aty

AUDIO MODULATION OF P^{31} SPECTRA

T. J. Flautt

The Procter and Gamble Company
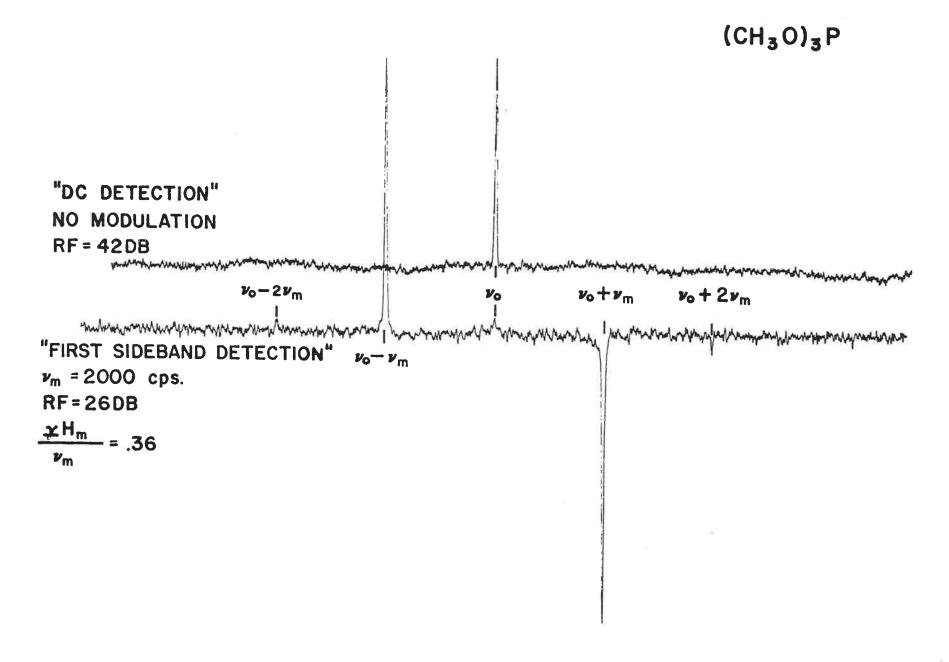Miami Valley Laboratories
Cincinnati 39, Ohio

In defining the experimental conditions for obtaining audio modulated spectra, the most important parameter is the modulation index

$$\beta = \frac{\gamma H_m}{\nu_m} ,$$

that is, the ratio of the modulation amplitude (in frequency units) to the frequency of modulation. For protons, the Varian V-3521 integrator is ordinarily adjusted to obtain spectra at a β of 1.8 and the nmr signal at ν_0 is utilized (center band detection). With the H_m available from the integrator, a large modulation index is not attainable for nuclei with smaller γ -- P^{31}, C^{13}, B^{11}, H^2, etc. In such a case detection of the nmr signal at $\nu_0 \pm \nu_m$ (first sideband detection) is appropriate, since β may be small -- it only serves to reduce the effective radio frequency power.

The accompanying figure shows a comparison between P^{31} spectra obtained under conditions of (1) no modulation and (2) first sideband detection. The first sideband spectra were obtained by inserting a 1 μf condenser in series with the probe modulation coils to achieve ~ π/2 phase shift of the modulation current and to reduce H_m to the modulation coils -- fine adjustments of the audio phase and amplitude were made by the appropriate controls on the integrator. The criterion of adjustment of audio phase was the disappearance of the nmr signal at ν_0. Audio amplitude was adjusted small enough so that the signals at $\nu_0 \pm 2 \nu_m$ were very small compared to the signals at $\nu_0 \pm \nu_m$. In the case of the spectrum presented in the figure, the modulation index was 0.36. The figures representing radio frequency power are the attenuator settings on the 24.3 MC 4311 radio frequency unit for maximum S/N. It is to be noted that considerably more RF power is needed for maximum S/N under first sideband detection conditions than for no modulation. The sweep rate for both spectra was 54 cps./sec. and frequency response was 1 cps.

It appears that maximum S/N for unmodulated spectra is better than for first sideband audio modulated spectra (theoretically it is better by $\sqrt{2}$) if long term baseline drift is ignored. However, for integration the baseline drift must be minimized -- under such conditions first sideband spectra are to be preferred. A secondary advantage of modulated spectra is that calibration of the spectrum is automatically achieved since the separation between the upper and lower sideband signals is always 2 ν_m. A disadvantage of modulation at 2000 cps. for P^{31} spectra is that the separation between the upper and lower sidebands is not large compared to the chemical shift range of P^{31} nuclei (~ 12,000 cps. at 14,100 gauss). Hence there may be interferences between the upper sideband of one nucleus and the lower sideband of another nucleus chemically shifted by 4000 cps. However, this practically never happens -- and if it does happen, the other sideband will not be interfered with -- at least by the same nucleus.

$(CH_3O)_3P$

"DC DETECTION"
NO MODULATION
RF = 42 DB

$\nu_0 - 2\nu_m$ ν_0 $\nu_0 + \nu_m$ $\nu_0 + 2\nu_m$

"FIRST SIDEBAND DETECTION" $\nu_0 - \nu_m$

ν_m = 2000 cps.

RF = 26 DB

$$\frac{\gamma H_m}{\nu_m} = .36$$
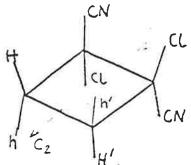
5-54

U. S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS
Washington 25, D.C.
June 22, 1962

"Urbi et Orbi."

Here is another case where geminal and vicinal proton-proton coupling constants have opposite signs. The molecule in question is trans-1,2-dichloro-1,2-dicyanocyclobutane. These are its NMR parameters:

a) Geminal coupling constants
$$J_{HH} = J_{H'h'} = \pm 9.4 \text{ c/s or } \mp 13.1 \text{ c/s}$$

b) Cis coupling constants
$$J_{Hh'} = J_{H'h} = \mp 13.1 \text{ c/s or } \pm 9.4 \text{ c/s}$$

c) Trans coupling constants (interchangeable)
$$J_{HH'} = \pm 9.3 \text{ c/s}; \quad J_{hh'} = \pm 4.5 \text{ c/s}$$

d) Relative chemical shift: 0.410 ppm.

The spectrum, of the A_2B_2-type, contains 2 x 9 resolvable lines, one pair being 0.8 c/s broad. A value for δ was obtained from the second moment, and then some guesses were made on the AB and the B patterns. Only with the above values can the entire spectrum be fitted. Frequencies check within 0.1 c/s, except for the pair of innermost lines (calc.: 1.9; obs.: 1.7 c/s), and intensities do so within 5 %. Aksel Bothner-By's Frequint III program was of immense help. LAOCOON may be able to refine the data some, but probably not much more. The lines are not too sharp (~0.5 c/s): to observe the outer weak lines, the concentration of the $CDCl_3$ solution has to be high, with a corresponding increase in viscosity and linewidths.

I think that the present case is of interest also for other reasons.
1. Not much averaging of J's can occur, as the ring is quite rigid.
2. The two carbons bearing the protons are not bonded to any substituents.
3. A distinction between cis and trans coupling constants can be made. J_{cis} is between non-equivalent and the J_{trans}'s are between equivalent protons.

Few J's are known for protons on four-membered rings. In cyclobutanone, and in trimethylene oxide and sulfide, $|(J_c + J_t)/2|$ are 8.2 and 7.6 c/s respectively[1] [2]. In β-propiolactones, these vicinal J's range from $|4.9|$ to $|6.1|$[3] In β-(p-nitrophenyl)-β-propiolactone, J_{gem} is $|16.6|$ c/s. From the ABX spectrum reported [4], the relative signs of J_{gem} and the J_{vic}'s cannot be determined, in spite of the authors' statement that the signs are all equal.

I hope that these data will contribute to the refinement, rather than to the demolition of Karplus' theory. In analogy with the J's in similar molecule, in the present one J_{cis} may be ± 9.4 c/s and $J_{gem} \mp 13.1$ c/s. The rather large difference in the J_{trans}'s could be due to the non-equivalence of the geminal protons, but also to the geometry of the molecule: if the ring is planar, the hCH angles may not be bisected by the plane of the ring; or the ring is twisted about the C_2-axis. In view of these uncertainties it may not be too meaningful to calculate parameters for the $\cos^2\varphi$ expression.

Ernest Lustig

1) Wiberg and Nist, JACS 83, 1223 (1961), Varian Spectra Catalog
2) Analysis of these spectra in progress   (and own data.
3) cf. Grant and Gutowsky, JCP 34, 699 (1961).
4) Gutowsky, Karplus and Grant, JCP 31, 1278 (1959).

MOUNT HOLYOKE COLLEGE
SOUTH HADLEY, MASSACHUSETTS

May 23, 1962

DEPARTMENT OF CHEMISTRY
CARR LABORATORY

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

Dear Dr. Bothner-By,

In order to determine the effect of substituents of
varying electronegativity and magnetic anisotropy on the
magnitude of the coupling constant between protons on ad-
jacent saturated carbon atoms, we have examined the spectra
of some Diels-Alder adducts of hexachlorocyclopentadiene
and various monosubstituted ethylenes:

This system is rigid, and there-
fore variations in the magnitude of
the coupling constants are not due to
variations in the dihedral angle be-
tween the coupling ABX protons. Fur-
thermore, since the system contains
a minimum number of coupling protons,
a complete, unequivocal ABX analysis is possible.

A correlation has been found between the sum of J_{cis} -
J_{trans} - J_{gem} and the electronegativity of the substituent
for a long series of vinyl compounds (J. S. Waugh and S.
Castellano, J. Chem. Phys. 35, 1900 (1962); T. Schaefer,
Can. J. Chem. 40, 1 (1962)). In the present work, however,
the sum of $|J_{AX}| + |J_{BX}| + |J_{AB}|$ is 24.5 ± 1 c.p.s. for the
six compounds, so a similar correlation for this saturated
system has no validity. A definite correlation does exist,
however, between the electronegativities of the substituents
(as defined by J. R. Cavanaugh and B.P. Dailey, J. Chem.
Phys., 34, 1099 (1961)) and the individual coupling constants
$|J_{AX}|$, $|J_{BX}|$, $|J_{AB}|$ (see Fig. 1).

In Fig. 2 the internal chemical shifts between the X
and A protons ($\delta_X - \delta_A$) and the X and B protons ($\delta_X - \delta_B$)
for the six compounds are plotted against the electronega-
tivities of the various substituents. The dashed line
represents the internal shifts between the α and β protons
in a series of ethyl derivatives upon which Cavanaugh and
Dailey have based their electronegativity values.

A complete discussion of these results will appear in
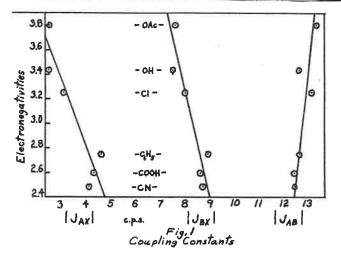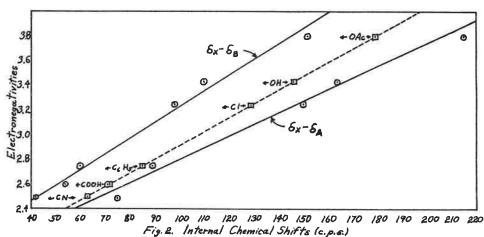a forthcoming publication.

Sincerely yours,

Kenneth L. Williamson

Kenneth L. Williamson

TABLE I
COUPLING CONSTANTS AND CHEMICAL SHIFTS

Substituent X	J_{AX}	J_{BX}	J_{AB}	δ_A	δ_B	δ_X	$\delta_X-\delta_A$	$\delta_X-\delta_B$	Electronegativities
	c.p.s.			c.p.s. from TMS at 60 mc.					(from Cavanaugh & Dailey)
CN	4.1	8.7	12.4	129	162	204	75	42	2.49
COOH	4.3	8.6	12.4	146	163	217	71	54	2.60
C_6H_5	4.6	8.9	12.6	143	172	232	89	60	2.75
Cl	3.1	8.0	13.1	133	185	283	150	98	3.25
OH	2.5	7.5	12.6	114	167	278	164	110	3.43
OAc	2.5	7.6	13.3	114	177	330	215	152	3.80

Fig. 1
Coupling Constants

Fig. 2. Internal Chemical Shifts (c.p.s.)

45-7

27.5.1962

Drs. A.A. Bothner-By and B.L. Shapiro,
Mellon Institute,
4400 Fifth Avenue,
Pittsburgh, Pa.,
U. S. A.

Dear Aksel and Barry:

Among other things, I have been playing with interpreting chemical shifts in terms of local electrostatic (assumed homogeneous) fields extending the original ideas of Buckingham and Buckingham, Schaefer and Schneider. I have a paper soon to appear in JCP giving a quantum chemical 'calculation' for k_E in the expression

$$\Delta\sigma = k_E \Delta E_z^{eff}$$

where ΔE_z^{eff} is the actual electric field along the axis, obtaining $k_E = -2.5 - 5 \times 10^{-12}$ (statvolts/cm)$^{-1}$ for a proton in a carbon-hydrogen bond, where the variation comes from possible choice of parameters. This serves to justify the estimate of -2×10^{-12} made by Buckingham, and agrees quite well with available data.

The recent data of Professor Goldstein and co-workers (JACS **84**, 1042 (1962)) on uracils provided another example of this electric field shift for a proton in a C-H bond, and the first such examples for a proton in a N-H bond. This paper correlates the chemical shifts of proton at the 1,3 and 6 positions as a function of 'Group dipole moment' of X, showing a reasonably linear plot

(allowing even for disagreements over the choices of 'bond moments') with the same slopes obtained for protons on the two N atoms as might be expected. When these are interpreted in terms of the intra-molecular fields and the local electric field differences are calculated assuming a certain geometry one obtains

$$k_E(C - H) = -3.0 \times 10^{-12}$$

and

$$k_E(N - H) = -6.2 \times 10^{-12}$$

This involves a slight change in the $\Delta\mu$ used, and neglected the 'reaction field' which should only change results by $\sim 10\%$ and is exceptionally difficult to estimate in view of the artificiality of the models existing in the literature.

This is reasonably in accord with the calculations, which depends in part on a parameter

$$R_{X-H} - \langle\sigma_X|z|\sigma_X\rangle$$

or the bond length minus the hybrid dipole. Since there is certainly considerably less hybridization in N-H bonds than in C-H bonds (Moffitt, Pople etc.), the second term which is .4A for carbon is almost zero for nitrogen. Further only the slightest polarization of a MO in favor of the nitrogen along with decreased overlap provides the rest of the increase in k_E for an N-H bond. It would be interesting to extend this to non-exchanging OH and SH bonds. From the experimental k_E's we can obtain information about the choice of bond parameters.

Keep up the excellent service you and the Mellon Institute provide to the NMR world with Mellonmr.

Best regards,

Sincerely,

J.I. Musher.

HARVARD UNIVERSITY

DEPARTMENT OF CHEMISTRY

12 Oxford Street
Cambridge 38, Massachusetts, U.S.A.

May 28, 1962

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

Dear Aksel:

Our determination of the relative signs of the geminal and vicinal H-F coupling constants in CH_3CH_2F (S.L. Stafford and J.D. Baldeschwieler, J.A.C.S., 83, 4473 (1961)) seems to be emerging as one of the few cases where the geminal and vicinal coupling constants have been shown to be of the same sign. These relative signs were determined by a complete analysis of the proton spectrum at 15 Mc.

Martin Karplus' recent note (MelloNMR, 43, 26) that these constants have "apparently" been shown to be of the same sign inspired us to check this result by proton-proton double resonance methods.

CH_3CH_2F is a particularly easy example for relative sign determination, since the spectrum at 40 or 60 Mc. consists of well separated pairs of triplets and quartets. We find that irradiation of the upfield quartet causes the collapse of the upfield triplet, and irradiation of the downfield quartet causes collapse of the downfield triplet. This is very good evidence that the H-F coupling constants are of the same sign, and confirms the single resonance work.

We now propose that the signs of these coupling constants "really" are the same.

Sincerely,

B. D. Nageswara Rao

J. D. Baldeschwieler

BDNR/JDB:br

RÉPUBLIQUE FRANÇAISE
PREMIER MINISTRE

COMMISSARIAT A L'ÉNERGIE ATOMIQUE

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ADRESSER LA CORRESPONDANCE :
BOITE POSTALE 269 - GRENOBLE

TÉL. 87-58-11 ET LA SUITE

D. GAGNAIRE & **F. CSAKVARY**
Chimie Organique Physique

LONG-RANGE COUPLING

RÉFÉRENCE A RAPPELER :	VOTRE RÉF. :	GRENOBLE, LE 2 8 Mai 1962
G/ MEL-1	VOTRE LETTRE DU	

Cher Dr. BOTHNER-BY,

Voici, avec quelque retard, notre contribution à Mellon-M-R. Il s'agit d'un cas interessant de couplage à longue distance.

Nous avons été amené à étudier une série de corps à squelette rigide afin d'établir les constantes de couplage en fonction de la géométrie moléculaire, et plus particulièrement la série dérivée du 2,3 dihydrofuranne.

Le spectre du 2,3 dihydro-5-methyl furanne (1) présente un cas de structure fine du groupement $-CH_3$, ainsi qu'en témoigne la figure jointe (*).

L'attribution des raies est en parfait accord avec celle proposée par L.M. JACKMAN (1) pour le spectre du 2,3 dihydrofuranne, et correspond aux ? suivants :

../..

τ p.p.m	CH$_1$	e	c	d
	8,28	3,35	4,46	5,15

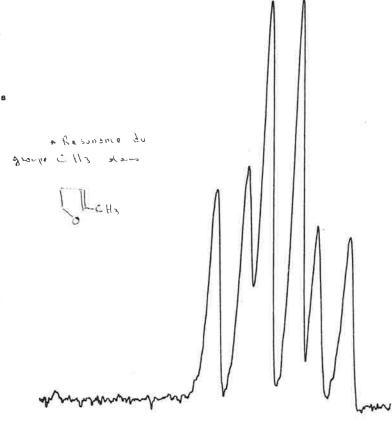| J c/s	CH$_3$	e	c
e	1,1		
c	?	0,9	
d	0	0,9	g

Le groupement méthyl est couplé non seulement à l'hydro-
gène (b) mais à deux autres protons. La résolution du spectre au premier
ordre, a conduit à attribuer ce couplage aux hydrogènes (c) et a permis
d'établir le tableau ces constantes de couplage, suivant.

Une étude plus détaillée de ce spectre est en cours. Mais
d'ores et deja ce couplage apparaît comme un couplage à longue distance
beaucoup plus intense que celui obtenu dans le 2-methyl furanne (de l'ordre
de 0,4 c/s) ou le 2,5 dimethyl-furanne par exemple (2). Nous pensons pouvoir
l'interpreter par hyperconjugaison.

Sincèrement vôtre,

* Résonance du
groupe CH$_3$ dans

(*) effectuée sur Varian A-60 par le Professeur OURISSON que nous remercions
ici
(1) "Application of NMR spectroscopy in Organic Chemistry" Pergamon Press
p.88
(2) Reddy, Goldstein, J.Phys.Chem. 1961, 65, 1539

HARVARD UNIVERSITY

DEPARTMENT OF CHEMISTRY

12 Oxford Street
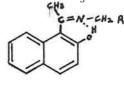*Cambridge 38, Massachusetts, U.S.A.*

June 12, 1962

Dr. Barry L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Barry,

Read all the comments on recorder ink for the A-60, and another opinion is that "Parker Quick" black fountain pen ink works as well as any we've tried.

Our stockroom now has about eight (8) of the more useful deuterated solvents in 1 and 2 gram ampoules and deuterochloroform in 5 and 10 gram ampoules. Merck of Canada charges for subdividing an order into these small sizes, but the convenience and decreased wastage makes up for the cost. Many would balk at buying 10 grams of deuterpyridine for a spectrum, but 1 gram is quite different.

I have an interesting case of long-range coupling. The spectra of the Schiff Bases derived from 2-hydroxy-1-acetonapthone are quite ordinary in DCCl$_3$ (methyl region diagramed):
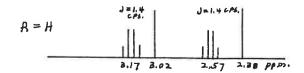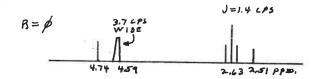
In Pyridine solution:

My present explanation is that in pyridine, the hydrogen bond in the Schiff Base can be broken and the aceto-imine group rotates 180°. In this rotamer, the 1.4 cps coupling appears. In the hydrogen bonded chelate, the hydrogen bond disturbs the system so the coupling is not transmitted. The coupling is not observed in 2-(N-methylimino)acetonapthone, so the coupling makes greater demands on the system than just a lack of a hydrogen bond. I'm making a few more compounds in an effort to discover what a few of these additional requirements are.

Yours truly,

Gerald Dudek

GOD/efr

June 14, 1962

Drs. A.A. Bothner-By and B.L. Shapiro
Mellon Institute
Pittsburgh, Pa.

Dear Aksel and Barry,

At the risk of burdening you with a second contribution from our laboratory for the same issue of MELLONMR we send on the following

We were pleased to see Ted Schaefer's paper giving NMR data on the cyclopropane ring (Hutton and Schaefer, Can. J. Chem. 40, 875 (1962)) and we thought your readers might be interested in the following additional data. The molecules were very kindly provided by Prof. H.M. Walborsky. The relative signs were determined both by the double quantum spectra and by analysis of the 30 Mc spectrum. The absolute values of J_{cis} and J_{trans} agree quite well with the values of H. and S. of 8.7 and 5.4 cps respectively. We assign cis and trans protons by observing that in propylene oxide the methyl group shifts the cis – proton upfield and the trans – downfield to give a differential of 18 cps. This turns out to be 17 cps in propylene sulfide and 15 cps here if the protons are assigned as follows. I wonder why this disagrees with the findings of Prof. Closs in JACS 82. From Schaefer's work it really appears that one of these two groups must have the wrong molecules. For the above reason, excluding all knowledge of organic chemistry, I favor Schaefer's (commercial) isomer assignments.

$J_{AB} = 4.65$ $\nu_A = 90.9$ (TMS/60 Mc)

J_{CH_3-A}, $J_{CH_3-B} \lessapprox 0.4$ $\nu_B = 145.5$ (TMS/60 Mc)

$J_{AB} = \pm 4.37$ $\nu_A = 92.1$

$J_{AC} = \mp 7.70$ $\nu_B = 132.8$

$J_{BC} = \mp 5.85$ $\nu_C = 159.0$

It is interesting to note that the ^2J (J_{gem}) and the ^3J's (J_{trans} and J_{cis}) are of opposite signs here in analogy with ethanes (Anet, Freeman, Kaplan, Lemieux, McLauchlan, et al.) but as differing from propylene oxide. It is probably a reasonable guess that the ^3J's which remain relatively constant in series of the O, N, S heterocycles and the carbocycle preserves its sign, while the ^2J's change sign. The conclusion from the literature data (particularly epichlorhydrin of Reilly and Swalen) would be that if ^3J in ethane is positive then ^2J (ethane) is negative but ^2J (cyclopropane) is positive and ^3J (cyclopropane) is negative, which, to use the vernacular, is a fine kettle of fish.

Yours sincerely,

J.I. Musher

A. Szöke

UNIVERSITY CHEMICAL LABORATORY,
LENSFIELD ROAD,
CAMBRIDGE.
TELEPHONE: 56491.

Dr. A. A. Bothner - By,   ENGLAND.   14ᵗʰ JUNE, 1962.
Mellon Institute
Pittsburgh, Pennsylvania.

Dear Dr. Bothner - By :

When reading Dr. Sheppard's copy of MelloNMR 44, we were interested to notice the data of Dr. J. P. Freeman on azo and azoxy compounds. The shift to high field on oxidation has, in fact, been recorded several times in the literature for molecules in the pyridine,[1] pyrroline[2] and furazan[3,4] series, but as far as we are aware has not been commented on previously. Until we noticed the articles[1-3] concerned, we were very puzzled by our results from a low temperature study of benzofuroxan (I), for we expected the resonance of the proton at position 7 to occur

to low field of that of H_4, and also to low field of the corresponding protons in benzofurazan (II). However, the latter prediction was certainly wrong (see Table), and this led us to question the former. It was not possible to solve the problem from a study of the spectra of the unsubstituted compounds , but the 4 - nitro derivatives showed us that in fact H_7 has a τ - value higher than that of H_4. The relevant data is shown in the Table. Figures (III), (IV) and (V) give the resonance shifts (in p.p.m.) on oxidation from a furazan to the corresponding furoxan (all the shifts are to high field).

In fact the molecules reported here are in some ways more suitable for theoretical study than those of Freeman, since the structure is now beyond doubt (see the recent X - ray work,[5,6] and all the atoms are in a single plane (since there are no rotating methyl groups). Undoubtedly, however, resonance structures of type (VI) contribute to the high field shift for H_5 and H_6 (presumably more than those of type (VII)). The shift at H_7, on the other hand, is probably due almost entirely to anisotropy of the (N,O) bond, especially as inductive effects act in the opposite

direction. It may be seen that H_7 is analogous in position with the protons at C_4 in Freeman's compounds in some of the possible rotamers.

A paper has been submitted to J. Chem. Soc. on the N.M.R. spectra of benzofuroxan and five nitro - derivatives, following our preliminary note in Chem. and Ind.[7] We would like to express our appreciation for the MelloNMR service (and we are grateful to Dr. Sheppard for the loan of his copy). Finally, one of us (R.K.H.) will no doubt feel himself at the centre of the N.M.R. world when he takes up his appointment at the Mellon Institute in September.

Cordially yours,

R. K. Harris   A R Katritzky

(R. K. Harris)   (A. R. Katritzky)

Table. τ - values of benzofurazan and benzofuroxan compounds.

Compound	4	5	6	7
benzofurazan [a]	2.05	2.41	2.41	2.05
benzofuroxan [a,c]	2.39	2.49	2.65	2.54
4-nitrobenzofurazan [a]	-	1.90	2.05	1.40
4-nitrobenzofuroxan [a]	-	1.48	2.41	1.44
4,7-dibromobenzofurazan [b,4]	-	2.49	2.49	-
4,7-dibromobenzofuroxan [b,4]	-	2.59	2.75	-

a in solution in acetone
b in solution in methylene dichloride
c at - 60° C. Values correspond to room temperature.

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Proton Magnetic Relaxation in Polyamides

by

David W. McCall and Ernest W. Anderson
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Murray Hill, New Jersey

ABSTRACT

Proton magnetic relaxation studies of three polyamides have been carried out. NMR relaxation times, T_1 and T_2, have been measured over a wide range of temperature and the transitions observed have been correlated with dielectric and mechanical loss transitions. The low temperature transition involves the entire specimen and is interpreted in terms of molecular reorientations about the long chain axes. The high temperature transition is associated with the onset of liquid-like motions in the noncrystalline regions. Between 130 and 190°C it is possible to decompose the resonances into a broad and a narrow component and to deduce a "rigid fraction".

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HARVARD UNIVERSITY

DEPARTMENT OF CHEMISTRY

June 15, 1962

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

Dear Aksel:

The proton NMR spectrum of CH_2CF_2 in the liquid phase includes 10 sharp lines, and is readily analyzed as an AA'XX' case. As is usual for this problem, only the relative signs of J_{HF} and $J_{HF'}$ can be obtained from an analysis of the spectrum, while the relative signs of the other coupling constants remain indeterminant.

The proton NMR spectrum of CH_2CF_2 in the gas phase consists of two sharp peaks, and a number of broad features. By a careful measurement of the splitting of the two sharp peaks as a function of pressure, it is possible to associate the sharp peaks in the gas phase spectrum with the innermost pair of lines in the liquid spectrum. As with the spectra of other fluorocarbons in the gas phase (Mello NMR 42, 12 (1962). The sharp features can be identified as transitions between states with the largest singlet fluorine spin character. This identification of the origin of the lines in an AA'XX' spectrum removes one of the ambiguities in the spectral assignment. In this way the relative signs of J_{HH} and J_{FF} can be obtained. In CH_2CF_2, J_{HH} and J_{FF} are opposite in sign.

We feel you may find this result an interesting addition to the rapidly growing collection of relative signs.

Sincerely yours,

George W. Flynn

John D. Baldeschwieler
George W. Flynn

JDB:dl

THE UNIVERSITY OF WESTERN ONTARIO
UNIVERSITY COLLEGE

DEPARTMENT OF CHEMISTRY   LONDON, CANADA

June 18, 1962

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

Dear Aksel,

In the course of a study of the factors contributing to the chemical shift of formyl protons, an examination of the effect of solvent was carried out. A number of aldehydes were run in a range of solvents and the peak position of the formyl proton determined relative to an internal tetramethylsilane marker. The most striking effects were observed for aromatic aldehydes in benzene solution and this solvent shift was found to be markedly dependent on the nature of the substituent of the solute molecule. Some typical results are presented in Fig. 1 in which the shift in a given solvent is shown relative to that observed in CCl_4 solution, except for the nitro derivatives whose shifts are given relative to $CDCl_3$ solution. Two aliphatic examples are included for comparison.

The results in benzene solution suggested that a rather specific solute-solvent interaction was involved and that the specificity was governed by the nature of the substituent grouping. For a benzene solvent molecule acting as a donor, one would expect association to occur at the electron-deficient region of the solute. Thus, in the case of a strong electron-withdrawing group such as p-NO_2, the aromatic carbon bearing the formyl group could be the centre of this association, while, for the p-NMe_2 derivative, the substituent grouping would be expected to be most strongly associated with the donor molecule. Further, a planar type of complex appears to be a most reasonable form for this association.

Since the shielding effect of an aromatic ring through space is well understood, one can predict, qualitatively at least, the effect of a closely associated ring on the chemical shifts of the solute protons. Therefore, if the suggested complex is actually involved, one would predict, for the p-NMe_2 derivative, that the N-methyl proton would be strongly shielded, the aromatic protons less so, and the formyl proton even less (if not deshielded slightly). [All of these shifts considered relative to those observed in a non-associating medium.] On the other hand, for the p-NO_2 derivative, the ortho-protons would be strongly shielded and the formyl and meta protons less shielded. In order to test these predictions a series of p-substituted benzaldehydes was examined in benzene and chloroform solution and the chemical shifts of all solute protons determined. (Due to solubility problems, $CDCl_3$ was chosen as the base case rather than CCl_4. We have found no evidence that this solvent causes differential shifts of the solute protons.) The relative shifts for the solute protons in these two solvents are shown in Fig. 2. Clearly the observed trends are quite compatible with the suggested model for this solute-solvent association. Similar studies were carried out for a series of p-substituted toluenes and acetophenones and the trends observed are completely analogous. The differential shifts of the solute protons, therefore, offer strong evidence for a planar complex whose stereochemistry is controlled by the electron distribution of the solute molecule. Variable temperature studies have also been done on two of these systems and the observed effects are in complete agreement with our model. Further, Hatton and Richards have recently presented evidence for a similar association in the case of some amides and three α,β unsaturated carbonyl derivatives in aromatic solvents.

We have also examined the solvent shifts of the various substituted benzaldehydes, toluenes and acetophenones in acetone solution. In this case the relative shifts are much smaller, however, the trends are clear. Our results are in accord with the suggestion made earlier by Schaefer and Schneider for similar systems.

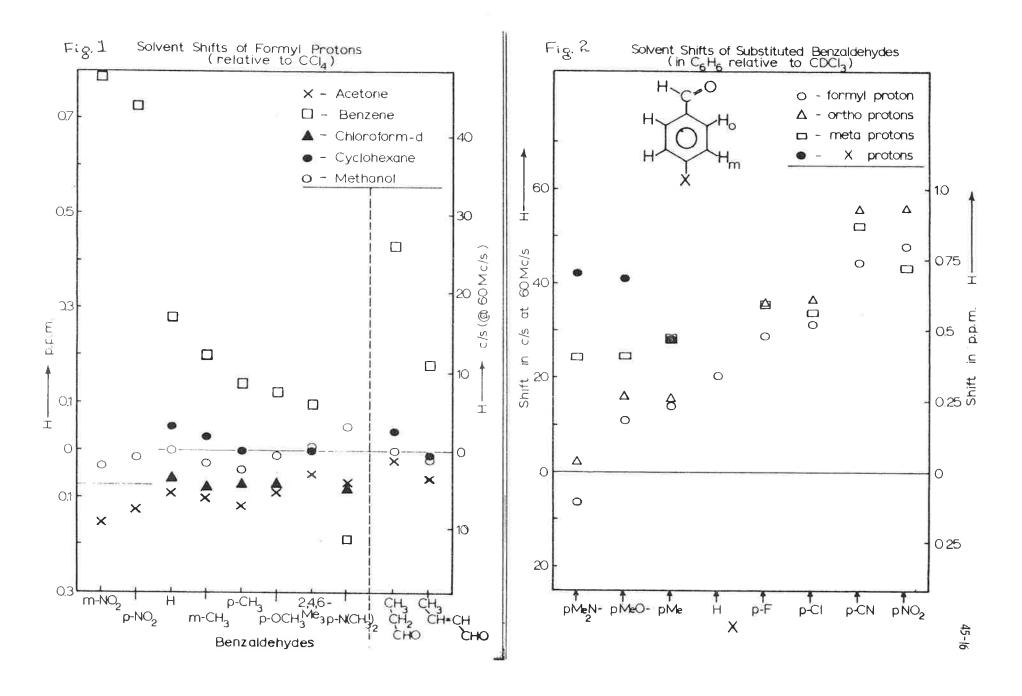Sincerely,

Jake

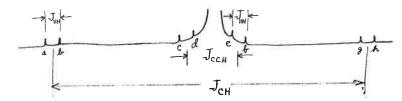J. B. STOTHERS
Assistant Professor

JBS:vl

Fig. 1   Solvent Shifts of Formyl Protons
(relative to CCl_4)

X – Acetone
☐ – Benzene
▲ – Chloroform-d
● – Cyclohexane
○ – Methanol

0.7
0.5
0.3
0.1
0
0.1
0.3

H ⟶ p.p.m.

40
30
20
10
0
10
20

H ⟶ c/s (@ 60Mc/s)

m-NO_2 p-NO_2 H   m-CH_3 p-CH_3 p-OCH_3 2,4,6-Me_3 p-$N(CH_3)_2$ CH_3 CH_2 CHO CH_3 CH=CH CHO

Benzaldehydes

Fig. 2   Solvent Shifts of Substituted Benzaldehydes
(in C_6H_6 relative to $CDCl_3$)

○ – formyl proton
△ – ortho protons
☐ – meta protons
● – X protons

60
40
20
0
20

Shift in c/s at 60Mc/s

H

1.0
0.75
0.5
0.25
0
0.25

Shift in p.p.m.

pMeN-$_2$ pMeO-   pMe   H   p-F   p-Cl   p-CN   pNO$_2$

X

Fig. 3

(TOP VIEW)

(a)

(SIDE VIEW)

(b)

On the Relative Signs of CH and HH Coupling Constants

In MELLON-M-R No. 43, p. 24, Karplus suggested that the absolute signs of HH coupling constants could be determined with near certainty by comparisons with couplings between directly bonded C^{13} and H^1, for which theory predicts, in a straight-forward manner, positive signs. We have carried out H^1 (C^{13}) double resonance experiments of the type proposed by Karplus with results outlined below.

The H^1 spectrum of cis-CHCl=CHCl, sketched below, permitted an easy test

of the experiment. Upon irradiation of the low frequency doublet in the C^{13} spectrum, lines d and f in the H^1 spectrum were observed to move toward one another and finally vanished under the central peak from the $C^{12}HCl=C^{12}HCl$ species. At an irradiation frequency (ν_2) about 200 cps higher, lines c and e moved in and vanished. Since the low frequency C^{13} doublet occurs at high field, and vice versa, this result shows that the HH and CH couplings have the same signs. As cis and trans HH couplings in olefins have been found to be of the same sign, we now know that both are positive. Relative signs of cis and/or trans couplings and geminal couplings have been measured in many olefins, and we can now say with virtual certainty which of the latter are positive and which negative. The following table summarizes some of the data found in the literature for vinyl compounds.

Table I

HH Coupling Constants in X-CH=CH$_2$

X	J			Ref
	cis	trans	gem	
H	+ 11.7	+ 19.1	+ 2.5	1
F	+ 4.7	+ 12.8	− 3.2	2
Cl	+ 7.2	+ 14.9	− 1.4	2
Br	+ 7.1	+ 15.0	− 1.7	2
CH$_3$	+ 10.02	+ 16.81	+ 2.08	3
CH$_3$CH$_2$	+ 10.4	+ 17.4	+ 1.9	4
(CH$_3$)$_2$CH	+ 10.4	+ 17.3	+ 1.6	2
(CH$_3$)$_3$C	+ 10.8	+ 17.5	+ 1.4	4
CCl$_3$	+ 10.07	+ 16.05	− 0.42	5

X	cis	trans	gem	Ref
C_6H_5	+ 11.0	+ 17.8	+ 1.1	6
$2,4,6-(CH_3)_3C_6H_2$	+ 11.6	+ 18.0	+ 2.3	6
CN	+ 11.8	+ 18.0	+ 1.0	2
CH_3O	+ 6.8	+ 14.4	- 2.2	2
$CH_2=CHO$	+ 6.4	+ 14.0	- 1.8	2
CH_3COO	+ 6.5	+ 14.1	- 1.5	6

Furthermore, a number of comparisons have been made between the signs of couplings in allylic groupings as shown below. The absolute

$$J_c$$
$$CH=CH-CH$$
$$J_a \quad J_b$$

signs can now be assigned as shown in Table II.

Table II

Compound	J_a cis	J_a trans	J_b	J_c cis	J_c trans	Ref.
$CH_3-CH=CH_2$	+ 10.02	+ 16.81	+ 6.40	-1.75	-1.33	3
trans-$CH_3CH=CH-CHO$	---	+ 15.6	+ 6.8	-1.6	---	7
trans-$CH_3-CH=CH-COOH$	---	+	+	-	---	7
cis-$CH_2Cl-CH=CHCl$	+ 7.2	---	+ 7.2	---	-0.9	8,(9)
trans-$CH_2Cl-CH=CHCl$	---	+ 13.1	+ 7.1	-0.5	---	8,(9)
trans-$CH_3-CH=CH-C_6H_5$	---	---	+ 6.6	-1.8	---	10

Because of the near constancy of the $CH_3-CH=C$ couplings, it seems permissible to assume further that the signs in 1-chloro-1,2-butadiene are as given below. The relative

+2.40
+7.20 H_3C $C=C=C$ Cl
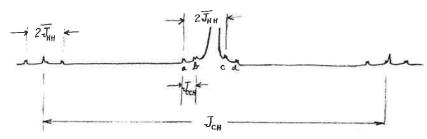   H   H
-5.80

sign data are from Snyder and Roberts (11).

In addition, we find from the work of Elvidge and Jackman (12) that the coupling shown below between vicinal hydrogens in diolefins is

$$=C \begin{array}{c} H \\ C= \\ H \end{array}$$

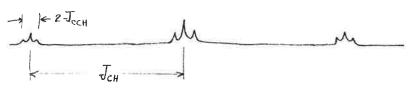of the same sign as those across the double bonds and therefore positive.

It also seems likely that the ortho HH couplings in substituted benzenes, which have about the same magnitudes as cis olefinic couplings, are also positive in sign. We are planning to check this point in the near future.

The corresponding couplings in 5-membered ring compounds become very small, and it is impossible to decide upon their probable signs by comparison with other compounds. Double resonance experiments will also be carried out on some compounds of this type.

Double resonance experiments were next carried out on $ClCH_2CH_2Cl$ to determine the signs of vicinal couplings between hydrogens on sp3 carbons. The spectrum is sketched below. $(2\bar{J}_{HH} \simeq J_{HH} + J'_{HH})$

The C^{13} spectrum would look, at high resolution, about as follows.

It was found that irradiation of the low field (high frequency) peaks in the C^{13} spectrum caused peaks a and b in the H^1 spectrum to move together, and that peaks c and d were affected at an irradiating frequency about 300 cps $(2J_{CH})$ lower. Therefore, the sum of the vicinal HH coupling constants is positive, and the accumulated evidence makes it seem very likely that all large vicinal HH coupling constants are positive. Furthermore, judging from the relative signs and magnitudes of the couplings in Table III, all large geminal HH couplings are probably negative, the

Table III

	Ref.

13

14

14

15

result considered most likely by Karplus.

Several other couplings whose signs relative to ordinary vicinal couplings are known are shown below.

16

17

17

We are continuing relative sign determinations on various types of compounds, and will report further results and more details in the near future.

Paul C. Lauterbur
Mellon Institute

R. J. Kurland
Carnegie Inst. of Tech.
Pittsburgh 13, Pa.

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UNION CARBIDE

INTERNAL CORRESPONDENCE ────────────────────

UNION CARBIDE CHEMICALS COMPANY   SOUTH CHARLESTON 3, WEST VIRGINIA

To (Name)	Dr. A. A. Bothner-By	Date June 21, 1962
Company	Mellon Institute	
Location	Pittsburgh 13, Pa.	Originating Dept. Research and Development Department
		Answering letter date
Copy to		Subject

Dear Aksel:

For your voracious MelloNMR fraternity, I have enclosed a Preview of a paper which, in the event of a prolonged interlude of comparative world peace, may someday appear in the Journal of Polymer Science. The Complete, Unabridged Text is, of course, available upon request.

I rather hope this will escape the notice of Paul Lindenmeyer, who somehow cannot let me forget that along about 1958, on the basis of my own brief but incisive pioneering experimentation in the field (which remains unpublished), I hooted at his intuitive conviction that high-resolution NMR studies of polymers might one day yield exciting results.

Thank you, once again, Aksel, for your valuable suggestion regarding the spectral interpretation. (There, that should help distribute the blame!)

Mundanely,

Just Plain Charlie

Chas.W.Wilson,III/s

"NMR Study of Molecular Chain Structure of Polyvinylidene Fluoride" by Chas. W. Wilson III, Research and Development Department, Union Carbide Chemicals Company, So. Charleston, W. Va.

Synopsis

Improved resolution of the 40 Mc and 56.4 Mc F^{19} NMR room temperature spectra of solutions of polyvinylidene fluoride in dimethyl acetamide has resulted in a clearer understanding - of the polymer chain structure.* The spectra indicate that the structure of polyvinylidene fluoride consists predominantly of head-to-tail sequences of $-CH_2-CF_2-$ monomer links, with 5% to 6% of the monomer links added "backwards" to give occasional $-CF_2-CF_2-CH_2-CH_2-$ configurations along the chain. Identifying the four principal chemically shifted lines in the NMR spectrum with four specific local chain structures, and applying simple probability theory to compare predicted and observed spectral intensities, it was possible to compute the probabilities of head-to-tail monomer addition (p), head-to-head addition (1-p), tail-to-tail addition (q), and tail-to-head addition (1-q). The values of both p and q varied somewhat from sample to sample, depending on the temperature and pressure of polymerization; however, both p and q were found to be in the general vicinity of 0.94. This is believed to be the first reported instance in which the relative probabilities of head-to-head, tail-to-tail, head-to-tail, and tail-to-head monomer addition in free-radical polymerization have been determined.

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*
Excellent earlier studies of F^{19} high-resolution NMR in polymers containing vinylidene fluoride have been made by: (a) R. C. Ferguson, JACS 82, 2416 (1960); (b) R. E. Naylor and S. W. Lasoski, J. Polymer Sci. 44, 1 (1960)
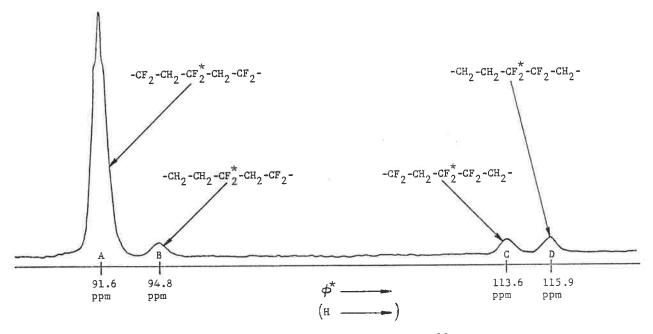
-CF$_2$-CH$_2$-CF$_2^*$-CH$_2$-CF$_2$-

-CH$_2$-CH$_2$-CF$_2^*$-CF$_2$-CH$_2$-

-CH$_2$-CH$_2$-CF$_2^*$-CH$_2$-CF$_2$-

-CF$_2$-CH$_2$-CF$_2^*$-CF$_2$-CH$_2$-

A 91.6 ppm B 94.8 ppm ϕ^* ——→ (H ——→) C 113.6 ppm D 115.9 ppm

Figure 1: Room Temperature 56.4 Mc F^{19} High-Resolution NMR Spectrum of 25% Solution of Polyvinylidene Fluoride in N,N-dimethyl acetamide. CFCl$_3$ Internal Reference

Figure 2: Most probable structure of the polyvinylidene fluoride molecular chain in the vicinity of a head-to-head linkage. Letters A, B, C and D below particular -CF$_2$- groups refer to spectral lines in Figure 1 associated with each structural position.