M. L. S. & A. A. B.

Snyder

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Polyvinylidene Fluoride

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 [E. 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 requested 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.
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,

\[
\begin{align*}
\text{HO}_2\text{C} & \quad \text{H}_1 \\
\text{H}_2 & \quad \text{Br} \\
\text{H}_3 & \quad \text{Br}
\end{align*}
\]

was made by Freeman, our data contra-indicate 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 \(\alpha\)-deuterostyrene and trans- \(\beta\)-deuterostyrene,

\[
\begin{align*}
\text{H} & \quad \text{C} = \text{C}^\text{H} \\
\text{D} & \quad \text{C}
\end{align*}
\]
TABLE OF SPECTRAL PARAMETERS

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<th>2</th>
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<tr>
<td>(\text{CH}_2\text{BrCHBrC}_6\text{H}_5)</td>
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<td>5.58</td>
<td>10.60</td>
<td>-10.27</td>
<td>8.45</td>
<td>Chloroform</td>
</tr>
</tbody>
</table>

\(\text{Chem. shift of methyls}\) | 5.1 | 16.5 | 13.1 | Benzenes |
| 5.9 | 6.0  | 12.3 | Chloroform |
| 7.1 | 11.0 |      | Carbon tetrachloride |

* Value measured from spectrum of dibromide from trans- \(\beta\)-deuterostyrene.

one can make an unambiguous spectral assignment to the \((1,2\text{-dibromo-ethyl})\text{benzene spectrum, assuming only that bromine adds }\text{trans}\) 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 never obtained. Continued iteration by either scheme resulted in an almost constant rate of change of \( J_{12} \) and \( J_{13} \), i.e., 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- \( \beta \)-deuterostyrene gives further support to this assignment. Again, \( J_{23} \) is quite solvent dependent. Because \( V_3 - V_2 > 0 \) in benzene, chloroform, and carbon tetrachloride but \( V_3 - V_2 < 0 \) 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 \( \text{[C}_6\text{H}_5\text{CHBrCBr(CH}_3\text{)}_2 \) and \( \text{[(CH}_3\text{)}_2\text{CBrCBrHCO}_2\text{H]} \) are quite broad, but no fine structure was resolved. (The half-width of internal TMS was \( \sim 0.3 \) cps., that of the methyls \( \sim 1 \) cps.) Since long-range coupling has been observed in

\[
\begin{align*}
\text{CH}_3 & \\
\text{CH}_2\text{Br} & \quad \text{CHBr} \quad \text{CO}_2\text{H}
\end{align*}
\]

and its ester, and in erythro-\( \text{CH}_3\text{CHBrCBrHCO}_2\text{H} \), 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 $^{31}\text{P}$ 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

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

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 $\beta$ of 1.8 and the nmr signal at $v_o$ is utilized (center band detection). With the $H_m$ available from the integrator, a large modulation index is not attainable for nuclei with smaller $\gamma$ -- $^{31}\text{P}$, $^{13}\text{C}$, $^{11}\text{B}$, $^{2}$H, etc. In such a case detection of the nmr signal at $v_o \pm u_m$ (first sideband detection) is appropriate, since $\beta$ may be small -- it only serves to reduce the effective radio frequency power.

The accompanying figure shows a comparison between $^{31}\text{P}$ spectra obtained under conditions of (1) no modulation and (2) first sideband detection. The first sideband spectra were obtained by inserting a 1 $\mu$F condenser in series with the probe modulation coils to achieve $\pi/2$ 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 $v_o$. Audio amplitude was adjusted small enough so that the signals at $v_o \pm 2 u_m$ were very small compared to the signals at $v_o \pm u_m$. 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 $u_m$. A disadvantage of modulation at 2000 cps. for $^{31}\text{P}$ spectra is that the separation between the upper and lower sidebands is not large compared to the chemical shift range of $^{31}\text{P}$ nuclei (about 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.
"DC DETECTION"
NO MODULATION
RF = 42 DB

"FIRST SIDEBAND DETECTION"  \( v_0 - v_m \)
\( v_m = 2000 \) cps.
RF = 26 DB
\( \frac{x H_m}{v_m} = 0.36 \)
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:

1) Geminal coupling constants
\[ J_{HH} = J_{HH'} = \pm 9.4 \text{ c/s or } \pm 13.1 \text{ c/s} \]

2) Cis coupling constants
\[ J_{HH} = J_{HH'} = \mp 13.1 \text{ c/s or } \mp 9.4 \text{ c/s} \]

3) Trans coupling constants (interchangeable)
\[ J_{HH} = \pm 9.3 \text{ c/s} ; J_{HH'} = \pm 4.5 \text{ c/s} \]

4) Relative chemical shift: 0.410 ppm.

The spectrum, of the A2B2-type, contains 2 x 9 resolvable lines, one pair being 0.8 c/s broad. A value for \( \delta \) was obtained from the second moment, and then some guesses were made on the AB and the \( \alpha \) 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 \%. Nils Bohr's frequent III program was of immense help. LACON may be able to refine the data some, but probably not much more. The lines are not too sharp (\( \sim 0.5 \) c/s): to observe the outer weak lines, the concentration of the CCl4 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 \( \beta \)-propiolactones, those vicinal J's range from \( 4.9 \) to \( 6.4 \) \(^3\). In \( \beta \)-(p-nitrophenyl)-\( \beta \)-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 \( \pm 9.4 \) c/s and \( J_{gem} = \pm 13.1 \) 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-C-axis. In view of these uncertainties it may not be too meaningful to calculate parameters for the cos\( \beta \) expression.

1) Wiberg and Nist, JACS 83, 1223 (1961), Varian Spectra Catalog
2) Analysis of those spectra in progress (and own data.
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 adjacent saturated carbon atoms, we have examined the spectra of some Diels-Alder adducts of hexachlorocyclopentadiene and various mono or disubstituted ethylenes:

This system is rigid, and therefore variations in the magnitude of the coupling constants are not due to variations in the dished angle between the coupling ABX protons. Furthermore, 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 Jcia - Jcjm and the electronegativity of the substituent for a long series of vinyl compounds (J. S. Maugh and J. S. Castellano, J. Chem. Phys., 25, 1000 (1961); T. S. Schaefer, Ind. Chem., 42, 25 (1962)). In the present work, however, the sum of $|J_{AX}| + |J_{BX}| + |J_{AB}|$ is 24.5 ± 1 c.p.m. 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. Dalley, J. Chem. Phys., 23, 1059 (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 ($6_X - 6_A$) and the X and B protons ($6_X - 6_B$) for the six compounds are plotted against the electronegativities of the various substituents. The dashed line represents the internal shifts between the X and B protons in a series of ethyl derivatives upon which Cavanaugh and Dalley 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**

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<tr>
<th>Substituent</th>
<th>$J_{AX}$</th>
<th>$J_{BX}$</th>
<th>$J_{AB}$</th>
<th>$6_A$</th>
<th>$6_B$</th>
<th>$6_X - 6_B$</th>
<th>$6_X - 6_A$</th>
<th>Electronegativities (from Cavanaugh and Dalley)</th>
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<td>CN</td>
<td>4.1</td>
<td>8.7</td>
<td>12.4</td>
<td>121</td>
<td>163</td>
<td>217</td>
<td>71</td>
<td>2.49</td>
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<td>COOH</td>
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<td>8.6</td>
<td>12.4</td>
<td>146</td>
<td>163</td>
<td>217</td>
<td>71</td>
<td>2.60</td>
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<td>283</td>
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<td>177</td>
<td>330</td>
<td>215</td>
<td>3.80</td>
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| \(\text{Fig. 1} \) Coupling Constants |

| \(\text{Fig. 2} \) Internal Chemical Shifts (c.p.m.) |
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 Bunkingham, Meinweiler and Scheibe. I have a paper soon to appear in JCP giving a quantum chemical 'calculation' for $k_e$ in the expression

$$\Delta \sigma = k_e \Delta n$$

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

The recent data of Professor Goldstein and co-workers (JACS 82, 1942 (1960)) on uracils provided another example of this electric field shift for a proton in a C-H bond, and the first such example 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, needing a reasonably linear plot

$$\Delta \sigma = k_e \Delta \mu$$

(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 intramolecular 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 $A$ 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

$$R_{X-H} = <\sigma_x^2/\sigma_x>$$

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 $A^2$ for carbon is almost zero for nitrogen. Further only the slightest polarization of a $N$ in favor of the nitrogen along with increased overlap causes the rest of the increase in $k_e$ for an N-H bond. It could 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 some parameters.

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

Just regards,

Sincerely,

[signature]

A.A. Dothen-Ado and D.L. Shapiro
Mellon Institute
27.5.1962

[Address]

500 Fifth Avenue
Pittsburgh, Pa.
U. S. A.
Dear Akel:

Our determination of the relative signs of the geminal and vicinal H-F coupling constants in CH3CllrF (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 (Mellon NMR, 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.

CH3CllrF 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. Nageswara Rao
J. D. Baldeschwieler
Le groupeement méthyl est couplé non seulement à l'hydrogène (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 déjà ce couplage apparaît comme un couplage à longue distance beaucoup plus intense que celui obtenu dans le 2-méthyl furanne (de l'ordre de 0,4 c/s) ou le 2,5-diméthyl furanne par exemple (2). Nous pensons pouvoir l'interpréter par hyperconjugaison.

Sincèrement vôtre,

(*) effectuée sur Varian A-60 par le Professeur CURISSON que nous remercions ici.

(1) "Application of NMR spectroscopy in Organic Chemistry" Ferguson Press p.38
(2) Reddy, Goldstein, J.Phy. Chem. 1961, 55, 1539
Dr. Barry L. Shapiro
Bennion Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

June 12, 1963

Dear Barry,

Read all the comments on recorder ink for the A-50, and another opinion is that "Parker Quill" 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. Norco 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 deuteropyridine 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-acetonaphthone are quite ordinary in DCCI₂ (methyl region diagramed):

\[ A = H \]

\[ 2.18 \text{ ppm} \]

\[ 2.53 \text{ ppm} \]

\[ R = \phi \]

\[ 4.77 \text{ ppm} \]

\[ 2.83 \text{ ppm} \]

My present explanation is that in pyridine, the hydrogen bond in the Schiff Base can be broken and the acetylamine group rotates 180°. In this rotation, the 1.4 cps coupling appears. In the hydrogen bonded cholate, the hydrogen bond disrupts the system so the coupling is not transmitted. The coupling is not observed in 2-(N-methylamino)acetonaphthone, 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 Dulich
June 14, 1962

Drs. A.A. Böhm and B.I. Shapiro
Mellon Institute
Pittsburgh, Pa.

Dear Akel and Barry,

At the risk of burdening you with a second contribution from our laboratory for the same issue of MELLOMBR 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 kindly provided by Prof. H.M. Walborsky. The relative signs were determined both by the double quantum spectra and by analysis of the 30 Ms spectrum. The absolute values of \( J_{\text{cis}} \) and \( J_{\text{trans}} \) agree quite well with the values of \( J_{\text{cis}} \) and \( J_{\text{trans}} \) reported for ethane by H.M. Walborsky.

The conclusions of Prof. Glos 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.

\[ J_{\text{cis}} = 4.65 \quad \nu = 90.9 \quad (\text{TMS/60 Ms}) \]

\[ J_{\text{CH}_{3}-A} \quad J_{\text{CH}_{3}-B} = 0.4 \quad \nu' = 145.5 \quad (\text{TMS/60 Ms}) \]

It is interesting to note that the \( ^2J_\text{gem} \) and the \( ^3J_\text{trans} \) (J. trans and \( J_{\text{cis}} \)) are of opposite signs in analogy with ethane (Anst, Freeman, Kaplan, Loucheux, McLauchlan, et al.) but as differing from propylene oxide. It is probably a reasonable guess that the \( ^3J_\text{cis} \) which remain relatively constant in series of the 0, N, S heterocycles and the carbocycle preserves its sign, while the \( ^3J_\text{trans} \) change sign. The conclusion from the literature data (particularly orthohydrogen of Kelly and Swalen) would be that \( ^3J_\text{cis} \) is positive then \( ^3J_\text{trans} \) is negative but \( ^3J_\text{cis} \) (cyclopropane) is positive and \( ^3J_\text{cis} \) (cyclopropane) is negative, which, to use the vernacular, is a fine kettle of fish.

Yours sincerely,

J.L. Mashar

A. Szoke
UNIVERSITY CHEMICAL LABORATORY,  
LENSFIELD ROAD,  
CAMBRIDGE.  

Dr. R. A. B. Bethune - Bt.  
Mallinckrodt Institute  
Pittsburgh, Pennsylvania.  

Dear Dr. Bethune - Bt.,  

When reading Dr. Shu-park's copy of I.M. I. N. N., we were interested to  
notice the data of Dr. J. F. F. 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, pyridazine and pyrazine series, but as far as we are  
aware has not been commented on previously. Until we noticed the articles 1,2, and 3  
concerned, we were very puzzled by our results from a low-temperature study of  
benzamiduronic (II), for we expected the resonance of the proton at position 7 to occur  
to low field of that of 7, and also to low field of the corresponding proton in  
benzamiduronic (III). 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 spectrum of the unsubstituted compounds, but the 4 - nitro derivatives  
demonstrated that in fact 7 has a value higher than that of 7. The relevant data is  
shown in the Table. Figures (III) (IV) and (V) give the resonance shifts (δ ppm)  
on oxidation from a benzamiduronic to the corresponding azoxy (all the shifts are to high  
field).  

In fact, the molecules reported here are in some ways more suitable for  
thetical study than those of Freeman, since the structure is less beyond doubt  
(see the recent R. W. B. patent) and all the azo's are in a single plane (since there  
are no resonating nitro groups). Unfortunately, however, resonance structures of type  
(IV) contribute to the high δ at δ 1.88 for 7, and δ 1.43 (presumably more than those  
of type (III)). The shift at 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 7 is anisotropic in position with the nitro-azo at  
Freeman's azoxy in one of the possible rotamers.  

A paper has been submitted to J. Chem. Soc. on the high  
spectra of benzamiduronic and five nitro-azo derivatives. Following our preliminary note  
in Chem. Soc. I, 2, we would like to express our appreciation for the kind way this  
and we are grateful to Dr. Shu-park for the loan of his copy. Finally, one of us  
(M.R.) will do his best to keep himself at the centre of the U.I.T., until then be taken  
up his appointment at the Mallinckrodt Institute in September.  

Genuinely yours,  

R. K. Harris  
(M. R.)  

APK  

(Asst. Res.  

CHARTS  

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ</th>
<th>5</th>
<th>6</th>
<th>7</th>
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</thead>
<tbody>
<tr>
<td>Benzamiduronic</td>
<td>2.46</td>
<td>2.68</td>
<td>2.45</td>
<td>2.65</td>
</tr>
<tr>
<td>Benzamiduronic</td>
<td>2.46</td>
<td>2.68</td>
<td>2.45</td>
<td>2.65</td>
</tr>
<tr>
<td>Lacto-benzamiduronic</td>
<td>2.46</td>
<td>2.68</td>
<td>2.45</td>
<td>2.65</td>
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<tr>
<td>Lacto-benzamiduronic</td>
<td>2.46</td>
<td>2.68</td>
<td>2.45</td>
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<tr>
<td>Lacto-benzamiduronic</td>
<td>2.46</td>
<td>2.68</td>
<td>2.45</td>
<td>2.65</td>
</tr>
</tbody>
</table>

1, 2, 3: in solution in deuteriochloroform  
4: in solution in deuteriochloroform  
5: at δ 6.45, Vitale monoxide, at room temperature.  

References:  
Proton Magnetic Relaxation in Polyamides

by

David W. McCall and Ernest W. Anderson
Bell Telephone Laboratories, Incorporated
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".
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 
\textit{CDCl}_3 solution, except for the nitro derivatives whose shifts are given relative to 
\textit{CCl}_4 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-NNMe_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-NNMe_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, 
\textit{CDCl}_3 was chosen as the base case rather than 
\textit{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 \( \alpha,\beta \) 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,

J. B. Stothers
Assistant Professor
Fig. 1  Solvent Shifts of Formyl Protons
(relative to $\text{CCl}_4$)

- Acetone
- Benzene
- Chloroform-d
- Cyclohexane
- Methanol

Fig. 2  Solvent Shifts of Substituted Benzaldehydes
(in $\text{C}_6\text{H}_6$ relative to $\text{CDCl}_3$)

- formyl proton
- ortho protons
- meta protons
- $\times$ protons

Benzaldehydes

<table>
<thead>
<tr>
<th>Substituent</th>
<th>m-NO$_2$</th>
<th>p-NO$_2$</th>
<th>m-CH$_3$</th>
<th>p-CH$_3$</th>
<th>2,4,6-</th>
<th>p-OCH$_3$</th>
<th>p-Me$_3$</th>
<th>p-N$_2$H$_5$</th>
<th>CH$_3$</th>
<th>CH$_2$</th>
<th>CH=CH</th>
<th>CHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c/s (at 60Mc/s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Shift in c/s at 60Mc/s

<table>
<thead>
<tr>
<th>Substituent</th>
<th>pMe$_2$N-</th>
<th>pMeO-</th>
<th>pMe</th>
<th>pF</th>
<th>pCl</th>
<th>pCN</th>
<th>pNO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shift in ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
On the Relative Signs of CH and BH Coupling Constants

In MELLOR-X-R No. 43, p. 28, Karplus suggested that the absolute signs of BH coupling constants could be determined with near certainty by comparisons with couplings between directly bonded C13 and H1, for which theory predicts, in a straightforward manner, positive signs. We have carried out H1 (C13) double resonance experiments of the type proposed by Karplus with results outlined below.

The H1 spectrum of cis-CH2=CHCl, sketched below, permitted an easy test of the experiment. Upon irradiation of the low frequency doublet in the C13 spectrum, lines 1 and 2 in the H1 spectrum were observed to move toward one another and finally vanished under the central peak from the C12H11ClC12H11 species. At an irradiation frequency (V0) about 200 cps higher, lines 3 and 4 moved in and vanished. Since the low frequency C13 doublet occurs at high field, and vice versa, this result shows that the BH and CH couplings have the same signs. As cis and trans BH 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

<table>
<thead>
<tr>
<th>X</th>
<th>BH Coupling Constants in X-CH=CH2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cis</td>
</tr>
<tr>
<td>H</td>
<td>+ 11.7</td>
</tr>
<tr>
<td>F</td>
<td>+ 4.7</td>
</tr>
<tr>
<td>Cl</td>
<td>+ 7.2</td>
</tr>
<tr>
<td>Br</td>
<td>+ 7.1</td>
</tr>
<tr>
<td>CH3</td>
<td>+ 10.02</td>
</tr>
<tr>
<td>CH2Cl2</td>
<td>+ 10.4</td>
</tr>
<tr>
<td>CH2Br2</td>
<td>+ 10.4</td>
</tr>
<tr>
<td>(CH3)2C</td>
<td>+ 10.8</td>
</tr>
<tr>
<td>(Cl)2C</td>
<td>+ 10.07</td>
</tr>
</tbody>
</table>

(TOP VIEW)

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

\[
\begin{align*}
\text{cis} & & \text{trans} & & \text{gem} & & \text{Ref} \\
\text{CH}_3\text{CHO} & & + & 6.8 & & + & 2.2 & & 2 \\
\text{cis}-\text{CH}_2\text{CH} & & + & 9.4 & & + & 4.0 & & 2 \\
\text{cis}-\text{CH}_2\text{CH}-\text{CHO} & & + & 7.2 & & + & 4.0 & & 2 \\
\text{cis}-\text{CH}_2\text{CH}-\text{COOH} & & + & 3.0 & & + & 7.1 & & 2 \\
\text{cis}-\text{CH}_2\text{CH}-\text{COCl} & & + & 5.5 & & + & 4.1 & & 2 \\
\text{cis}-\text{CH}_2\text{CH}-\text{COCl} & & + & 6.5 & & + & 1.5 & & 6 \\
\end{align*}
\]

The signs can now be assigned as shown in Table II.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( J_a )</th>
<th>( J_b )</th>
<th>( J_c )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{cis}-\text{CH}_2\text{CH}-\text{CHO} )</td>
<td>+10.0 &amp; +16.6 &amp; +6.40 &amp; ( \text{cis} ) ( \text{trans} )</td>
<td>1,25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{trans}-\text{CH}_2\text{CH}-\text{CHO} )</td>
<td>--- &amp; +15.6 &amp; +6.60 &amp; ( \text{cis} ) ( \text{trans} )</td>
<td>1,25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{trans}-\text{CH}_2\text{CH}-\text{COOH} )</td>
<td>--- &amp; +15.6 &amp; +6.60 &amp; ( \text{cis} ) ( \text{trans} )</td>
<td>1,25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{cis}-\text{CH}_2\text{CH}-\text{COCl} )</td>
<td>+7.2 &amp; --- &amp; +7.2 &amp; ( \text{cis} ) ( \text{trans} )</td>
<td>1,25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{trans}-\text{CH}_2\text{CH}-\text{COCl} )</td>
<td>--- &amp; +15.6 &amp; +7.1 &amp; ( \text{cis} ) ( \text{trans} )</td>
<td>1,25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{cis}-\text{CH}_2\text{CH}-\text{COCl} )</td>
<td>--- &amp; +6.6 &amp; +1.5 &amp; ( \text{cis} ) ( \text{trans} )</td>
<td>1,25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Because of the near constancy of the \( \text{CH}_2\text{CH}-\text{C} \) couplings, it seems permissible to assume further that the signs in 1-chloro-1,2-butadiene are as given below.

The relative

\[ J_{\text{cis}} = 1.0 \quad J_{\text{trans}} = 2.0 \quad J_{\text{gem}} = 1.0 \]

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 dienes is 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 \( \text{CICH}_2\text{CHCl} \) to determine the signs of vicinal couplings between hydrogens on sp^3 carbons. The spectrum is sketched below. (\( E_{\text{HH}} = J_{\text{HH}} + J_{\text{HH}}' \))

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 \( o \) and \( p \) in the HH spectrum to move together, and that peaks \( g \) and \( d \) were affected at an irradiating frequency about 5000 cps (2500 Hz) 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

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.

1. N. Sheppard, MELLONRE, #58, p. 11.
Dear Aksel:

For your voracious MellonNMR 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 about 1958, on the basis of my own brief but incisive pioneering experimentation in the field (which remains unpublished), I boasted at this 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!)

Mundaneely,

Just Plain Charlie

Chas. W. Wilson III

"NMR Study of Molecular Chain Structure of Polyvinylidene Fluoride"

Synopsis

Improved resolution of the 40 Mc and 56.4 Mc F19 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 -CH2-CF2- monomer links, with 5% to 6% of the monomer links added "backwards" to give occasional -CF2-CF2-CH2-CF2- 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 0.9%. 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.

* Excellent earlier studies of F19 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)
Figure 1: Room Temperature 36.4 Mc F¹⁹ High-Resolution NMR Spectrum of 25% Solution of Polyvinylidene Fluoride in N,N-dimethyl acetamide. CFCl₃ 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 -CF₂- groups refer to spectral lines in Figure 1 associated with each structural position.