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Deadline Dates: No: 85: 18 October 1965 [NOTE CHANGE]
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A monthly collection of informal private letters from laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as "Private Communication".
Professor Barry L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616

Dear Barry:

Several months ago when we were busy studying proton and deuteron relaxation in HD in a gas phase (B.D. Nagaswara Rao and L.R. Anders, Phys. Rev.) (in press), Paul Lauterbur pointed out that an interesting dividend from these experiments might be a measurement of the HD-H$_2$ isotope shift. A crude measurement of the isotope shift in the dueterium resonances of HD and D$_2$ has been given by Wimett in 1953. His value for the D$_2$-HD isotope shift is 0.048 ± 0.037 ppm. Although deuterium isotope effects in the proton NMR spectra of a number of compounds have been reported recently (Gutowsky (1959), Bernheim (1964), Bernheim and Lavery (1965)), a precise experimental value of the HD-H$_2$ isotope shift does not appear to be available for comparison with calculated values. Perhaps our measurement of the HD-H$_2$ isotope effect by high-resolution techniques will be of interest to people who have modern programs for calculating this sort of thing.

A sample containing HD, H$_2$, and CO$_2$ was prepared by condensing sufficient quantities of the gases in a 5 mm OD, thick-walled NMR tube to give pressures at room temperature of 7 atm. H$_2$, 15 atm. HD, and 20 atm. CO$_2$. CO$_2$ is quite efficient for reducing the proton resonance linewidths as noted by Johnson and Waugh (1962). The HD was prepared by the reaction of LiAlH$_4$ and D$_2$O as described by Fookson et al. (1950). The H$_2$ and CO$_2$ (Mathe\'sion) were used without further purification.

The proton NMR spectrum of the HD$_2$-H$_2$-CO$_2$ mixture obtained at 100 Mcps. is shown in Fig. 1. The spectrum is the superposition of the proton resonance of H$_2$ and the triplet multiplet of HD. The separation of the high and low field components of the HD multiplet determined by the usual sideband technique is 86.4 ± 0.5 cps. The shift of the central peak from the center of the high and low field components of the HD multiplet is 3.4 ± 0.8 cps at 100 Mcps. Where the apparent shift is the average from 34 traces, and the uncertainty is the RMS deviation of these measurements.
Since the central peak of the spectrum shown in Fig. 1 is the superposition of the \( H_2 \) resonance and the center peak of the HD multiplet, the resulting complex lineshape yields an apparent shift slightly smaller than the true isotope shift. A correction to the apparent shift can be readily obtained if the complex lineshape \( I(\omega) \) is assumed to be composed from the superposition of two Lorentzian lines:

\[
I(\omega) = \frac{I_{HD}}{1 + \left( \frac{\omega - \delta}{T_{2HD}} \right)^2} + \frac{I_{H_2}}{1 + \left( \frac{\omega}{T_{2H_2}} \right)^2}
\]

where \( I_{HD} \) and \( I_{H_2} \) are the peak heights of the central HD and \( H_2 \) resonances, \( T_{2HD} \) and \( T_{2H_2} \) are the half-widths at half-height of the HD and \( H_2 \) resonances, and \( \delta \) is the true isotope shift.

This is obtained from the outer peaks since measurements with HD/CO\(_2\) mixtures in the gas phase indicate that the widths of the center and outer components of the HD multiplet are not significantly different. The \( H_2 \) parameters, and \( \delta \) can then be adjusted to give the best fit to the experimental lineshape. The true isotope shift, obtained by this procedure from the calculated curve shown in Fig. 1 is \( 0.038 \pm 0.008 \) ppm. These parameters yield an apparent shift of 1.7 cps at 60 Mcps, which is close to the experimental value of \( 1.6 \pm 0.8 \) cps obtained from 92 traces.

Although there have been some crude calculations of isotope shifts in \( H_2 \), HD, and \( D_2 \), (Marshall (1961), Saika and Narumi (1964)), perhaps this result will provide the motivation for a more detailed calculation of the \( H_2 - HD \) isotope shift.

With best regards,

Leslie R. Anders

John D. Baldeschwieler

Paul C. Lauterbur

REFERENCES

Carbonyl Carbon Shieldings of Some Cyclopropyl Ketones

An interesting extension of our studies of the $^{13}$C N.M.R. spectra of carbonyl compounds appeared to be the use of the technique as a test for conjugative interactions in systems which lack $\alpha,\beta$-unsaturation but possess other structural features thought to be capable of electron donation to carbonyl functions. One such system which we have been examining is that in which a cyclopropyl ring is $\alpha,\beta$ to the carbonyl group. Other physical methods have, of course, been employed for this purpose but our $^{13}$C NMR results for carbonyl compounds, in general, show clearly that the carbonyl carbon shieldings reflect the influence of conjugative interactions. We have published detailed accounts of these earlier results in Can. J. Chem. 43 479,498,596 (1965).

To test for conjugation in the cyclopropyl ketones, a number of simple alkyl methyl ketones were examined first to determine the effect of alkyl substitution on the carbonyl carbon shielding in a simple ketone. The results for methyl ethyl ketone and all possible derivatives methylated on the ethyl group i.e. $\text{R}^1\text{R}^2\text{C}=$ were $\text{COCH}_3$ show that substitution on the $\beta$-carbon does not affect the carbonyl shielding appreciably while methylation at the $\alpha$-carbon tends to deshield the carbonyl carbon (see Table). On the basis of these data and the earlier results, it was expected that the cyclopropyl ketones should exhibit carbonyl resonances at higher field than the saturated cases if there are conjugative interactions between the cyclopropyl and carbonyl groups. This was found to be the case (cf. No.2,7 and 8) in the Table). The cyclopropyl ketones give rise to carbonyl peaks at field positions which are intermediate between the saturated and $\alpha,\beta$-unsaturated analogs. Some of the pertinent data are included in the Table. We have several other examples which are entirely in agreement with these representative results.

Since it is generally accepted that the relative orientation of the cyclopropyl ring with respect to the carbonyl group is important, some bicyclic cases have also been examined. For these systems, it appears that the effect of the cyclopropyl ring is more pronounced for bicyclo[3.1.0]hexan-2-one system than for bicyclo[4.1.0]heptan-2-one derivatives as one would expect since in the former case the plane of the three-membered ring is more nearly coplanar with the carbonyl \(\pi\) system, but the differences are small. Alkyl substitution in the bicyclic series does not
affect these general trends as a number of other examples show.

It is interesting that these results do support the contention that a
cyclopropyl ring is capable of conjugative electron-donation to a carbonyl function
in the ground state.

I trust that this contribution will renew my subscription for a few more
months.

Sincerely,

J. B. Stothers
Associate Professor

Carbonyl Shieldings of Some Simple Ketones

<table>
<thead>
<tr>
<th>Compound</th>
<th>Carbonyl shift*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. methyl ethyl ketone</td>
<td>-13.5</td>
</tr>
<tr>
<td>2. methyl iso-propyl ketone</td>
<td>-16.3</td>
</tr>
<tr>
<td>3. methyl t-butyl ketone</td>
<td>-18.3</td>
</tr>
<tr>
<td>4. methyl n-propyl ketone</td>
<td>-13.8</td>
</tr>
<tr>
<td>5. methyl isobutyl ketone</td>
<td>-13.5</td>
</tr>
<tr>
<td>6. methyl neopentyl ketone</td>
<td>-13.6</td>
</tr>
<tr>
<td>7. methyl cyclopropyl ketone</td>
<td>-13.1</td>
</tr>
<tr>
<td>8. methyl isopropenyl ketone</td>
<td>-4.8</td>
</tr>
<tr>
<td>9. cyclopentanone</td>
<td>-24.4</td>
</tr>
<tr>
<td>10. 2-cyclopentenone</td>
<td>-15.3</td>
</tr>
<tr>
<td>11. bicyclo[3.1.0]hexan-2-one</td>
<td>-20.9</td>
</tr>
<tr>
<td>12. cyclohexanone</td>
<td>-16.1</td>
</tr>
<tr>
<td>13. 2-cyclohexenone</td>
<td>-4.3</td>
</tr>
<tr>
<td>14. bicyclo[4.1.0]heptan-2-one</td>
<td>-13.8</td>
</tr>
</tbody>
</table>

* in p.p.m. from CS₂
Hindered Rotation in Some Biphenyls

Thank you for your subscription reminder. For our contribution, I would like to report some work that Jim Jahnke has been doing on hindered rotation in some naturally occurring biphenyls.

Podototarin (I, R=H) is a naturally occurring optically active biphenyl. The room temperature NMR spectrum of podototarin itself has no unusual features but that of the diacetate (I, R=Ac) shows the presence, in unequal concentration, of two species with slightly different spectra. In particular, the acetyl methyl resonance shows two components of unequal intensity separated by a few c/s. The spectrum has a reversible temperature dependence, the methyl peaks collapsing to a singlet when the temperature is raised. When the temperature of the dimethyl ether (I, R=Me) is lowered sufficiently the presence of two species is again indicated, the methoxyl methyl peak broadening and then splitting into two components.

Evidently, rotation about the central biphenyl bond is sufficiently slow and the two conformers are sufficiently different owing to the asymmetry in the molecule for their spectra to be distinguishable.

From the temperature dependence of the acetyl and methoxyl methyl resonances, we have been able to evaluate the energy barriers to free rotation in the diacetate and dimethyl ether. The line shapes of the methyl resonances as a function of the average lifetimes, $\tau_A$ and $\tau_B$, of the two conformers in each case were computed using the general line shape equation of Gutowsky and Holm. As the separation between the lines was small compared to
the line width, it was not possible to estimate the lifetimes directly from the line widths. Instead, it was necessary to determine the lifetimes by comparison between theoretical and experimental spectra. Curve fitting was carried out by means of an iterative non-linear regression least squares program on a 7074 computer, 36 to 49 data points being used. Five parameters could be varied by the computer - $\tau_A$, $\tau_B$, a scaling factor, and the chemical shifts of the methyl groups in the absence of exchange. The latter had to be treated as parameters as they could not be estimated accurately from the spectra. The computer varied the parameters until the best least squares fit was obtained. An experimental spectrum derived from the input data and the theoretical spectrum which was the best fit were drawn on the same chart by a Calcomp digital plotter, enabling a rapid check on the success of the calculation to be made. The line width term in the Gutowsky equation was retained since its omission was found to result in the introduction of a significant error.

Useful spectra were obtained over the temperature range 49 to 73°C for the diacetate and -11 to -25°C for the dimethyl ether, using an A-60 spectrometer and variable temperature controller. The upper temperature limit proved to be just below the coalescence point. The lower limit was set by the point at which the Arrhenius plot became non-linear. Apparently at sufficiently low temperatures there are secondary effects involving the acetyl and methoxyl groups which result in the lines being somewhat broader than expected.

The activation energies, obtained from a least squares Arrhenius calculation involving the first order rate constants $1/\tau_A$ and $1/\tau_B$, are as follows (for CDCl$_3$ solutions):

Podototarlin diacetate: 7.8 and 7.0 kcal.
Podototarlin dimethyl ether: 5.5 and 5.3 kcal.

Yours sincerely,

L. D. Colebrook

LDC/pn


Dear Dr. Shapiro:

We have been looking recently at some vicinal difluorocyclopentane derivatives of which Ia and Ib (trans' and cis' 1,2-difluoro, 2-methylindane) and three substitutedacenaphthalenes (II) are examples:

Table I (some of which is provisional) shows $J_{H_1F_2}$ to be 14.6 cps in isomer 'Ia' and 9 cps in isomer 'Ib'. On the assumption that H-F coupling constants follow a trend of angular dependence analogous to that of H-H couplings, isomer 'a' is trans difluoro adduct and 'b' is cis. The ring geometry is assumed planar (no temperature effects were found down to -85°C.), making $<HF_{vic} \sim 0^\circ$ for the trans and $<HF_{vic} \sim 110^\circ$ for the cis.
Table I

<table>
<thead>
<tr>
<th></th>
<th>acenaphthalene</th>
<th>2-methylindene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$F, F$-trans</td>
<td>$F, F$-cis</td>
</tr>
<tr>
<td>$J_{HF}$ vic trans</td>
<td>5.5</td>
<td>2.0</td>
</tr>
<tr>
<td>$J_{HF}$ vic cis</td>
<td>19.0</td>
<td>12.0</td>
</tr>
<tr>
<td>$J_{HF}$ gem</td>
<td>53.0</td>
<td>53.5</td>
</tr>
<tr>
<td>$J_{HH}$ vic</td>
<td>0.0</td>
<td>6.0</td>
</tr>
<tr>
<td>$J_{FF}$ gem</td>
<td></td>
<td>266.0</td>
</tr>
<tr>
<td>$J_{FF}$ vic trans</td>
<td>1.0</td>
<td>3.0</td>
</tr>
<tr>
<td>$J_{FF}$ vic cis</td>
<td>18.0</td>
<td>8.0</td>
</tr>
</tbody>
</table>

The coupling of the methyl group to $F_2$, the geminal fluorine, is about 22 cps in each case. However in isomer 'a', there is a further coupling (4 cps) to another $\frac{1}{2}$ nucleus. The $F_1$ resonances are also very broad in this isomer, and we presume this coupling to be due to the 'cis' proximity of $F_1$ and the methyl group, in agreement with the $J_{HF}$ vic considerations.

The $F-F$ coupling is curiously small in both isomers. For Ia it is 2.8 cps; for Ib, it is provisionally about 10 cps. The same trend holds for the acenaphthalenes, i.e., $J_{FF}$ trans is quite small and $J_{FF,cis}$ is larger.

The $0^\circ H'-H'$ coupling is larger (6 cps) in the acenaphthalene $F,F$-cis isomer than the $110^\circ H'-H'$ coupling ($\sim$ 0 cps) in the $F,F$-trans isomer, as expected from the Karplus curve. (The AA'XX' spectra do not uniquely determine $J_{HH}$ and $J_{FF}$, of course. We have chosen $J_{FF} > J_{HH}$ in each case.) The vicinal $J_{HF}$'s of the acenaphthalenes follow the same trend ($J_{cis} > J_{trans}$) as do the $J_{FF}$'s.

We expect to polish up the NMR data and add some dehydrofluorination rate data shortly.

Sincerely,

Richard F. Merritt

Frederic A. Johnson
Professor B.L. Shapiro,
Illinois Institute of Technology,
Chicago, 60616,
U.S.A.

Dear Professor Shapiro,

In two recent papers on fluorine chemical shifts in fluoroaromatic compounds (Mol. Phys., 8, 133 (1964) and Mol. Phys., 8, 467 (1964) it has been suggested that an internal Van der Waals type of interaction makes an important contribution to the chemical shifts. In the aromatic compounds there are also major changes in the chemical shifts from changes in π-electron densities. I have recently completed a study of fluorine chemical shifts in some perfluorocyclohexane derivatives, and in these compounds the chemical shifts produced by replacing a fluorine atom by say chlorine should be due entirely to what might be called the "neighbour polarvisability effect". From the simple theory given in the earlier papers the shift produced by a substituent will be given by:

\[ \delta = -B \Delta \langle E^2 \rangle \]

where \( \langle E^2 \rangle \) is the mean square electric field and the \( \Delta \) signifies a difference between sample and reference. \( B \) is a constant whose value depends on the type of C-F bond. The value of \( \langle E^2 \rangle \) is given approximately by:

\[ E^2 = \sum P I \tau^{-b} \]

where \( \sum \) signifies a sum over all other atoms or electron groups in the molecule, \( P \) is the polarvisability, \( I \) the first ionisation potential and \( \tau \) the distance separating the atoms etc. Because of the rapid change in \( \langle E^2 \rangle \) with distance the shifts produced by a substituent will fall off rapidly with distance, and this is indeed observed. The value of \( B \) can be calculated from the shifts produced at the adjacent fluorines and then used to calculate the other shifts. If this is done for \( C_6F_{11}Cl \) compared with \( C_6F_{12} \) then the following results are obtained:

<table>
<thead>
<tr>
<th>( ^{19}F ) nucleus</th>
<th>observed shift</th>
<th>calculated shift, (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 axial</td>
<td>8.72</td>
<td>7.86</td>
</tr>
<tr>
<td>2 equatorial</td>
<td>7.62</td>
<td>7.86</td>
</tr>
<tr>
<td>3 axial</td>
<td>0.63</td>
<td>0.67</td>
</tr>
<tr>
<td>3 equatorial</td>
<td>4.25</td>
<td>0.28</td>
</tr>
<tr>
<td>4 axial</td>
<td>0.72</td>
<td>0.44</td>
</tr>
<tr>
<td>4 equatorial</td>
<td>0.65</td>
<td>0.12</td>
</tr>
</tbody>
</table>
the chlorine is at position 1 equatorial, and the value of B used was $24.92 \times 10^{-18}$ e.s.u. Very similar results are obtained for C$_6$F$_{11}$Br compared with C$_6$F$_{12}$. The calculations assume that the molecules exist as chair forms, and hence the identical results for the positions 2 axial and equatorial since these two fluorines are equidistant from the chlorine. The fact that the fluorines in these two positions have different chemical shifts is readily explained by invoking a distortion from the symmetric structure. The $r^{-6}$ dependence of the chemical shift means that very small changes in structure can produce very large chemical shifts, and indeed only a very small distortion of the molecule is necessary to explain even the surprisingly large difference between calculated and observed chemical shifts and the position 3 equatorial. The success of the simple theory suggests that it might also be used to explain the chemical shift difference between axial and equatorial fluorines in perfluorocyclohexane itself. In this case the electric fields along the two C-F bonds differ and hence a term $-A \alpha \cdot E \cdot z$ will also contribute to the chemical shift difference. Using a value for $A$ of $-10 \times 10^{-22}$ e.s.u. and the value for B already quoted gives a chemical shift of $\sim 71$ ppm between the two fluorines compared with the observed value of $18.2$ ppm. In view of the very many approximations made in the calculation then perhaps this is quite good agreement.

Best wishes,

J. Emsley

J.W. Emsley
Dr. B. L. Shapiro
Illinois Institute of Technology
Department of Chemistry
Chicago, Illinois 60616

Dear Dr. Shapiro:

I should like to make my contribution to the newsletter so I may continue to receive them.

Enclosed is a copy of the spectrum we obtained when \( \alpha \)-cellulose was dissolved in a new solvent system we are studying. The spectrum should be of some interest since our analysis indicates we are separating the cellulose into small units by hydrolysis. We base the analysis on the doublet which appears near 6.6 ppm from TMS. It is assigned to the (a) proton and has a J value of about 4 cps.¹ This suggests the (a) and (b) proton are axial-equatorial rather than axial-axial as they are in \( \alpha \)-cellulose. Thus by breaking the O-O bond near the (a) proton this allows freedom of movement so that the equitorial position is achieved.

Our assignments are based on the following reasoning. The (a) proton is expected at low field since it is near two oxygens. The (b) and (c) protons are expected at lower fields than (d) (e) and (f) since they are connected to secondary alcohols. The (d) (e) and (f) protons are in similar environment and appear together at the highest field.

The OH protons occur under the solvent peak.

The integration results agree with our assignments.

This work was carried out by Mr. Robert Yelin as part of his master's degree research.

Sincerely,

Dr. Herman A. Szymanski
Chairman
Department of Chemistry

Has/am
Encl.
\[ \alpha - \text{cellulose in solvent X} \]
Dr. B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Technology Center  
Chicago, Illinois  60616

Dear Dr. Shapiro:

Recently we have determined the NMR parameters for three unsymmetrical ortho dihalobenzenes. For comparison purposes, their symmetrical analogs were redetermined also. The spectra for the chloroiodo and the bromoiodobenzenes were treated as ABX cases; while the chlorobromobenzene required the full ABCD treatment. The spectrum for 1-chloro-2-bromobenzene is shown in the figure. Line assignments follow from the considerations given by Reilly and Swalen. All parameters are given in Table I. The values in parentheses are calculated from the additivity rule of Martin and Dailey. As expected, the protons adjacent to the halogens do not fit the predicted values.

Examination of the ortho protons shows a marked dependence on the adjacent halogen and little or no effect due to the nonadjacent halogen. The most reasonable explanation for this observation is that offered by Hruska, Rutton, and Schaefer, and a plot of the ortho hydrogen shifts in Table I vs. their Q factor produced an excellent straight line with benzene also falling on the line.

Yours sincerely,

W. B. Smith  
Professor of Chemistry

WBS/dc

<table>
<thead>
<tr>
<th>Dihalobenzenes</th>
<th>$J_{34}$</th>
<th>$J_{45}$</th>
<th>$J_{56}$</th>
<th>$J_{35}$</th>
<th>$J_{46}$</th>
<th>$J_{36}$</th>
<th>$\gamma_3$</th>
<th>$\gamma_4$</th>
<th>$\gamma_5$</th>
<th>$\gamma_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-Dichloro</td>
<td>8.0₂₈</td>
<td>7.4₂₈</td>
<td>8.0₂₈</td>
<td>1.5₂₈</td>
<td>1.5₂₈</td>
<td>0.3₈₈</td>
<td>2.6₃(2.8₀)</td>
<td>2.₈₈(2.₉₅)</td>
<td>2.₈₈(2.₉₅)</td>
<td>2.₆₃(2.₈₀)</td>
</tr>
<tr>
<td>1,2-Dibromo</td>
<td>8.₄₂₈</td>
<td>7.₄₂₈</td>
<td>8.₄₂₈</td>
<td>1.₃₂₈</td>
<td>1.₃₂₈</td>
<td>0.₄₂₈</td>
<td>2.₄₅(2.₇₀)</td>
<td>2.₉₁(2.₉₃)</td>
<td>2.₉₁(2.₉₃)</td>
<td>2.₄₅(2.₇₀)</td>
</tr>
<tr>
<td>1,2-Diiodo</td>
<td>7.₉₂₈</td>
<td>7.₉₁₂₈</td>
<td>7.₉₂₈</td>
<td>1.₉₂₈</td>
<td>1.₉₂₈</td>
<td>0.₀₂₈</td>
<td>2.₁₉(2.₆₃)</td>
<td>3.₀₄(3.₀₇)</td>
<td>3.₀₄(3.₀₇)</td>
<td>2.₁₉(2.₆₃)</td>
</tr>
<tr>
<td>1-Chloro-2-bromo</td>
<td>8.₂₂₈</td>
<td>7.₄₂₈</td>
<td>8.₂₂₈</td>
<td>1.₃₂₈</td>
<td>1.₆₂₈</td>
<td>0.₅₂₈</td>
<td>2.₄₇(2.₆₄)</td>
<td>2.₉₉(3.₀₂)</td>
<td>2.₈₆(2.₈₇)</td>
<td>2.₆₂(2.₈₆)</td>
</tr>
<tr>
<td>1-Chloro-2-iodo</td>
<td>7.₇₂₈</td>
<td>7.₅₂₈</td>
<td>7.₉₂₈</td>
<td>1.₇₂₈</td>
<td>2.₀₂₈</td>
<td>0.₃₂₈</td>
<td>2.₂₁(2.₄₃)</td>
<td>3.₁₆(3.₁₆)</td>
<td>2.₇₉(2.₈₇)</td>
<td>2.₆₃(2.₉₉)</td>
</tr>
<tr>
<td>1-Bromo-2-iodo</td>
<td>7.₉₂₈</td>
<td>7.₂₂₈</td>
<td>8.₂₂₈</td>
<td>1.₆₂₈</td>
<td>1.₆₂₈</td>
<td>0.₄₂₈</td>
<td>2.₂₂(2.₅₀)</td>
<td>3.₁₂(3.₀₇)</td>
<td>2.₉₀(2.₉₃)</td>
<td>2.₄₅(2.₈₄)</td>
</tr>
</tbody>
</table>

(a) Chemical shifts are in $\tau$ units. Values in parentheses are predicted from the values of Martin and Dailey.
Dr. Barry L. Shapiro  
Chemistry Department  
Illinois Institute of Technology  
Chicago, Illinois 60616  

August 20, 1965

Dear Barry:

Your timely reminder finds us with the following information.

Concerted rotation: We recently examined the n.m.r. spectrum of 1,2,3,4-tetrahydro-1-benzyl-N-acetyl-6,7-dimethoxyisoquinoline, I and II, as a function of temperature. At -20° there are equal doublets for each of the two methoxy groups, the acetyl methyl, H3 and H4. The other hydrogens give unresolved structure and the benzyl ring appears as a multiplet of eight peaks. With increasing temperature these doublets collapse into single lines at their centers and the benzyl ring absorption becomes quite sharp. Assuming this behavior results from some kind of rotation we calculated rates of exchange and activation energies for the H3 and acetyl methyl doublets. They both turn out to be the same, 17 kcal. What seems to be happening is that there are present in equal amounts two major species corresponding to the two rotational states of the acetyl group. Rotation of the latter proceeds in concert with rotation of the benzyl substituent from one environment to the other. Inspection of models indicates that the third possible rotamer, not shown, is badly hindered so steric effects are responsible for the concerted rotations. The same sort of thing takes place in 1,2-dineopentyl-tetramethylbenzene where the CH2 groups turn in a conrotatory fashion. (see Tetrahedron Letters, September, 1965).

Li7 and P31: The Varian 19.4 Mc RF unit can be used for Li7 and P31 resonance at the appropriate fields. In this way we looked for but did not find a Knight shift in solutions of sodium in hexamethylphosphoramide. The lithium work concerns the existence of fine structure in the spectra of certain organolithium compounds.

Error: The C13, H(?) coupling constant reported by us for toluene-α-d is not 131 but 126 cps.

We greatly appreciate your work with this Newsletter.

Sincerely,

Gideon Fraenkel  
Associate Professor
30 August 1965

Dr. B.L. Shapiro
Associate Professor
Chemistry Department
Illinois Institute of Technology
Technology Centre
Chicago, Illinois 60616

Dear Barry,

Theory of Chemical Exchange Effects in Magnetic Resonance

Simon Fraser University is about to open, and since no Chemistry Department can afford to be without your excellent newsletter, may I open a subscription with an account of some work just completed at Illinois in collaboration with Dr. H.S. Gutowsky and R.L. Vold.

We were interested in generalising recent theories ¹, ², ³ of the effect of chemical exchange between two uncoupled sites on the echo amplitudes of a Carr-Purcell pulse train to account for more general exchange permutations of the nuclei in a spin-coupled assembly. Alexander's density matrix treatment ⁴ can handle the latter case for the steady state line shapes but this method involves carrying density matrix elements about which one has no information, and which do not contribute to the rotating magnetization. On the other hand, the pulse experiment is most elegantly treated by the matrix method of Anderson and Weiss ⁵. The two methods can be grafted together by picking out the relevant density matrix elements and arranging them as a column vector which becomes the usual relaxation function. The differential equations which the vector elements obey are then a set of Hahn-Maxwell-McConnell equations generalised to include spin-coupling. There is a 1:1 correspondence between lines in the steady state high resolution spectrum and elements of the relaxation function in the eigenstate basis. We call the magnetization associated with each element a spectral magnetization by analogy with the site magnetization of the usual HMM equations. The process sounds involved, and for the exchanging AB case at least, the HMM coefficients can be written directly in matrix form by noting that the spectral magnetizations are just the expectation values of the symmetrized super-operators of Banwell and Primas ⁶. In applications to the calculation of echo amplitudes, the Anderson-Weiss method is then just the matrix integral solution of the generalised HMM equations, subject to the boundary conditions imposed by the pulses.

..2..
Dr. B.L. Shapiro  
Illinois Institute of Technology  
30 August 1965

We have treated some specific systems in detail, and obtained closed formulae for the decay of the Carr-Purcell echo amplitudes in exchanging coupled AB systems, and in ABX and ABXq systems with exchange between the A and B sites. A feature of the results is the appearance of a rather pretty analogy between the effects of nuclear exchange and of nuclear spin coupling. Just as it is possible to remove the decay effects of exchange (or of molecular self-diffusion, which is related) on the Carr-Purcell echo amplitudes by pulsing rapidly, so it is possible to remove the modulation effects of spin coupling by the same device. This analogy leads us to believe that it should be possible to treat exchange by modifying the spin Hamiltonian to include an operator related to Dirac's exchange operator, but we have been unable to formulate this approach as yet.

The theory can be applied to the calculation of line shapes in steady state spectra, and for the exchanging uncoupled two site case it predicts in the fast exchange region a low intensity band centred at the mean frequency, and with a width directly dependent on the exchange rate. This line is in addition to the usual collapsed "fast exchange" line and has not been previously described. Intuitively its presence is required to maintain constancy of the second moment. Similarly, two weak extra lines appear in the fast exchange region of the exchanging AB system. This phenomenon seems to be related to, but not the same as, that reported recently in your newsletter by Anderson and Lichtenstein. Theirs would seem to arise because of non-linear response to the driving term. In our theory the driving term is omitted, apart from specifying the frequency.

Here at Simon Fraser we are looking forward to the arrival of our A56/60 at the end of October, and I hope to have some results on fluorine systems to report next time.

With all best wishes,

Yours sincerely,

E.J. Wells
Assistant Professor
Department of Chemistry
Simon Fraser University

2. A. Allerhand and H.S. Gutowsky, J.Chem.Phys.41, 2115(1964); 42, 1587 and 4203(1965)
Professor B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chic ago Ill. 60616.

"Virtual long range and partial virtual coupling" for pedestrians.

Dear Barry,

I would like to suggest that the mystical phenomenon of "virtual long range coupling and partial virtual coupling" is explained using straightforward effective Larmor frequency arguments.

To start with let us look at an ABX-case. Its X-part shows a four line spectrum even if \( J_{AX} = 0 \) (so called "virtual long range coupling"). This can be explained from the fact that the AB-part of the spectrum is a superposition of two in general different ab-type subspectra with effective chemical shifts:

\[
\delta_{AB}^* = \delta_{AB} \pm \frac{1}{2} (J_{BX} - J_{AX})
\]

and equal coupling constants \( J_{AB} \). These two subspectra are still different if we put \( J_{AX} = 0 \).

The X-part can be constructed as the possible transitions between the levels of two different ab-subspectra (Fig. 1.)

![Diagram](Fig. 1)
The existence of "virtual coupling" is equivalent to the following relations between transitions
\[ X_2 \neq X_5 \neq X_1 \neq X_6 \quad \text{or (and)} \]
\[ X_3 \neq X_4 \neq X_1 \neq X_6 \]
which can immediately be confirmed from "closed loop" relations in Fig. 1:
\[ B_1 + X_2 = X_1 + B_1 \quad X_2 = X_1 + B_1 - B_1 \]
\[ A_1 + X_5 = X_1 + A_1 \quad X_5 = X_1 + A_1 - A_1 \]
\[ B_1 + X_3 = X_1 + A_1 \quad X_3 = X_1 + A_1 - B_1 \]
\[ A_1 + X_4 = X_1 + B_1 \quad X_4 = X_1 + B_1 - A_1 \]

\( X_1 \) and \( X_6 \) are first order effective Larmor frequency transitions and therefore with \( J_{AX} = 0 \) given by the following relations
\[ X_1 = v_X + \frac{1}{2} J_{BX} \quad \text{IV.} \]
\[ X_6 = v_X - \frac{1}{2} J_{BX} \]

Relations III show, that "virtual coupling" disappears only if we fulfill a number of very special conditions.

From relation I it can be seen that the phenomenon should not be explained as due to the coupling between the nuclei \( A \) and \( B \) being strong enough so that \( X \) "sees" \( A \) although it is not coupled to it. The origin of "virtual coupling" lies in the dissimilarity of the two ab-subspectra. This dissimilarity can still arise for weak \( J_{AB} \) if \( J_{BX} \) is large.

For the ABMX-case the explanation for the 10 different M-transitions (although \( J_{BX} = J_{MX} = 0 \)) is very similar. We have now 4 different ab-sub-spectra with effective chemical shifts:
\[ \delta_{AB}^* = \delta_{AB} \pm \frac{1}{2} (J_{BX} - J_{AX}) \pm \frac{1}{2} (J_{DM} - J_{AM}) \quad \text{V.} \]
Again these are still different for \( J_{BX} = 0 \). There are now in principle 12 M-transitions possible (Fig. 2).
Using the same arguments as in the ABX case one can immediately see that all the transitions 2, 3, 4, 5, 8, 9, 10 and 11 are in general different from each other.

Transitions 1, 6, 7 and 12 again are of first order

\[
\begin{align*}
M_1 &= \nu_M + \frac{1}{2} J_{MX} + \frac{1}{2} J_{AX} + \frac{1}{2} J_{BX} \\
M_6 &= + - - - \\
M_7 &= - + + + \\
M_{12} &= - - - - \\
\end{align*}
\]

So that for \( J_{MX} = 0 \) we have

\[
\begin{align*}
M_1 &= M_7 \\
M_6 &= M_{12} \\
\end{align*}
\]

and finally observe 10 transitions ("partial virtual coupling").
Cher Professeur Shapiro,

Continuant l'étude de l'interaction phosphore-proton par résonance dans le champ magnétique terrestre, nous avons pu déterminer les signes relatifs des constantes de couplage phosphore-proton dans le triethyl thiophosphate

\[ S = P - (0 \text{CH}_3\text{CH}_2)_3 \]

\[
\begin{align*}
J_{\text{P}-\text{H}_2^+} &= 9.85 \text{ Hz} \quad \text{mêmes signes} \\
J_{\text{P}-\text{H}_3^-} &= 0.73 \text{ Hz}
\end{align*}
\]

Ce résultat est à comparer à ceux déjà obtenus par la même technique sur le triethyl phosphate et phosphite et sur le tripropyl phosphate.

D'autres expériences sont en cours, qui ont pour but de comparer les signes des constantes phosphore-proton à celui de \( J_{\text{H}_2^+ - \text{H}_3^-} \). On utilise, pour ce faire la technique de double irradiation en champ fort. Certaines transitions du phosphore sont irradiées, tandis que l'on observe le spectre du proton.

Pouvant connaître par comparaisons successives le signe absolu de \( J_{\text{H}_2^+ - \text{H}_3^-} \), ces mesures permettront de connaître le signe absolu des constantes d'interaction phosphore-proton.

Il s'avère que les deux méthodes utilisées se complètent, car d'une part il n'est pas possible de comparer le signe des constantes \( J_{\text{P}-\text{H}_2^+} \) et \( J_{\text{H}-\text{H}} \) en champ faible, les transitions étant difficiles à identifier sur le spectre, et d'autre part il n'est pas possible de déterminer les signes relatifs de \( J_{\text{P}-\text{H}_3^-} \) et \( J_{\text{H}-\text{H}} \) par double irradiation en champ fort du fait que \( J_{\text{P}-\text{H}_3^-} \) est inférieur à 1 c/s.

Veuillez agréer, cher Professeur Shapiro, avec nos excuses pour ce nouveau retard, nos salutations distinguées.

E. Duval

Prof. G.J. Béné
A-60 Magnet Troubles; NMR of Nitrosoureas

Dr. Bernard Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Dr. Shapiro:

Since my last contribution to IIT NMR Newsletter, we spent six months trying to locate the source of a weird problem with our A-60. The most obvious symptom was the appearance of the acetaldehyde quartet on a 50-cps sweep width. It appeared to have alternate broad and narrow peaks. A different manifestation was the appearance of step-like changes of slope on the water peak of the homogeneity-adjust sample, also best observed on a 50-cps sweep width. Naturally, adjusting the field was practically impossible, and we were not able to obtain reproducible spectra of anything on a 50- or 100-cps sweep width. The effect was present but less obvious on the other sweep widths. After everything electronic, cooling, and environmental had been eliminated, the villain turned out to be the styrofoam insulation around the magnet poles. Our changes in slope on the water peak and changing peak-widths on acetaldehyde coincided with the on-off cycle of the magnet cooling water, and the styrofoam was apparently transmitting a physical shock from the 3-way valve to the magnet poles. Since the Varian service engineer dug out the styrofoam, we have had no further trouble. We have no idea why this problem should suddenly arise after the magnet had been in use for three years. I understand newer magnets were made with a softer insulation around the magnet poles.

What NMR work we have accomplished recently has been mostly structure confirmation for our organic chemists. We have found NMR especially useful on a series of substituted ureas of the types

\[ R-N-C-N-CH_2-CH_2-Cl \]

\[ NO \quad H \]
Over a large range of substituents, it has always been possible to distinguish the two forms by the symmetry of the $A_2B_2$ spectrum from the chloroethyl group of II, or the asymmetry of the $A_2B_2X$ spectrum from the $-\text{NH-CH}_2\text{-CH}_2\text{-Cl}$ group of I. With a mixture it has been possible to estimate the proportions of each form with reasonable accuracy, despite overlapping peaks.

In addition, we have continued work on azido-tetrazole equilibria. Some of this work appeared in the July 1965 Journal of Organic Chemistry, and we hope to have more in shape to present for publication soon.

Sincerely yours,

Martha C. Thorpe
Research Chemist
September 1, 1965

Dr. B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois, 60616

Dear Dr. Shapiro,

Comment Concerning 2,3-Dichloro-1,4-Dioxane

I would like to comment on the letter of R. R. Fraser (IITNN; 82, 18) concerning 2,3-dichlorodioxane. I have looked at various spectra on an A-60 where two different isomers were present as approximately pure materials or where the two were found as a mixture. I shall designate as isomer (I) the one with the more deshielded CHCl groups and as isomer (II) the one with the less deshielded CHCl groups.

In our spectra, all 20% w/v in CCl₄, isomer (I) had the less complex A₂B₂ pattern for the CH₂ groups. Isomer (II) had the more complex one, which was visually identical to the one presented in figure 1-A, on page 22 of IITNN # 82. It turns out that in the case of isomer (I) the ¹³CCH satellite on the low field side of the CHCl groups is a slightly broadened singlet, J_HH between the CHCl groups being less than 2 cps.

The point of interest is that, following Fraser's arguments, isomer (I) must have the chlorines trans on the six-membered ring. In addition to rigid and interconverting chair conformations, two boat conformations may be conceived for the trans-molecule. The low (or zero ?) value of J_HH between CHCl groups may be used to rule out a large contribution of either the chair or the boat conformations with these protons trans- and axial. Thus the trans-molecule may be either in a chair conformation with both chlorines axial most or all of the time or in a boat conformation with the protons spending most or all of their time with a dihedral angle of, say, between 60° and 120°.

This low value of the H-H coupling between the two CHCl groups is in agreement with the x-ray and dipole moment evidence of Altona, Romers, and Havinga, cited by Fraser in his opening paragraph, that the chlorines are axial in the trans-compound, if I may assume that my isomer (I) is the same as the isomer melting at 31°C. The compound I am calling isomer (I) was obtained from Distillation Products Industries, Eastman Kodak Co., their number 3603 in their list #43, with boiling point given as 88-89° at 19 mm Hg.

Please credit this contribution to the subscription of Dr. J. P. Heeschen, same address as mine.

A. W. Douglas
Chemical Physics Research Laboratory
1603 Building
Phone ME 6 5325
Dr. B. L. Shapiro
Illinois Institute of Technology
Department of Chemistry
Chicago, Illinois 60616

Dear Dr. Shapiro:

Relative Signs of the Coupling Constants of a Thionosulfite

During work on the structure proof of the thionosulfites, a new class of organic oxygen-sulfur compounds, we obtained and analyzed the NMR spectra of several of these compounds [Q. E. Thompson, M. M. Crutchfield and M. W. Dietrich, J. Org. Chem. 30, 2696 (1965)]. Subsequent to this work while evaluating the integrator of our HR-60 spectrometer as a spin decoupler, we determined the relative signs of the coupling constants of one of these thionosulfites

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_b \\
\text{CH}_3 & \quad \text{CH}_a
\end{align*}
\]

(Trans).

From some partially decoupled spectra obtained, \(J_{ab}\) and \(J_{ac}\) appear to be opposite in sign.

Binders for A-60 Spectra

In the short time in which our A-60 has been in operation, we have accumulated what seems to be a vast number of A-60 spectra. The size and number of these spectra create a filing and retrieval problem. We have found that an economical solution to this problem is the use of a post binder notebook which will easily hold 500 spectra. The notebooks are available by special order from Loose Leaf Devices Company, 1724 North 13th Avenue, St. Louis, Missouri, as "Style End Storage Binder with Additional Posts, 11-1/2" X 26-1/2", 8-1/2" Between Posts." The inclusion of a sheet of A-60 paper with the order will assure an exact fit. The price depends on order size, three being $11.

Yours sincerely,

M. W. Dietrich
R. E. Keller
Dear Barry,

I'd like to share with readers of this marvelously useful Newsletter some results which Dr. Daniel Traficante and myself recently obtained in a study of C\(^{13}\) chemical shifts of acetic acid-1-C\(^{13}\), benzoic acid-1-C\(^{13}\) and mesitylic acid-1-C\(^{13}\) in solutions of concentrated sulfuric acid and oleum. Our results are only partly consistent with those of previous studies and indicate the existence of a new species present in solutions of the former two acids in the oleum solutions of highest SO\(_3\) contents. Dilute enough solutions were employed (about one percent) so that the effective acidities of the solvents were not appreciably altered.

Acetic acid. — In 100% sulfuric acid the observed chemical shift of -5.3 p.p.m. (all shifts reported here are with respect to benzene) is assigned to the protonated carboxyl species I \(\text{RC}^{13}\text{OH}_2^+\) in agreement with the results of a previous investigation.\(^1\) No signal was observed when the oleum composition was between 5% excess SO\(_3\) and 25% excess SO\(_3\). From Deno's proton magnetic resonance measurements\(^2\) we had expected to observe I up to SO\(_3\) concentrations of about 10% and the acylium ion II \(\text{RC}^{13}\text{O}^+\) at all SO\(_3\) concentrations higher than about 20%. Olah and co-workers\(^3\) had found C\(^{13}\) chemical shifts (by the INDIR technique) of the CH\(_3\)C\(^{13}\)O\(^-\)SbF\(_6\)\(^-\) complex in HF to be -30.9 p.p.m. with respect to CF\(_3\)C\(^{13}\)O\(^-\)H or -45.4 p.p.m. with respect to CH\(_3\)C\(^{13}\)OF. From our measurements on these reference compounds these correspond to -64.7 and -77.8, respectively, p.p.m. with respect to benzene. In solutions which contained 40% or 60% excess SO\(_3\) a strong peak at -43.5 p.p.m. was observed; this is so different from what one would expect for II from the INDIR results on CH\(_3\)C\(^{13}\)O\(^-\)SbF\(_6\)\(^-\) that it seems reasonable to assign it to a heretofore un-reported species, perhaps of the type CH\(_3\)C\(^{13}\text{OR})^2_ or CH\(_3\)C\(^{13}\text{OR})_3 or CH\(_3\)C\(^{13}\text{OR})_3 where OR is a sulfate group. Presumably the absence of observable peaks in the 5% to 25% SO\(_3\) range is due to exchange phenomena.

Benzoic acid. — In 98% H\(_2\)SO\(_4\)2H\(_2\)O, in pure H\(_2\)SO\(_4\) or in oleum with 2% excess SO\(_3\) a peak at -54.4 p.p.m. was observed which is assigned to the species I.\(^1\)
September 13, 1965

page 2

Professor Bernard L. Shapiro:

In oleum solutions with compositions ranging from 10% excess SO₃ to 35% excess SO₃ a peak at about -51.6 p.p.m. was observed, and this is tentatively assigned to a species of type II. In an oleum solution containing 68% excess SO₃ a peak at -26.2 p.p.m. was observed which we believe is due to a "new" species with structure analogous to that responsible for the -23.5 p.p.m. signal in the acetic acid system.

Mesitoic (2,4,6-trimethyl benzoic) acid.— This system had been well characterized previously by U.V. and proton magnetic resonance studies. Accordingly, we assigned the signal at -59.3 p.p.m. in 91% sulfuric acid to a species of type I and the signal at -32.2 p.p.m. in pure H₂SO₄ to the acylum ion II. The latter peak remained the only major resonance line in oleum solutions with SO₃ contents ranging up to 68%.

These sulfuric acid/carboxylic acid systems seem to be largely reversible, so that reproducible signals can be observed corresponding to a particular solvent composition regardless of how that composition was attained. Infrared measurements are now underway to test these assignments.

References


Sincerely yours,

Gary E. Maciel
Assistant Professor
in Chemistry

GEM/ds
September 13, 1965

Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois

Dear Professor Shapiro:

There are at present no subscribers to the ITT Newsletter (or whatever the current name is) at Hopkins. I would like to remedy this situation with the following contribution:

In the widely used high-resolution NMR method for measuring fast exchange processes, it has usually been assumed that the observed lineshape can yield only one experimental parameter, the rate of exchange. The chemical shifts, \( \delta \nu \), between the exchanging sites have been measured at temperatures sufficiently low to "freeze out" the exchange process, and then these values have been introduced into the appropriate lineshape equations to obtain the rates of exchange at higher temperatures. This method may lead to errors in the rate if the chemical shifts are temperature dependent. A suggestion to this effect has been made for the widely studied hindered internal rotation in N,N-dimethylformamide.

It has already been shown that if the Spin-Echo NMR method is used, it is possible to obtain both the rate and the chemical shift at each temperature. It is shown below that the high resolution lineshape, up to the coalescence temperature \( T_c \), can also yield the rate and chemical shift at each temperature.

The simplest possible case is a system that satisfies the following conditions: (A) It consists of two equally populated sites which are uncoupled or very weakly coupled, so that coupling between the sites may be neglected. (B) The temperature is below \( T_c \), so that two resolved peaks are observed. (C) The "natural" and instrumental contributions to the lineshape are negligible with respect to the exchange contribution.

Under these conditions, the following equations hold:

\[
\frac{1}{2\tau} = \frac{\pi}{2} (\delta \nu - \delta \nu_e) \frac{k_B}{2}
\]

\[
\frac{1}{2\tau} = \frac{\pi}{2} \delta \nu [r + (r^2 - r_e)^{3/2}]^{-3/2}
\]
Professor B. L. Shapiro  
Page 2  
September 13, 1965

where \( \tau \) is the lifetime, in sec, between exchanges, \( \delta \nu \) is the chemical shift in cps, \( \delta \nu_e \) is the experimental peak separation, and \( r \) is the peak-to-valley ratio. Equations (1) and (2) have been widely used for determining \( \tau \) below the coalescence temperature \( T_c \). In all cases \( \delta \nu \) was obtained from the low temperature spectrum, and it was assumed that \( \delta \nu \) is temperature independent.

We can combine Eqs. (1) and (2) and eliminate \( \tau \). The result, after some rearrangement, is:

\[
\delta \nu = \left[ \frac{r}{(r - 1)} \right]^{\frac{1}{6}} \delta \nu_e
\]

Equation (3) can be used at each temperature to calculate the chemical shift \( \delta \nu \) from the measured values of \( r \) and \( \delta \nu_e \). It is important to remember that Eq. (3) is valid only when conditions (A)-(C), given above, apply. When this is not the case, it may still be possible to extract the value of the chemical shift from an NMR spectrum strongly affected by exchange, by using computer methods. Work on such cases is in progress.

We have tested the applicability of Eq. (3) to the case of hindered internal rotation in \( N,N \)-dimethyltrichloroacetamide. The low temperature value of \( \delta \nu \) has been reported as 17.6 cps and 18 cps. Previous Spin-Echo work indicated the possibility of a temperature dependent chemical shift, but the results were not conclusive. We have applied Eq. (3) to the high resolution spectra of \( N,N \)-dimethyltrichloroacetamide below \( T_c \). Within experimental error, the chemical shift is temperature independent in the range 1.5-15.5°C, with a value in agreement with that obtained at -27°C. It would be interesting to repeat the Spin-Echo measurements at a higher frequency than the previously used 26.9 Mc/sec, and with less "aged" instrumentation.

Finally, it should be pointed out that when conditions (A)-(C) apply, the linewidth at half-height is exactly equal to \( \delta \nu \) at the coalescence temperature. This provides a way of extending the measurement of \( \delta \nu \) up to the coalescence temperature.

Sincerely yours,

[Signature]

Adam Allerhand  
Assistant Professor of Chemistry

AA/\( \delta \nu \)
References


(4) The range of temperatures over which both (B) and (C) hold increases with the chemical shift between the sites.

(5) A. Allerhand, H. S. Gutowsky, and R. Meinzer, to be published.


Professor B.L. Shapiro,
Illinois Institute of Technology,
Chicago 60616
USA

Dear Professor Shapiro,

We have recently completed an analysis of the ABC type spectrum of monochlorocuineone at 100 Mc/s. This has been carried out using a Mercury Autocode computer, programmed for parameter refinement. The final parameters are given below in the table, and in the figures we show the computed spectra at 100 Mc/s and 60 Mc/s below the corresponding observed spectra. (The 60 Mc/s case is intended as a check; it was computed using the parameters derived from the 100 Mc/s analysis).

<table>
<thead>
<tr>
<th></th>
<th>Chem. Shifts (cps, rel. to TMS)</th>
<th>Coupling Constants (cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 Mc/s</td>
<td>60 Mc/s</td>
</tr>
<tr>
<td></td>
<td>A 705.18</td>
<td>423.11</td>
</tr>
<tr>
<td></td>
<td>B 696.18</td>
<td>417.71</td>
</tr>
<tr>
<td></td>
<td>C 686.68</td>
<td>412.01</td>
</tr>
</tbody>
</table>

The most interesting point arising from this analysis is the value of $J_{\text{para}}$. This is, so far as we are aware, the first case of a negative para coupling constant. In benzene and its derivatives this coupling is of similar size but is positive. The spectrum is, however, less sensitive to $J_{\text{para}}$ than to the other coupling constants, and the accuracy of our value cannot be better than $\pm 0.1$ cps.

Yours sincerely,

G. T. Jones
Professor J. N. Murrell

I would like this letter to be credited to my account.
Observed and computed spectra of 2-chloroquinone at 100 Mc/sec.
Observed and computed spectra of 2-chloroquinone at 60 Mc/sec
Dear Barry,

Since I reported last on the benzeneoxide-oxepin-equilibrium (IITNMI-Newsletter 76-20, 78-16), Dr. Friebolin and I have been able to obtain good low-temperature spectra of oxepin as well as of α-methyloxepin, synthesized by VOGEL and SCHUBART. A mixture of CF₃Br and pentane (2:1) was used as solvent for the former compound and pure CF₃Br for the latter.

Equilibrium constants have been obtained from peak areas in the spectra below coalescence and from shift measurements above coalescence. Lifetimes of the isomers have been calculated from linewidth measurements in the slow and fast exchange limit. The signal of the internal reference TMS was used for field inhomogeneity corrections. In the case of oxepin the measurements were made on the α-proton signal. In the case of α-methyloxepin both, methylsignal and α-proton signal, have been used. The linewidth was corrected for coupling with the β-proton, which proved to be important in both cases. For this purpose the signal was treated as superposition of two singuletts. A similar procedure has been used previously by PHAEKEL and FRANCONI (J.A.C.S. 82, 4478 [1960]).

The results for both equilibria studied are summarized in the following table:
\[ A \quad \text{↔} \quad B \]

\[
\begin{array}{ccccccccc}
\tau_{\alpha} & \tau_{B} & \tau_{\gamma} & J_{\alpha B} & K(-100^\circ) & \Delta H^0[1] & E_a[2] & A[3] & \Delta S^0[4] \\
A & 6.0 & 3.7 & 3.7 & \sim 2.7 & 1.0 & 1.7 \pm 0.4 & 9.1 \pm 0.8 & 10^{14.4} \pm 1.1 & 10.5 \pm 8.3 \\
B & 4.3 & 4.3 & 3.7 & \sim 5.9 & & 7.2 \pm 1.0 & & 10^{12.1} \pm 1.4 \\
\end{array}
\]

\[
\begin{array}{ccccccccc}
\tau_{\alpha} & \tau_{CH_3} & J(CH_3,H_B) & K(-100^\circ) & \Delta H^0 & E_a & A & \Delta S^0 \\
A' & 6.3 & 8.45 & \sim 0 & 3.7 & 0.4 & 9.3 & 10^{14.2} & \sim 2.3 \\
B' & 4.2 & 8.09 & \sim 1.0 & & & 9.3 & 10^{13.7} \\
\end{array}
\]


Samples of the compounds were kindly provided by Dr. W. A. Böll and R. Schubart.
The values for the $\alpha$-methylloxepin case are subject to further studies. Spectra in the coalescence region will be analysed by the complete lineshape expression of GUTOWSKY and HOLM.

The entropy increase in going from A to B is certainly due to the conformational equilibrium between two boatforms, which should be possible for the monocyclic compound:

This also shows, that the $8\pi$-electron system of B is not in one plane. Together with the finding, that B has the higher groundstate energy as compared with A, the conclusion can be drawn, that the conjugated $8\pi$-electron system of B is not aromatic, as expected after HÜCKEL's predictions.

As can be seen from the results for $\alpha$-methylloxepin, the substituent stabilizes B with respect to A and the transition state. The introduction of a second $\alpha$-methylgroup will probably lead to a negative $\Delta H^0$. It is therefore not surprising, that no indication of an equilibrium was found for $\alpha,\alpha'$-dimethylloxepin (VOGEL, BÖLL and GÜNThER, Tetrahedron Letters 1965, 609).

The results for the unsubstituted oxepin will appear in Tetrahedron Letters shortly.

Best regards,

H. Günther

* $H_B^0 < H_A^0$
20 September 1965

Dear Barry:

We have been using the field-frequency-lock device of Freeman and Anderson¹ and Manatt and Elleman² for $^{19}$F studies of some fluorosilanes. The upper trace in Figure 1 shows the recorded $^{19}$F spectrum of $\text{Si}_2\text{F}_6$; the lower trace shows the spectrum calculated for $F_3^{28}\text{Si}^{29}\text{SiF}_3$ by LAOCOON II.

The central line, A, in the observed spectrum is due to the $^{28}\text{Si}_2\text{F}_6$ (92% of the sample); it was recorded at reduced gain. B denotes lines due to the $^{29}\text{Si}_2\text{F}_6$ (0.22% of the sample). C denotes lines arising from an impurity which appeared after the sample had been kept for 2 months at room temperature. Spectral parameters were obtained by fitting the calculated to the observed spectrum, using 92 of the observed lines. Observed and calculated line positions agree with an r.m.s. error of 0.156 Hz. The results for $\text{Si}_2\text{F}_6$ and $(\text{SiF}_3)_2\text{O}$ are given in Table I.

The separation, $K$, between the two most intense lines in the $A_3\Delta^{\text{XX'}}$ spectrum of $^{29}\text{Si}_2\text{F}_6$ (which are the only two lines observed here) is given by $K = |J_{\text{SiF}} + J_{\text{SiF'}}|$. The observed value of $K$, 231.2 Hz, confirms the relative signs obtained from the analysis of the $F_3^{28}\text{Si}^{29}\text{SiF}_3$ spectrum.

Sincerely,

[Signature]

Thomas D. Coyley
Chief
Inorganic Chemistry Section

Thomas C. Farrar
Inorganic Chemistry Section

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### Table 1

NMR Spectral Parameters\(^a\) for Si\(_2\)F\(_6\) and (SiF\(_3\))\(_2\)O

<table>
<thead>
<tr>
<th></th>
<th>Si(_2)F(_6)</th>
<th>(SiF(_3))(_2)O</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>(J_{\text{SiF}})</td>
<td>(\pm 321.83 \pm 0.09) Hz</td>
<td>167.63 (\pm 0.06) Hz</td>
<td>b</td>
</tr>
<tr>
<td>(J'_{\text{SiF}})</td>
<td>(90.48 \pm 0.11) Hz</td>
<td>(&lt; 2.5) Hz</td>
<td>b</td>
</tr>
<tr>
<td>(J_{\text{FF}})</td>
<td>20.91 (\pm 0.08) Hz</td>
<td>0.74 (\pm 0.03) Hz</td>
<td></td>
</tr>
<tr>
<td>(\delta_{\text{F}})</td>
<td>-42.25 (\pm 0.002) p.p.m.</td>
<td>-6.13 (\pm 0.002) p.p.m.</td>
<td>c</td>
</tr>
<tr>
<td>(\delta'_{\text{F}})</td>
<td>.009 (\pm 0.0008) p.p.m.</td>
<td>.008 (\pm 0.002) p.p.m.</td>
<td>d</td>
</tr>
<tr>
<td>(\delta^*_{\text{F}})</td>
<td>.004 (\pm 0.0009) p.p.m.</td>
<td></td>
<td>e</td>
</tr>
<tr>
<td>(\delta^\prime_{\text{F}})</td>
<td>.008 (\pm 0.002) p.p.m.</td>
<td></td>
<td>f</td>
</tr>
</tbody>
</table>

**Notes**

a. Values refer to \(^{28}\)Si\(^{29}\)Si species unless otherwise specified. All errors are average errors. The errors for the \(^{28}\)Si\(^{29}\)SiF\(_6\) spectral parameters were obtained from the error vectors calculated by the LAOCOON II program.

b. Relative signs of \(J_{\text{SiF}}\) and \(J'_{\text{SiF}}\) determined for Si\(_2\)F\(_6\) only. Signs of other \(J's\) indeterminate.

c. Chemical shift of \(^{28}\)Si\(^{29}\)Si species relative to internal \(^{28}\)SiF\(_4\). Negative value indicates shift to lower field.

d. Isotope shift relative to \(^{28}\)Si\(^{29}\)Si species, fluorine bonded to \(^{29}\)Si.

e. Isotope shift relative to \(^{28}\)Si\(^{29}\)Si species, fluorine bonded to \(^{28}\)Si.

f. Isotope shift in \(^{29}\)Si\(^{28}\)Si species.

---

**Figure 2**
\[ \text{Si}_2\text{F}_6 \]

56.4 MHz.

Figure 1

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