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NMR Study of Acetaldehyde-Water Mixtures

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Acetaldehyde and trimethylamine are known to be the principal products of the radiation decomposition of crystalline choline chloride<sup>3</sup>. In order to investigate the migration of protons from the ethanol group of the choline molecule during the radiation decomposition it is necessary to know whether acetaldehyde hydrogen atoms can be exchanged with water. This, in turn, must be known because water must be used to separate the radiation products. For this reason we undertook the study of mixtures of acetaldehyde and water. Using the technique of high resolution NMR we have established that there is no exchange between the protons of acetaldehyde in water and in D<sub>2</sub>O. We have also calculated a value for the equilibrium constant between the two forms (free and hydrated). The general expression of this equilibrium is:



We have used samples of acetaldehyde, propionaldehyde, and isobutyraldehyde that were purified by distillation. The purity of H<sub>2</sub>O and D<sub>2</sub>O was ascertained by NMR. All the spectra have been taken with a Varian Model V-4300 B spectrometer working at 40 Mc. The chemical shifts are expressed in ppm of the external magnetic field by the relation:

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3. R.M. Lemmon, M.A. Parsons, D. Chin, J. Am. Chem. Soc. 77, 4139 (1955).

$$\delta = (\text{H} - \text{H}_{\text{ref}}) \times 10^6 / \text{H}_{\text{ref}}$$

where H is the resonance field for the sample and H<sub>ref</sub> is the resonance field of protons in water.

The spectrum of pure acetaldehyde consists of a quadruplet at  $\delta = -4.3$  and a doublet at  $\delta = +4.1$ . The quadruplet represents absorption by the aldehydic proton, which has been split by spin-spin interaction with the three protons of the methyl group, while the doublet represents absorption by the methyl group, split by the aldehydic proton.

When D<sub>2</sub>O is added to pure acetaldehyde (Fig. 1) we observe the same acetaldehyde spectrum consisting of a quadruplet at  $\delta = -4.3$  and a doublet at  $\delta = +4.1$ . In addition, a quadruplet at  $\delta = +0.7$  and a doublet at  $\delta = +5$  appear. We have assigned these additional lines to the hydrated form of the acetaldehyde, with the new quadruplet representing absorption by the proton of the acetal group, and the new doublet representing absorption by the methyl group.

The intensities, but not the positions, of the peaks assigned to the hydrated form depend on the relative proportions of acetaldehyde and water. The assignment is further supported by the fact that the hydrated form is less polarized than the aldehydic form.

The same effect has been observed in mixtures of propionaldehyde/water or D<sub>2</sub>O, and isobutyraldehyde/water or D<sub>2</sub>O<sup>4</sup>. The data are reported in Table I.

4. However, in the case of mixtures of acetone and water no formation of the hydrated form has been observed.

It is possible to calculate the value of the equilibrium constant using the relation:

$$K_{eq} = x / (a-x)(b-x)$$

where:  $x$  = equilibrium concentration in moles/liter of the hydrated form

$a$  = initial concentration of aldehyde in moles/liter

$b$  = initial concentration of  $H_2O$  or  $D_2O$  in moles/liter

From the areas under the absorption peaks of the pure and the hydrated form we obtain the ratio  $x/a-x$  from which we calculate  $x$ .

The results of many experiments, using different amounts of acetaldehyde and water or  $D_2O$ , gave for acetaldehyde at  $25^\circ C$ :

$$K_{eq} = \frac{(2.7 \pm 0.1) (10^{-2})}{\text{moles/liter}}$$

Table I

Chemical Shift\* of Nonequivalent Protons in Aldehydes and their Hydrated Forms

	Acetaldehyde	Acetaldehyde + $H_2O$	Acetaldehyde + $D_2O$
-CHO	-4.3	0.6	0.7
-CH <sub>3</sub>	4.1	5.0	5.0
	Propionaldehyde	Propionaldehyde + $H_2O$	Propionaldehyde + $D_2O$
-CHO	-4.3	0.3	0.4
-CH <sub>2</sub>	2.7	3.6	3.6
-CH <sub>3</sub>	4.1	4.1	4.1
	Isobutyraldehyde	Isobutyraldehyde + $H_2O$	Isobutyraldehyde + $D_2O$
-CHO	-4.1	0.8	0.8
CH	3.0	3.7	3.7
-CH <sub>3</sub>	4.3	4.3	4.3

\* The values are estimated to be accurate to  $\pm 0.2$  ppm.

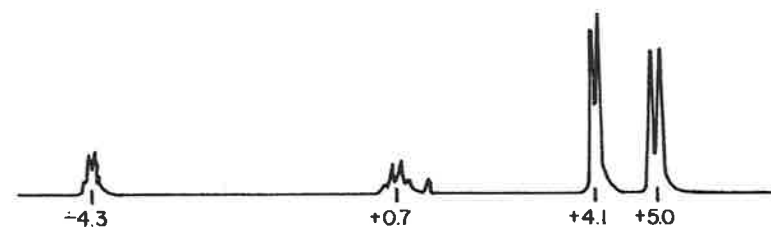


Fig. 1. NMR spectra of mixture containing 1 part acetaldehyde to 1 part  $D_2O$ .

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October 7, 1959

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Gentlemen:

We found the excellent results obtained by Weinberg and Corio (MELLON N.M.R. 12 and J. Chem. Phys. 31, 569 (1959)) on the NMR spectra of methylthiophenes very interesting, since as you may know we are currently studying long-range methyl couplings (Acta Chem. Scand. in press) as well as substituted thiophenes (Arkiv Kemi and Acta Chem. Scand. in press). We think that the results obtained at 60 Mc/s and our results at 40 Mc/s complement each other in a fortunate way.

The methyl group in 2-methylthiophene is a simple doublet at 40 Mc/s having a splitting of  $0.95 \pm 0.05$  c/s and a line width of each component of 0.5 c/s (fig. 1). Thus the  $J_{\text{CH}_3 \rightarrow 4}$  splitting of 0.4 c/s reported by Corio and Weinberg is apparently absent in <sup>the</sup> 40 Mc/s spectrum.

In the pure  $\text{ABX}_3$  case the field dependent splitting ( $J_{\text{AX}} - J_{\text{BX}}$  at large  $\delta_{\text{AB}}$ ) should decrease with decreasing field (cf. accompanying note). Thus the collapsing of the quartet structure into a doublet at small  $\delta_{\text{AB}}$  should indicate unequal signs of the coupling constants  $J_{\text{CH}_3 \rightarrow 3}$  and  $J_{\text{CH}_3 \rightarrow 4}$ . This arguments may be oversimplified in the present case because we neglect the 5-hydrogen. In 2-methyl-5-thiophencarboxaldehyde (fig. 2), however, the presence of the  $J_{\text{CH}_3 \rightarrow 4}$  coupling is observed at 40 Mc/s.

The methyl group splittings indicate couplings equal to 1.1 c/s and 0.5 c/s respectively.

In the 40 Mc/s spectrum of 3-methylthiophene, the methyl group shows a complex multiplet, which could not be interpreted since the ring protons form an uncompletely resolved multiplet (Arkiv Kemi 13, 279 (1958)). We have found, however, (Acta Chem. Scand. in press) through a study of substituted 3-methylthiophenes that there is a coupling  $J_{\text{CH}_3 \rightarrow 2}$  of the order of 1 c/s. This confirms our theories on the connection between hyperconjugation and these splittings. The 3-methyl group can only conjugate effectively to the 2-position (Arkiv Kemi 13, 295 (1958)) and not to the 4- and 5-positions in the thiophene nucleus and this fact may explain the much larger coupling constant of the 3-methyl group with the 2-hydrogen than the 4- and 5-hydrogens.

Yours sincerely,

*Salo Gronowitz*

Salo Gronowitz

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Ragnar A. Hoffman

Determination of relative signs of coupling constants  
in the ABX and related cases

By Ragnar A. Hoffman and Salo Gronowitz

In connection with our work on the relation between long range couplings of methyl groups and hyperconjugation, we were interested in determining relative signs of coupling constants.

An analysis similar to that of Bothner-By in # 11 of your bulletin shows that the field dependence of the multiplet structure may be used to determine relative signs in an extremely simple way.

Let us consider an ABX-case as being representative. Here the analysis by Bernstein, Pople and Schneider shows that the X-hydrogen resonance consists of two doublets, one with the field independent splitting

$$|J_{AX} + J_{BX}|,$$

the other with the field dependent splitting

$$2|D_+ - D_-|,$$

which may be written

$$f(x) = \sqrt{(x + \alpha)^2 + \gamma^2} - \sqrt{(x + \beta)^2 + \gamma^2} \quad [1]$$

where  $x$  equals  $\eta_{H_0} |\sigma_B - \sigma_A|$  and  $\alpha > \beta$  and  $\gamma$  are dependent of coupling constants only.

$f(x)$  is a monotonic function of  $x$  and the difference is largest in magnitude when  $x \rightarrow +\infty$  being in the limit equal to

$$\alpha - \beta = |J_{AX} - J_{BX}|;$$

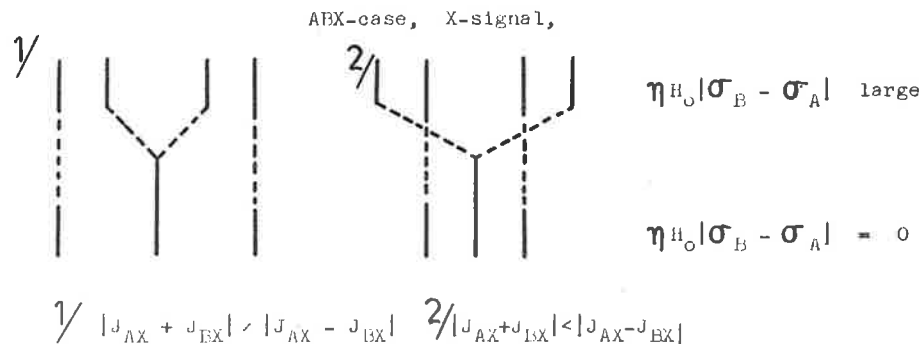
we thus see, that the field dependent lines of the quartet always move inwards as the shift  $\eta_{H_0} |\sigma_B - \sigma_A|$  is decreased.

The effect of this field dependence may appear quite different, depending on the relative signs of  $J_{AX}$  and  $J_{BX}$ ; if the couplings have equal sign, then always the inner lines will approach when resonance is observed at a lower field. The reverse is not true, however, because even if  $|J_{AX} - J_{BX}| > |J_{AX} + J_{BX}|$  it is not necessarily true that

$$2|D_+ - D_-| > |J_{AX} + J_{BX}|$$

one may, however, conclude that if the observed quartet collapses into a doublet when resonance is observed at a lower field (assuming equal resolution of the spectrometer) then the coupling constants must differ in sign.

In the ABX<sub>3</sub>-case one obtains four pairs of lines, but for every field dependent splitting we obtain an expression of the form [1]. Thus the conclusions reached are the same.



P.S. Dr V.J. Kowalewsky just pointed out to us that our extension to the  $AEX_3$ -case is not generally valid.

A closer examination reveals that here  $f(x)$  vanishes for one pair of lines if  $\eta_{H_0} |\sigma_B - \sigma_A| = |J_{AX} - J_{BX}|$ . Thus our conclusions in the  $AEX_3$ -case are valid only if  $\eta_{H_0} |\sigma_B - \sigma_A| \gg \gg |J_{AX} - J_{BX}|$ .

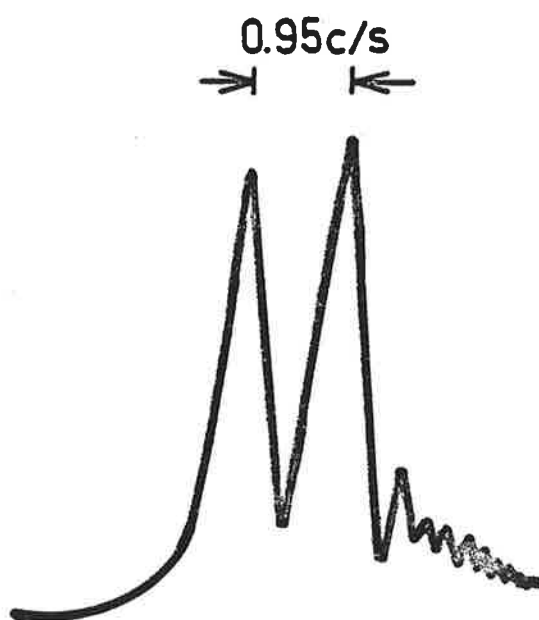


Fig. 1. NMR spectrum of methyl group of 2-methylthiophene at 40 Mc/s.

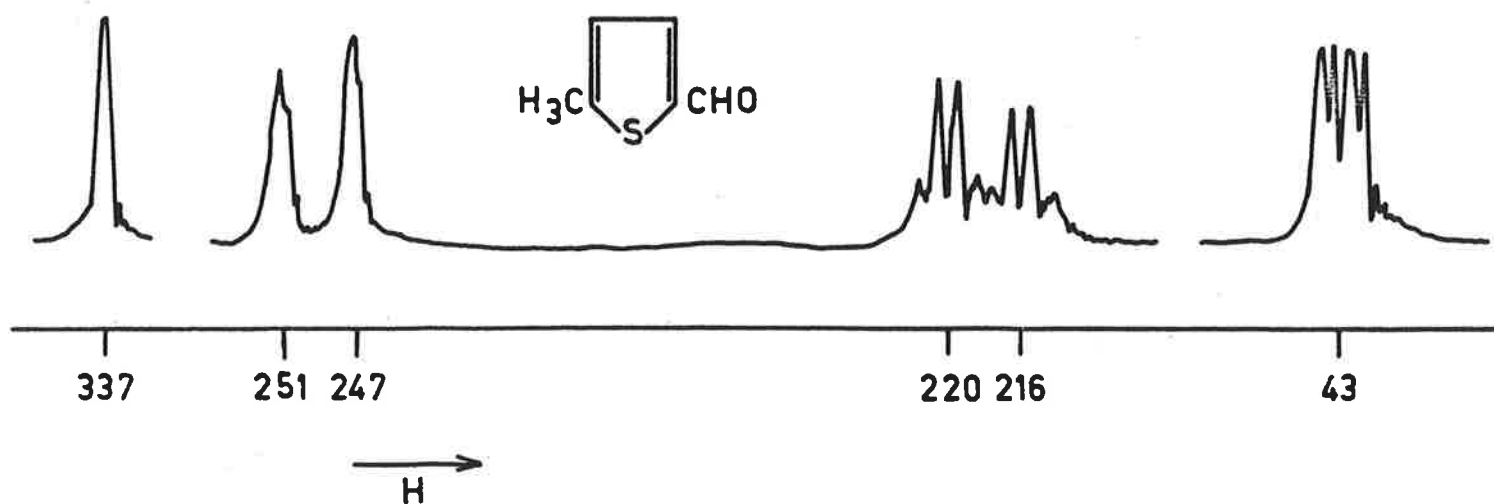


Fig. 2. NMR spectrum of 2-methyl-5-thiophenecarboxaldehyde at 40 Mc/s. Shifts in c/s rel. to cyclohexane. The different sections are not to scale.



*Fysiska Institutionen, Upsala, october 12, 1959.*

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Gentlemen:

This is in certain way in reply to your kind letter of april 14. As we have been informed that our university has bought a Varian instrument we expect to be in position to make some contributions to M.E.L.L.O.N.M.R. from there, beginning next year. In the meanwhile I would like to report about some results we obtained here, in Upsala, working in the  $ABX_3$  case which are quite similar to the  $ABX$  case which is fully explained in the letter by R. Hoffman and S. Gronowitz.

In the  $ABX_3$  case, like in the  $ABX$ , for sufficiently strong values of the  $H_0$  field ( $\sigma \gg J$ ), the  $X_3$  group is a quadruplet and has two components separated by a distance equal to  $|J_{AX} + J_{BX}|$  and which is independent of the applied field. When the spectrum is observed at a lower frequency the other components move inwards. When both couplings are of the same sign the field independent lines are the external ones. In case the signs are different the internal lines are the field independent ones.

We have been studying this in connection with the spectrum of the N-methylformamide. At 40 Mc. a quadruplet is seen with the internal lines separated 4.1 c.p.s. and the external ones 5.9 c.p.s. A spectrum at 25 Mc. was kindly run by prof. R. Freymann (Paris) giving 4.3 c.p.s. for the internal doublet and, just about the limit of resolution, 5.2 c.p.s. for the external one. This result seems to prove the existence of a negative J-coupling associated to a C-N bond.

It seems to me it would be interesting to have some calculations made for the  $X_3$  group, in a way similar to the  $AXX'$  case which appeared in Nr. 11 of M.E.L.L.O.N.M.R., taking  $J_{AB}/\delta_{AB}$  as sensitive parameter, because when this parameter approaches unity, the  $X_3$  group splits into eight lines whose behaviour is no longer so simple.

Yours sincerely,

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PROTON RESONANCE SPECTRA OF PORPHYRINS

The proton magnetic resonance spectra of several porphyrins display chemical shifts of unusual magnitudes. For example, the attached figure shows the spectrum of coproporphyrin-1 methyl ester. The probable assignments of the peaks are given in the caption to the figure. The most remarkable features of the spectrum are the peak at  $\delta = -9.96$ , which is clearly due to the four methine protons, and the peak at  $\delta = +3.89$ , which we assign to the NH protons. The methine peak is 2.7 ppm lower in field than the resonance of benzene and about 4 ppm lower than typical olefinic protons. The N-H line is 13 ppm higher in field than the analogous line in pyrrole. Other features, such as the  $\text{CH}_3$  resonance, are also shifted from the usual positions, but the differences are not nearly so marked.

These unusual shifts can be accounted for qualitatively by the effect of ring currents in the large conjugated porphyrin system. Using a current of  $18 \pi$  electrons, we compute from the magnetic dipole approximation<sup>1</sup> a shift for the methine protons of -5.4 ppm, compared with the observed difference of -4 ppm between these protons and typical olefinic analogues. With the magnetic ring model<sup>2</sup>, taking the spacing of the magnetic rings used for benzene<sup>3</sup>, we compute a shift of -8 ppm for the methine protons and +25 ppm for the NH protons.

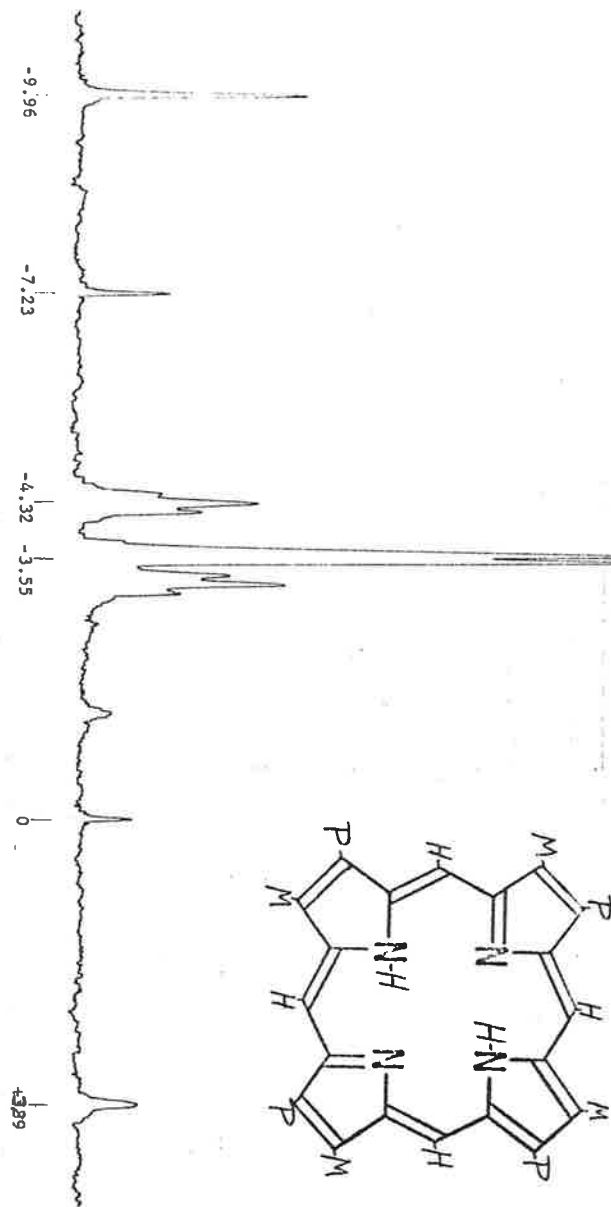
A description of this work is scheduled to be published as a Communication in the November issue of the Journal of Chemical Physics, and spectra of additional porphyrins will be reported later.

1. Pople, J. Chem. Phys. 24, 1111 (1959).
2. Johnson and Bovey, *ibid* 29, 1012, (1958).

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PMR spectrum (60 mc) of coproporphyrin-1 methyl ester in  $\text{CDCl}_3$  ( $\sim 0.05$  molar), ( $\text{H}=\text{CH}_3$ ;  $\text{P}=\text{CH}_2\text{CH}_2\text{OOCCH}_3$ ). Shifts expressed in ppm from internal tetramethylsilane. Probable assignments:  $\delta = -9.96$ ,  $\text{CH}$ ;  $-4.32$ ,  $\text{CH}_2\text{CH}_2\text{OOC}$ ;  $-3.67$ ,  $\text{CH}_3$  OOC;  $-3.55$ ,  $\text{CH}_3$ ;  $-3.20$ ,  $\text{CH}_2\text{CH}_2\text{OOC}$ ;  $+3.89$ ,  $\text{NH}$ ;  $-7.23$ ,  $\text{CHCl}_3$ ;  $\text{C}$ ,  $32(\text{CH}_3)_4$ ;  $-1.43$ , impurity.





FLUORINE N.S.R. SPECTROSCOPY. II. A "DISTANT" CARBON-13

ISOTOPE EFFECT

By George Van Dyke Tiers

Contribution No. 167

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A nuclear spin resonance (N.S.R.) "isotope effect" upon shielding values for fluorine atoms attached to  $C^{13}$  has recently been discovered.<sup>1</sup> In each case the heavy isotope produced a band displacement of 0.1 to 0.2 parts-per-million in the direction of greater shielding.

Although spin-spin interaction was observed in the system  $F - C^{12} - C^{13}$ , no isotopic shift was detected.<sup>1</sup> As both the sign and the magnitude of such a  $C^{13}$  effect might be theoretically interpretable, particular attention has been given to precision measurement in the present work.

The purity of the compounds studied was excellent, no spurious bands being found in the N.S.R. spectra. The  $CF_2=CCl_2$  was obtained from the General Chemical Co., the  $CFCl=CCl_2$  from the Columbia Organic Chemical Co. (Columbia, South Carolina, U.S.A.), while the  $CF_3CO_2H$  and the  $CF_3CCl_3$  were synthesized in our laboratories. The  $C^{13}$  isotopic isomers were present at their natural abundances.

-2-

The undiluted compounds were employed for the  $C^{13}$  studies. For the measurement of the following  $\phi^*$ -values,<sup>2</sup> dilute solutions in  $CCl_3F$  were used;  $CF_2=CCl_2$ ,  $+88.54 \pm 0.01$  (3%);  $CFCl=CCl_2$ ,  $+79.33 \pm 0.01$  (10%);  $CF_3CO_2H$ ,  $+76.542 \pm 0.005$  (5%);<sup>2</sup> and  $CF_3CCl_3$ ,  $+82.209 \pm 0.002$  (3%).<sup>2</sup>

The N.S.R. spectrometer and the measurement techniques used have been described in great detail,<sup>3,4</sup> the latter having been developed for the detection of the exceedingly small  $C^{13}$ -H isotope effect.<sup>4</sup> The results, presented in Table I, are in each case the averaged values from 6 to 8 separate measurements.

Table I

The Excess Fluorine N.S.R. Shielding  
Produced by Distant  $C^{13}$  in Two-Carbon Compounds

Compound	$\Delta\phi$ , p.p.m. <sup>a</sup> ( $F-C^{12}-C^{13}$ )	$J$ , c/s <sup>a</sup> ( $F-C^{12}-C^{13}$ )	$\Delta\phi$ , p.p.m. <sup>b</sup> ( $F-C^{13}$ )	$J$ , c/s <sup>b</sup> ( $F-C^{13}$ )
$CF_3CCl_3$	+ 0.014	43.1	+ 0.131	282.5
$CF_3CO_2H$	+ 0.021	44.1	+ 0.129	283.2
$CF_2=CCl_2$	+ 0.030	44.2	+ 0.103	288.9
$CFCl=CCl_2$	+ 0.032	43.7	+ 0.112	303.1

- (a) Standard deviations of the averaged values are  $\pm 0.002$  p.p.m. and  $\pm 0.10$  c/s for  $CF_3CCl_3$  and  $CF_3CO_2H$ , and  $\pm 0.003$  p.p.m. and  $\pm 0.20$  c/s for the olefins.
- (b) Standard deviations of the averaged values are  $\pm 0.002$  p.p.m. and  $\pm 0.13$  c/s. These values are quoted from Ref. 1 for purposes of comparison.

The small excess shielding produced by "distant"  $C^{13}$  is shown to vary by a statistically significant factor of two among the compounds of Table I. No correlation is observed between this strongly varying quantity and the presumably closely related other measurements listed in Table I, nor to the fluorine shielding values,  $\phi^*$ ,<sup>2</sup> listed for the compounds. A new influence apparently must be sought. A tentative suggestion (which cannot at present be verified) has to do with the structure of carbon atoms in the valence-bond system concerned. The magnitude of the  $C^{13}$  effect increases with the number of trigonal carbons in the F-C- $C^{13}$  system; this "correlation" may perhaps extend (with the opposite sign!) to the smaller F- $C^{13}$  system. Gutowsky has offered an explanation of isotope effects in the systems H- $C^{12}$ -D and F- $C^{12}$ -D, based on a simple electrostatic model,<sup>5</sup> which if extended to the F- $C^{12}$ - $C^{13}$  case would appear to imply a relatively large amplitude for the in-plane F-C=C bending vibration of the fluorinated olefins.

It is of particular theoretical interest that the "distant" spin-coupling constant,  $J(F-C^{12}-C^{13})$  appears virtually invariant in the compounds of Table I. One might have expected the opposite result, in view of the very large variations in structure. Experiments are currently under way to determine the relative sign of the two  $C^{13}$  coupling constants.

I am particularly indebted to P. C. Lauterbur of the Mellon Institute for the privately-communicated results of Ref. 1, without which it is probable that the present work would not have been begun. I thank Professor H. S. Gutowsky of the University of

Illinois for a pre-publication copy of Ref. 5. Donald Hotchkiss is responsible for the careful maintenance and operation of our N.S.R. equipment.

#### References

- (1) P. C. Lauterbur (paper in course of preparation)
- (2) G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.* **61**, 761 (1959)
- (3) G. V. D. Tiers, *J. Phys. Chem.* **62**, 1151 (1958)
- (4) G. V. D. Tiers, *J. Phys. Chem.*, in press.
- (5) H. S. Gutowsky, *J. Chem. Phys.*, in press.

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Preprint available: "Medium Effects in the Nuclear Magnetic Resonance Spectra of Liquids. IV. Nature of the Effects"  
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