

SUBSTITUTION AND SOLVENT EFFECTS ON C¹³-F¹⁹ COUPLING CONSTANTS

BY M. M. DHINGRA, G. GOVIL* AND C. L. KHETRAPAL

(Tata Institute of Fundamental Research, Colaba, Bombay-5)

(Communicated by Dr. B. V. Thosar, F.A.Sc.)

Received January 22, 1966

ABSTRACT

C¹³-F¹⁹ coupling constants have been measured in *p*-substituted fluorobenzenes. It has been shown that they vary linearly with Hammett's constant (σ_p). Further the change in the ionic character of the C-F bond in fluorobenzenes calculated on the basis of the change in the coupling constants agrees well with that calculated from F¹⁹ chemical shifts.

The coupling constant in trifluoroacetic acid has also been measured in various solvents at several concentrations. A remarkable solvent effect on these couplings has been discovered; this appears to be related to the dipole moment of the solvent.

INTRODUCTION

RECENTLY the study of C¹³-F¹⁹ coupling constants has attracted the attention of various workers (Govil, 1963; Lauterbur, 1962; Muller and Carr, 1963; Pople and Santry, 1964; Tiers, 1962). As a result of theoretical investigations of Pople and Santry (1964) and experimental work of Tiers (1962), it is known that the absolute sign of C¹³-F¹⁹ coupling constant for directly bonded nuclei is negative. Although the predominant contribution to these couplings still comes from the contact term (Pople and Santry, 1964), the experimental evidences show that the rules obeyed by C¹³-H couplings do not hold good for such couplings (Lauterbur, 1962; Govil, 1963; and Muller and Carr, 1963). There is no direct relation between the hybridisation of the carbon orbitals and the C¹³-F¹⁹ coupling constants. As has been pointed out by Govil (1963) and Muller and Carr (1963), changes in the ionic character of the C-F bond (which is 43% ionic on Pauling Scale, 1960) compared with those of the C-H bond (which is about 2% ionic) may produce significant changes in the C¹³-F¹⁹ couplings. The

* Present address: National Physical Laboratory, Teddington, England.

earlier work (Lauterbur, 1962; Tiers, 1962) shows that the electronegative groups attached to the carbon atoms generally increase the coupling when changes in other bond properties are not likely to be large.

The present work throws further light on the influence of ionic character on the C^{13} - F^{19} couplings.

EXPERIMENTAL

(1) *Chemicals* :

(a) All the samples used in this work are obtained from commercial sources.

(b) Purity of each sample was checked by determining boiling point.

(c) Nitrogen was bubbled through every solution to drive away any dissolved oxygen.

(2) *NMR Measurements* :

(a) Measurements of C^{13} - F^{19} coupling constants were made on varian spectrometer operating at 56.445 Mc/s frequency.

(b) C^{13} - F^{19} satellites were recorded on either side of the main band with signal to noise ratio of 3:1 for most of the compounds except for CF_3COOH in which case signal to noise ratio was larger (Fig. 1) because of the larger concentration of F^{19} nuclei attached to ^{13}C .

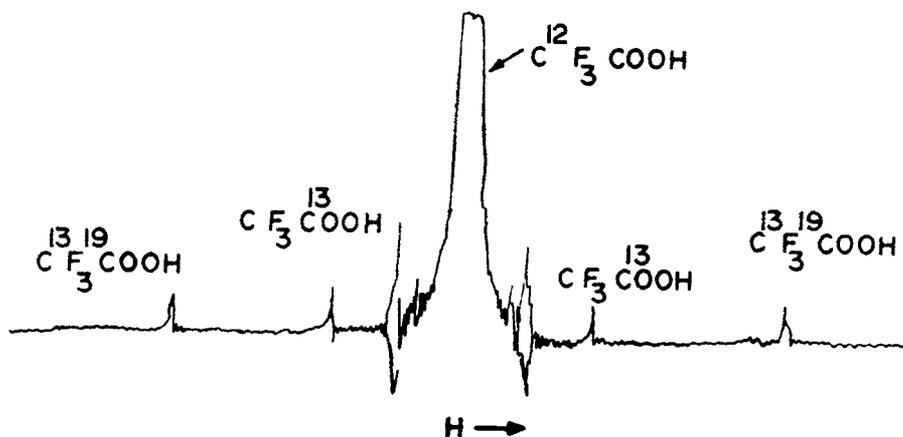


FIG. 1. F^{19} spectrum of pure CF_3COOH .

(c) Determination of C^{13} - F^{19} coupling was tried for *ortho*-, *meta*- and *para*-substituted fluorobenzenes. Since the four protons in the *ortho*- and

meta derivatives are placed unsymmetrically about the fluorine, the C^{13} - F^{19} bands were broadened out almost to noise level. Hence the coupling could be measured only for *para* fluorobenzenes.

(d) Since C^{13} - F^{19} bands in all the compounds except CF_3COOH are broadened out by the interaction with the four ring protons, the accuracy of measurement of the coupling constants cannot be claimed to be more than ± 5 c/s. For CF_3COOH , however, a much larger accuracy (about ± 0.5 c/s.) could be achieved upto a concentration of 0.2 mole fraction.

(e) Concentration dependence of the C^{13} - F^{19} couplings in CF_3COOH was studied in A.R. grade dioxane, CCl_4 , acetone and methyl cyanide.

RESULTS AND DISCUSSION

(1) Substitution Effects on $J_{C^{13}-F^{19}}$ in Monosubstituted Fluorobenzenes:

$J_{C^{13}-F^{19}}$ for *para* fluorobenzenes are given in Table I. It is evident from the table that the variations in the coupling constant are beyond experimental error. It may be noted that the electron withdrawing groups which have a tendency to increase the electronegativity of carbon attached to F^{19} and thus increase the covalent character of the C-F bond increase the coupling. In fact a linear relation has been observed between Hammett's constant (σ_p) and $J_{C^{13}-F^{19}}$ within experimental error (Fig. 2). These

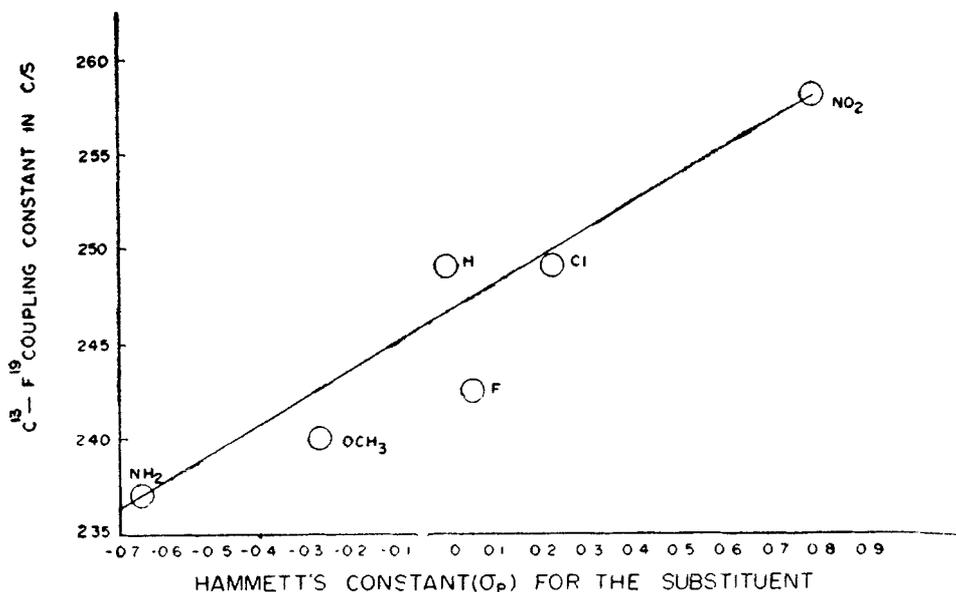


FIG. 2. Relation between Hammett's constant and C^{13} - F^{19} coupling constant,

TABLE I

C¹³-F¹⁹ coupling constants in para-substituted fluorobenzenes

Substituent	σ_p	$J_{C^{13}-F^{19}}$ in C/S	$\Delta \lambda F$ calculated from $J_{C^{13}-F^{19}}$	$\Delta \lambda F$ from the results of Wu and Dailey
-NO ₂	0.778	258	-0.010 ± 0.005	-0.003
-Cl	0.227	249	.000 ± 0.005	.005
-F	0.062	243	.007 ± 0.005	.010
-H	0.000	249
-OCH ₃	-0.268	240	0.12 ± 0.005	.017
-NH ₂	-0.660	237	0.014 ± 0.005	.021

results can be analysed on a semiempirical basis in terms of the theory of Pople and Santry (1964) for the coupling constants of directly bonded nuclei. Let λ and μ be the coefficients of the wave functions which determine the distribution of electrons between C and F. They can be explicitly expressed in terms of the ionic character parameter λ_F (Wu and Dailey, 1964) as follows:

$$\lambda = (1 + \lambda_F)^{\frac{1}{2}}; \quad \mu = (1 - \lambda_F)^{\frac{1}{2}}$$

The dominant contribution to $J_{C^{13}-F^{19}}$ arises from a negative term proportional to $\lambda^2 \mu^2 x^2 / (\epsilon_2 - \epsilon_3)$ with a smaller contribution from the term proportional to $\lambda^2 x^2 / (\epsilon_1 - \epsilon_3)$, where x is a positive parameter which determines the mixing of the orbital function [SF] with others and $\epsilon_i - \epsilon_j$ is the excitation energy ${}^3\Delta E_j - i$. If the latter contribution and variations in $\epsilon_2 - \epsilon_3$ and x are neglected in different substituted fluorobenzenes, $J_{C^{13}-F^{19}}$ is proportional to $\lambda^2 \mu^2$ or $(1 - \lambda_F^2)$. For two different fluorobenzenes x and y , the corresponding coupling constants are related by:

$$\frac{J_x}{J_y} = \frac{1 - (\lambda_F^2)_x}{1 - (\lambda_F^2)_y}$$

Taking $\lambda_F = 0.75$ for unsubstituted fluorobenzene and $J_{C^{13}-F^{19}} = 249$ c/s., one can derive the following relation:

$$\Delta\lambda_F = -1.17 \times 10^{-3} \Delta J$$

where $\Delta\lambda_F$ is the change in ionic character of C-F bond in the substituted fluorobenzene from that in the unsubstituted one and ΔJ the difference in the C¹³-F¹⁹ coupling constants in the two compounds. The changes in the ionic character of the C-F bond calculated from the above formula using values of ΔJ are given in Table I along with the results of Wu and Dailey obtained from F¹⁹ chemical shifts. In view of the approximations involved in either method, the agreement between the two seems to be quite satisfactory.

(2) *Solvent Effects on $J_{C^{13}-F^{19}}$ in Trifluoroacetic Acid:*

Trifluoroacetic acid gives sharp C¹³-F¹⁹ bands separated by 283.2 c/s. The value has been found to increase with dilution in all the solvents studied except CCl₄ which has no dipole moment. Solvent effect is maximum in methyl cyanide for which the dipole moment is also maximum. A plot of the mole fraction of acid against $J_{C^{13}-F^{19}}$ is shown in Fig. 3.

A polar solvent can affect the solute molecules through the following possible mechanisms (Moeller, T., 1960).

- (1) Dipole-dipole attractions leading to alignments of the dipole of the solute and the solvent.
- (2) Ion dipole and ion-induced dipole attractions causing the solvation of the ions of the solute.
- (3) Formation of hydrogen bonds between the solute and the solvent.
- (4) Dipole-induced-dipole attractions: The solvent may induce dipole in a nonpolar solute and then attract it.

In the case of trifluoroacetic acid, the solvent dipoles can interact with the solute by aligning themselves either with the C-F bonds or with the -COOH bonds. They can also change in a remarkable way the hydrogen bonding in pure trifluoroacetic acid. All these effects change the ionic character of the C-F bond which in turn is responsible for the changes in $J_{C^{13}-F^{19}}$ values. Since in this case several factors are responsible for changing the ionic character of the C-F bonds, it is difficult to interpret the results explicitly. A detailed study on simpler molecules which do not involve hydrogen bonding and where the dipolar attraction takes place only at one end may throw further light on this problem. Such work is in progress.

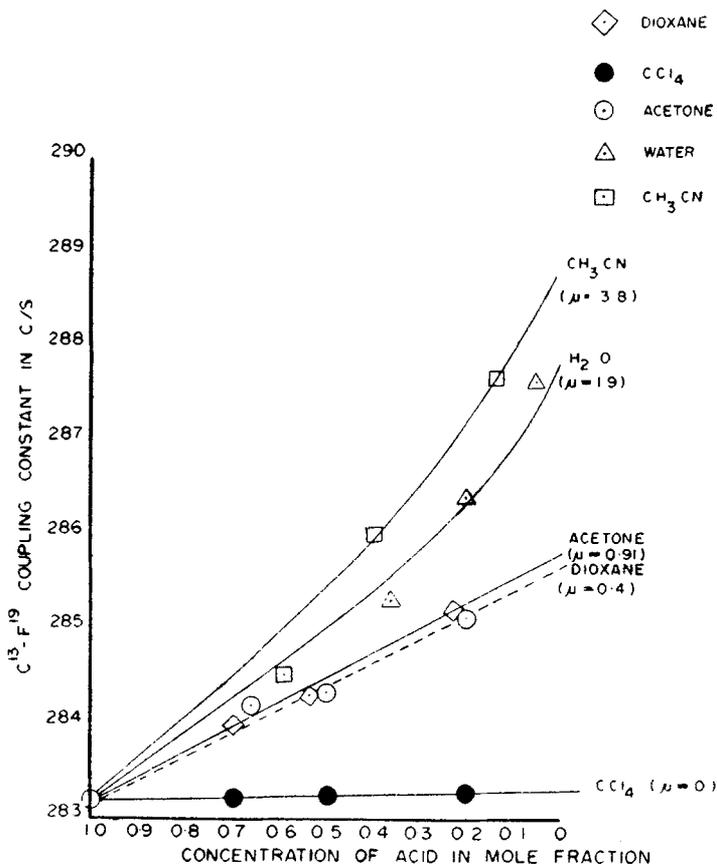


FIG. 3. Effect of the solvent on the $C^{13}-F^{19}$ coupling constant in CF_3COOH .

ACKNOWLEDGEMENTS

The authors are grateful to Dr. C. R. Kanekar and (the late) Professor S. S. Dharmatti for valuable discussions.

REFERENCES

- Govil, G. .. *Ph.D. Thesis*, Bombay University, 1963.
- Lauterbur, P. C. .. *Determination of Organic Structures by Physical Methods*, Vol. 2, Academic Press, New York and London, 1962, p. 505.
- Moeller, T. .. *Inorganic Chemistry*, Asia Publishing House, 1960, p. 186.
- Muller, N. and Carr, D. T. *J. Phys. Chem.*, 1963, **67**, 112.
- Pauling, L. .. *Nature of Chemical Bond*, 3rd edition, Cornell University Press, 1960, pp. 98, 240.
- Pople, J. A. and Santry, D. P. *Mol. Phys.*, 1964, **8**, 1.
- Tiers, G. V. D. .. *J. Am. Chem. Soc.*, 1962, **84**, 3972.
- Wu, T. K. and Dailey, B. P. *J. Chem. Phys.*, 1964, **41**, 2796.