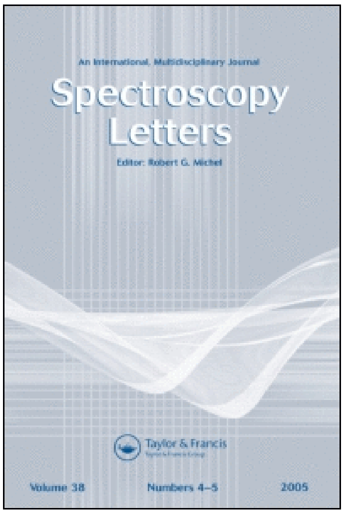

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SOLVENT DEPENDENCE OF H-F COUPLING PARAMETERS IN FLUOROBENZENE

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Solvent dependence of NMR spectral parameters has been the object of considerable interest in recent years (see Ref. 1 for a brief summary). More recently attention has been devoted to the solvent dependence of NMR parameters in fluorine-containing compounds. In their investigation of fluorobenzene, Mohanty and Venkateswarlu observed the effect of solvents on the proton and fluorine chemical shifts, but did not report any dependence of the H-H or H-F couplings on the solvent medium.[2] For 1,2-dichlorofluoroethylene Bell and Danyluk found a linear correlation between the directly bonded ^{13}C-H and ^{13}C-F couplings and the H-F couplings.[3] These results, along with linear correlations between the ^{13}C-H (or ^{13}C-F) coupling and the proton (or fluorine) chemical shift, led to the inference that the medium effect acts to change the coupling parameters and shieldings by a similar mechanism.

Hutton and Schaefer have reported the results of a solvent study on 1-chloro-1-fluoroethylene.[1] They found that the cis H-F coupling increases in a roughly linear fashion with the square root of the dielectric constant of the solvent. In another study, Hutton, *et al*, reported changes as large as 0.85

Hz for the ortho H-F coupling in 3-chloro-4,6-dinitrofluorobenzene with changes in solvent.[4] They noted an algebraic increase of J_o^{HF} and of the sum, $J_o^{HF} + J_m^{HF}$, with increasing dielectric constant of the medium for a series of substituted fluorobenzenes.

Recently, Castellano, et al, reported the fluorobenzene parameters for the neat liquid and for solutions in CCl_4 and CCl_3CF_3.[5] The observed variations were no larger than 0.10 Hz and 0.20 Hz in the H-H couplings and the H-F couplings, respectively.

In the recent analysis of fluorobenzene conducted in this laboratory, however, significant changes were observed in the H-F couplings at several concentrations in TMS, [6] which suggested the desirability of an extension of the study to include a series of solvents. The proton spectra were obtained at 60 MHz for ten mole per cent solutions of the compound in seven solvents. For each sample, the observed frequencies were obtained as averages of three forward and three reverse sweeps. In no case was the root-mean-square deviation between experimental and calculated frequencies greater than 0.06 Hz. The probable errors in the parameter sets are conservatively estimated to be no greater than 0.05 Hz. The results of these analyses are collected in Table I.

Variations of up to 0.80 Hz were observed in the H-F couplings, the largest change being in J_o^{HF} Variations of this magnitude are considerably larger than the estimated uncertainty in the parameters. There is a generally monotonic relationship between J_o^{HF} and the square root of the dielectric constant of the solvent, except with N-methylpropionamide as solvent.

Table I. Solvent Effects on the NMR Parameters in Fluorobenzene

Parameter[a]	TMS	Acetone	Methanol	DMF	Acetonitrile	N-methyl-propionamide	CCl_4
o[b]	-415.27	-424.77	-422.80	-428.68	-424.93	-423.75	-418.22
m	-430.96	-442.25	-440.32	-444.50	-441.97	-440.43	-434.76
p	-418.99	-429.28	-427.83	-431.24	-429.77	-427.70	-422.24
$J_{12}=J_{45}$[c]	8.35	8.37	8.38	8.38	8.40	8.36	8.37
$J_{13}=J_{35}$	1.03	1.04	1.03	1.11	1.03	1.11	1.03
$J_{14}=J_{25}$	0.40	0.42	0.44	0.43	0.42	0.36	0.40
J_{15}	2.58	2.75	2.75	2.62	2.80	2.64	2.59
$J_{23}=J_{34}$	7.50	7.46	7.46	7.46	7.48	7.49	7.50
J_{24}	1.76	1.84	1.87	1.78	1.86	1.71	1.72
$J_{16}=J_{56}=J_o^{HF}$	8.90	9.31	9.28	9.38	9.44	9.02	8.64
$J_{26}=J_{46}=J_m^{HF}$	5.57	5.79	5.76	5.79	5.83	5.82	5.68
$J_{36}=J_p^{HF}$	0.20	0.34	0.33	0.51	0.39	0.24	0.29
o- m	15.69	17.48	17.52	15.82	17.04	16.68	16.54
o- p	3.72	4.51	5.03	2.56	4.84	3.95	4.02

[a] Numbering begins with proton adjacent to fluorine. [b] At 60 MHz, relative to TMS, in Hz. [c] In Hz.

The H-H couplings showed no significant dependence on solvent except in the case of J_{15}, the meta H-H coupling across the fluorine substituent, which varied by 0.22 Hz. In a recent study of a series of monosubstituted benzenes, the substituent effect was shown to be the greatest on this meta H-H coupling across the substituent.[7] Since the greatest effects of solvent medium occur for couplings involving the F nucleus and the two adjacent protons, it seems reasonable to suppose at least tentatively, that the medium effect is associated with the substituent. The possibility that other mechanisms may be involved will require further study.

The results described here indicate that solvent effects cannot be disregarded in the analysis and interpretation of the NMR spectra of fluorinated aromatic compounds.

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