Participation of Hydrogen-bonded Donor Molecules in Vicinal H–F Spin–Spin Coupling

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Summary The participation of hydrogen-bonded donor molecules in H–F spin–spin coupling is proposed to explain the drastic increase of the vicinal H–F coupling constants in $CCl_3COOCH_2CF_3$ and $CF_3COOCH_2CF_3$ in good electron-donor solvents.

IN strongly basic solvents the ^1H n.m.r. spectra of the esters $CCl_3COOCH_2CF_3$ (I) and $CF_3COOCH_2CF_3$ (II) exhibit either a quartet at lower field to that in n-heptane, consistent with the formation of a simple hydrogen-bonded complex, or a quartet at higher field, or both, with vicinal H–F coupling constants as indicated in the Table. Relative to that in n-heptane, the H–F coupling constant increases by more than 0·50 Hz in the low field quartet and by 1·5 Hz in the high field quartet. Similar coupling constants have been obtained in about 12 other solvents and solvent mixtures and these results will be presented subsequently. The esters were recovered unchanged from the solvents and solvent mixtures.

TABLE. *Vicinal* H–F *coupling constants and chemical shifts*[a] *of the methylene protons of* $CCl_3COOCH_2CF_3$ *and* $CF_3COOCH_2CF_3$ *in various solvents*[b]

Solvent	Mol ratio	$CCl_3COOCH_2CF_3$		Peak area ratio	CF_3COOCH_2CF		Peak area ratio
		δ (p.p.m.)	*J* (Hz)		δ (p.p.m.)	*J* (Hz)	
n-Heptane		4·53	7·83		4·47	7·79	
Pyridine		4·18	9·35		5·21	8·37	1
					4·18	9·28	3
Pyridine/CCl_4	1:1	4·97	8·19	3	4·97	8·18	5
		3·98	9·17	1	3·97	9·21	3
Acetone		5·10	8·38		3·97	9·26	

[a] Internal reference TMS. [b] 5% *W/W* solutions at 34 °C.

The i.r. spectrum of a dilute solution of (I) or (II) in pyridine shows two absorption bands at 6·12 and 6·73 μm, which were also observed for the reaction of pyridine with carboxylic acids, and were attributed to hydrogen-bonded ion pair formation of the pyridine.[1] The high field quartets observed in the strongly basic solvents of high dielectric constant are therefore attributed to hydrogen-bonded ion pair formation, this tentative interpretation being the most probable. The ion pair hydrogen bonding interaction has been shown to be much stronger than the simple hydrogen bonding interaction.[2]

When hydrogen bonding involves the H vicinal to the F nuclei, the donor site and the fluorine nuclei would be held in close proximity and the unshared electrons of the donor are expected to provide an additional pathway for spin–spin coupling between the vicinal H and F nuclei. Although the nitrogen donor has only one lone pair, the large range of the lone-pair electron distribution should facilitate this spin coupling mechanism. This H–F spin–spin coupling through intermolecular nonbonded interactions should be more effective when a stronger hydrogen bond is formed in the case of ion pair formation, giving rise to the more drastic enhancement of the vicinal H–F couplings observed for (I) and (II). Also, since the electronic structure of the trifluoroethyl fragment is altered by the presence of a partial negative charge on the methylene carbon in the hydrogen-bonded ion pair, it is possible that a part, possibly a major part of the increase in the H–F spin coupling is bond-mediated, and this is being investigated. The H–F spin–spin coupling through intra-molecular nonbonded interactions has been amply substantiated.[3]

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