An Anomalously Large Nuclear Overhauser Effect in the ^{13}C N.M.R. Spectra of Strongly Hydrogen-bonded Systems

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Summary The carboxy carbons of neat liquid carboxylic acids display an anomalously large nuclear Overhauser effect that is further enhanced by the addition of potassium fluoride which is capable of forming strong hydrogen bonds between the fluoride anion and the acid hydroxy group.

WORKERS in the field of ^{13}C n.m.r. spectroscopy are accustomed to low intensities for carbonyl and carboxy carbons as a result of long relaxation times and the lack of a significant nuclear Overhauser effect (n.O.e.) in the absence of directly bonded hydrogens. As part of our continuing study of strong hydrogen-bonding to fluoride ion,[1] we have examined the ^{13}C n.m.r. spectra of a series of neat liquid carboxylic acids and solutions of potassium fluoride in these acids. Compared with the carbonyl carbon of acetone or the carboxylate carbon of acetic anhydride which displayed no n.O.e. enhancement under the same conditions, all acid systems under study showed a significant n.O.e. enhancement (n.O.e. $= 1 + \eta$, where 1·98 is the theoretical maximum η for any carbon) which was increased on the addition of potassium fluoride (Table). Formic acid, which contains

TABLE

Acid	$^{13}CO(OH)$		$^{13}CH_2CO_2H$		$^{13}CH_2CH_2CO_2H$		$^{13}CH_3$	
	T_1/s[a]	η_c	T_1/s	η_c	T_1/s	η_c	T_1/s	η_c
Formic	6·6	2·0	—	—	—	—	—	—
Formic + KF[b]	0·54	1·4	—	—	—	—	—	—
Acetic	21·1	0·7	—	—	—	—	7·1	1·2
Acetic + KF	2·1	1·1	—	—	—	—	0·7	1·1
Propionic	25·1	0·4	5·1	1·7	—	—	4·9	1·4
Propionic + KF	2·8	1·9	0·5	1·1	—	—	2·1	1·4
n-Butyric	13·2	0·9	2·9	1·7	4·3	1·8	5·1	1·7
n-Butyric + KF	2·1	1·3	0·3	1·0	0·7	1·2	1·5	1·4

[a] ^{13}C spectra were obtained on a Bruker WP-60 FT n.m.r. spectrometer at 15·08 MHz using modified Bruker disk based T_1 programs.
[b] In all cases a saturated solution of KF in the neat acid was used.

a directly bonded C–H hydrogen, was the one exception in that it showed a full n.O.e. which decreased on addition of fluoride. The methylene and methyl carbons in the acids showed reduced n.O.e.'s on addition of fluoride while all T_1's, including carboxy, methyl, and methylene are also reduced by an order of magnitude under the same conditions as might be expected for solutions of increasing viscosity. In a recent report,[2] Couperus *et al.* reported the ^{13}C n.m.r. spectra of a series of carboxylic acids without commenting on the n.O.e.'s but for the ester, methyl heptanoate, they reported $\eta = 1{\cdot}3$ without comment. Levy *et al.* have also reported significant n.O.e. factors for carbons not directly bonded to hydrogens in polymethacrylates[3] and in some aromatics.[4] In the case of phenol, Levy observed a large n.O.e. ($\eta = 1{\cdot}3$) for the hydroxy-carrying carbon and suggested that the OH proton and the two *ortho* protons were responsible for the ^{13}C–^{1}H dipole–dipole relaxation of that carbon.[4]

While contributions from the two hydroxy protons in the acid H-bonded dimers might explain the significant n.O.e.'s of the carboxy carbons in the neat carboxylic acids as compared to the essentially zero n.O.e. in acetic anhydride, we must conclude that the increasingly large η values for the fluoride–acid solutions arise from the very strong hydrogen-bonding that occurs between the fluoride ion and the acid hydroxy group in these systems.[5]†

It would seem therefore, that the presence and strength of hydrogen-bonding involving functional groups bonded to carbons that possess no directly bonded hydrogens may play an important role in determining the n.O.e's. of those carbons. It may be possible to take advantage of this phenomenon by deliberately strengthening the hydrogen-bonding in such systems so as to enhance the intensity of otherwise weak carbon-13 signals.

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† A referee suggests that if two or more carboxylic acid molecules hydrogen-bond to a single F^-, a long axis may be created for this complex resulting in very anisotropic molecular reorientation. The slowing of the modulation of the C–H dipolar interactions would shorten T_1's and increase the n.O.e. This situation is somewhat analogous to the ^{13}C resonance of C-4 in pyridine hydrogen-bonded to alcohols (I. D. Campbell, R. Freeman, and D. L. Turner, *J. Magnetic Resonance*, 1975, **20**, 172), and is consistent with the known MF(carboxylic acid)$_2$ stoicheiometry of the solid hydrogen-bonded solvates of aliphatic carboxylic acids, but not with their i.r. spectra (J. Emsley and O. P. A. Hoyte, *J.C.S. Dalton*, 1976, 2214).

[1] See for examples: J. H. Clark and J. M. Miller, *J. Amer. Chem. Soc.*, 1977, **99**, 498; *J.C.S. Perkin I*, 1977, 1743; *ibid.*, 1978, 941; *J.C.S. Chem. Comm.*, 1978, 466.

[2] P. A. Couperus, A. D. H. Clague, and J. P. C. M. van Dongen, *Org. Magnetic Resonance*, 1978, **11**, 590.

[3] G. C. Levy, D. E. Axelson, R. Schwartz, and J. Hochmann, *J. Amer. Chem. Soc.*, 1978, **100**, 410.

[4] G. C. Levy, J. D. Cargioli, and F. A. L. Anet, *J. Amer. Chem. Soc.*, 1973, **95**, 1527.

[5] J. H. Clark and J. Emsley, *J.C.S. Dalton*, 1973, 2154; J. Emsley, O. P. A. Hoyte, and R. E. Overill, *J.C.S. Perkin II*, 1977, 2079.