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SPECIFITY OF HIGH RESOLUTION ^{1}H AND ^{13}C NMR SPECTRA OF SOLID FATTY CARBOXYLIC ACIDS

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Abstract High resolution ^{1}H and ^{13}C NMR spectra of fatty carboxylic acids from C_{15} to C_{19} have been studied at various temperatures. The existence of narrow NMR lines has been found for the studied acids in the solid phase. The new line at 4.1 ppm in the ^{1}H NMR spectra of odd-carbon acids in the solid phase has been observed and assigned to the signal of the monomers.

High resolution NMR studies of organic solids reveal the very interesting fact that fairly sharp NMR lines occur in the spectra of plastic crystals where extensive molecular self-diffusion is allowed.[1-3] The plastic crystal phase is normally found in the case of bulky molecular systems,[4] but in the molecules of solid long chain compounds, parafins and saturated fatty acids, considerable freedom of motion is to be expected. The present paper investigates the high resolution ^{1}H and ^{13}C NMR spectra of fatty carboxylic acids from C_{15} to C_{19} at various temperatures.

The spectra were recorded at 90.02 MHz (^{1}H) and 22.64 MHz (^{13}C) on a Fourier transform Bruker CXP 100 spectrometer employing the broad-band ^{1}H - ^{13}C decoupling. The chemical shifts were measured relative to the line of $(CH_2)_n$ group, chemical shift of which was found to be temperature independent, and converted to the delta scale. The temperature of samples was stabilized to within ± 0.5 K by means of the B-ST 100/700 c temperature control unit.

Commercially obtained fatty acids (99.5 %) were carefully purified by vacuum sublimation. Note that the degree of purification was found to have no effect on the spectra.

The existence of narrow ^{1}H and ^{13}C NMR lines has been found for the studied acids in the solid phase (Fig.1). The line-widths vary from about 15 Hz to 70 Hz with the temperature change. However, the temperature dependences of the chemical shift of the carboxyl proton and carbonyl carbon (Fig.2) are essentially different from the analogous ones for plastic pivalic acid,[5,6] where an increase of chemical shift with decreasing temperature has been found. All the acids included in the present study show dependences of same type as heptadecanoic acid (Fig.2). The variation of chemical shift of the carboxyl proton and the carbonyl carbon for a liquid acid above the melting point is caused by a monomer-self-associate (cyclic dimer, open chain n-mer) exchange process and by the temperature dependence of the chemical shift of the associates.[7] The carboxyl proton line for the solid acids studied cannot be assigned to the signal of pure cyclic

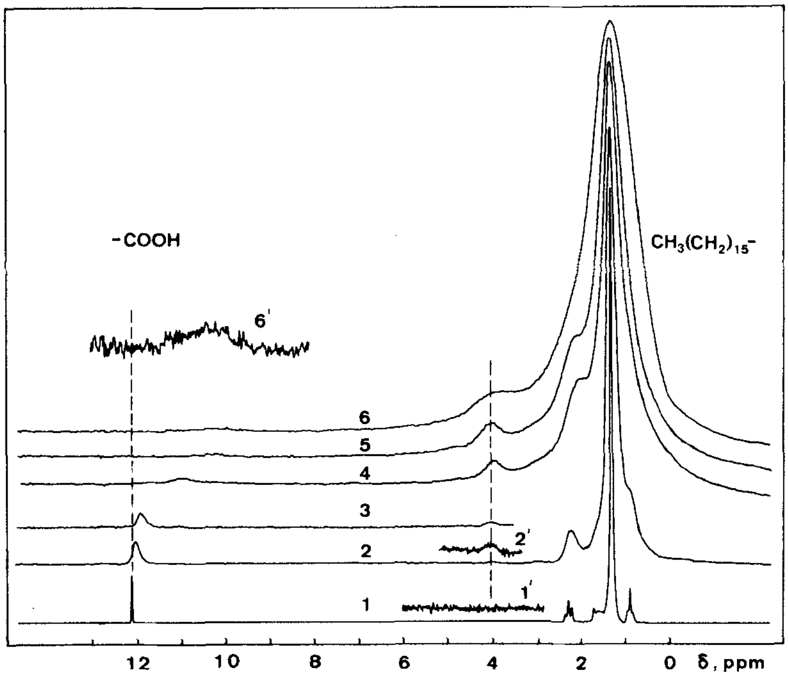

FIGURE 1. The ^1H NMR spectra of heptadecanoic acid (T_m = 334.4 K) at different temperatures: (1) 336, (2) 331, (3) 330, (4) 320, (5) 313, and (6) 313 K (without spinning of sample); (1'), (2'), and (6') - with increased amplitude of the vertical display. The spectra are recorded after accumulation of 50 - 1000 transiets at the same height of the highest peak.

dimers, because of a sharp decrease of its chemical shift with decreasing temperature (Fig.2). Note that the values of chemical shift for the solid

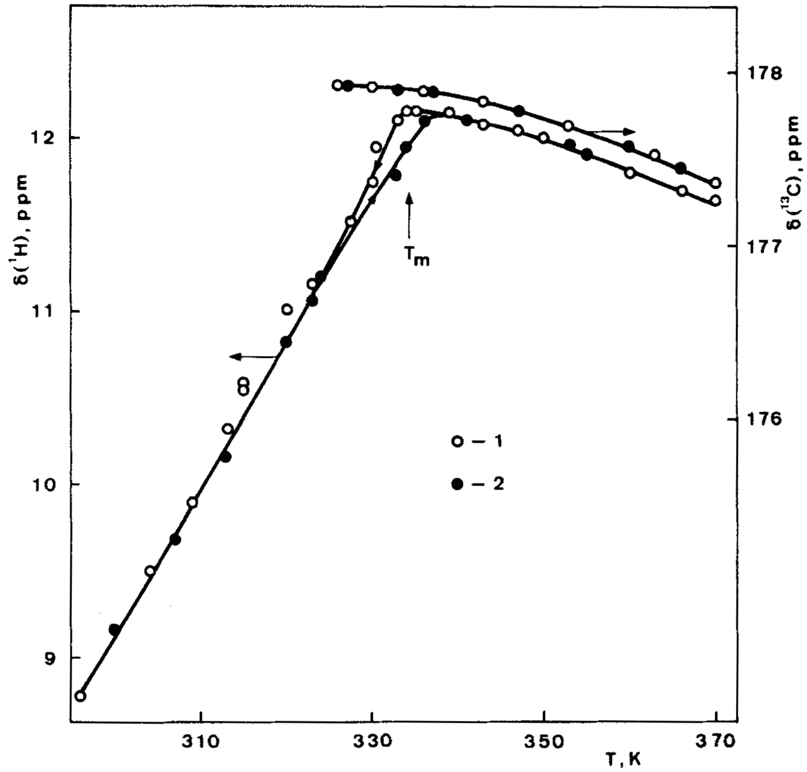

FIGURE 2. Chemical shift of carboxyl proton and carbonyl carbon of heptadecanoic acid as a function of decreasing (1) and increasing (2) temperature.

acids have been found to be stable during a period of measurement of about 10 hours. The direction of temperature change has no effect on the chemical shifts with the exception of a small divergence near the melting point (Fig.2).

The other unexpected fact is the appearance of a new line at 4.1 ppm in the ^1H spectra of odd-

-carbon acids in the solid phase (Fig.1). As the temperature decreases, the intensity of this line increases while the intensity of the carboxyl proton line decreases correspondingly. That result allows the assumption that the observed new line, which is absent for the acids in the liquid phase (Fig.1), may be assigned to the carboxyl proton and, probably, results from the presence of the monomers. The chemical shift of that line is quite close to the average value of the chemical shift for aliphatic acid monomers 5 ± 1 ppm, as calculated from the concentration dependences,[7,8] or temperature dependences of chemical shift for acid in the vapour phase;[9] direct measurement is impossible in the liquid phase.

The existence of the line at 4.1 ppm for only odd-carbon acids appears to be a peculiar result, however differences in crystalline structures[10] and IR spectra[11] have been found for odd and even-carbon acids previously.

The line of the carbonyl carbon has been observed in a narrower temperature range than the carboxyl proton line, because of extensive intensity decreases. The character of temperature dependence of the chemical shift of the carbonyl carbon (Fig.2) is different from the analogous one for the carboxyl proton, and no additional line has been found, inspite of using a large number of transiets (50000) and a different interval between the pulses (3 - 50 sec).

The experimental data obtained may be significant in elucidating the nature of the dynamics of crystallization of the fatty acids.

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