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Specific Changes in the High Resolution ^{1}H and ^{13}C NMR Spectra of Triethyl- and Trimethylacetic Acids at the Liquid-Solid Phase Transition

Liudvikas L. Kimtys [a]
[a] Department of General Physics and Spectroscopy, Vilnius V. Kapsukas State University, Vilnius, SSR, Lithuanian, 232734
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SPECIFIC CHANGES IN THE HIGH RESOLUTION ^{1}H AND ^{13}C NMR SPECTRA OF TRIETHYL- AND TRIMETHYLACETIC ACIDS AT THE LIQUID-SOLID PHASE TRANSITION

Liudvikas L. KIMTYS

Department of General Physics and Spectroscopy, Vilnius V.Kapsukas State University, 232734 Vilnius, Lithuanian SSR

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Abstract High resolution ^{1}H and ^{13}C NMR spectra of triethylacetic and trimethylacetic (pivalic) acids have been studied at different temperatures. A sharp decrease in the chemical shift of the carboxyl proton and hysteresis of chemical shift have been found for triethylacetic acid at the liquid-solid phase transition. A new line at 5.3 ppm has been observed for both acids in the brittle crystal phase and assigned to the signal of the non-hydrogen-bonded carboxyl proton. The difference of experimental data for the studied acids indicates, that triethylacetic acid does not exist in the plastic crystal phase.

The plastic crystal phase is normally found in the case of bulky molecular systems,[1] for which the entropy of fusion is very small. Trimethylacetic acid (TA) is one of the most studied plastic crystals, and it is particularly suitable for high resolution NMR

experiments.[2-6] The absence of high resolution ^{1}H NMR lines for other aliphatic derivatives of acetic acid less bulky than TA has been found.[7] The changes in the NMR spectra at the liquid-solid phase transition of the carboxylic acids more bulky than TA have not been studied. The present paper investigates the temperature dependence of the high resolution ^{1}H and ^{13}C NMR spectra of triethylacetic acid (TE) and compares this with the analogous data for TA.

The spectra were recorded at 90.02 MHz (^{1}H) and 22.64 MHz (^{13}C) on a Fourier transform Bruker CXP 100 spectrometer; experimental details were the same as in Ref.6,8. Commercially obtained TE (99 %) was purified additionally by vacuum sublimation and azeotropic distillation. Monocrystals grown in a vacuum at 0.1 mm Hg were used in preparing the spectral samples. The same TA as in Ref.6 was used for the continued ^{1}H NMR study.[4]

Figure 1 presents the ^{1}H NMR spectra of TE at different temperatures as well as the temperature dependence of the chemical shifts of carboxyl proton and carbonyl carbon. The existence of narrow ^{1}H and ^{13}C NMR lines has been found for TE in the solid phase (Fig.1a). The line-widths vary from about 30 Hz to 80 Hz with the temperature change. While the change in the spectra of TE at the liquid-solid phase transition is very similar to that found for the odd-carbon fatty carboxylic acids,[8] it is very different from the case of TA (Fig.2). A comparison of the temperature dependences of the chemical shift of the carboxyl proton of TE (Fig.1b) and of TA (Fig.2b) indicates, that the character of phase transition at the melting point for TE is similar to

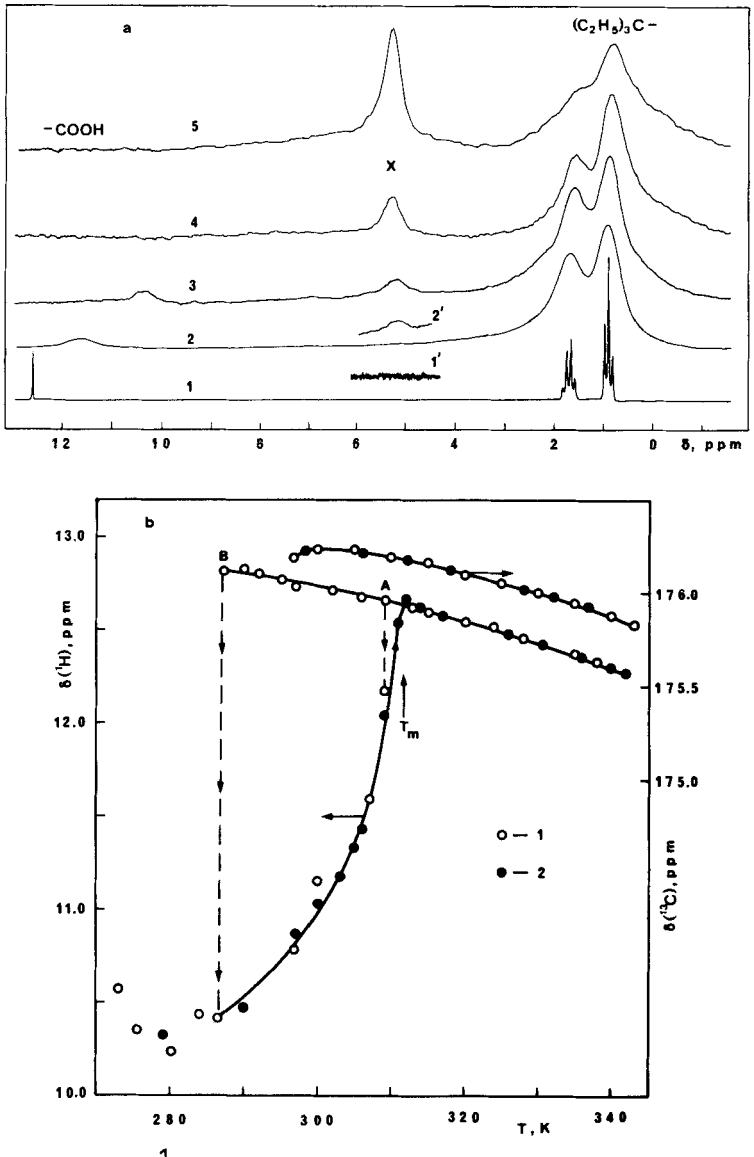

FIGURE 1. The ^{1}H NMR spectra (a) of TE (T_m=312 K) at: (1) 315, (2) 295, (3) 284, (4) 273, (5) 250 K, and (b) the chemical shifts of carboxyl proton and carbonyl carbon as a function of decreasing (1) and increasing (2) temperature (A-B - supercooled liquid). The spectra are recorded after accumulation of 10 - 500 transiets at the same height of the highest peak.

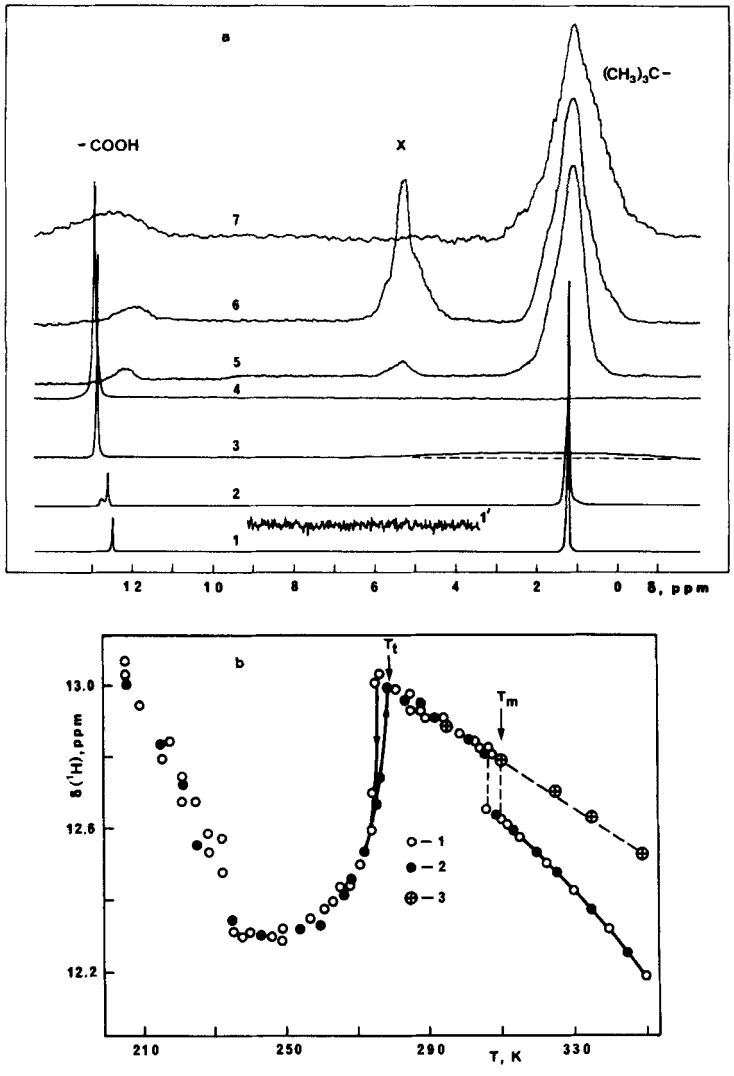

FIGURE 2. The ^{1}H NMR spectra (a) of TA (T_m=309.6 K, T_t=280 K) at: (1) 327, (2) 309, (3) 300, (4) 295, (5) 265, (6) 240, (7) 225 K, and (b) chemical shift of carboxyl proton as a function of decreasing (1) and increasing (2) temperature; (3) the chemical shifts of the cyclic dimers.[9] The spectra are recorded after accumulation of 10 - 500 transiets at the same height of the highest peak.

the plastic-brittle crystal phase transition of TA at T_t. Consequently, TE, unlike TA, does not show a plastic crystal phase.

A sharp decrease in the chemical shift of the carboxyl proton of TE at $T < T_m$ (Fig.1b) and of TA at $T < T_t$ (Fig.2b), and the hysteresis of chemical shift have been found. A new line at 5.3 ppm, which is absent in the spectra of liquid TE and TA, has been observed (Fig.1a and 2a). As the temperature decreases, the intensity of this line increases while the intensity of the carboxyl proton line decreases correspondingly. This fact allows the assignment of that line to the carboxyl proton. This conclusion accords with the absence of such a line for deuterated TA ($(CH_3)_3CCOOD$, 99.3 %). The chemical shift of the observed line is comparable with the value of the chemical shift of the monomers 5.2 ± 0.6 ppm calculated from the concentration dependences of TA in cyclohexane.[9] While it is likely that this line is due to the presence of monomers, it may also be explained as being the signal of the end-proton of the carboxyl group of the open-chain polymers, the chemical shift of which is expected to be the same as for the monomers.

The ^1H NMR lines of the ethyl group of TE at the liquid-solid phase transition show no sudden change but only broadening (Fig.1a). Extensive broadening is found for the methyl line of TA at the liquid-plastic crystal phase transition and narrowering is observed at the plastic-brittle crystal phase transition (Fig.2a).

The high resolution ^{13}C NMR spectra of solid TE have been observed in a narrower temperature range

than the proton, because of extensive intensity decreases. The character of temperature dependence of the chemical shift of the carbonyl carbon of TE (Fig.1b) is different from the analogous one for the carboxyl proton. No change in the chemical shift of the ethyl carbons of TE, only broadening of the lines to about 80 Hz, has been observed at the phase transition. These facts are essentially different from the results for TA.[6]

The obtained experimental high resolution NMR data for the studied acids at the phase transitions indicate the great potential of NMR for such studies.

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