^{13}C-NMR Chemical Shift Anisotropy of Acetylene

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The ^{13}C-NMR spectrum at 22.63 MHz and the PMR spectrum at 90 MHz of ^{13}C enriched acetylene oriented in a nematic liquid crystal were measured by the pulsed Fourier technique and analysed. From the chemical shift difference between the nematic and the isotropic phase the anisotropy of the ^{13}C shielding tensor of acetylene $\Delta\sigma = +253 \pm 17$ ppm was calculated.

Chemical shifts of organic compounds provide valuable information on the structural features of the molecules. However, in isotropic solution only the average shielding can be measured due to the rapid molecular tumbling motion. It is to be expected that measurement of the complete shielding tensor should yield considerably more information, since the elements of the shielding tensor will be differently influenced by changes in the molecular structure.

Very recently, Waugh et al. [1, 2] have demonstrated that proton-enhanced nuclear induction spectroscopy of solids can be successfully applied to the determination of the elements of ^{13}C chemical shielding tensors.

Another frequently used method for the determination of shielding anisotropies is to measure the chemical shift difference between the signals of molecules dissolved in the isotropic and in the nematic phase of a liquid crystal [3]. In the latter, the preferential orientation of the solutes will affect the chemical shifts. This approach has been used in numerous cases for the calculation of chemical shift anisotropies of ^{1}H and ^{19}F nuclei [4, 5]. However, only few measurements of ^{13}C anisotropies obtatined by this technique seem to have been published [6–8].

In a previous PMR study we have shown that acetylene in contrast to several substituted acetylenes was preferentially oriented perpendicular to the H_0 direction in nematic 4,4-di-n-hexyloxy-azoxybenzene [9]. This was later confirmed by SPIESECKE [10] for a different liquid crystal from a PMR study of ^{13}C enriched acetylene. In this note we report on the determination of $\Delta\sigma(^{13}\mathrm{C})$ of ^{13}C enriched acetylene. The experimental details were similar to those used previously for the measurement of $\Delta\sigma(^{13}\mathrm{C})$ of benzene-1-^{13}C [8]. A 5 mm sample tube with acetylene (ca. 7 atm pressure) consisting of roughly 45% of molecules with one ^{13}C, 40% with two and 15% with ^{12}C only, dissolved in N-(p-ethoxybenzylidene)-p-n-butylaniline (EBBA) was used (l. c. [11]). For the ^{13}C measurements, the tube was enclosed in a 10mm o. d. tube containing D_2O (D-lock). The reduced filling factor had to be compensated by a corresponding increase in the accumulation time. The PMR-spectrum shown in Fig. 1 (top) was obtained in a 5 mm insert without lock. No line splittings or field drift were detected after the accumulation time of 2.2 minutes. The spectra were taken on a Bruker HX90/15 FT-spectrometer equipped with a Nicolet 1083 computer. The sample temperatures were 25 °C (nematic) and roughly 70 °C (isotropic).

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Results

The two symmetrical partial spectra of ^{13}C and ^{1}H in the nematic phase are shown in the Figure. The center of gravity of the ^{13}C part was arbitrarily chosen as 5000 Hz. The lines can easily be assigned to the different isotopical molecular species as indicated. The ^{13}C part of the 4-spin spectrum was first analysed with the aid of the iterative computer program LAOCOONOR. With fixed values of

$J_{HH} = 9.6$ Hz, $J_{CH} = 249.0$ Hz and $J_{CCH} = 49.15$ Hz,

a slightly changed value for $J_{CC} = 169.6 \pm 0.9$ Hz (instead of 171.5 Hz) and the following direct couplings were iteratively obtained (RMS = 0.9 Hz):

$D_{HH} = 182.6 \pm 0.3$ Hz, $D_{CCH} = 143.3 \pm 0.3$ Hz,
$D_{CH} = 1340.9 \pm 0.3$ Hz, $D_{CC} = 229.4 \pm 0.3$ Hz.

Iteration of the ^{1}H part (RMS = 0.3 Hz) with J_{CH}, J_{CCH} and J_{CC} fixed gave $J_{HH} = 9.5 \pm 0.3$ Hz and a set of 4 direct couplings which were all greater than the above given ones by a factor of 1.010 ± 0.005 indicating a small increase in the degree of orientation.

With an assumed C,C-distance of $r_0 = 1.207$ Å the degree of order of the molecular axis was calculated from the given value of D_{CC}:

$$S = -0.0531 .$$

The negative sign, implying a preferential perpendicular alignment of the molecules with respect to the H_0 direction, follows from the relative signs of the indirect and direct couplings. It is in agreement with previous work in other nematic solvents [9, 10].

In the isotropic phase the relatively strong singlet signal detected in the noise-decoupled ^{13}C spectrum was shifted upfield by $\Delta\delta = 8.95 \pm 0.2$ ppm. The external referencing method may additionally contribute to the error because of changes in the bulk susceptibility (~ 0.2 ppm). Temperature effects may also contribute to the possible error. However, it seems safe to assume that $\Delta\delta$ is accurate within ± 0.6 ppm. If the components of the shielding tensor are denoted by $\sigma_{\parallel}$ and $\sigma_{\perp}$ for parallel and perpendicular orientation of the molecular axis with the external magnetic field, the anisotropy can be calculated from:

$$\Delta\sigma(^{13}\mathrm{C}) = \sigma_{\parallel} - \sigma_{\perp} = \frac{3}{2}\,(\sigma_{nem} - \sigma_{iso})\,\frac{1}{S} = +253 \pm 17 \text{ ppm}.$$

The sign of $\Delta\sigma$ for ^{13}C is the same as for ^{1}H. It is in agreement with the naive expectation based on the simple model of a delocalized π current leading to an increase in shielding for a parallel orientation of the molecule to the magnetic field.

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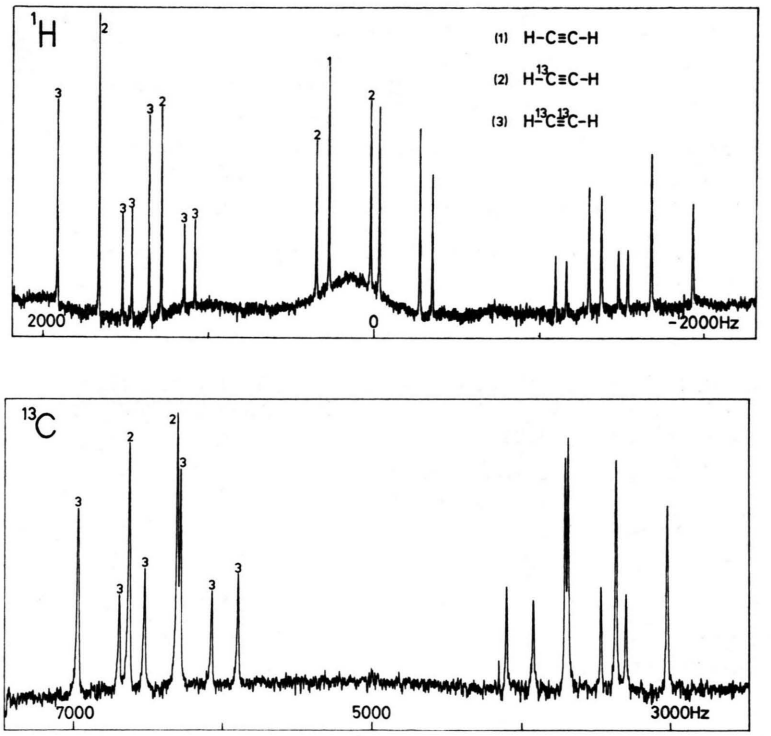

Fig. 1. Fourier Transform NMR spectrum of ^{13}C labeled acetylene in the nematic phase of EBBA at ca. 25 °C. *Top:* ^{1}H-part at 90 MHz. 150 pulses of 15 μsec, 0.9 sec repetition, 8 K interferogram, absorption mode, sweep-width 4500 Hz, line-width ca. 4—7 Hz. *Bottom:* ^{13}C-part at 22.63 MHz. 192,000 pulses of 6 μsec, 0.82 sec repetition (44 h), 8 K interferogram, exponential filtering TC = −4, absorption mode, sweep-width 5000 Hz, line-width ca. 12 Hz.

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