

¹³C-NMR Chemical Shift Anisotropy of Acetylene

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The ¹³C-NMR spectrum at 22.63 MHz and the PMR spectrum at 90 MHz of ¹³C 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 ¹³C 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 ¹³C 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 crystal³. 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 ¹H and ¹⁹F nuclei^{4,5}. However, only few measurements of ¹³C anisotropies obtained by this technique seem to have been published⁶⁻⁸.

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-azoxybenzene⁹. This was later confirmed by SPIESECKE¹⁰ for a different liquid crystal from a PMR study of ¹³C enriched acetylene. In this note we report on the determination of $\Delta\sigma(^{13}\text{C})$ of ¹³C enriched acetylene. The experimental details were similar to those used previously for the measurement of $\Delta\sigma(^{13}\text{C})$ of benzene-1-¹³C⁸. A 5 mm sample tube with acetylene (ca. 7 atm pressure) consisting of roughly 45% of molecules with one ¹³C, 40% with two and 15% with ¹²C only, dissolved in N-(p-ethoxybenzylidene)-p-n-butylaniline (EBBA) was used (l. c.¹¹). For the ¹³C measurements, the tube was enclosed in a 10mm o. d. tube containing D₂O (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).

Results

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

$J_{\text{HH}} = 9.6$ Hz, $J_{\text{CH}} = 249.0$ Hz and $J_{\text{CCH}} = 49.15$ Hz, a slightly changed value for $J_{\text{CC}} = 169.6 \pm 0.9$ Hz (instead of 171.5 Hz) and the following direct couplings were iteratively obtained (RMS = 0.9 Hz):

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

Iteration of the ¹H part (RMS = 0.3 Hz) with J_{CH} , J_{CCH} and J_{CC} fixed gave $J_{\text{HH}} = 9.5 \pm 0.3$ 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 ¹³C 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 σ_{\parallel} and σ_{\perp} for parallel and perpendicular orientation of the molecular axis with the external magnetic field, the anisotropy can be calculated from:

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

The sign of $\Delta\sigma$ for ¹³C is the same as for ¹H. 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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Reprint requests to Dr. G. ENGLERT, c/o F. Hoffmann-La Roche & Co., Abt. VI/Phy., CH-4002 Basel, Schweiz.

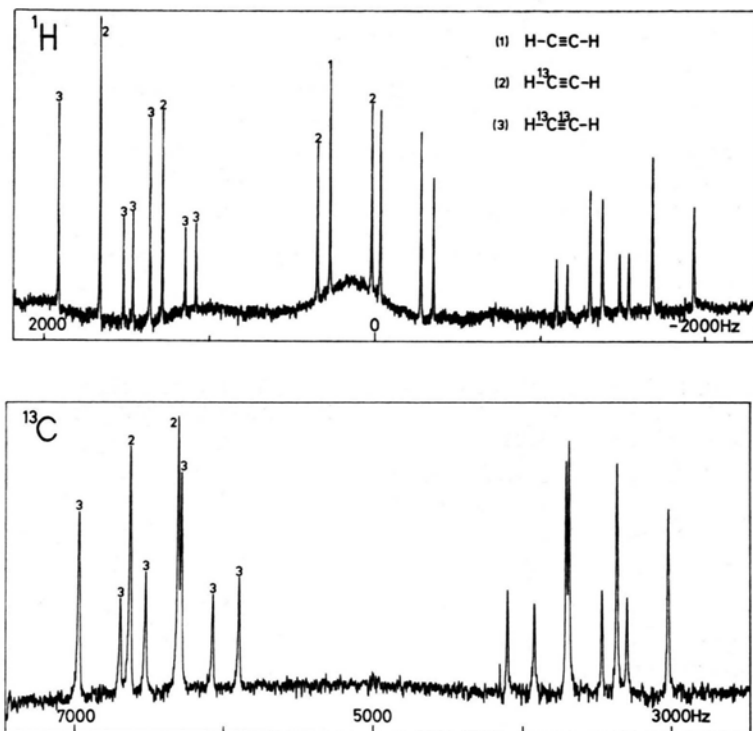


Fig. 1. Fourier Transform NMR spectrum of ^{13}C labeled acetylene in the nematic phase of EBBA at ca. 25°C . Top: ^1H -part at 90 MHz. 150 pulses of $15\ \mu\text{sec}$, 0.9 sec repetition, 8 K interferogram, absorption mode, sweep-width 4500 Hz, line-width ca. 4–7 Hz. Bottom: ^{13}C -part at 22.63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

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¹¹ This sample was kindly provided by Prof. Dr. P. DIEHL and Dr. W. NIEDERBERGER, Basle.