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^{13}C-NMR Chemical Shift Anisotropy in Benzene-1-^{13}C

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The ^{13}C-NMR spectrum obtained by the pulsed Fourier technique, of benzene-1-^{13}C oriented in a nematic liquid crystal was analysed. From the chemical shift difference between the nematic and isotropic phase a value for the ^{13}C chemical shift anisotropy in benzene-1-^{13}C of +190 ppm was determined.

Recently, we reported the ^{1}H-NMR spectra of benzene and benzene-1-^{13}C in isotropic and nematic solution[1]. In the meantime we have investigated the ^{13}C-NMR spectra of benzene-1-^{13}C in both phases applying the pulsed Fourier NMR technique. It was the aim of this investigation to obtain information on the anisotropy of the ^{13}C chemical shift. A recent communication by Yannoni and Bleich[2] on the ^{13}C shift anisotropy in polycrystalline benzene (^{13}C in natural abundance) at −40 °C prompted us to report our own results obtained by a different method.

The ^{13}C- and ^{1}H-NMR spectra of 38 mg of benzene and benzene-1-^{13}C in 450 mg of N-[p-ethoxybenzylidene]-p-n-butylaniline in a 5 mm o. d. tube were recorded at 22.63 and 90 MHz. The tube which was the same as previously used[1], was enclosed in a 10 mm o. d. tube containing D_2O to serve as a lock-signal. A Bruker HX 90/15 NMR spectrometer equipped with a Nicolet 1083 computer was used.

In the nematic phase the non-spinning sample yielded a ^{13}C spectrum which, as in the PMR case, is mainly determined by the direct dipolar couplings. The ^{13}C part of the spectrum, which is shown in the Fig. 1 (top), and the ^{1}H part, were both obtained by the pulsed Fourier technique at 24 °C (probe temperature). They were analysed using the computer program LAOCOONOR. The following indirect couplings (in Hz) were assumed[1]:

$$J_{\text{HH}}(\text{ortho}) = 7.54\,, \qquad {}^{1}J_{^{13}\text{CH}} = 158.17\,,$$
$$J_{\text{HH}}(\text{meta}) = 1.38\,, \qquad {}^{2}J_{^{13}\text{CH}} = 1.13\,,$$
$$J_{\text{HH}}(\text{para}) = 0.64\,, \qquad {}^{3}J_{^{13}\text{CH}} = 7.62\,,$$
$${}^{4}J_{^{13}\text{CH}} = -1.16\,.$$

The direct couplings and their standard deviations (in Hz) iteratively obtained upon assignment of 104 transitions in the ^{13}C part and 62 transitions in the ^{1}H part of the spectrum were:

$$D_{\text{HH}}(\text{ortho}) = -307.14 \pm 0.08, \qquad D_{^{13}\text{CH}} = -848.73 \pm 0.22,$$
$$D_{\text{HH}}(\text{meta}) = -58.72 \pm 0.10, \qquad D_{^{13}\text{C[C]H}} = -116.57 \pm 0.15,$$
$$D_{\text{HH}}(\text{para}) = -38.41 \pm 0.15, \qquad D_{^{13}\text{C[CC]H}} = -30.03 \pm 0.16,$$
$$D_{^{13}\text{C[CCC]H}} = -19.91 \pm 0.22.$$

The computer simulated spectrum (see Fig. 1, bottom) is in excellent agreement with the experimetal one. The RMS-deviation between observed and calculated transitions was 1.0 Hz. Assumption of a H–H (ortho) distance of 2.481 Å lead to the degree of order of the molecular C_6-symmetry axis:

$$S_{C_6} = -0.078\,.$$

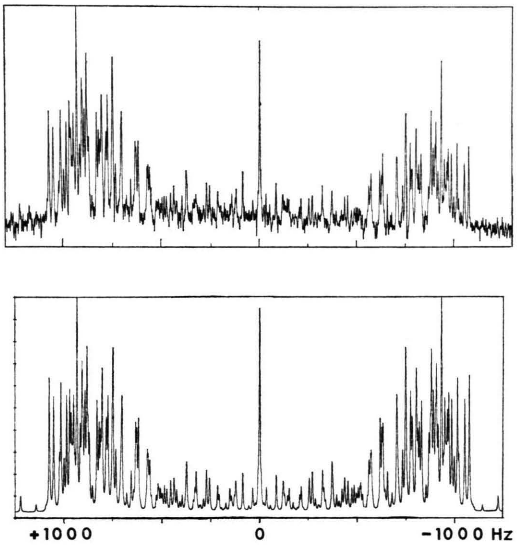

Fig. 1. Experimental and theoretical ^{13}C-NMR spectrum of benzene-1-^{13}C oriented in a nematic liquid crystal. *Top:* Experimental spectrum, obtained by pulsed (Fourier transform) NMR-technique. *Conditions:* 374 000 pulses of ca. 4 µsec, pulse repetition 0.68 sec (total measuring time 71 h), 4 K interferogram, exponential filtering (TC = −3), 24 °C, 22.63 MHz. *Bottom:* Computer simulated spectrum (for parameters used see text), half-width of the lines: 5.0 Hz.

The ^{13}C chemical shift (center of gravity of the symmetrical ^{13}C part) coinciding with the strong center line was arbitrarily chosen in the figure as 0 Hz.

In the isotropic phase the spectrum of the spinning sample under the condition of complete ^{1}H noise decoupling consisted of 14 singlets due to the 14 different (by symmetry) ^{13}C nuclei of the solvent. The total range of the chemical shifts was 3340 Hz (148 ppm). In the aromatic region a further slightly more intense singlet of benzene-1-^{13}C was observed. This singlet was shifted upfield compared to the center of the spectrum in the nematic phase. This implies that the ^{13}C and the ^{1}H shielding anisotropies are of opposite sign. If the components of the shielding tensor are denoted by $\sigma_{\parallel}$ and $\sigma_{\perp}$ for parallel and perpendicular orientation of the sixfold axis with the external field, values for the ^{1}H-anisotropy $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$ between -2.9 and -3.9 ppm have been reported for benzene [3, 4]. The possible sources of error encountered when measuring ^{1}H shielding anisotropies have been discussed by several authors [4–6]. The difficulties are expected to be considerably reduced, however, with ^{13}C-NMR because the observed shift differences between the two phases are usually larger. Actually, we observed:

$$\sigma_{\mathrm{NEM}} - \sigma_{\mathrm{ISO}} = -9.9 \pm 0.2 \text{ ppm}.$$

The ^{13}C anisotropy is given by:

$$\Delta\sigma = \tfrac{3}{2} \cdot (\sigma_{\mathrm{NEM}} - \sigma_{\mathrm{ISO}}) \cdot 1/S_{C6} = +190 \pm 4 \text{ ppm}.$$

This value is in good agreement with the reported one of $+180$ ppm obtained in polycrystalline benzene [2].

The error stated above only takes into account the deviation from the mean of two independent measurements. Other sources of error might be the neglection of vibrational corrections to the observed D_{HH}(ortho)-coupling [1] (~ 4%), the small change in susceptibility between nematic and isotropic phase (~0.1 to 0.2 ppm) [6], and the temperature dependence of the chemical shifts [5] due to local shielding contributions. Although the total influence of these effects is difficult to estimate, we feel that the reported value for $\Delta\sigma$ is accurate to ±10%.

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The Critical Solution Points of Some Hydrocarbons in Deuterated Nitromethane *

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As a part of our group research program on liquid systems containing hydrocarbons, the influence of nitromethane deuteration on the upper critical solution points (ucsp's) of binaries, where component **1** was nitromethane and component **2** was a $(C_5 - C_9)$-n. alkane, 1-octene or cyclooctane, was studied.

The apparatus and the adopted procedure were those previously described by FRANZOSINI [1]. Fluka CD_3NO_2 (purum, ≧ 99 at.% D), n. pentane (puriss., ~ 99.98%), n. hexane (puriss., ~ 99.96%), n. heptane (puriss., ~ 99.87%), n. octane (puriss., ~ 99.81%), n. nonane (puriss., ~ 99.68%), 1-octene (puriss., ≧ 99.7%) and cyclooctane (purum, ≧ 98%) were employed.

The demixing curves we obtained are shown in Figures 1 and 2.

In the investigated composition ranges, the liquid-liquid equilibrium temperatures could be generally detected with a very satisfactory degree of accuracy, each measurement being, as a rule, reproducible within a few hundredths of a °K. Only for the (CD_3NO_2 + n. heptane)-system the boundaries of the miscibility gap could be drawn in a merely approximate way, owing to the fact that in most samples the demarcation line between the two liquid phases was nearly evanescent.

In Table 1 the ucsp co-ordinates of the binaries where **1** = CD_3NO_2 and **2** = n. alkane are summarized with those reported in recent literature for the corresponding binaries where **1** = CH_3NO_2.

Table 1. Coordinates of the ucsp's in binaries where **2**=n. alkane.

component **1**	component **2**	$N_{2,\,\mathrm{max}}$	T_{max} (°K)	Ref.
CD_3NO_2	n. pentane	0.43 ±0.01	372.0	this work
	n. hexane	0.37_5 ±0.01	376.8	
	n. heptane	0.33_5 ±0.01	$382._3$	
	n. octane	0.31 ±0.01	388.9	
	n. nonane	0.28 ±0.01	395.1	
CH_3NO_2	n. pentane	0.45 ±0.01	370.7	2
	n. hexane	0.41_5 ±0.01	375.4	3
		0.3775	375.55	4
	n. heptane	0.36 ±0.005	381.0	3
		0.350	381.45	4
	n. octane	0.33 ±0.01	387.2	3
		0.315	387.65	4
	n. nonane	0.30_5 ±0.005	393.8	3
		0.280	393.45	4

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