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 $\sigma_{||}$ and $\sigma_{\perp}$ for parallel and perpendicular orientation of the sixfold axis with the external field, values for the ^{1}H-anisotropy $\Delta\sigma = \sigma_{||} - \sigma_{\perp}$ 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:

$$\Delta\sigma = \tfrac{3}{2} \cdot (\sigma_{\mathrm{NEM}} - \sigma_{\mathrm{ISO}}) \cdot 1/S_{\mathrm{C}_6} = +190 \pm 4 \text{ ppm} .$$

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] ($\sim 4\%$), 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 $\pm 10\%$.

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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, $\geqq 99$ at. % D), n. pentane (puriss., $\sim 99.98\%$), n. hexane (puriss., $\sim 99.96\%$), n. heptane (puriss., $\sim 99.87\%$), n. octane (puriss., $\sim 99.81\%$), n. nonane (puriss., $\sim 99.68\%$), 1-octene (puriss., $\geqq 99.7\%$) and cyclooctane (purum, $\geqq 98\%$) 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	$0.37_5 \pm 0.01$	376.8	
	n. heptane	$0.33_5 \pm 0.01$	$382._3$	
	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	$0.41_5 \pm 0.01$	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	$0.30_5 \pm 0.005$	393.8	3
		0.280	393.45	4

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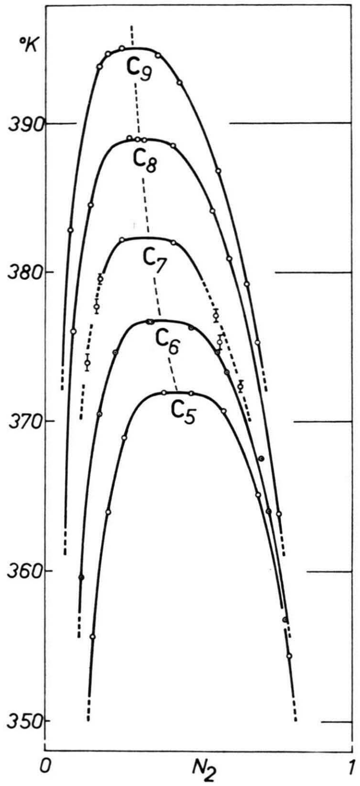

Fig. 1. Miscibility gaps in binary mixtures of trideuteronitromethane with (C_5-C_9)-n. alkanes.

The comparison between the two sets of data allows to conclude that, in each couple of corresponding binaries, the main effect of nitromethane deuteration is to raise up the ucsp temperature by an amount averaging 1.3 °K. This temperature effect is similar to that observed by Riccardi et al.[2] in mixtures formed with the same n. alkanes and acetone or hexadeuteroacetone, respectively.

It seems moreover that, component **2** remaining the same, the $N_{2,\max}$ value tends to be lowered by substituting CH_3NO_2 with CD_3NO_2, though this composition effect is apparent only when the comparison is restricted to the data from Refs. [2] and [3], which were taken by employing the same apparatus and procedure we adopted: anyway, the fact that Malesinska[4] (in order to obtain an easier detection of demixing) added some methylene blue to nitromethane is also to be mentioned.

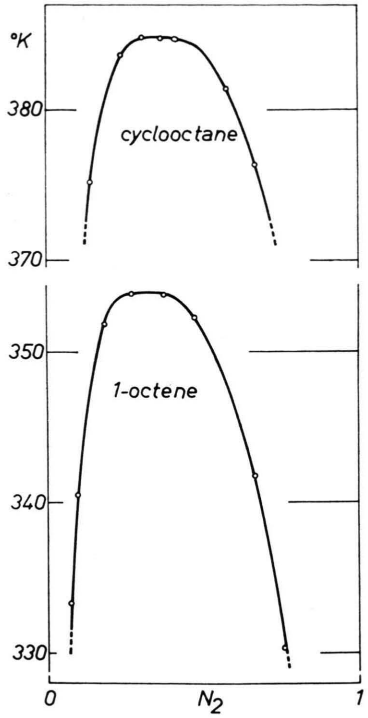

Fig. 2. Miscibility gaps in binary mixtures of trideuteronitromethane with 1-octene and cyclooctane.

Table 2. Coordinates of the ucsp's in binaries where **2** = 1-octene or cyclooctane.

component 1	component 2	$N_{2,\max}$	$T_{\max}$ (°K)	Ref.
CD_3NO_2	1-octene	$0.31_5 \pm 0.01$	354.0	this work
	cyclooctane	0.37 ± 0.01	384.8	
CH_3NO_2	1-octene	0.33 ± 0.01	351.9	5
	cyclooctane	$0.39_5 \pm 0.01$	382.7	2

Concerning the systems containing 1-octene and cyclooctane (see Table 2), it may be finally observed that, the composition effect remaining approximately the same as before, the ucsp temperature increase is larger by a factor ~ 1.6.

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