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Orientalional properties of liquid-crystalline 4-*n*-alkyloxybenzilidene-4'-fluoroanilines

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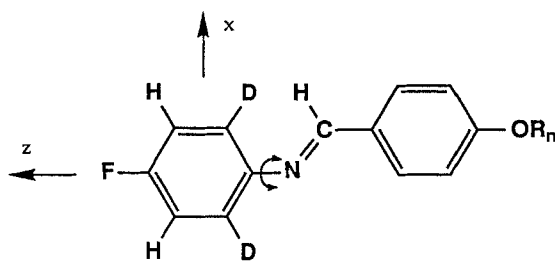
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The orientational order of 4-*n*-hexyloxybenzilidene-4'-fluoroaniline, (FAB-OC6) and its 4-*n*-heptyloxy analogue, (FAB-OC7), studied by means of ²H NMR and ¹⁹F NMR is reported. The entire temperature range of the liquid-crystalline phases (S_B, S_A and N for FAB-OC6, S_B and S_A for FAB-OC7) have been investigated. The results are discussed in relation to previous X-ray diffraction measurements. The chemical shift tensor components of the fluorine bond, evaluated from the ¹⁹F NMR spectra are compared with previous results.

Recently a series of 4-alkyloxybenzilidene-4'-fluoroanilines has been investigated by polarizing microscopy and X-ray diffraction [1]. A smectic polymorphism was found in the compounds studied (alkyl chain lengths of between 4 and 8 carbon atoms), consisting of a S_B phase with either (and sometimes both) a S_A phase or a nematic phase. We have investigated the orientational behaviour of these liquid crystals by fluorine NMR and also deuterium NMR of partially deuteriated samples. The entire temperature ranges of the liquid-crystalline phases of the hexyloxy homologue (FAB-OC6), which exhibits the most abundant polymorphism, i.e. nematic, S_A, and S_B phases, and the heptyloxy homologue (FAB-OC7), which does not have a nematic phase, have been studied. We are, at present, in the process of looking at all the other homologues which have been studied by X-ray diffraction. The molecular structures are shown in figure 1.

The deuterium spectra were taken using samples deuteriated in the ortho position, with respect to the amino group, of the benzene ring with the fluorine atom, by a standard method [2]. A VXR 300 spectrometer was employed operating at 46.04 MHz for deuterium (using a spectral width of 50 kHz and acquiring 32 K points) and 282.2 MHz for fluorine (using otherwise similar parameters). The temperature dependence was recorded by starting in the isotropic phase and cooling the sample slowly taking spectra every 0.2 K and equilibrating at each temperature for 10 min. The deuterium spectra were analysed by calculating the deuterium quadrupolar splitting and the major, ortho-meta, dipolar splitting (caused by the nearest ring proton) from the line positions. Notice that the Schiff's base proton will give rise to a smaller coupling, because it is averaged by rotational motion about the C_{ring}-N bond. A typical spectrum is shown in figure 2 (a); a doublet (quadrupolar coupling) of doublets (smaller

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FAB-OC_n; n = 6,7

Figure 1. 4-Alkyloxybenzilidene-4'-fluoroanilines with the molecular axes and site labelling.

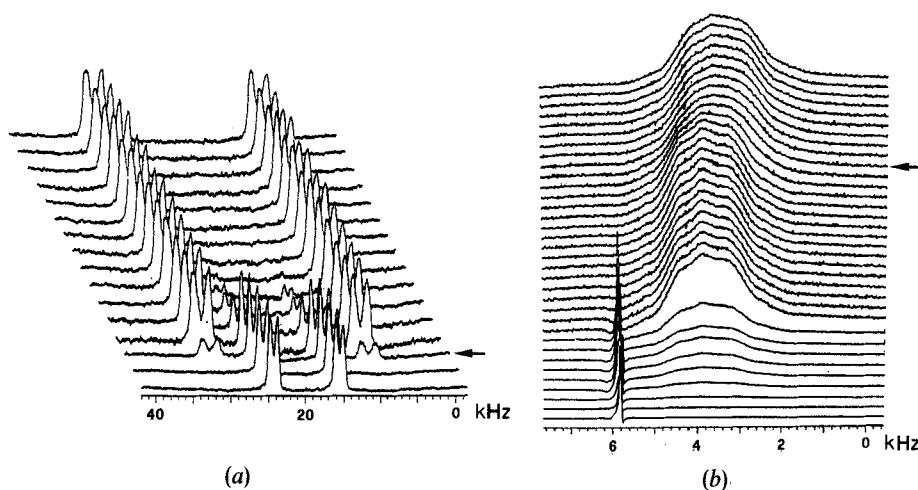
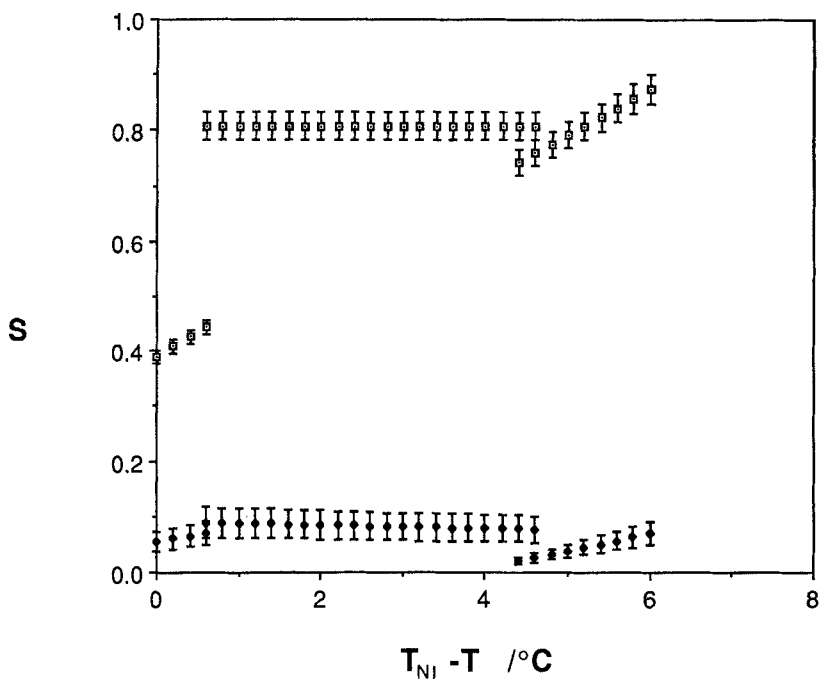


Figure 2. (a) ^2H NMR spectra (46.04 MHz) of partially deuteriated FAB-OC6 in the nematic and smectic A phase. The spectra were taken every 0.2 K. The arrow indicates the S_A -N transition at 58.2°C. (b) ^{19}F NMR spectrum of FAB-OC6 in the smectic A and smectic B phase. The spectra were taken every 0.2 K. The arrow indicates the S_B - S_A transition at 53.8°C.

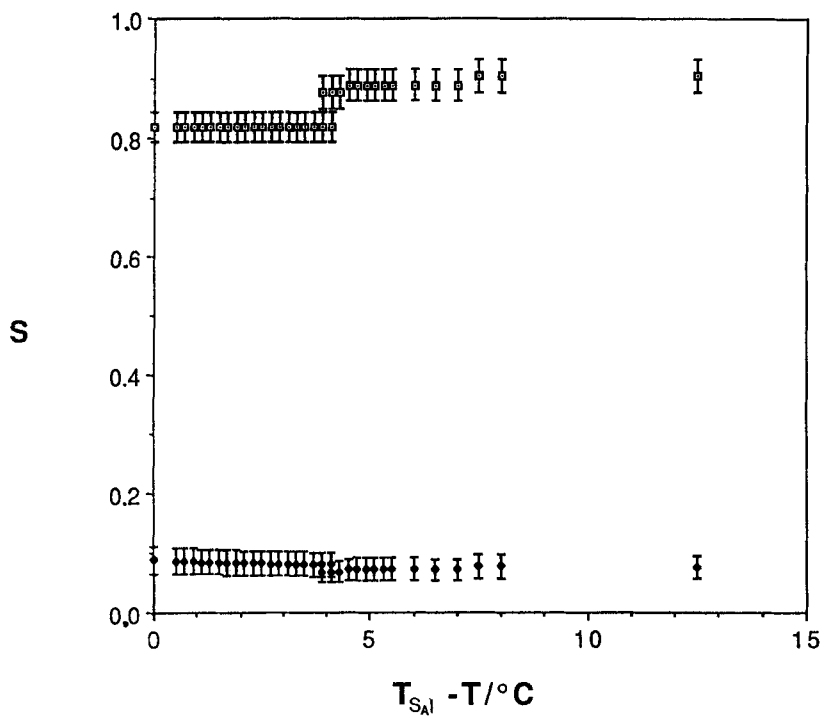
dipolar coupling) is observed in each liquid crystal phase. The fluorine spectra were analysed by measuring the chemical shift difference, $\Delta\sigma$, of the resonances in the liquid crystal phases with respect to that in the isotropic phase. The liquid crystal spectra exhibit a partially resolved triplet pattern originating from the dipolar coupling to the two adjacent protons, broadened by other dipolar couplings. Unfortunately, as can be seen in figure 2(b), this structure is not well resolved, and we could not extract couplings which were accurate enough to be useful.

Molecular order parameters can be calculated from the deuterium splittings with respect to the axis system shown in figure 1, using well-known relations [2]. Thus the dipolar splitting is related to the internuclear vector order parameter, presumed parallel to the z axis ($S_{\text{DH}} = S_{zz}$), by

$$\Delta\nu_{\text{DH}} = -(\gamma_{\text{D}}\gamma_{\text{H}}h/4\pi r^3)4S_{zz}, \quad (1)$$



(a)



(b)

Figure 3. Order parameters of FAB-OC6 and FAB-OC7, (\square) S_{zz} and (\blacklozenge) $S_{xx} - S_{yy}$, plotted against the shifted temperature $T_{xl} - T$. The error bars have been roughly evaluated allowing the C-D bond angle with the *para* axis to vary between 61.5° and 60.5° .

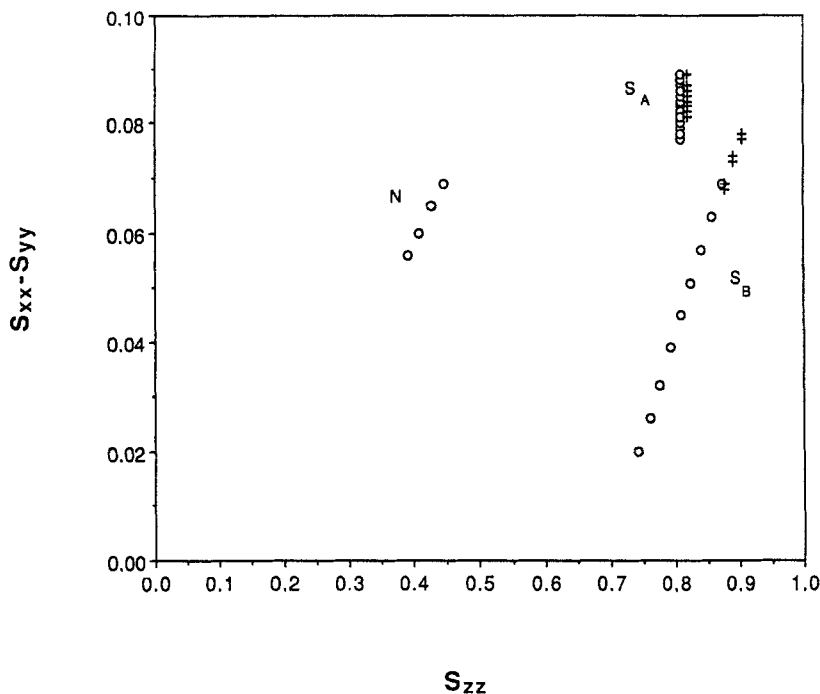


Figure 4. Order parameters of (O) FAB-OC6 and (+) FAB-OC7 plotted against each other.

where γ_D and γ_H are the gyromagnetic ratios of deuterons and protons, respectively. The internuclear distance, r , is taken to be 2.46 Å. S_{zz} is known to be positive, given the orientational properties of these molecules. The quadrupolar splitting is related to the major order parameter, S_{zz} , and the biaxiality, $S_{xx} - S_{yy}$, by

$$\Delta\nu_q = (3/4)q\{S_{zz}[3l_{zb}^2 - 1 + \eta(1 - l_{zb}^2)] + (S_{xx} - S_{yy})[1 - l_{zb}^2 + (1/3)\eta(1 + l_{zb}^2)]\}, \quad (2)$$

where q is the quadrupolar coupling constant and η is the asymmetry parameter, taken to be 186 kHz and 0.03, respectively, values typical for aromatic deuterons [3]. The direction cosine between the z axis and the C-D bond, l_{zb} , is given by the C-D bond angle with the *para* axis, and is assigned a value of 61°. This angle is near 60° in fluorobenzene [4], and if an angle less than 60° is used a negative biaxiality results, which is unlikely given the molecular shape (the out-of-plane axis order parameter, S_{yy} , should be the most negative). The order parameters are plotted against the shifted temperature ($T_{XI} - T$, where T_{XI} is the nematic (N)/smectic A (S_A) to isotropic transition temperature) in figures 3(a) and (b), and against each other in figure 4.

The chemical shift difference, $\Delta\sigma$, for fluorine can be related to the chemical shift tensor, σ , by [5]

$$\Delta\sigma = (2/3)S_{zz}\{\sigma_{zz} - (1/2)(\sigma_{xx} + \sigma_{yy})\} + (1/3)(S_{xx} - S_{yy})(\sigma_{xx} - \sigma_{yy}). \quad (3)$$

Therefore, by using the order parameters calculated from the deuterium spectra at the same temperature the components of the fluorine chemical shift tensor may be found for these molecules, the only assumption being that the isotropic value does not change significantly with phase or over the temperature ranges studied. Thus $\Delta\sigma$ is measured with respect to the isotropic value determined in the isotropic phase, so that we can take

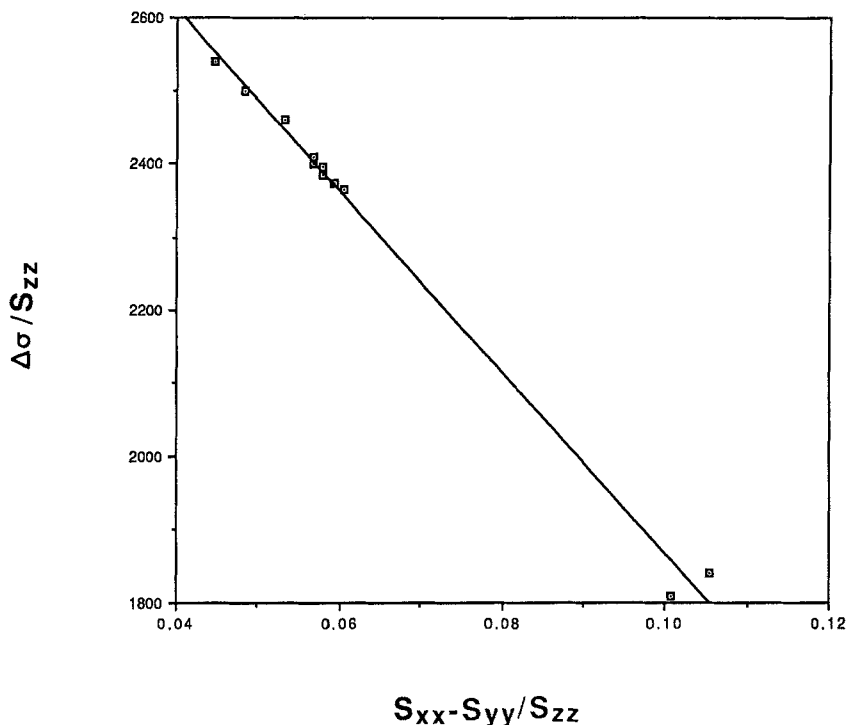


Figure 5. $\Delta\sigma/S_{zz}$ versus $S_{xx} - S_{yy}/S_{zz}$ for FAB-OC6 at different temperatures.

the trace of σ to be zero (i.e. $\sigma_{xx} + \sigma_{yy} + \sigma_{zz} = 0$). Looking at equation (3) it can be seen that the slope and intercept of a plot of the ratio $\Delta\sigma/S_{zz}$ against the ratio $(S_{xx} - S_{yy})/S_{zz}$ will give us the other necessary relations, which will allow us to determine the complete chemical shift tensor. In figure 5 we show this plot for FAB-OC6 for points measured in the nematic and smectic A phases, and a straight line is obtained to within the experimental error. A similar result was obtained for FAB-OC7 by looking at the smectic A and B phases. Note that the order parameters were taken from the deuterium spectra, and so the temperature had to be controlled very carefully; this was checked by comparing the regions where two different phases coexist, giving us at least two different reference points in each sample. Not unsurprisingly the components of σ for each liquid crystal molecule are similar: $\sigma_{xx} = -71$ ppm, $\sigma_{yy} = 60$ ppm, $\sigma_{zz} = 11$ ppm for FAB-OC6, and $\sigma_{xx} = -63$ ppm, $\sigma_{yy} = 50$ ppm, $\sigma_{zz} = 13$ ppm for FAB-OC7. Unfortunately since there are relatively large errors in measuring the biaxial order parameter, $S_{xx} - S_{yy}$, because it is so small, the error associated with our measurement of the fluorine chemical shift tensor is about 20 per cent. These values, taking the large differences between the molecules into consideration, are in reasonable agreement with those calculated for 4-fluoronitrobenzene partially oriented in a nematic liquid crystal [5].

We now turn our attention directly to the order parameters calculated from the deuterium spectra and plotted in figures 3 (a) and (b), and 4. One of the most interesting results is that the order parameters in the smectic phases are very close to their theoretical maxima, and thus for the S_A phase we are seeing some of the highest order parameters ever recorded for a low molar mass material [6]. Perhaps even more

unusual is the observation that the order parameters in the S_A phase do not vary with temperature, whereas the molecular reorientations over which the orientational average must be taken are known to be extremely sensitive to temperature. Such an observation can only arise if there exists a strong coupling between the orientational and translational ordering in the smectic phases, so that as the temperature rises the excess thermal energy is dissipated into motions which mainly affect the translational ordering. In the smectic B phase, however, the translational ordering is near its maximum value (the X-ray data show that the molecules are fully extended in this phase [1]) and therefore the orientational ordering should again vary with temperature, as is in fact observed; the translational ordering can no longer act as a heat sink. Chain motions are the most likely heat sink in the smectic A phase. Conformational freedom will reduce the layer spacing and, as is usually observed [7, 8], the X-ray data show that there is a jump down in layer spacing going from the S_B phase to the S_A phase [1]. In addition changes in conformational freedom are less likely to affect the ordering of the phenyl rings, whereas it is expected that the chain order parameters would be affected. We are therefore in the process of obtaining chain deuteriated molecules in order to test this hypothesis by deuterium NMR.

References

- [1] GANDOLFO, C., GRASSO, D., BUEMI, G., and TORQUATI, G., 1988, *Nuovo Cim.*, **10**, 1363.
- [2] EMSLEY, J. W., and LINDON, J. C., 1975, *NMR Spectroscopy Using Liquid Crystal Solvents* (Pergamon).
- [3] VERACINI, C. A., 1985, *Nuclear Magnetic Resonance of Liquid Crystals* (Vol. 141, NATO ASI Series C), edited by J. W. Emsley (Reidel).
- [4] NYGAARD, L., BOJESEN, I., PEDERSEN, T., and RASTRUP-ANDERSEN, J., 1968, *J. molec. Struct.*, **2**, 209.
- [5] VAN DER GIESSEN, J., and DE LANGE, C. A., 1978, *Chem. Phys. Lett.*, **50**, 122.
- [6] CATALANO, D., FORTE, C., VERACINI, C. A., EMSLEY, J. W., and SHILSTONE, G. N., 1987, *Liq. Crystals*, **2**, 345.
- [7] ALBERTINI, G., FANELLI, E., GUILLON, D., MELONE, S., POETI, G., RUSTICHELLI, F., and TORQUATI, G., 1983, *J. chem. Phys.*, **78**, 2013.
- [8] FANELLI, E., MELONE, S., TORQUATI, G., PISIPATI, V. G. K., and RAO, N. V. S., 1987, *Molec. Crystals liq. Crystals*, **146**, 235.