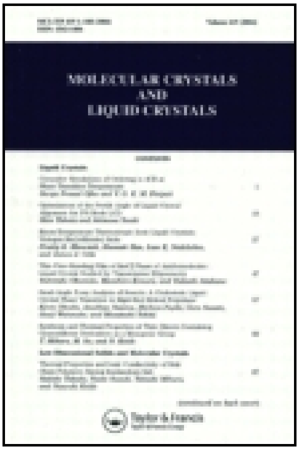

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Liquid Crystal Ordering in the Magnetic and Electric Fields Studied in 4,4'-di-*n*-heptyloxyazoxybenzene by EPR†

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Abstract—The 4,4'-di-*n*-heptyloxyazoxybenzene (PAH) liquid crystal ordering in the presence of the magnetic and dc electric fields was studied in the smectic and nematic mesophase. In the smectic phase the molecules are aligned with the long molecular axes perpendicular to the dc electric field direction, as contrasted to the parallel orientation with the dc electric field direction in the nematic phase. Effects of anisotropy in the plane perpendicular to the long molecular axes are observed.

1. Introduction

Electron paramagnetic resonance can be used to study the ordering of a liquid crystal mesophase, but first a paramagnetic impurity has to be introduced to make the measurement possible. The axially symmetric vanadylacetylacetonate (VAA) complex was found to be a convenient paramagnetic centre since a satisfactory alignment with the solvent molecules is obtained.⁽¹⁾ The nematic phase of *p*-azoxyanisole (PAA) was studied by electron paramagnetic resonance in the presence of a dc electric field.⁽²⁾ From the angular dependence in the magnetic field it was concluded that the molecular distribution about their long molecular axes is not axially symmetric. In order to extend the same technique to another liquid crystal, where the nematic and smectic mesophase measurements are possible the 4,4'-di-*n*-heptyloxyazoxybenzene (PAH) was used.

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2. Results and Discussion

PAH, a higher homologue of PAA, undergoes three liquid crystal transitions (solid-smectic $T = 65°$, smectic-nematic $T = 90°$ and nematic-isotropic $T = 118\,°\mathrm{C}$). The smectic mesophase, where the nematic order in magnetic field was partially maintained, was studied by Francis and Luckhurst.(3) An angular dependence of the hyperfine splitting do to the dissolved vanadylacetylacetonate (VAA) paramagnetic complex was followed and a decrease of the long range orientational order was observed.

When a dc electric field was applied on the PAH in the nematic phase the molecules do orient with the long molecular axes along the electric field direction and the results of the angular dependence resembles those of PAA (Fig. 1). The hyperfine splitting between

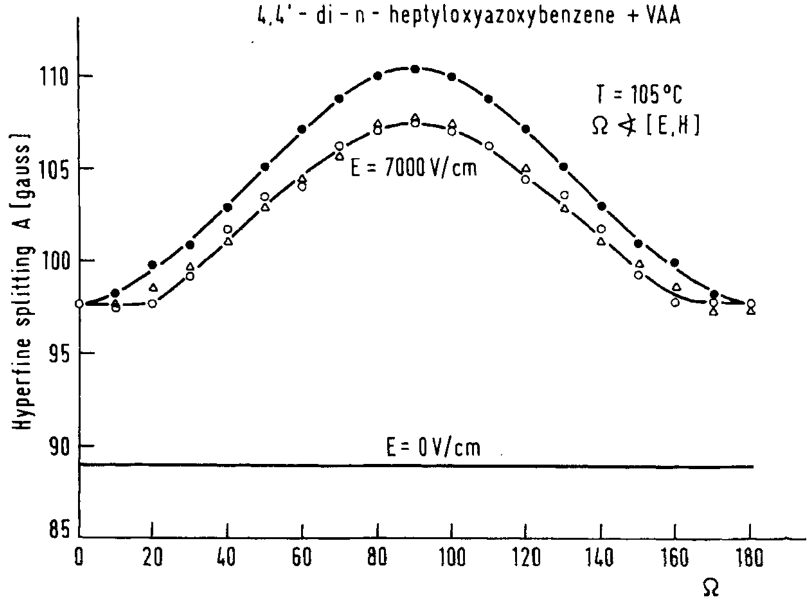

Figure 1. The angular dependence of the VAA complex hyperfine splitting in the PAH nematic phase matrix with respect to the relative orientation of the dc electric and magnetic fields directions. (○○○ represent the experimental values, ●●● the calculated values for an axial distribution of $A_{\parallel}$ direction about the electric field, △△△ the calculated values for unaxial distribution of $A_{\parallel}$).

the lines corresponding to the nuclear spin projections m and $-m$ is given by the equation:

$$\frac{\Delta E_{m,-m}}{2m} = a + \tfrac{1}{3}(A_{\parallel} - A_{\perp})\,(\overline{3\cos^2 U - 1})$$

where a, $A_{\parallel}$ and $A_{\perp}$ are the isotropic, and the general components of the hyperfine tensor. U is the angle between the magnetic field direction and the $A_{\parallel}$ hyperfine component, which can be expressed:

$$\cos^2 U = \sin^2\Omega\ \overline{\sin^2\alpha\ \sin^2\phi} + \cos^2\Omega\ \overline{\cos^2\alpha}$$
$$+ 2\sin\Omega\ \cos\Omega\ \overline{\sin\alpha\ \cos\alpha\ \sin\phi}$$

for an asymmetric distribution of the $A_{\parallel}$ axis orientation about the electric field. Ω is an angle between the electric and magnetic field, α and ϕ are spherical coordinates of the $A_{\parallel}$ direction. Assuming that the optical axis and the electric field coincide, the experimental values for the averages are:

$$\overline{\cos^2\alpha} = 0.261 \quad \overline{\sin^2\alpha\ \sin^2\phi} = 0.347 \quad \overline{\sin\alpha\ \cos\alpha\ \sin\phi} = -0.005$$

A qualitative explanation of the above coefficients could be given assuming that the distributions of the normals to the molecular plane of the paramagnetic complex in α and ϕ about the optical axis are not correlated, and that $\sin^2\phi \leqslant 0.5$. The value of $\sin^2\phi$ is limited according to the collective ordering of the liquid crystal molecules with their planes preferentially oriented in the magnetic field direction.(2) Since the calculated curve is well aligned with the experimental one it can be concluded that the molecular order does not change with the relative orientation of both fields.

From the values of the PAA coefficients(2):

$$\overline{\cos^2\alpha} = 0.186 \quad \overline{\sin^2\alpha\ \sin^2\phi} = 0.478 \quad \overline{\sin\alpha\ \cos\alpha\ \sin\phi} = -0.055$$

we can suggest that during the angular dependence measurements, when H and E are not parallel, the magnetic field partially increases the order along the long molecular axes. This is not the case for PAH, which is explainable since the molecules are heavier and longer according to the end group attached. Therefore, the effect of the inplane orientation is directly observable and the curves are well aligned as compared to the discrepancies in the PAA case.

The angular dependence measurement on Fig. 1 could also be explained with the deviation of the optical axis from the electric field direction reflected in a decreased ordering parameter according to the fast molecular diffusional motion. But it is necessary to assume that the optical axis direction is changing with the relative orientation of the electric and magnetic fields. In this case the saturation effects on Fig. 4 are hard to explain. Therefore, we have chosen the inplane ordering of molecules, being in agreement with the nonaxially symmetric molecular shape.

When the electric field is switched on at 105 °C the 50 % decrease in the ordering parameter from $S = -0.223$ to $S = -0.108$ is obtained which is contrasted by only a 1 % decrease from -0.24 to -0.22 for PAA. S is the ordering parameter defined for the $A_{\parallel}$ direction of the VAA paramagnetic solute.(1,4)

When the crystal is cooled down from the nematic phase to the smectic one, (Fig. 2) the molecules retain the preferential direction

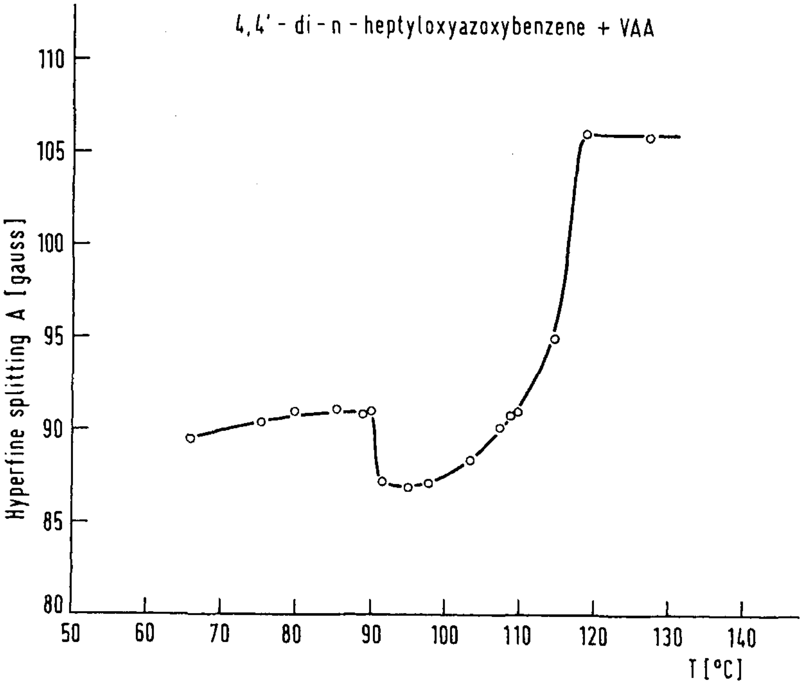

Figure 2. Temperature dependence of the VAA hyperfine splitting in the PAH.

along the magnetic field, with a lowering of order from $S = -0.245$ to $S = -0.191$ just below the transition point which slowly increases to $S = -0.212$, near the smectic-solid transition temperature, being thus in a close agreement to the results of Francis and Luckhurst.(3) Therefore the angular dependence measurements in the magnetic field are possible (Fig. 3). Just as in the nematic phase we can try

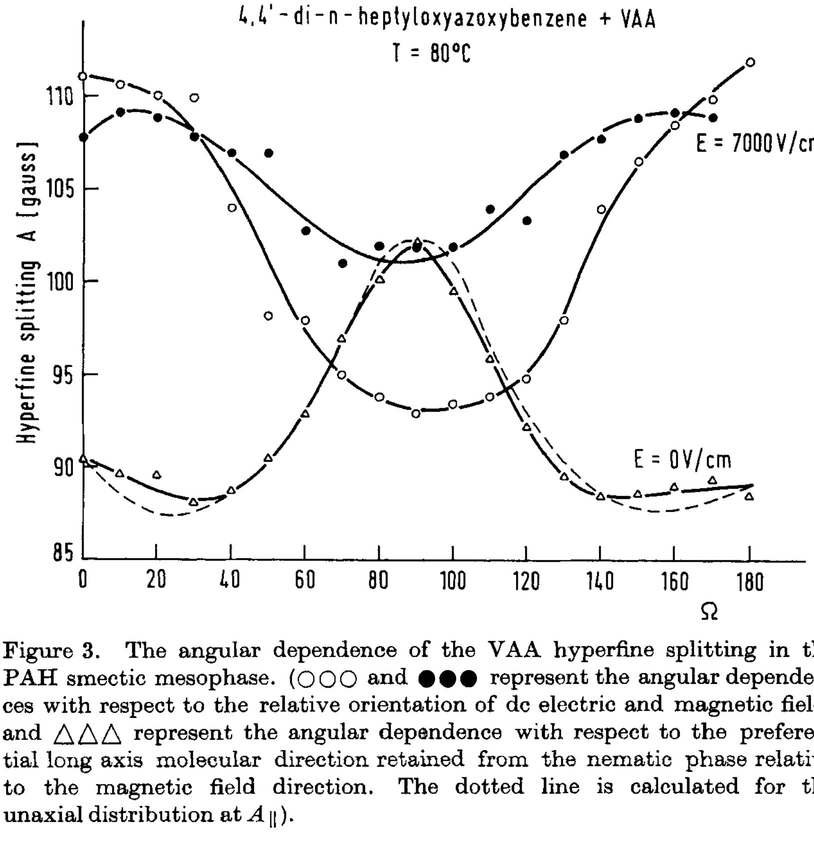

Figure 3. The angular dependence of the VAA hyperfine splitting in the PAH smectic mesophase. (○○○ and ●●● represent the angular dependences with respect to the relative orientation of dc electric and magnetic fields and △△△ represent the angular dependence with respect to the preferential long axis molecular direction retained from the nematic phase relative to the magnetic field direction. The dotted line is calculated for the unaxial distribution at $A_{\parallel}$).

to define the long range orientational ordering and the averages, defining the nonaxial distribution as follows:

$$\overline{\cos^2\alpha} = 0.201 \quad \overline{\sin^2\alpha \sin^2\phi} = 0.229 \quad \overline{\sin\alpha \cos\alpha \sin\phi} = -0.057$$

Here a larger disturbance of molecular ordering or the preferential orientation of both anisotropy defining directions takes place. This disturbance is reversible since the angular dependence is symmetric about the 90° value (Fig. 3). The deeps at 35° could be explained as the start of the inplane anisotropy influence.

When the dc electric field is applied to the smectic phase along the magnetic field, the direction of the long molecular axes are turned by 90° and a complete change of the collective molecular orientation is evident. In the electric field a preferential direction for the long molecular axes is not defined except for being in the plane perpendicular to the electric field and therefore the measured angular dependence is not reproducible. These are in fact the two extreme experimental values presented on (Fig. 3). It is therefore hard to estimate the ordering parameters for the smectic phase in an electric field.

It is interesting that the electric field effect is saturated in both mesophases at the same dc value, $E = 4500$ V/cm, when H and E are perpendicular (Figs. 4, 5). This value is nearly twice as high as measured for PAA. As expected the preferential direction in the smectic phase is only slightly disturbed when the electric field is removed.

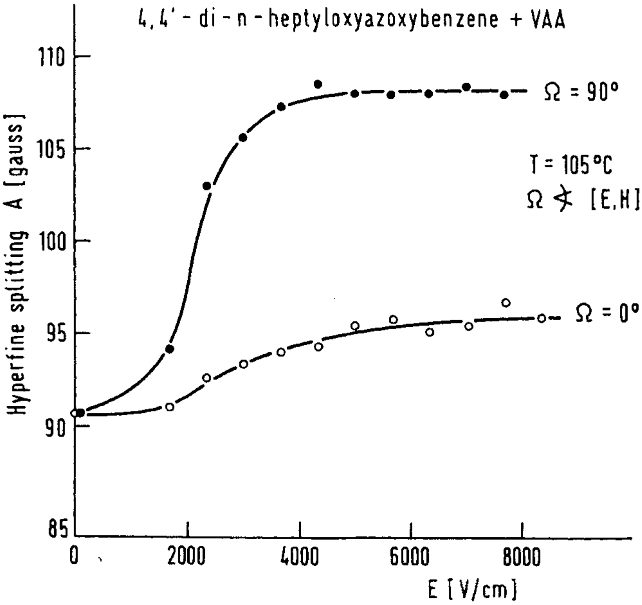

Figure 4. The hyperfine splitting of VAA complex dissolved in the PAH nematic mesophase as a function of the dc electric field strength ○○○ for E and H parallel and ●●● for E and H perpendicular.

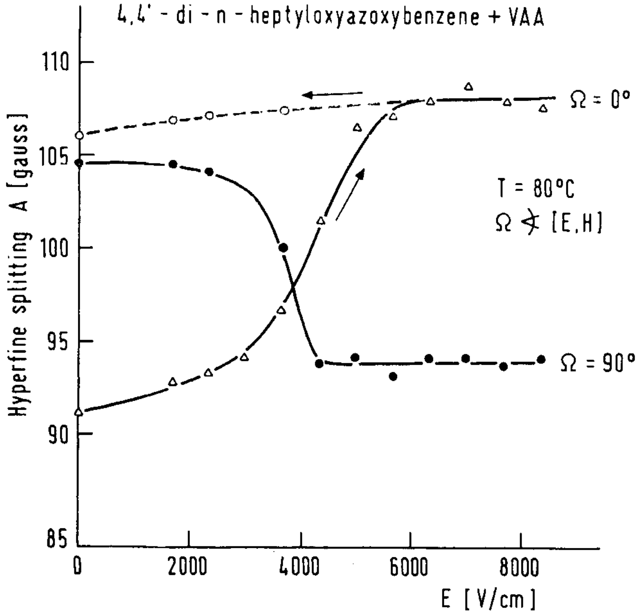

Figure 5. The hyperfine splitting of VAA complex dissolved in the PAH smectic mesophase as a function of the dc electric field strength ●●● for *E* and *H* perpendicular, and △△△ for *E* and *H* parallel.

3. Conclusion

The results presented have only a relative value since the VAA complex does only partly follow the solvent mesophase order.$^{(1)}$ But it can be suggested that the liquid crystal molecules should not be treated as axially symmetric about their long molecular axes. Therefore, two preferential directions can set in with respect to the collectively ordered molecules in the two mesophases of PAH.

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