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MOLECULAR ROTATION IN HEXATIC B MESOPHASE STUDIED BY THE EPR METHOD

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Molecular motions have been examined by EPR method in materials with the SmA-HexB-CryB phase sequence doped by paramagnetic copper (II) complex. It has been found that while in the SmA phase molecules rotate freely around their long molecular axes in the hexatic phase rotation can be either free or restricted. The restricted rotation is likely attributed to the herring-bone packing of the molecules in smectic layer.

INTRODUCTION

From x-ray studies it is known that in the crystal B phase in-plane molecular distance is distinctly smaller than the molecular diameter and thus only co-operative molecular rotations in which molecules locally correlate orientations of their short axes are permitted[1]. It has been commonly believed that in the smectic B phase during co-operative motions on average all orientation of short molecular axes are reached[2]. Recently the existence of the hexatic B phase with in-plane herring-bone (HB) arrangement of molecules has been assumed[3]. The long range HB order must result in molecular rotation with anisotropic distribution of short molecular axes.

In this paper we report results of EPR study of the molecular motions in the smectic A and hexatic B phases. Among variety of experimental methods, the EPR spectroscopy proved to be particularly fruitful for the investigation of molecular dynamic and mesophase structure[4-11].

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EXPERIMENT

Generally, in our work we followed the principles of the EPR method developed for paramagnetically doped liquid crystals[4-11]. As a spin probe the bis(dimethyldithiocarbamato) copper(II) complex ((dmdtc)$_2$Cu) was used[12]. The molecular structure of (dmdtc)$_2$Cu is shown in the inset in Figure 1 together with the principal axes of the magnetic interaction tensor that are very close to the axes of the inertia momentum.

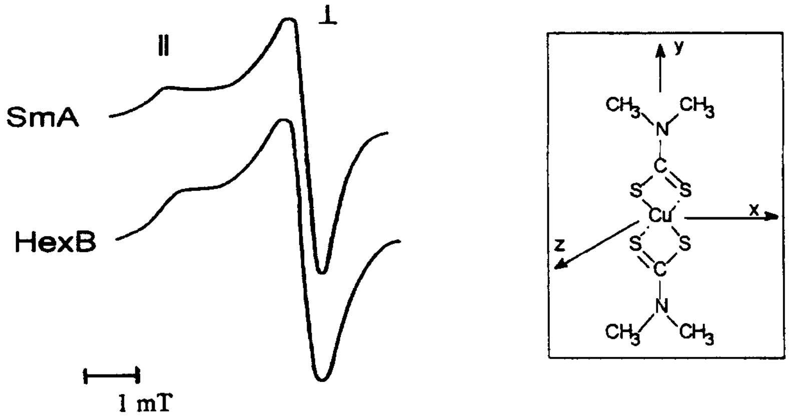

FIGURE 1 M_I = -3/2 peak of the (dmdtc)$_2$Cu EPR spectra in the SmA and HexB phases of the RFL6 host matrix. In the inset - molecular structure of (dmdtc)$_2$Cu and orientation of the magnetic molecular frame, z-axis is perpendicular to the co-ordination plane of the Cu(II) ion.

The (dmdtc)$_2$Cu complex has been chosen for our studies due to its high ratio of the magnetic parameters anisotropy to the EPR line width that makes it easy to observe fine details of the EPR spectra. In the experiment the isotope ^{63}Cu was used to reduce EPR line broadening resulting from the presence of the second isotope ^{65}Cu in all natural copper compounds. The concentration of the spin probe in the sample was about 0.1 wt % and did not affect the mesophase sequence of the host substances.

The X-band EPR spectra were recorded using Radiopan spectrometer equipped with a temperature controller capable stabilising the temperature within less than 0.05K.

For our studies two enaminoketone derivatives REF10, RFL6 with the sequence of orthogonal SmA-HexB-CryB phases were selected[13]. These compounds exhibit broad (>20 K) temperature range of the SmA phase in order to avoid influence of the layer fluctuations on the hexatic structure[14]. The EPR spectra were recorded in the smectic A and hexatic B phases as well as for the glassy state. Aligned LC samples were prepared in the 10 kG magnetic field by slow cooling from the isotropic to SmA phase The glassy

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state was obtained by fast cooling of isotropic melt to the temperature of liquid nitrogen.

RESULTS

The EPR spectra obtained for both studied substances in the glassy at room temperature are similar and give values of the molecular magnetic g and A tensors: g_{xx}=2.025+0.002, g_{yy}=2.019+0.002, g_{zz}=2.087+0.002, A_{xx}=4.1+0.1mT, A_{yy}=3.6+0.1mT, A_{zz}=15.8+0.1mT. In the isotropic phase fast tumbling of the molecules leads to full averaging of the g and A magnetic tensors. The obtained isotropic parameters are g_0=2.046, A_0=7.4 mT. Difference between isotropic hyperfine A_0 value and the value calculated by averaging of the glassy state parameters (A_0=7.8 mT) is due to the small temperature dependence of A tensor[15].

M_I = -3/2 peaks of the EPR spectra in the SmA phase are shown in Figures 1 and 2.

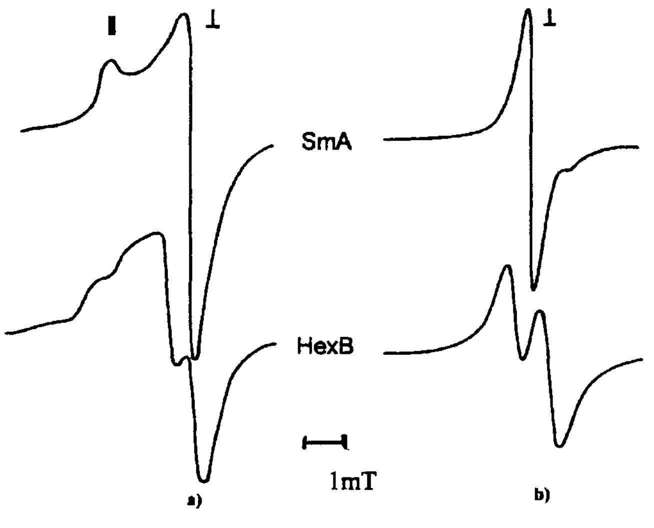

FIGURE 2 M_I = -3/2 peak of the $(dmdtc)_2Cu$ EPR spectra in the SmA and HexB phases for a) non-aligned and b) aligned REF10 sample. For b) director is perpendicular (γ = 90) to the external magnetic field.

The SmA phase spectrum is axial symmetric and reflects the fast isotropic rotation of the molecules around their long axes capable of averaging x and z elements of the g and A tensors. This feature is consistent with what might be expected from the common ideas about the structure of the SmA phase.

In the HexB phase we found two essentially different behaviours:

i The spectrum of the RFL6 compound does not change appreciably in the temperature range of the HexB phase as compared with the spectra in the SmA phase (Figure 1). It

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keeps the axial symmetry and only slight broadening of the lines was observed. Thus, we can conclude that the character of the rotational motion of the molecules in the SmA and HexB phases is similar in this substance.

ii The spectrum of the REF10 compound undergoes changes from the axial symmetry in the SmA phase to the rhombic symmetry in the HexB phase. The changes are noticeable in the non-aligned sample (Figure 2a) but they are especially pronounced in the spectra of the aligned sample when the director is perpendicular (γ=90) to the magnetic field (Figure 2b). A single line related to the short molecular axes observed in the SmA phase spectrum splits in the HexB phase. This points out unambiguously that in the HexB phase the distribution of the molecular short axes is no longer isotropic. The molecular motions do not allow the x and z-elements of the **g** and **A** tensors to be averaged completely. It is worthwhile mentioning, that each component of the doublet in the HexB spectrum is virtually equal in width to the single peak from which it has arisen. Since the EPR line width reflects the rate of the molecular motions, we can conclude that the mobility of the molecular short axes does not decrease remarkably at the SmA-HexB phase transition.

Under assumption that the nematic order parameter in HexB phase is S=1, splitting in the doublet (Figure 2b) defines the diagonal elements of new effective tensors $\tilde{\mathbf{g}}$ and $\tilde{\mathbf{A}}$ with the principal axes x′ and z′ which lies in the plane of the molecular axes x and z. The tensors $\tilde{\mathbf{g}}$ and $\tilde{\mathbf{A}}$ results from averaging of the molecular tensors g and **A** over short axes distribution function $f(\phi)$, which is symmetrical in the new frame.

$$\tilde{A}_{x'x'} = \overline{A} + \frac{\Delta A}{2} < \cos 2\phi >_f ; \quad \tilde{A}_{z'z'} = \frac{\overline{A}}{2} - \frac{\Delta A}{2} < \cos 2\phi >_f$$

$$\tilde{g}_{x'x'} = \overline{g} + \frac{\Delta g}{2} < \cos 2\phi >_f ; \quad \tilde{g}_{z'z'} = \overline{g} - \frac{\Delta g}{2} < \cos 2\phi >_f$$

where ϕ is the angle between the x, z and x′, z′ frames and:

$$\Delta g = (g_{xx} - g_{zz}); \quad \overline{g} = \frac{(g_{xx} + g_{zz})}{2}; \quad \Delta A = A_{xx} - A_{zz}; \quad \overline{A} = \frac{A_{xx} + A_{zz}}{2}.$$

Thus from the value $\Delta H_{3/2}$ of the splitting of the M_I = -3/2 peak, the parameter $< \cos 2\phi >_f$, reflecting order of short molecular axes was obtained from the relation:

$$< \cos 2\phi >_f = \left(\frac{h\nu}{\beta} \frac{\Delta g}{\overline{g}^2} - \frac{3}{2} \Delta A \right)^{-1} \Delta H_{3/2}$$

where $h\nu$ - the photon energy of applied electromagnetic field , β - the Bohr magneton. In the HexB phase of REF10 $<\cos 2\phi>$ = 0.13 has been found.

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Two interpretations of the result are possible. If the motion of molecules around their long axes is assumed to be continuous but restricted within some sector of angle ω then the relation $<\cos 2\phi> = (\sin\omega)/\omega$ is fulfilled and $\omega = 159^0$ has been obtained. In more realistic model of the smectic structure described by Levelut, the short molecular axes are locally arranged in the herring-bone fashion[16], and the molecules rotate by subsequent fast jumps followed by residing in a six fold potential well. The difference in occupation probability of the molecular equilibrium positions reflects the strength of the HB order. If the occupation probability of particular two states (separated by π) is p_1 and remaining four - p_2 the parameter $<\cos 2\phi>$ is equal $2(p_1-p_2)$[18] . Under condition $2p_1+4p_2=1$, our result provide $p_1 = 0.20$ and $p_2 = 0.15$ values close to that reported for the tilted crystalline phase CryG of TBBA[18] but distinctly different form that detected in CryB phase of IBPBAC where nearly isotropic distribution of the molecules among the six equivalent positions was found by the N^{14} quadruple resonance method[19].

However, it should be mentioned that based only on the EPR measurements it is not possible to discriminate between the 'uniform motion' and the 'jump' models.

CONCLUSION

Although REF10 and RFL6 are chemically similar, both exhibit the SmA-HexB-CryB phase sequence and similar in-plane molecular distance (D ~ 5.0 A), the character of the molecular motions detected in the HexB phase of these compounds differs qualitatively. From the EPR studies it has been deduced that in RFL6 the local orientational order of the short molecular axes in HexB and SmA is similar. In both phases, while molecule rotates around its long axis, the distribution of the short axis remains isotropic. For REF10, in the SmA phase rotation is still isotropic but in the HexB phase it becomes anisotropic.

The character of the motions is likely attributed to the strength of the coupling between the herring bone order and the bond order parameters[3]. In RFL6 the coupling must be weak and the hexatic phase without the herring bone order is observed. In such a phase all six directions of the short axis are on average equally probable when molecule rotates. In REF10 possibly stronger coupling takes place and the hexatic phase with the herring-bone order is established. In such a phase the rotation is hindered and the short molecular axes are not equally distributed among the six equilibrium directions. However, it should be noticed that the difference in the probability of the occupation equilibrium positions, reflecting the strength of the herring-bone order, is too small to be detected as the HB order in X-ray measurements. Neither the distortion of the hexagonal lattice nor the broken glide symmetry was observed in hexatic phase by X-ray method.

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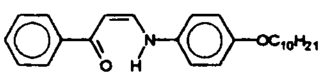
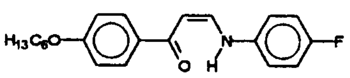


RFL6



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