ORIENTATIONAL ORDERING OF FULLERENE C70 IN SMECTIC LIQUID CRYSTAL

V.K.Dolganov, K.P.Meletov, Yu.A.Ossipyan

Institute of Solid State Physics, RAS

142432 Chernogolovka, Moscow distr., Russia

Polarized absorption spectra of fullerene C70 have been measured in a smectic liquid crystal. The polarization ratio has been found to dif- fer significantly for different electronic transitions. The orientation of the transition dipole moment, the orientation order parameters have been specified. It has been concluded that higher fullerenes may form liquid crystalline structures.

The discovery of the novel molecular form of carbon - fullerenes [1] has opened up new fields in molecular physics and chemistry. Fullerenes are extraordinary both in molecular structure (polyhedra comprising sixty and more carbon atoms) and in the interaction of their molecules with environment (e.g. high $- T_c$ superconductivity of doped crystals [2]). By the present time fullerene C60, its molecular, crystalline structure and electronic states are best studied. Fullerenes of exotic nonspheric shapes with the number of carbon atoms more than sixty are less extensively studied. Marcus et al [3] reported that fullerene C70 molecules are oriented in the nematic phase of liquid crystals. We studied the orienting action of smectic A on C70 molecules. A significant difference in the intensities of the polarized light absorption spectra was observed for three electronic transitions. The preferential orientations of the electronic transitions, the molecular orientation order parameters were determined.

Fullerene was synthesized by electric arc graphite vaporization in helium atmosphere using the technique employed by Kratschmer et al [4]. A mixture of fullerenes of various molecular mass was first separated by extraction with organic solvents after which chromatographic methods were used. This ensured C70 yield of purity not worse than 97%. The measurements were carried out for smectic A phase of liquid crystal (SLC). The concentration of C70 in the SLC was ~ 0.03 wt %. The polarized light absorption spectra were measured for monodomain specimens (200 μm in thickness) having homogeneous molecular orientation. The orientation was achieved by depositing a polyvinyl alcohol film onto the surface of a quartz vessel and a subsequent directed rubbing of the vessel surface. The SLC self-absorption and the spectral dependence of the scattered light were accounted for in concurrent measurements of C70-free SLC transmission spectra. The C70 spectra referred to in this work were obtained by dividing the transmission spectrum of doped crystal by the spectrum of undoped SLC of the same polarization. The orientational order parameter of SLC $S_0 = 0.5^*(< 3\cos^2\Theta > -1)$ was inferred from the polarization ratio of the absorption spectrum of 4-diethylamino-4-nitrostilbene admixture whose molecular form is close to that of SLC and an electronic transition dipole moment is parallel with the longer axis of molecule [5]. The absorption spectra of C70 for polarizations parallel with and perpendicular to the director (n) of liquid crystal are illustrated in fig.1. The principal spectral features of C70 are observed in both polarizations, however, the spectral forms

are markedly different. The long-wave transition $(\lambda \sim 4700$ Å$)$ intensity, like in nematic liquid crystal [3], is stronger in the $T \perp n$ polarization. The intensity of $\lambda \sim 3800$ Å and $\lambda \sim 3600$ Å transitions, which were not observed in [3], are stronger in the $T \parallel n$ polarization that indicates that these transitions are oriented with respect to different molecular axes.
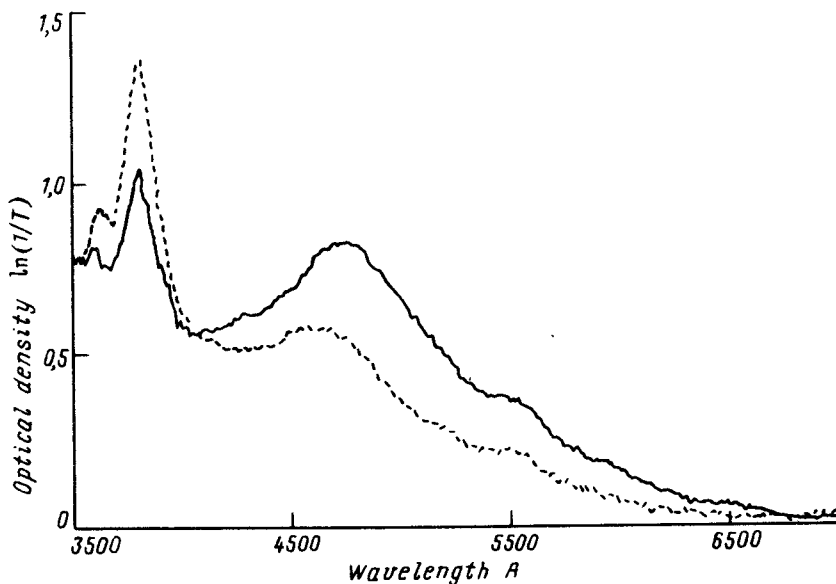

Fig.1. Absorption spectra of fullerene C70 for polarization parallel with (dashed curve) and perpendicular (solid curve) to the liquid crystal director, 81°C
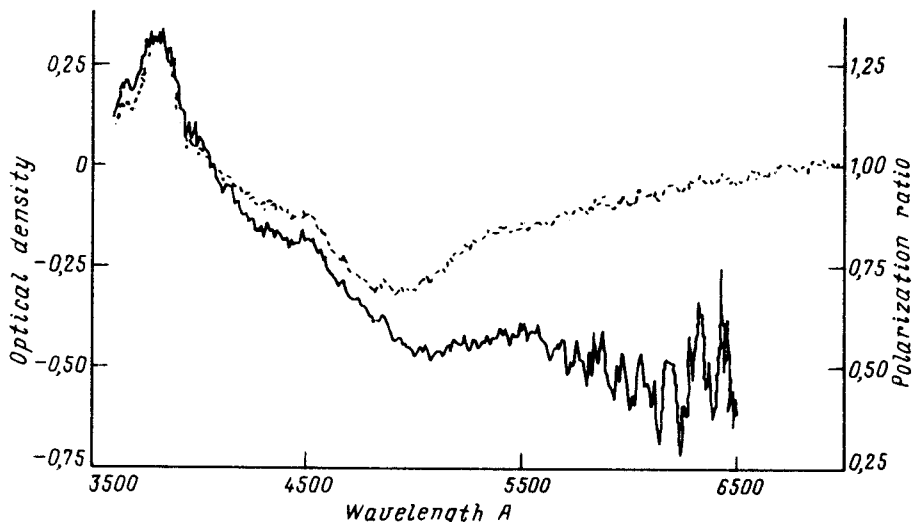

Fig.2. Polarization ratio $P = D_{\parallel}/D_{\perp}$ (solid curve) and the $D_{\parallel} - D_{\perp}$ difference spectrum (dashed curve) of fullerene C70 in smectic liquid crystal

Fig.2 illustrates the difference spectrum $D_{\parallel} - D_{\perp}$ and the spectral dependence of the polarization ratio $P = D_{\parallel}/D_{\perp}$. For the long-wave transition the spectral

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maximum position is different in the two polarizations, the polarization ratio grows for $\lambda < 4700$ Å. This may partly be attributed to overlapping of the spectrum with the short-wave absorption spectrum with the opposite polarization ratio. Intermolecular static interaction may also lead to splitting of electronic bands in the two polarizations [6]. The observable shifts of bands in the two polarizations are consistent with the earlier calculations [6] in the case that the electronic transition dipole moment is perpendicular to the molecular longer axis.

Difference of the polarization ratio from unity (for the long-wave transition $P \sim 0.53$ in $\lambda \sim 5000$ Åregion) is indicative of a significant orientation of C70 molecules in SLC. A C70 molecule consists of 25 hexagons and 12 pentagons forming a "rugby-ball", i.e. the egg-shaped structure, the difference from the sphere is, however, not very strong (the axes differ in length less than 12%) [7]. Therefore the strong orientation cannot be attributed to geometric factor alone, it rather bears witness to an essential anisotropy of the intermolecular interaction of C70 molecules. If the degree of orientational ordering of fullerene is considered to be the same as of liquid crystals then the direction of the electronic transition dipole moment in a molecule can be estimated as $\sin^2 \alpha = [2(P-1) + S_0(P+2)]/3S_0(P+2)$ [8], where α is the angle the transition dipole moment direction and the plane perpendicular to the molecular axis oriented with respect to the director ("long" axis of C70), $S_0 = 0.7$ is the order parameter of SLC. No absorption dichroism was observed for the spheric C60 molecule, therefore the internal fields in liquid crystal may be ignored in a determination [9]. For the long-wave transition we get $\alpha \cong 23^0$. Inasmuch as fullerene molecules differ in shape from liquid crystal molecules, one should expect that the degree of their orientational ordering S_F is smaller than that of liquid crystal molecules. Consequently, the value of α determined by us, is the largest possible angular value. However, even in the limiting case with $\alpha = 0$ for $S_F = 2(1 - P)/(P + 2)$ we get a large value of $S_F \cong 0.37$. This value of S is realized in liquid crystal near the transition to the isotropic liquid. The liquid crystal local molecular orientation order S_L^* exceeds the macroscopic orientational ordering. Under the assumption that $S_L^* \cong 1$, the values of S_0 and S_F allow the estimation of the degree of local ordering of C70 molecules S_{LF}. S_F is made up of local ordering of C70 with respect to the nearest liquid crystal molecules and orientational ordering of the liquid crystalline structure. For S_{LF} a simple expression $S_{LF} = S_F/S_0$ can be obtained, i.e. $S_{LF} = 0.53$.

C60 is a plastic crystal having the ideal spheric molecular shape. The classic statistic theories [10,11] predict the formation of liquid crystalline structures for the systems of rigid long rods (Onsager's approximation), spherocilinders of finite length (cylinders terminated in semispheres at both ends), elongated ellipses. Precisely this molecular shape is clearly and ideally realized by nature in higher fullerenes whose isolation has been recently reported [12]. Large degrees of orientational ordering S_F and S_{LF} substantiate the assumption that liquid crystalline structure may form in fullerenes composed of a large number of carbon atoms in the case when the temperature of transition to the orientationally ordered phase (thermotropic liquid crystal) or the required concentrati on of the material (concentrational transition) are not too high.

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