

Orientational ordering of fullerene C₇₀ in a smectic liquid crystal

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

The discovery of a novel molecular form of carbon (fullerenes¹) has opened up new fields in molecular physics and chemistry. Fullerenes are extraordinary in molecular structure (polyhedra comprise sixty or more carbon atoms) and in the interaction of their molecules with the environment (e.g., high- T_c superconductivity of doped crystals²). At present, fullerene C₆₀, its molecular structure, its crystal structure, and electronic states have been studied most extensively. Fullerenes of exotic nonspheric shapes, with the number of carbon atoms more than sixty, have been studied less extensively. 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 and the molecular orientation order parameters have been 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 masses was first separated by extraction with organic solvents, after which chromatographic methods were used. This ensured C₇₀ yield of purity no worse than 97%. The measurements were carried out for the smectic *A* phase of the liquid crystal (SLC). The concentration of C₇₀ in the SLC was ~0.03 wt. %. The polarized light absorption spectra were measured for single-domain samples (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 by 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 discussed here 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, $S_0 = 0.5 * (\langle 3 \cos^2 \Theta \rangle - 1)$, 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 the electronic transition dipole moment is parallel to the longer axis of the molecule.⁵ The absorption spectra of C₇₀ for polarizations parallel to and

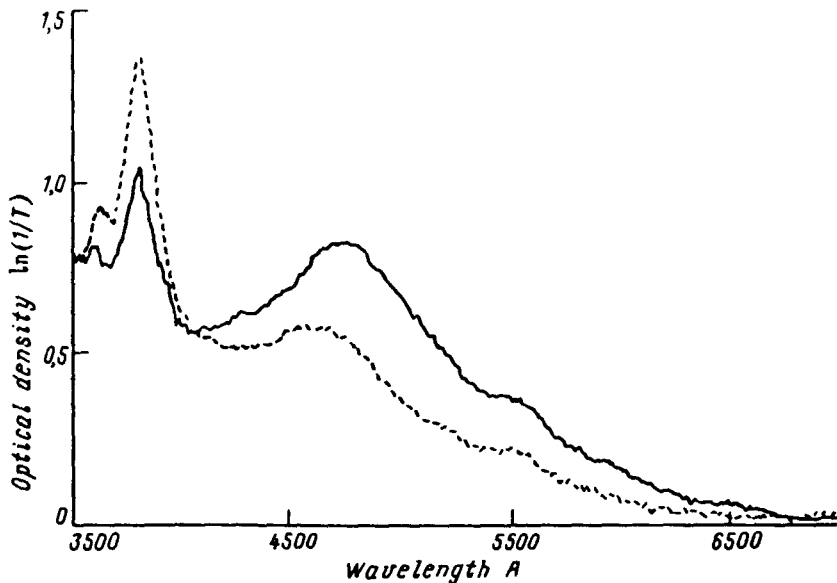


FIG. 1. Absorption spectra of fullerene C_{70} for polarization parallel to (dashed curve) and perpendicular to (solid curve) the liquid-crystal director, 81°C .

perpendicular to the director (\mathbf{n}) of the liquid crystal are shown in Fig. 1. The principal spectral features of C_{70} are seen in both polarizations; however, the spectral forms are markedly different. The long-wave transition ($\lambda \sim 4700 \text{ \AA}$) intensity, like in a nematic liquid crystal,³ is stronger in the $\mathbf{T} \perp \mathbf{n}$ polarization. The intensity of $\lambda \sim 3800 \text{ \AA}$ and $\lambda \sim 3600 \text{ \AA}$ transitions, which were not observed in Ref. 3, are stronger in the $\mathbf{T} \parallel \mathbf{n}$ polarization, indicating that these transitions are oriented with respect to different molecular axes.

Figure 2 shows 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 maximum position is different in the two polarizations, and the polarization ratio increases at $\lambda < 4700 \text{ \AA}$. This behavior may be partly attributed to overlapping of the spectrum with the short-wave absorption spectrum with an opposite polarization ratio. Intermolecular static interaction may also lead to splitting of electronic bands in the two polarizations.⁶ The observable shifts of the bands in the two polarizations are consistent with the earlier calculations⁶ for the case in which the electronic transition dipole moment is perpendicular to the longer molecular axis.

Difference of the polarization ratio from unity (for the long-wave transition $P \sim 0.53$ in $\lambda \sim 5000\text{-}\text{\AA}$ region) is indicative of a strong orientation of C_{70} molecules in SLC. A C_{70} molecule consists of 25 hexagons and 12 pentagons which form a "rugby-ball," i.e., an egg-shaped structure. It differs, however, only slightly from a sphere (the axes differ in length less than 12%).⁷ Therefore, the strong orientation cannot be

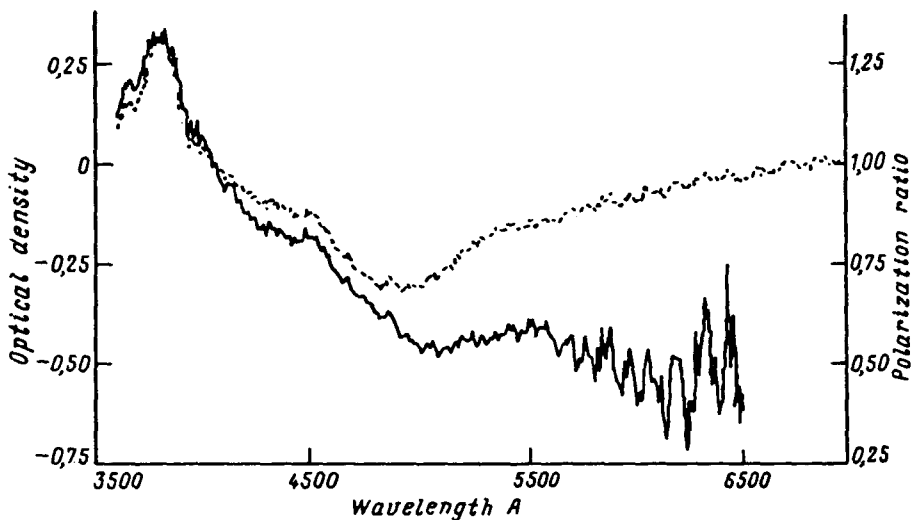


FIG. 2. Polarization ratio $P = D_{\parallel} / D_{\perp}$ (solid curve) and the $D_{\parallel} - D_{\perp}$ difference spectrum (dashed curve) of fullerene C_{70} in a smectic liquid crystal.

attributed to the geometric factor alone; it rather indicates a strong anisotropy of the intermolecular interaction of C_{70} molecules. If the degree of orientational ordering of fullerene is assumed to be the same as that of liquid crystals, then the direction of the electronic transition dipole moment in a molecule is estimated to be $\sin^2 \alpha = [2(P-1) + S_0(P+2)] / 3S_0(P+2)$,⁸ where α is the angle between the transition dipole moment direction and the plane perpendicular to the molecular axis oriented with respect to the director (the "long" axis of C_{70}), and $S_0 = 0.7$ is the order parameter of SLC. Since no absorption dichroism was observed in a spherical C_{60} molecule, the internal fields in a liquid crystal may be ignored in a calculation.⁹ For the long-wave transition we obtain $\alpha \approx 23^\circ$. Since fullerene molecules differ in shape from liquid crystal molecules, we 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 obtain a large value of $S_F \approx 0.37$. This value of S is realized in a 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 $S_L^* \approx 1$, the values of S_0 and S_F can be used to estimate the degree of local ordering of C_{70} molecules S_{LF} . S_F consists of local ordering of C_{70} with respect to the nearest liquid crystal molecules and orientational ordering of the liquid crystal structure. For S_{LF} a simple expression $S_{LF} = S_F / S_0$ can be obtained, i.e., $S_{LF} = 0.53$.

C_{60} is a plastic crystal which has an ideal spherical molecular shape. The classical statistical theories^{10,11} predict the formation of liquid crystal structures for the systems

consisting of long rigid rods (Onsager's approximation), spherocylinders of finite length (cylinders terminated in hemispheres at both ends), and 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 crystal structure may form in fullerenes which consist of a large number of carbon atoms in the case where the temperature of the transition to an orientationally ordered phase (thermotropic liquid crystal) or the required concentration of the material (concentrational transition) is not too high.

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