Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Gunyakov, V. A. , Shestakov, N. P. and Shibli Corresponding author, S. M.(2003) 'Density and refractive index measurements in hexaheptyloxytriphenylene, a discotic liquid crystal', Liquid Crystals, 30: 7, 871 — 875
To link to this Article: DOI: 10.1080/0267829031000121224
URL: http://dx.doi.org/10.1080/0267829031000121224

Liquid Crystals, Vol. 30, No. 7, July, 2003, 871–875

Density and refractive index measurements in hexaheptyloxytriphenylene, a discotic liquid crystal

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(*Received 14 October 2002; in final form 5 February 2003; accepted 27 February 2003*)

Density and refractive index measurements in the discotic liquid crystal hexaheptyloxytriphenylene were performed in the hexagonal columnar $\mathrm{Col_{ho}}$ and isotropic I phases. The temperature dependence of the density $\rho(T)$ for this compound was obtained by combining small angle X-ray data and capillary methods. The ordinary n_o extraordinary n_e and isotropic liquid n_i refractive indices were measured using a modified Abbe refractometer to an accuracy of about 10^{-3}. To check the consistency of the density and the refractometry experiments we used the Lorentz–Lorenz relation. An anomaly in the empirical relationship $\left(\overline{n^2}-1\right)\Big/\rho\left(\overline{n^2}+2\right)=\left(n_i^2-1\right)/\rho_i\left(n_i^2+2\right)$ at the $\mathrm{Col_{ho}}$–I phase transition, which holds for many uniaxial liquid crystals, was detected. A discrepancy between low birefringence $\Delta n \sim 0.109$ and a relatively high local electric field anisotropy for hexaheptyloxytriphenylene is discussed.

1. Introduction

Molecules which exhibit discotic nematic and columnar liquid crystal phases (LCs) generally have a flat, rigid, disc-like central core attached to which are six or eight long flexible chains. The uniaxial columnar phase consists of discs stacked one on top of the other to form columns, arranged on a two-dimensional lattice [1]. The director **n** denotes the preferred axis of orientation of the disc-normals. The molecular cores are highly ordered relative to the director **n**, while the disordered long chains fill the space between the columns [2]. Columnar discotic phases are characterized by unusually large charge carrier mobilities, which have important potential in molecular electronics and other applications [3]. To analyse the quasi-one-dimensional electric conductivity of the hexagonal columnar $\mathrm{Col_{ho}}$ phase, information is required on the parameters of the local field of a light wave acting on the molecules. Recently these parameters for the discotic LC hexaheptyloxytriphenylene were obtained from an infrared (IR) study [4]. It was shown that the ratio of the parallel and perpendicular components of the local field tensor, related to the director **n**, corresponds to a higher conductivity of the $\mathrm{Col_{ho}}$ discotic sample along the columns. It was shown also that the two-dimensional crystalline ordering of the molecular columns reduces the anisotropy of the local field in the columnar phases. This factor is absent in discotic nematics, which show only orientational ordering of the disc-like molecules. In fact, the approximation of an isotropic local field can be used for discotic nematics having low optical anisotropy Δn [5]. It would be interesting to elucidate the role of the optical anisotropy of the columnar phases in determining the local field. Density is another relevant parameter in the investigation of liquid crystal systems, particularly in studies of phase transitions. Furthermore, such basic physical parameters as density and refractive indices of columnar phases are important for analysing their molecular-optical properties of relevance to technical applications. Surprisingly, no attempt to measure these characteristics has been reported to date. In the present work, we studied a hexagonal columnar discotic phase using small angle X-ray scattering, capillary and refractometry techniques. We also checked the consistency of our measurements by means of the Lorentz–Lorenz relation.

2. Experimental

The sample studied, 2,3,6,7,10,11-hexaheptyloxytriphenylene, is a discotic liquid crystal (H7T). The transition temperatures for H7T are: Cr-68°C-$\mathrm{Col_{ho}}$-92.5°C-I, where Cr, $\mathrm{Col_{ho}}$, I are crystalline, hexagonal ordered columnar and isotropic phases, respectively.

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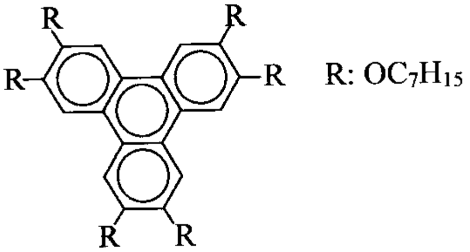
Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2003 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/0267829031000121224

The temperatures of these phase transitions were confirmed using a differential scanning calorimeter, Shimadzu DSC-50, at a scanning rate of 20°C h^{-1}.



The refractive indices of hexaheptyloxytriphenylene were measured using a temperature controlled Abbe refractometer (Carl Zeiss). This is the most convenient technique, since the direct measurement of the ordinary n_o and extraordinary n_e refractive indices of H7T is the only way of obtaining information about the optical anisotropy of the columnar phase. The main difficulty precluding the use of the refractometer for measuring the extraordinary refractive index, is related to the alignment of the liquid crystal director normal to the surfaces of the prisms. A reliable homeotropic orientation of a columnar mesophase can be obtained within a flat capillary of thickness about 10 μm [6]. As a rule, an Abbe refractometer has a 100–200 μm gap between the two working prisms. To obtain the oriented layer of H7T, the prism block of the refractometer was modified. We replaced the upper illuminating prism by a glass plate with a high refractive index and reduced the gap between the working surfaces to 10 μm using appropriate spacers. The orientation of the director **n**, normal to the surface of the measuring prism, was achieved by filling the capillary in the isotropic phase and slowly cooling to the discotic phase. This orientation of the director ensures the observation of both sharp boundary lines corresponding to the internal reflection angles of the ordinary and extraordinary refractive indices within the mesophase. To exclude any doubt about the validity of the refractive index measurements a calibration procedure was carried out over the temperature range of the mesophase. Distilled water was used as the calibrant. Both values of the refractive indices for distilled water, measured before and after the modification of the refractometer, coincided within the accuracy of the experiment. The precision of the refractive index measurements was about 10^{-3}. The temperature corrections of the refractive indices due to the variation of the refractive index of the prism, on increasing the temperature, were performed as described elsewhere [7].

For density measurements we used the capillary method. A small amount of hexaheptyloxytriphenylene was introduced into a glass capillary of about 0.2 mm internal diameter. The capillary was isolated in a glove box filled with dry air and thermostated to ±0.05°C. Thus, the sample was protected against the risks of sublimation and degradation due to oxidation, or to the ambient humidity [8]. We used an electric furnace containing an oven; the temperature was monitored using a thermocouple connected to the capillary. The discotic sample was thoroughly degassed before use, the degassing being performed by successive heating and cooling stages. By melting and recrystallizing alternately, the sample was gradually purged of dissolved air.

The temperature dependence of the length of the liquid crystal columns inside the capillary and of the internal diameter of the capillary were measured by means of a laser interferometer. The capillary and special prism reflector of the interferometer were mounted on the base of an optical comparator. This optical system made possible measurements of precision of about 1 μm, with the possibility of detecting volume changes of 1.6×10^{-6} cm^3. The main error in the determination of density arose from the weighing process, given the very small amounts of H7T inside the capillary. To evaluate the mass of H7T inside the capillary to a higher precision we used the value of the specific gravity obtained from X-ray data.

X-ray diffraction patterns of hexaheptyloxytriphenylene were obtained using a conventional set-up consisting of a focusing monochromator adjusted to give a parallel beam. The sample was held in a Lindemann glass capillary tube of *c.a.* 1 mm diameter perpendicular to the incident beam. The temperature control of the sample was about ±0.05°C, using a custom-built apparatus. The scattered intensity was recorded using X-ray photoplates. Photographic images were digitized using an optical scanner, 'Storm 820' (Molecular Dynamics). Sample-to-detector distance was evaluated using the diffraction pattern of the *n*-dodecylsulphate sodium salt $C_{12}H_{25}NaO_4S$ (Merck) at known angles of X-ray scattering.

3. Results and discussion

The DSC thermogram for hexaheptyloxytriphenylene is given in figure 1. The sample exhibits two transitions: the lower temperature one can be attributed to the melting of the solid crystal to a mesophase and the higher temperature one to the isotropization of the mesophase. On the basis of the heating data, the mesophase temperature region was estimated. We use the reduced temperature $\Delta T = T_c - T$, where $T_c = 92.5$°C is the clearing point of the discotic mesophase.

The results of measurements of the refractive indices are presented in figure 2. The dashed line is

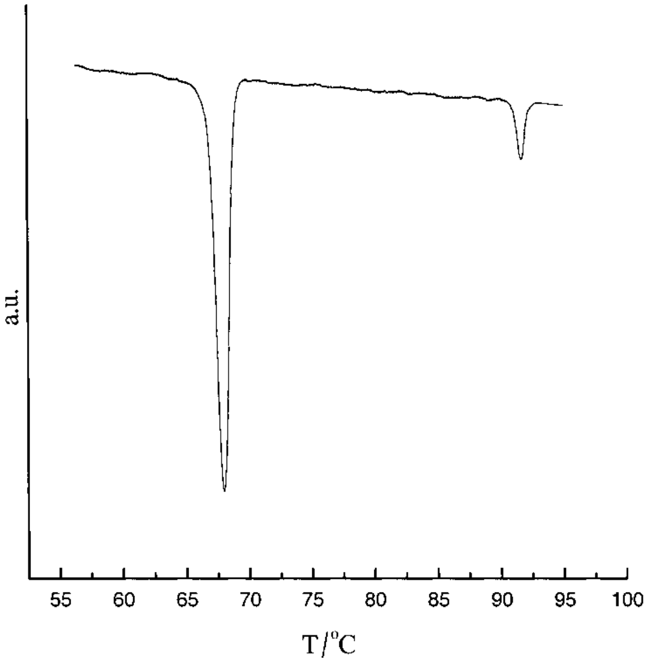


Figure 1. DSC thermogram of 2,3,6,7,10,11-hexaheptyloxytriphenylene.

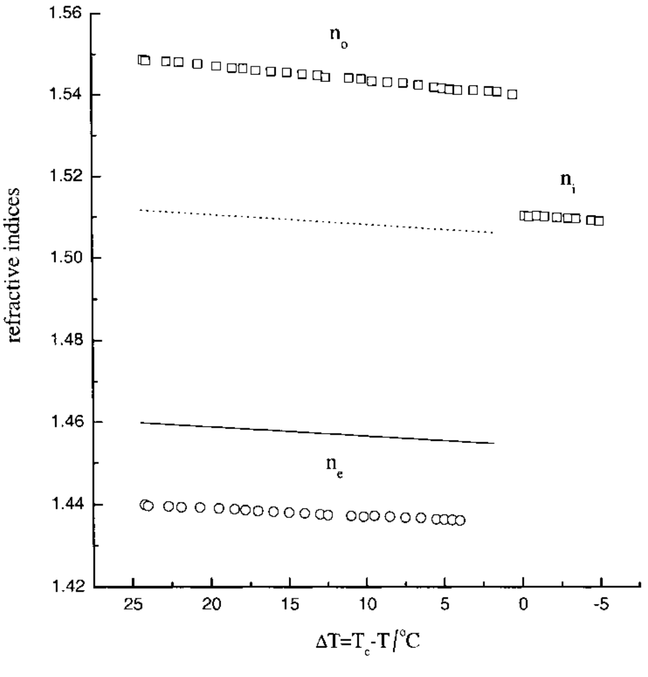


Figure 2. Refractive indices of H7T as a function of the reduced temperature $\Delta T = T_c - T$, where T_c is the clearing point, at 589 nm. The dashed line is the value of $[(n_e^2+2n_o^2)/3]^{1/2}$. The solid line is the temperature dependence of the extraordinary refractive index n_e calculated from equation (2).

the temperature dependence of the mean value of the refractive index $\left(\overline{n^2}\right)^{1/2} = \left[\left(n_e^2+2n_o^2\right)/3\right]^{1/2}$ in the columnar mesophase. As shown in figure 2 the change in the refractive indices at the Col$_{ho}$–I phase transition is not in good agreement with the expression $\left(\overline{n^2}\right)^{1/2} = n_i$, where n_i is the refractive index of the isotropic phase. Below the temperature $\Delta T = 3.8$°C we could not measure the extraordinary refractive index because the corresponding boundary line in the refractometer was not sharp enough. It should be noted that an inspection of the homeotropic sample of H7T inside the optical cell under the polarizing microscope, confirms the breakdown in the perfect orientation near to the Col$_{ho}$–I phase transition. We observed that the optical anisotropy $\Delta n = n_o - n_e$ is negative, as expected for disc-like polyaromatic molecules. A slight decrease of Δn on increasing the mesophase temperature originates from a reduction of the orientational order parameter S of the hexagonal columnar phase.

The diffraction pattern of the unoriented sample of H7T (figure 3) is consistent with the assignment of a Col$_{ho}$ mesophase [9]. In the wide angle region, two diffuse reflections are observed. The broad one at $q \approx 2\pi/4.5$ Å^{-1} (b) corresponds to a liquid-like ordering of the flexible chains of the molecules, whilst the relatively narrow one, observed at $q \approx 2\pi/3.59$ Å^{-1} (a), is due to the stacking periodicity of the molecular cores within the columns. It is known that the X-ray scattering from the intracolumnar stacking in a Col$_{ho}$

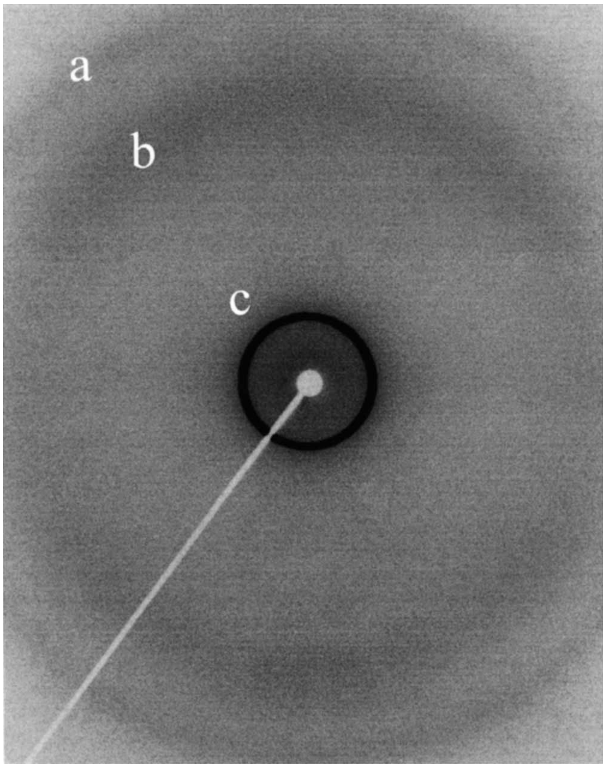


Figure 3. X-ray diffraction pattern of the hexagonal columnar phase of an unoriented sample of H7T.

phase does not give Bragg reflections, but rather relatively narrow diffuse peaks with a corresponding correlation length of the order of 100 Å [10]. Thus, in the ordered $\mathrm{Col_{ho}}$ phase the molecules in each column are correlated over 30–50 intermolecular distances, in contrast to the disordered $\mathrm{Col_{hd}}$ phase, in which liquid-like correlations within the columns extend over only a few neighbouring molecules. In the low angle region a strong sharp Bragg ring (c) originates from the long range hexagonal order of molecular columns. From the radius of the Bragg ring, one can derive the period of the hexagonal lattice $a \approx 22.83$ Å. It should be noted that the intermolecular distance d is the same as the one used in [9], but the parameter of the hexagonal lattice a is 0.9 Å higher. In a simple hexagonal phase the unit cell volume of hexaheptyloxytriphenylene can be evaluated using parameters a and d of the two-dimensional lattice using the equation $V=\sqrt{3}da^2/2$ [11]. The general rule, as in the case of H7T, is that the molecular volume is equal to the unit cell volume in an hexagonal mesophase of typical discotic compounds [12]. The specific gravity of the mesophase of H7T is calculated as $1.07\,\mathrm{g.cm^{-3}}$. This parameter allows us to evaluate the mass of the liquid crystal column inside the capillary. The mass remains constant with temperature variation of the volume. Then, the density of H7T in the mesophase and the isotropic phase was evaluated using the temperature dependence of volume obtained from capillary measurements. The temperature dependence of density is presented in figure 4. The value of the $\mathrm{Col_{ho}}$–I transition temperature shows good agreement with the calorimetry and refractometry results.

To check the consistency of density and refractometry measurements we used the Lorentz–Lorenz relation. An analogue of this relation, for uniaxial LCs, can be written as [13]

$$\frac{\overline{n^2}-1}{\overline{n^2}+2}=\frac{4\pi N_\mathrm{A}}{3M}\rho\bar{\gamma}A. \tag{1}$$

Here $\bar{\gamma}=\left(\gamma_\parallel+2\gamma_\perp\right)/3$ is the mean effective polarizability of the molecules. The values $\gamma_\parallel$ and $\gamma_\perp$ are the average longitudinal and transverse polarizabilities of molecules relative to the director **n** of the uniaxial liquid crystal phase, respectively. M and ρ are the molecular mass and the density of the mesophase, respectively; N_A is the Avogadro number. The value A depends on the order parameter S, the optical Δn and the structural $\tau=\left(L_\parallel-L_\perp\right)/3$ anisotropies of LCs, as well as on the anisotropy of the local field Δf and the anisotropy of molecular polarizability $\Delta\gamma=\gamma_\parallel-\gamma_\perp$: $A=1+2\left[\left(n_\mathrm{e}^2-n_\mathrm{o}^2\right)\tau+S\Delta\gamma\Delta f/3\bar{\gamma}\right]/\left(\overline{n^2}+2\right)$. Here $L_\parallel$ and $L_\perp$ are the parallel and perpendicular components of the Lorentz tensor relative to the director, respectively. In the approximation of an isotropic local field $\Delta f\approx 0$ $\left(L_\parallel\approx L_\perp\right)$ the value A is equal to unity. On the other hand, the empirical equality

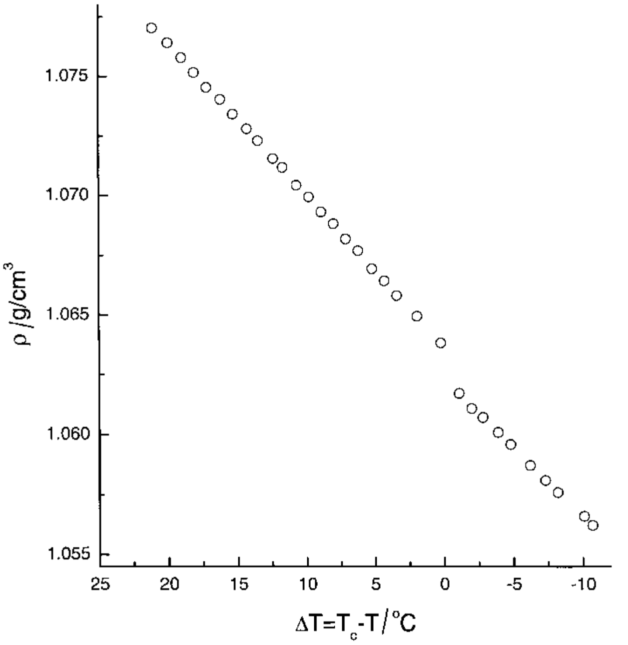


Figure 4. Temperature dependence of the density in the $\mathrm{Col_{ho}}$ and I phases of hexaheptyloxytriphenylene.

$$\frac{\overline{n^2}-1}{\rho\left(\overline{n^2}+2\right)}=\frac{n_\mathrm{i}^2-1}{\rho_\mathrm{i}\left(n_\mathrm{i}^2+2\right)} \tag{2}$$

holds for many uniaxial calamitic nematic and smectic A phases and discotic nematic phases. We assume that equation (2) is also true for columnar discotics. This equality is satisfied in the experiment owing to the constancy of the product $\bar{\gamma}A$. It means that the left-hand side of the Lorentz–Lorenz relation plotted as a function of temperature corresponds only to the temperature variation of the liquid crystal density. In figure 5 the temperature dependence of the function $\left(\overline{n^2}-1\right)/\left(\overline{n^2}+2\right)$ for hexaheptyloxytriphenylene in the $\mathrm{Col_{ho}}$ and I phases is presented. As seen in this figure, the behaviour of this function at the $\mathrm{Col_{ho}}$–I transition is different from the behaviour of the density shown in figure 4.

We calculated the extraordinary refractive index using equation (2) and found that this (solid line in figure 2) does not coincide with the experimental data (circles in figure 2). The difference between the calculated and experimental values of the birefringence Δn is about 20% within the mesophase. These results allow us to comment on an anomaly in the empirical equation (2) for H7T. The X-ray patterns of H7T reveal that the distance between two stacks in the columnar phase is smaller than the diameter of the fully extended molecule in the isotropic phase [9]. It would appear,

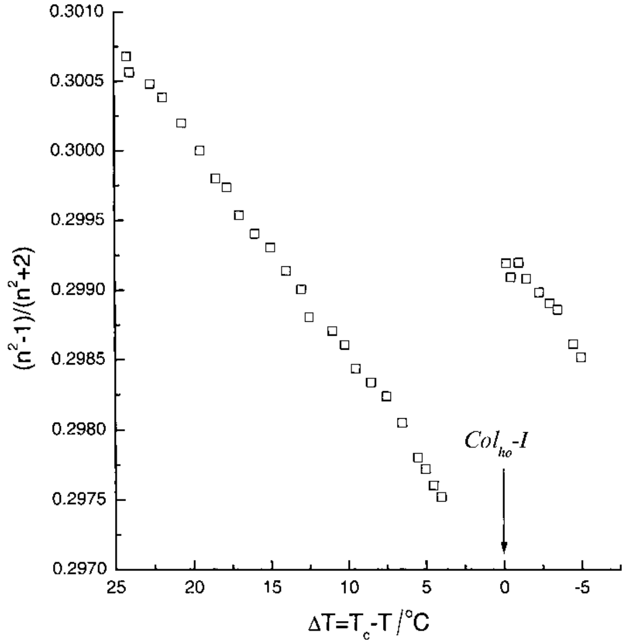


Figure 5. Temperature dependence of the function $\left(\overline{n^2}-1\right)/\left(\overline{n^2}+2\right)$ in the columnar and isotropic phases.

therefore, that the Col_{ho}–I transition is accompanied by a variation of the distribution of the polarizability over the molecular volume due to conformational variations of the disc-shaped molecules. It is surprising that variations of the molecular polarizability imply an additional decrease of the extraordinary refractive index n_e from 1.46 to 1.44 and an increase of Δn from 0.090 to 0.109. This leads to an anomaly in equation (2) for the columnar discotic phase.

Refractometry measurements for truxene derivatives exhibiting the discotic nematic phase have been performed [14]. These LCs have a low optical anisotropy $\Delta n \sim 0.1$, and the approximation of an isotropic local field is valid for these compounds [5]. In spite of an additional increase in the birefringence of hexaheptyloxytriphenylene in the Col_{ho} phase, we obtained a relatively low value of $\Delta n \sim 0.109$, comparable to that of the truxene derivatives. As well as the low optical anisotropy, the two-dimensional crystalline ordering of the molecular columns also reduces the anisotropy of the local field in the Col_{ho} phase. One would therefore expect the effect of the isotropization of the Lorentz tensor, but in fact IR data revealed the anisotropy of the tensor. The parallel and perpendicular components of the Lorentz tensor are $L_{\|}=0.66\pm0.02$ and $L_{\perp}=0.17\pm0.01$, respectively [4]. The total anisotropic component of the local field correction consists of two parts: the anisotropy of the molecular shape, which is directly connected to the local environment of the molecule, and the optical anisotropy of the medium [15]. We suppose that, for columnar phases, the local environment of the disc-like molecules plays a more important role in determining the local field than the value of the optical anisotropy. This issue has not been completely clarified and requires further investigation.

4. Conclusion

To conclude, we have experimentally determined the density and refractive indices of the columnar and isotropic phases of hexaheptyloxytriphenylene. We used the equations of the molecular optics for uniaxial LCs to check the results of our measurements. An anomaly of the empirical equation (2) was revealed, related to conformational variations of the disc-shaped molecules at the Col_{ho}–I transition. The molecular polarizability is sensitive to these variations. To study features of the polarizability distribution over molecular volume, however, we need further information about the orientational, statistical and structural properties of hexaheptyloxytriphenylene in addition to the density and refractive index data obtained in this work.

The authors are in debt to Bruna B. Postacchini and Renata L. Rosa for the DSC and X-ray measurements, respectively. We would also like to acknowledge Fundação de Amparo à Pesquisa de São Paulo (FAPESP) for financial support.

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