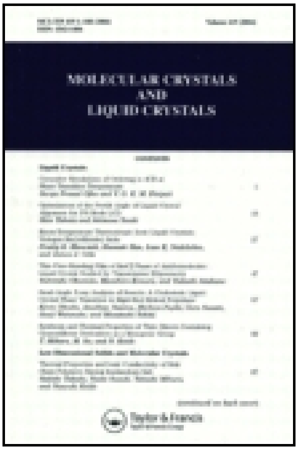

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Order Parameters from Magnetic Susceptibility Measurements on Some Nematogens

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Order Parameters from Magnetic Susceptibility Measurements on Some Nematogens

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The diamagnetic susceptibility of three alkoxyphenyl trans-4-alkyl cyclohexane carboxylates and p-cyanophenyl trans-4-pentyl cyclohexane carboxylate are reported as a function of temperature in the solid, nematic and isotropic phases. Assuming that the molecules are effectively axially symmetric, the temperature dependence of orientational order parameter $\langle P_2 \rangle$ has been investigated from the anisotropy of the susceptibility at different temperatures. The values of $\langle P_2 \rangle$ agree reasonably well with the predictions from Maier and Saupe theory except near the clearing point where the values of $\langle P_2 \rangle$ are lower than theoretical prediction, whereas $\langle P_2 \rangle$ values obtained from X-ray diffraction studies show good agreement with theoretical values. The possible cause of this discrepancy has been discussed.

Keywords: diamagnetic anisotropy, order parameters, density, nematogens

INTRODUCTION

The determination of diamagnetic properties is of great importance in the study of liquid crystals.[1] All anisotropic properties of liquid crystals are related to the orientational order parameter $\langle P_2 \rangle$, in a more or less complicated way. So, anisotropy of diamagnetic susceptibility, $\Delta\chi$, can be used to evaluate $\langle P_2 \rangle$, which is one of the fundamental quantities for describing the behavior of liquid crystals. In addition, a knowledge of the diamagnetic anisotropy is required to determine the elastic constants of nematic liquid crystals from Frederiks transition and to understand the magnetic field effects.[2]

The relation between the anisotropy of the magnetic susceptibility and the order parameters can be derived after making a few assumptions.[3–6] The anisotropy of the diamagnetic susceptibility, $\Delta\chi$, is given by

$$\Delta\chi = (\chi_{\parallel} - \chi_{\perp}), \tag{1}$$

where $\chi_{\parallel}$ and $\chi_{\perp}$ are the diamagnetic mass susceptibility parallel and perpendicular to the director. In most cases $\Delta\chi$ is positive. Since we can not measure $\chi_{\perp}$ directly, we replace eqn. (1) by the following

$$\Delta\chi = \frac{3}{2}(\chi_{\parallel} - \bar{\chi}), \tag{2}$$

$\bar{\chi}$ [$\equiv 1/3(\chi_{\parallel} + 2\chi_{\perp})$] being the mass susceptibility in the isotropic phase.

Order parameter $\langle P_2 \rangle$ is expressed by

$$\langle P_2 \rangle = \frac{\Delta\chi}{\Delta\chi_o}, \tag{3}$$

$\Delta\chi_o$ being the diamagnetic susceptibility anisotropy of completely ordered nematic phase.

In this paper we are reporting our measurements of the diamagnetic susceptibility at different temperatures of following four nematogens:

(I) p-methoxyphenyl trans-4-pentyl cyclohexane carboxylate,
(II) p-propoxyphenyl trans-4-pentyl cyclohexane carboxylate,
(III) p-ethoxyphenyl trans-4-butyl cyclohexane carboxylate, and
(IV) p-cyanophenyl trans-4-pentyl cyclohexane carboxylate.

They have the structure shown below:

I, $R_1 = C_5H_{11}$, $R_2 = OCH_3$
II, $R_1 = C_5H_{11}$, $R_2 = OC_3H_7$
III, $R_1 = C_4H_9$, $R_2 = OC_2H_5$
IV, $R_1 = C_5H_{11}$, $R_2 = CN$

The samples were kindly donated by M/s. Hoffman-La-Roche and Co., Basel, Switzerland. In their catalogue the transition temperatures of the compounds are as follows:

I, Solid $\xrightarrow{40^\circ 7^\circ\text{C}}$ Nematic $\xrightarrow{71^\circ 1^\circ\text{C}}$ Isotropic
II, Solid $\xrightarrow{43^\circ 3^\circ\text{C}}$ Nematic $\xrightarrow{71^\circ 1^\circ\text{C}}$ Isotropic
III, Solid $\xrightarrow{36^\circ 3^\circ\text{C}}$ Nematic $\xrightarrow{74^\circ 6^\circ\text{C}}$ Isotropic
IV, Solid $\xrightarrow{47^\circ\text{C}}$ Nematic $\xrightarrow{78^\circ 7^\circ\text{C}}$ Isotropic

All the samples were supplied to us in pure form and were used without further purification.

Description of the experimental set-up

Most of the usual methods for measuring susceptibilities consist of estimating the translational force on a sample placed in an inhomogeneous magnetic field. Considering all these methods we have selected Curie torsion balance technique for better accuracy and stability for our system. We have designed an electromagnetic balance for this purpose. Figure 1 shows the schematic diagram of the apparatus.

It consists of a horizontal light glass balance beam A, secured in its place with two phosphor-bronze strips. The upper strip B is soldered to a torsion head T used for adjusting tension and orientation of the beam, whereas, the lower strip B′ terminates in a spring E, made of phosphor-bronze, secured to an adjustable holder H which can be moved horizontally in two directions. The torsion head is fixed to a brass pillar S and the holder H is fixed on a flat brass plate b resting on levelling screws.

A perspex block R is attached to one end of an arm of the balance beam. The sample holder can be hung by a glass capillary tube from this perspex block. A damping vane V made of thin mica sheet, dipping into diffusion pump oil, fixed to the other arm of the glass beam effectively damps out all unwanted vibrations. To that arm of the beam is attached a balancing coil of 15 turns of 42 s.w.g. enamelled copper wire wound over a hollow perspex cylinder C and the coil is free to move inside a hollow magnet M with a radial field of about 200 gauss. Here the phosphor-bronze strips serve double purpose; they act as suspension wire as well as electrical connection to the coil. A greased ground bell-jar J forms a convenient cover for the balance assembly. Two holes are drilled in the base plate P. In one of these (h_1) is one porcelain sleeve, sealed vacuum tight with araldite, for leading wire in for the coil current. The other terminal of the coil is attached to the brass base plate which completes the circuit. The second aperture h_2, about 3 cm. in diameter, is fitted with a brass

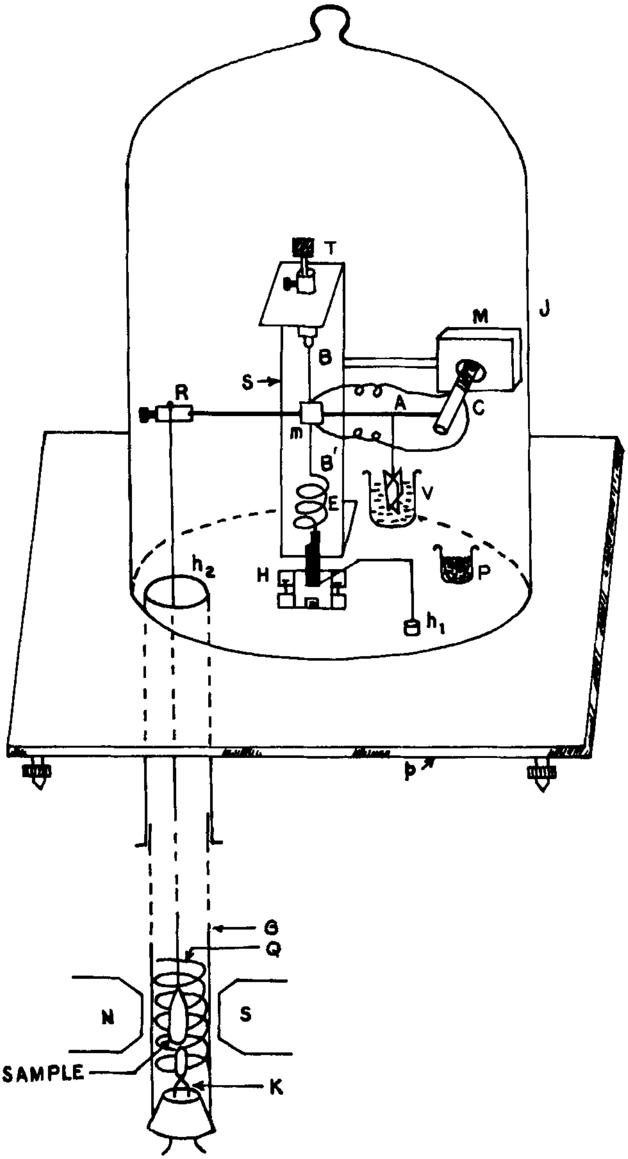

FIGURE 1 Schematic diagram of the apparatus for measuring magnetic susceptibility. T-Torsion head, S-Brass pillar, B,B'-Phosphor-bronze strips, m-Mirror, A-Balance beam, M-Magnet, C-Coil, E-Spring, G-Glass tube, Q-Heater, K-Thermocouple, P-Beaker containing calcium chloride, V-Vane, H-Adjustable platform, J-Bell-jar, p-Brass plate, R-Perspex block.

collar for fitting the glass tube extension of the experimental chamber. The joint of the glass tube G and brass tube is made vacuum tight with O-ring. The glass tube carries a heater Q of constantant wire (non-magnetic) fitted in a non-inductive way and a thermocouple K, placed close to the sample holder, through a rubber stopper tightly fitted to the glass tube with araldite. The sample holder, thermocouple and the heater are placed between the pole pieces of an electromagnet. Inside the bell-jar a small beaker P partially filled with calcium chloride is kept to absorb atmospheric water vapour. The system can be evacuated to avoid instability due to convectional currents.

The Sucksmith form of pole-pieces is adopted and the detection of the change in the position of the sample has been made with the help of a pair of matched photo cells.

EXPERIMENTAL

The magnetic susceptibilities have been measured by the classical Faraday-Curie method. The formula used in this case is given by,[11]

$$\chi(t) = \frac{F}{F_r} \times \frac{m_r}{m}\left[\chi_r - \frac{\rho_o(t_o)}{\rho_r(t_o)} \times \chi_o(t_o)\right] + \frac{\rho_o(t)}{\rho(t)}\chi_o(t) \qquad (1)$$

Where χ, F, m, ρ and t stand for susceptibility, force, mass, density and temperature respectively. Subscript 'r' and 'o' stand for reference sample and air and t_o represents the temperature at which the reference measurement has been done.

The sample was put in a cylindrical quartz container having a volume of nearly .1 cm^3. It was hung by a glass capillary between the pole-pieces, the values of dH^2/dx being 1.1 K.gauss^2/cm approximately. The value of dH^2/dx is constant within 1% for 1 cm. length along x-direction. Along y and z directions dH^2/dx is practically constant over sufficiently large distances. So, we assumed that in every case we put the samples in constant dH^2/dx. The temperature of sample was maintained with ± 0.5°C of the desired temperature by an automatic temperature controller (Indo-therm, India). About 30 minutes were allowed for the sample to reach the thermal equilibrium. The accuracy of the measurement using this balance is about 1%.

We used trans-Decaline ($\chi_r = -.779 \times 10^{-6}\text{cm}^3\text{gm}^{-1}$)[7], a non-volatile liquid at room temperature as a reference substance. Density of reference sample is .869 gm/cc[8]. Using the magnetic susceptibility of air ($\chi_o = 106.3 \times 10^{-6}\mathrm{cm}^3\mathrm{gm}^{-1}$ at 20°C)[9], the Curie's law $\chi_o \sim 1/T$, the tabulated density of air,[10] the necessary corrections as given by Eq. (1) can be calculated. Error due to influence of dissolved oxygen has been discussed and has been ignored by de Jeu *et al.*[11] This has been neglected by us as well.

The force on the sample is exactly balanced by the force exerted on the horizontal coil, rigidly attached to the balance beam, placed inside a hollow permanent magnet with a uniform radial field and carrying a suitable electric currient i. This force, F, on the coil due to the uniform field is given by

$$F = 2\pi r n i H,$$

where

n = number of turns in the coil,
r = radius of the coil,
H = magnetic field

In general the suspended system will experience a force even in the absence of any sample due to the diamagnetism of the sample holder. To balance this pull, we must employ an initial current i_o through the coil. In our set up, instead of the current we measured voltage drop across a standard resistance of the order of 10 K. ohms with the help of a high precision digital voltmeter. So the final expression for susceptibility becomes

$$\chi(t) = \frac{V - V_o}{V_r - V_o} \times \frac{m_r}{m}\left[\chi_r \frac{\rho_o(t_o)}{\rho_r(t_o)}\chi_o(t_o)\right] + \frac{\rho_o(t)}{\rho(t)}\chi_o(t) \qquad (2)$$

We tested the experimental setup by measuring the susceptibility of p-azoxyanisole (PAA) as a function of temperature and the values we got are within 1% to the values reported by de Jeu *et al.*[12]

RESULTS AND DISCUSSION

The transition temperatures of the compounds as observed by us by using a polarising microscope with a hot stage agree well with the literature values during heating but during cooling we got supercooled nematic phase in all the samples. From X-ray diffraction studies and optical birefringence measurements[13] also we confirmed the presence of supercooled nematic phases. The transition temperatures reported by Beens *et al.*[14] are slightly different from our findings. The transition temperatures of the compounds as obtained by us are given below:

$$\text{I, Solid} \xrightleftharpoons[\sim 11{\cdot}5^\circ\text{C}]{40{\cdot}7^\circ\text{C}} \text{Nematic} \xrightleftharpoons{71{\cdot}1^\circ\text{C}} \text{Isotropic}$$

$$\text{II, Solid} \xrightleftharpoons[37^\circ\text{C}]{43{\cdot}3^\circ\text{C}} \text{Nematic} \xrightleftharpoons{71{\cdot}1^\circ\text{C}} \text{Isotropic}$$

$$\text{III, Solid} \xrightleftharpoons[\sim 11^\circ\text{C}]{36{\cdot}3^\circ\text{C}} \text{Nematic} \xrightleftharpoons{74{\cdot}6^\circ\text{C}} \text{Isotropic}$$

$$\text{IV, Solid} \xrightleftharpoons[\sim 11^\circ\text{C}]{47^\circ\text{C}} \text{Nematic} \xrightleftharpoons{78{\cdot}7^\circ\text{C}} \text{Isotropic}$$

The Figure 2 shows the variation of $\Delta\chi$ with temperature of the four compounds. The values of densities in the nematic and isotropic phases are listed in Table I which also contains the results of $\Delta\chi$ of the compounds. Since we have no crystallographic data of the first three compounds we could not measure $\Delta\chi_o$ from the completely ordered crystalline phase. Crystallographic data for the compound IV are available.[15] But we did not try to measure $\Delta\chi_o$ directly from

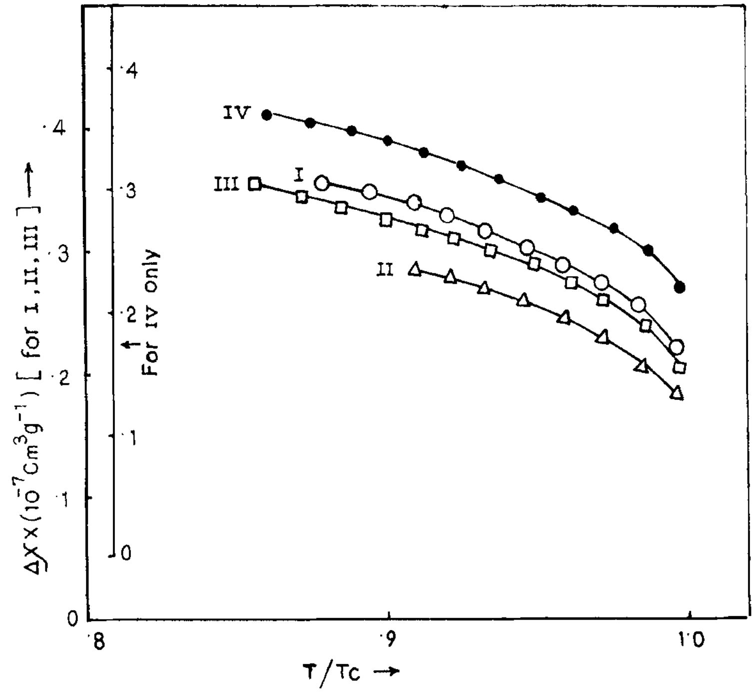

FIGURE 2 Variation of $\Delta\chi$ with reduced temperature.

TABLE I

Temperature (°C), anisotropy ($\Delta\chi$) in $10^{-7}\text{cm}^3\text{g}^{-1}$ and density (ρ) in g cm^{-3} and order parameter $\langle P_2 \rangle$ for the compounds

Sample I				Sample II				Sample III				Sample IV			
t	$\Delta\chi$	ρ	$\langle P_2 \rangle$	t	$\Delta\chi$	ρ	$\langle P_2 \rangle$	t	$\Delta\chi$	ρ	$\langle P_2 \rangle$	t	$\Delta\chi$	ρ	$\langle P_2 \rangle$
29.5	.356	1.073	.6500	40	.285	1.036	.6250	25	.357	1.056	.6839	30	.363	1.071	.6700
35	.348	1.068	.6363	44	.278	1.035	.6086	30	.347	1.057	.6639	35	.356	1.069	.6562
40	.339	1.060	.6105	48	.269	1.034	.5888	35	.336	1.058	.6437	40	.348	1.065	.6423
44	.329	1.055	.6006	52.5	.260	1.032	.5691	40	.327	1.059	.6264	44	.339	1.061	.6257
48	.315	1.050	.5759	57	.246	1.029	.5395	44	.318	1.070	.6092	48	.329	1.057	.6063
52.5	.302	1.045	.5513	61.5	.231	1.026	.5066	48	.311	1.069	.5948	52.5	.318	1.053	.5869
57	.287	1.040	.5238	65.5	.213	1.020	.4671	52	.302	1.066	.5776	57	.308	1.050	.5676
61.5	.275	1.035	.5019	70	.186	1.009	.4079	57	.290	1.053	.5546	61.5	.296	1.046	.5454
65.5	.255	1.025	.4662					61	.276	1.050	.5287	65.5	.282	1.042	.5205
70	.221	1.002	.4032					65	.263	1.046	.5029	70	.267	1.036	.4928
								70	.240	1.039	.4600	74	.249	1.028	.4596
								74	.209	1.028	.4000	78	.221	1.010	.4070

For sample I, $\Delta\chi_o^M = 16.63\ \text{cm}^3\text{Mol}^{-1}$;
For sample II, $\Delta\chi_o^M = 15.14\ \text{cm}^3\text{Mol}^{-1}$;
For sample III, $\Delta\chi_o^M = 15.87\ \text{cm}^3\text{Mol}^{-1}$;
For sample IV, $\Delta\chi_o^M = 16.20\ \text{cm}^3\text{Mol}^{-1}$; all in Gaussian System of units.

the single crystal since we do not possess a set-up for accurate determination of anisotropy in crystals. So, for all the compounds studied the well-known extrapolation procedure due to Haller[16] was used to get the value of $\Delta\chi_o$. The values of order parameters at different temperatures are also tabulated in Table I. Variation of order parameters, of the four samples, obtained from magnetic susceptibility measurement and X-ray data[13] with reduced temperature is shown in Figure 3. The continuous curves correspond to Maier-Saupe[6,17] mean field theory. The figure shows that near isotropic temperatures the experimental order parameter values are lower than the theoretical values. This trend has also been observed in $\langle P_2 \rangle$ values obtained from optical birefringence measurements of these mesogens.[13]

The rapid decrease in order parameter values obtained from re-

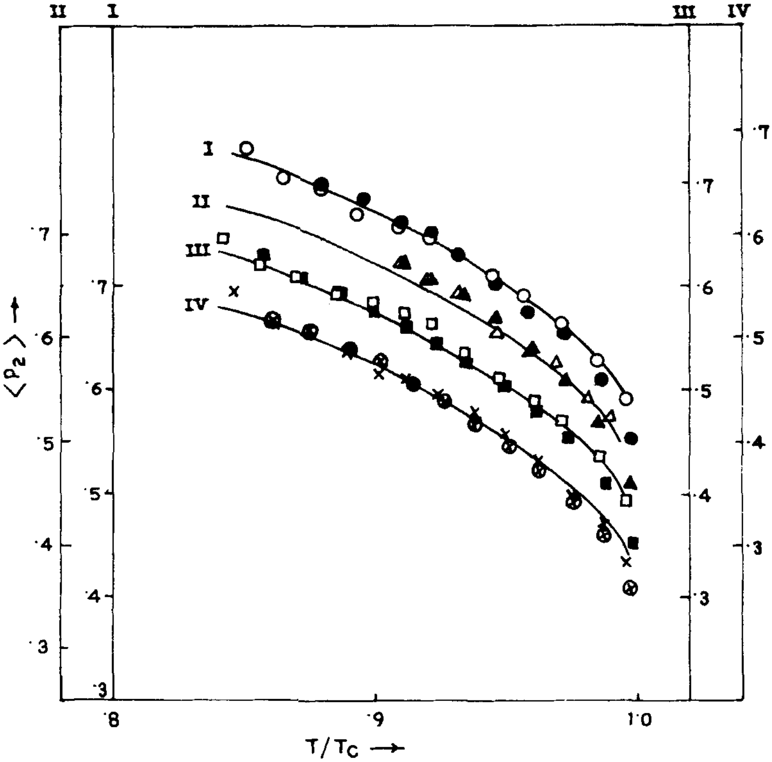

FIGURE 3 Variation of order parameter with reduced temperature. Continuous curves are from Maier-Saupe theory.
$\langle P_2 \rangle$ from magnetic susceptibility data: ●—sample I, ▲—sample II, ■—sample III, ⊗—sample IV;
$\langle P_2 \rangle$ from X-ray data, ○—sample I, △—sample II, □—sample III, x—sample IV.

fractive index and magnetic susceptibility close to nematic isotropic transition temperature has been observed by many workers.[18–21] This may be due to fluctuations of the director, which is more pronounced near transition temperature. In the present work, all the compounds have cyclohexane ring, which may vibrate more with rise of temperature and thus lower the order parameter in addition to the lowering effect due to aliphatic chain vibrations. However, our X-ray diffraction measurement of these compounds[13] shows good agreement of $\langle P_2 \rangle$ values with Maier and Saupe values. Since in X-ray studies we get the diffraction pattern due to neighbouring molecules, what we measure is essentially the short range order parameter. Whereas, in refractive index or magnetic susceptibility we clearly measure the long range order of the sample. Hence, in effect we are measuring two different order parameters depending upon the experimental method used. It is also well known that the long range order parameter decreases rapidly near transition temperature T_c and vanishes at $T = T_c$. On the other hand, short range order is expected to decrease less rapidly near T_c and should persist even above T_c. This explains apparent contradiction between order parameters obtained from X-ray diffraction on one hand and those obtained from refractive index and magnetic anisotropy on the other hand.

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