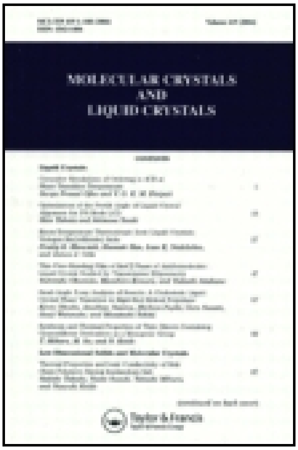


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Magnetic Susceptibility Studies of EPAP Acetate and EPAP Valerate

L. V. Choudary [a] , J. V. Rao [b] & P. Venkatacharyulu [b]

[a] R.V.R. & J.C.O.P. College of Engineering, GUNTUR, -522 006, India

[b] Department of Physics, Nagarjuna University, Nagarjuna Nagar 522 510, Andhra Pradesh, India

Version of record first published: 13 Dec 2006.

To cite this article: L. V. Choudary , J. V. Rao & P. Venkatacharyulu (1987): Magnetic Susceptibility Studies of EPAP Acetate and EPAP Valerate, Molecular Crystals and Liquid Crystals, 146:1, 463-471

To link to this article: http://dx.doi.org/10.1080/00268948708071830

Mol. Cryst. Liq. Cryst., 1987, Vol. 146, pp. 463–471
Photocopying permitted by license only

Printed in the United States of America

Magnetic Susceptibility Studies of EPAP Acetate and EPAP Valerate

L. V. CHOUDARY
R.V.R. & J.C.O.P. College of Engineering, GUNTUR–522 006, India

and

J. V. RAO and P. VENKATACHARYULU
Department of Physics, Nagarjuna University, Nagarjuna Nagar 522 510, Andhra Pradesh, India

(*Received January 12, 1987*)

The temperature variation of the magnetic susceptibility (χ_g) of the liquid crystals EPAP Acetate and EPAP Valerate is reported in the isotropic liquid and nematic phases. Abrupt changes in χ_g and $S \cdot \Delta\chi_g$ are observed at isotropic liquid–nematic transition. The isotropic liquid–nematic transition is found to be of first order in both the compounds. The order parameter is calculated using an estimated value for the molar susceptibility anisotropy.

INTRODUCTION

In nematic liquid crystals[1,2] there is orientational order. The order parameter can be determined by several techniques.[3–5] It is shown that the diamagnetic susceptibility can be used to determine the order parameter in nematic liquid crystals. These measurements are useful, too, for understanding the phase transitions of the liquid crystals. In this paper we report the diamagnetic susceptibility investigations on *P*-(Ethoxyphenyl azophenyl) acetate and *P*-(Ethoxyphenyl azophenyl) Valerate which forms part of our systematic studies on liquid crystal phase transitions.[6–9]

THEORY

The relation between Q, the macroscopic tensor order parameter and X^a the anisotropic part of the diamagnetic susceptibility tensor (per unit volume) can be expressed as[4]

$$Q = G\chi^a \tag{1}$$

Where the constant G can be determined by setting $Q_{zz} = 1$ in a perfectly aligned state.

$$\text{Hence } Q_{\alpha\beta} = GX^a_{\alpha\beta} \quad \text{where } \alpha\beta = x, y, z \tag{2}$$

G is given by

$$G = \frac{3}{N(2\chi_{33} - \chi_{22} - \chi_{11})} \tag{3}$$

where N is the number of molecules per unit volume and χ_{11}, χ_{22} and χ_{33} are the principal volume susceptibilities of an isolated molecule.

If one defines the macroscopic diamagnetic susceptibility anisotropy of a completely ordered nematic phase as

$$\Delta\chi = N\left[\chi_{33} - \frac{1}{2}(\chi_{22} + \chi_{11})\right] \tag{4}$$

then

$$Q_{\alpha\beta} = \frac{3}{2}\frac{\chi^a_{\alpha\beta}}{\Delta\chi} \tag{5}$$

Thus it is possible to define the macroscopic order parameter $Q_{\alpha\beta}$, which is independent of any assumption regarding the rigidity of the molecule.

Rotating the diamagnetic susceptibility tensor of a single rod like molecule by an arbitrary rotation R (ϕ, θ, ψ), where ϕ, θ and ψ are the Euler angles of the rotation and then taking the statistical average we find that

$$\chi_{\parallel} - \chi_{\perp} = \frac{1}{2}(3\langle\cos^2\theta\rangle - 1)\Delta\chi \tag{6}$$

Where $\Delta\chi$ is the anisotropy of the diamagnetic susceptibility of a perfectly aligned nematic phase, $\chi_{\parallel}$ and $\chi_{\perp}$ are the volume susceptibilities parallel and perpendicular to the nematic director, respectively, and θ is the angle between the long molecular axis and the nematic director.

The microscopic order parameter S is defined as

$$S = \frac{1}{2}(3\,\langle\cos^2\theta\rangle - 1)\,\Delta\chi \tag{7}$$

From (6) and (7) we get

$$S = (\chi_{\parallel} - \chi_{\perp})/\Delta\chi \tag{8}$$

The average susceptibility is given by

$$\chi_{\nu\nu} = \frac{1}{3}(\chi_{\parallel} + 2\,\chi_{\perp}) = \frac{1}{3}\sum_{\nu}\chi_{\nu\nu}$$

Equation (8) can be written as

$$\chi_{\parallel} = \bar{\chi} + \frac{2}{3}S\,\Delta\chi \tag{9a}$$

$$\chi_{\perp} = \bar{\chi} - \frac{1}{3}S\,\Delta\chi \tag{9b}$$

Hence

$$\chi_{\parallel} - \chi_{\perp} = \frac{3}{2}(\chi_{\parallel} - \bar{\chi}) \tag{10}$$

EXPERIMENTAL

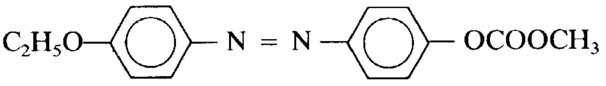
Synthesis of EPAP acetate and EPAP valerate

P-Ethoxy-P-hydroxy azobenzene was prepared by following the diazotization procedure,[10] P-Ethoxy-P-hydroxy azobenzene was stirred with acetic anhydride in the presence of pyridene at room temperature. The mixture was poured in ice. The orange crystals which separated were washed with water and dried in vacuum.

The above procedure is repeated by taking Valeric anhydride instead of acetic anhydride (for EPAP Valerate).

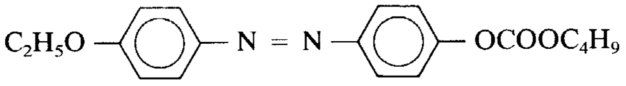
The samples were purified chromotographically with silicagel as absorbent and benzene as elucent. The pure samples were recrystallised from anhydrous ethyl-alcohol until the constant nematic–isotropic transition temperature was found. The phase transition temperatures of the two compounds were determined using polarising microscope and are given below.

P-(Ethoxyphenyl azophenyl) acetate (EPAP Acetate)



Solid $\xleftrightarrow{121^\circ\mathrm{C}}$ Nematic $\xleftrightarrow{136^\circ\mathrm{C}}$ Isotropic liquid

P-(Ethoxyphenyl azophenyl) Valerate (EPAP Valerate)



Solid $\xleftrightarrow{78^\circ\mathrm{C}}$ Nematic $\xleftrightarrow{126^\circ\mathrm{C}}$ Isotropic liquid

The diamagnetic susceptibility was measured as a function of temperature by means of a sensitive balance using the Faraday method at about 10 KOe. The corrections due to the force experienced by the suspension fibre, the sample container and the surrounding atmosphere in the applied field were also made. The susceptibility measurements were accurate up to 1%. The accuracy of the temperature control was ± 0.1°C.

Since the magnetic field was strong enough to align the director parallel to H, the mass susceptibility measured in the liquid crystalline phase was $(\chi_g)_\parallel$). In the isotropic liquid phase and in the solid phase the molecules are randomly oriented and hence $\bar{\chi}$ was obtained.

Evaluation of $\Delta\chi_g$

The susceptibility anisotropy, $\Delta\chi_g$ (= $\Delta\chi/\rho$ where ρ is the density) can be very accurately calculated by mass susceptibility measurements on a single crystal for which one has single crystal X-ray and magnetic data. If $\Delta\chi_g$ is not known the order parameter can not be separated. However there are some possibilities to estimate $\Delta\chi_g$.[11]

(a) As the molecule under consideration consists of two benzene rings it is considered to be equivalent (magnetically) to the biphenyl molecule, provided that there is no conjugation between the two benzene rings of the biphenyl.[12] In such a case the susceptibility anisotropy is completely due to the delocalized electrons of the benzene rings as far as the contributions of the end and central groups to the magnetic susceptibility are small with respect to those of the benzene rings. In such a case[13] the molar susceptibility anisotropy can be taken as

$$\Delta\chi_M = \Delta\chi_g \cdot M = 55.1 \times 10^{-6}\mathrm{Cm}^3\,\mathrm{mol}^{-1}.$$

Where M is the molecular weight.

We have followed the extrapolation procedure of Haller[14] in which $\log(S \cdot \Delta\chi_g)$ Vs $\log(-\tau)$ gives a straight line in the temperature region $\tau < -0.016$. τ is the reduced temperature, $\tau = (T - T_c)/(273 + T_c)$ where T_c is the nematic to isotropic liquid transition temperature. The intercepts of the extrapolated straight lines for EPAP Acetate are on X-axis 0.63 and on Y-axis 0.114 and for EPAP Valerate on X-axis 0.34 and on Y-axis 0.054.

The slopes and molar susceptibility anisotropies for EPAP Acetate and EPAP Valerate are given in Table I. The estimated molar susceptibility anisotropy value is in good agreement with extrapolation procedure value for both the compounds.

RESULTS AND DISCUSSION

Values are calculated by using Equation (8). The diamagnetic susceptibility χ_g and the quantity $S \cdot \chi_g$ reflecting the temperature dependence of the order parameter S, are shown in Figures 1 and 2 respectively for EPAP Acetate and EPAP Valerate. Figure 3 represents the variation of $\log(S \cdot \Delta\chi_g)$ with $\log(-\tau)$.

TABLE I

The slopes and molar diamagnetic anisotropies obtained by extrapolating to absolute zero

Compound	Slope	10^6 ($\mathrm{Cm}^3\,\mathrm{mol}^{-1}$)
EPAP Acetate	0.1809	54.285
EPAP Valerate	0.1588	54.308

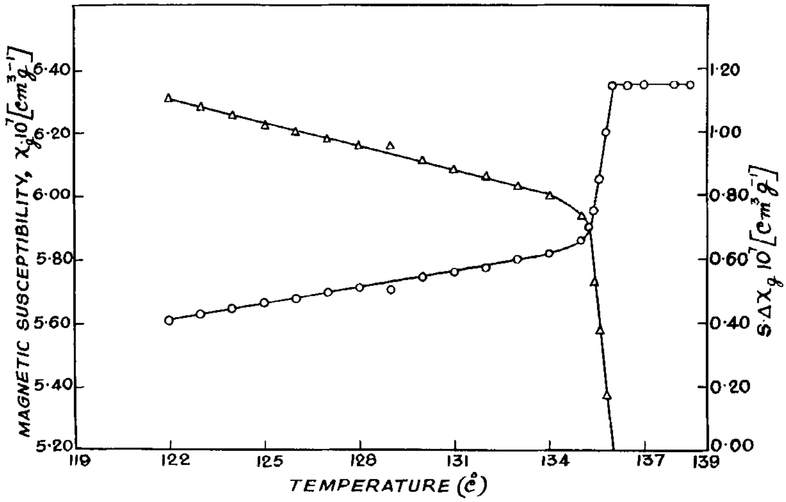


FIGURE 1 Temperature variation of magnetic susceptibility, (○–○) and S · $\Delta\chi_g$ (△–△) for EPAP Acetate.

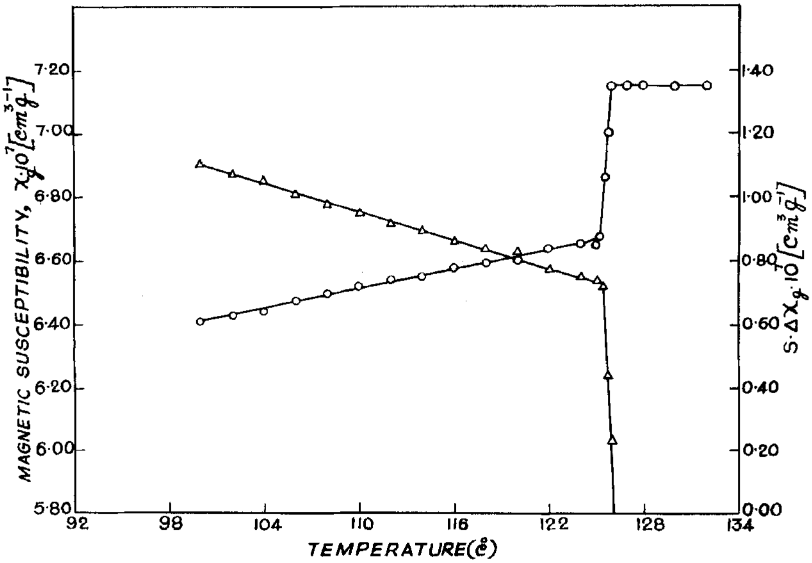


FIGURE 2 Temperature variation of magnetic susceptibility, (○–○) and S · $\Delta\chi_g$ (△–△) for EPAP Valerate.

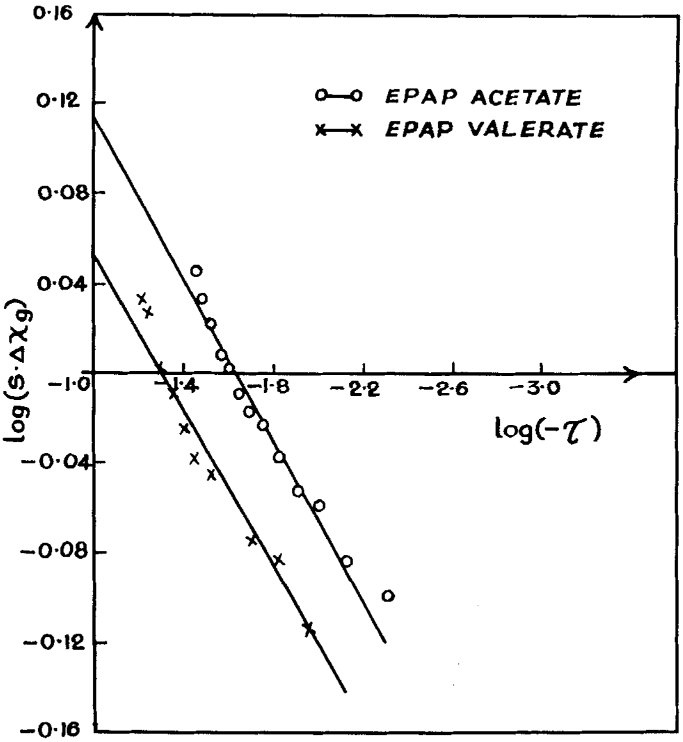


FIGURE 3 Variation of log (S · $\Delta\chi_g$) with log ($-\tau$) for EPAP Acetate and EPAP Valerate.

The diamagnetic susceptibility values of EPAP Acetate and EPAP Valerate in the isotropic liquid phase and in the solid phase (not shown in Figures 1 and 2) are nearly equal and practically independent of temperature. With decrease of temperature the diamagnetic susceptibility decreases abruptly at the isotropic liquid–nematic transition and consequently $S \cdot \chi_g$ undergoes sudden jump. This is due to the alignment of nematic director in the field direction. As the orientational order parameter ($S \cdot \chi_g$) undergoes a discontinuous change during the isotropic liquid–nematic transition, it may be regarded as a first order transition. The increase in χ_g and $S \cdot \Delta\chi_g$ with decrease in temperature in the nematic phase indicate the increase of order of the nematic phase.

The χ_g and $S \cdot \Delta\chi_g$ also increase with decrease of temperature in the nematic phase indicating that the degree of order of the nematic phase increases with decreasing temperature. According to the Equa-

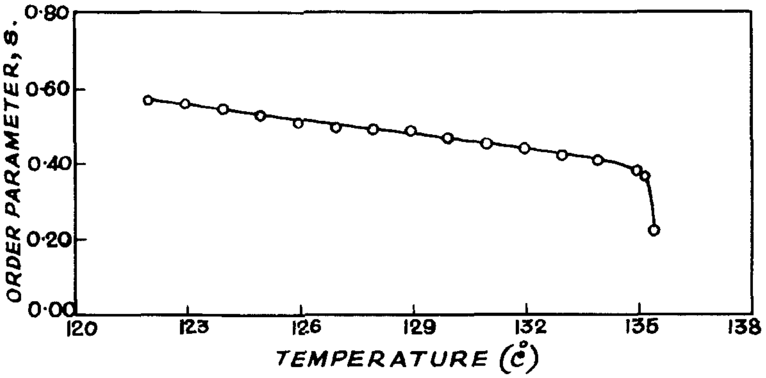


FIGURE 4 Variation of order parameter with temperature for EPAP Acetate.

tions 8 and 10 the order parameter is calculated using the estimated value for the molar susceptibilty anisotropies (procedure a). The temperature variation of the order parameter is shown in Figures 4 and 5 respectively for EPAP Acetate and EPAP Valerate. The order parameter increases with decrease of temperature in the nematic phase as is general in liquid crystals.

Acknowledgments

The authors thank Dr. P. R. Kishore for his help during the process of the work. L. V. Choudary is grateful to Prof. S. R. K. Paramahamsa for his encouragement.

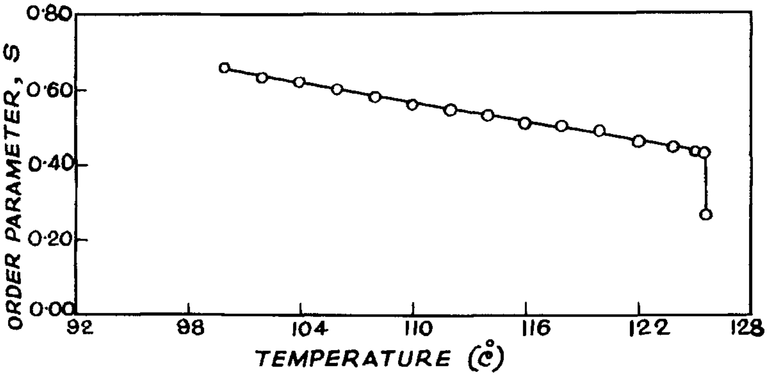


FIGURE 5 Variation of order parameter with temperature of EPAP Valerate.

References

1. M. J. Stephen and J. P. Straley, *Rev. Mod. Phys.*, **46**, 617 (1974).
2. P. G. de Gennes, "*The Physics of Liquid Crystals*" Clarendon Press, Oxford (1974).
3. S. Chandrasekhar and N. V. Madhusudana, *Mol. Cryst. Liq. Cryst.*, **10**, 151 (1970).
4. I. H. Ibrahim and W. Haase, *Z. Naturforsch*, **31a**, 1644 (1976).
5. P. L. Sherrell and D. A. Crellin, *J. de Physique*, **40**, C3-211 (1979).
6. J. V. Rao and C. R. K. Murty, *Phase Transitions*, **5**, 67 (1985).
7. J. V. Rao and C. R. K. Murty, *Phase Transitions*, **5**, 139 (1985).
8. K. R. K. Rao, J. V. Rao, L. V. Choudary and C. R. K. Murty, *Acustica*, **57**, 98 (1985).
9. L. V. Choudary, J. V. Rao, P. N. Murty and C. R. K. Murty, *Z. Naturforsch*, **38a**, 762 (1983).
10. Arthur I. Vogel, Practical Organic Chemistry. E. L. B. S. Edition and Longmans, Green & Co, Ltd., London 1968.
11. K. R. K. Rao, J. V. Rao, L. V. Choudary and P. Venkatacharyulu, *Z. Phys. Chem. Zeuefolge* (in press).
12. A. Hargreaves and S. H. Rizvi, *Acta Cryst.*, **15**, 365 (1962).
13. M. A. Lasheen, *Phil. Trans. Roy. Soc.*, **A256**, 357 (1964).
14. I. Haller, H. A. Huggins, H. R. Lilinthal and T. R. McCuire, *J. Phys. Chem.*, **77**, 950 (1973).