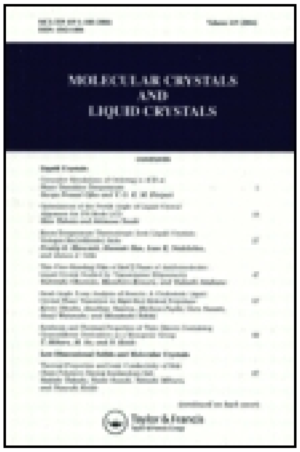

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High Pressure Studies on Hexa-n-alkoxy Triphenylene Homologous Series

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High Pressure Studies on Hexa-*n*-alkoxy Triphenylene Homologous Series

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High pressure investigations have been carried out on four successive homologues of the hexa-*n*-alkoxy triphenylene series exhibiting the hexagonally ordered columnar mesophase. The most remarkable feature is that the slope of the mesophase to isotropic phase boundary $(dT/dP)_{1\,\mathrm{bar}}$ shows a strong decrease with increasing chain length becoming zero for the 8th homologue. To explain this feature we propose an argument based on the ratio of the volume of the triphenylene core to the total volume.

Keywords: High pressure studies; alkoxy triphenylene series; Clausius-Clapeyron equation; transition volume; Simon-Glatzel equation

INTRODUCTION

Although the first high pressure studies [1] on discotic liquid crystals were carried out almost immediately after their discovery [2], this field has not attracted much attention. Here we report pressure–temperature phase diagrams on the first four mesogenic homologues of the hexa-*n*-alkoxy triphenylenes (HnTP for short, where *n* indicates the number of carbon atoms in the alkyl chain), a series which has been well studied otherwise.

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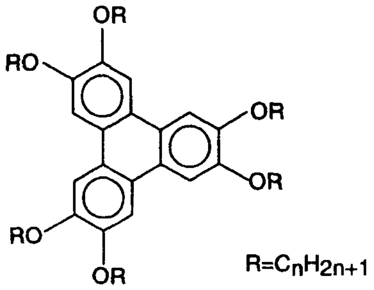
EXPERIMENTAL

The structural formula of HnTP is shown below. These materials were synthesised using standard procedures, following an improved route reported recently [3].



The transition temperatures and enthalpies obtained from both optical microscopy and DSC (Perkin Elmer DSC7) scans are in agreement with the literature values [4]. The transition temperatures (obtained in the heating mode) *versus* chain length phase diagram is shown in Figure 1. In the 5th,

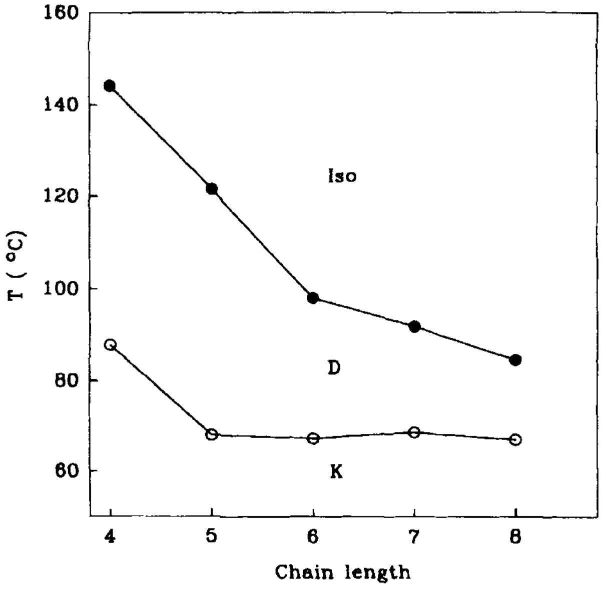


FIGURE 1 Temperature-chain length phase diagram for the homologues studied. The D phase for the 5th to 8th homologue is of the D_h type whereas it is of the recently found plastic (D_p) type for the 4th homologue.

6th and 7th homologues the columnar mesophase is of the hexagonally ordered D_h type whereas the mesophase of the 4th homologue was recently [5] found to be a more ordered columnar phase referred to as a plastic D phase. However, for convenience, we shall refer to the mesophases of all the homologues as simply the D phase.

The schematic diagram of the optical high pressure set up used to map the pressure–temperature phase diagrams is shown in Figure 2. The liquid crystalline sample was sandwiched between two optically polished sapphire cylinders and was isolated from the fluid pressure transmitting medium (Octoil-s) by an elastomeric tube (Fluran). The transition temperatures were detected by the optical transmission technique. Light from a He-Ne laser (Melles Griot) was incident normally on the sapphire window. The intensity of light transmitted by the sample was measured by using a photodiode (OSI5) the output of which was fed to one of the channels of a 8-channel multiplexer card (Dynalog). The output of a calibrated thermocouple, located very close to the sample inside the pressure cell, was connected to another channel of the multiplexer card. A high speed switching card alternately selected the channel to be read and thus allowed both the intensity and temperature to be measured using a single digital multimeter (HP, DMM 34401A). The DMM was in turn interfaced to a PC using the serial port connection facilitating the data acquisition process to be automated. The experiments were always conducted along isobars, *i.e.*, the pressure was kept constant and the temperature of the sample was varied at a controlled rate (typically ~ 1°C/min). Pressure was measured using a Heise guage with a precision of 1.5 bar.

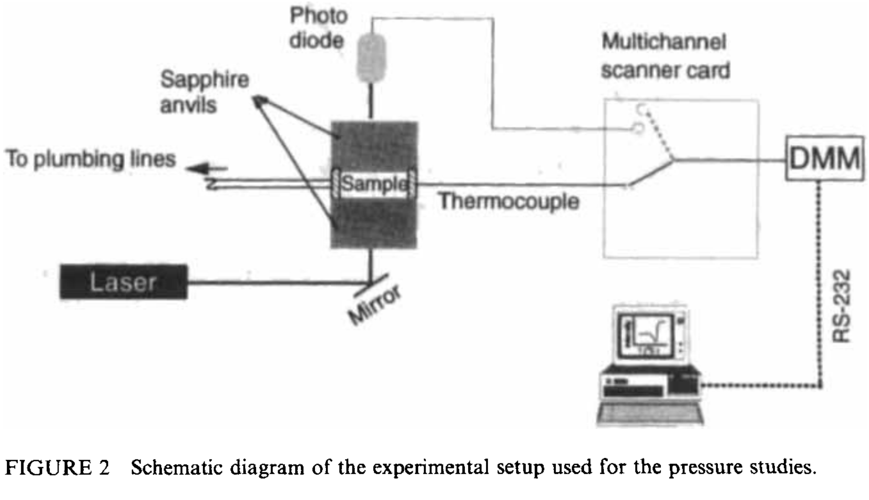


FIGURE 2 Schematic diagram of the experimental setup used for the pressure studies.

RESULTS AND DISCUSSION

The pressure – temperature phase diagram obtained both in the heating and cooling modes are given in Figures 3(a) – (d). In the case of H4TP the temperature range of the D phase is seen to increase slightly with increasing pressure both in the heating and cooling mode. As the phase boundary corresponding to the crystal to mesophase melting remains almost parallel to the D-Iso transition line the D phase continues to be enantiotropic at higher pressures also. In contrast to this, the range of the D phase decreases with increasing pressure for the higher homologues. For H5TP this decrease is only marginal and occurs only at lower pressures, so that the D phase is enantiotropic till the highest pressure studied. However the reduction in the temperature range of the mesophase with pressure is appreciable in both

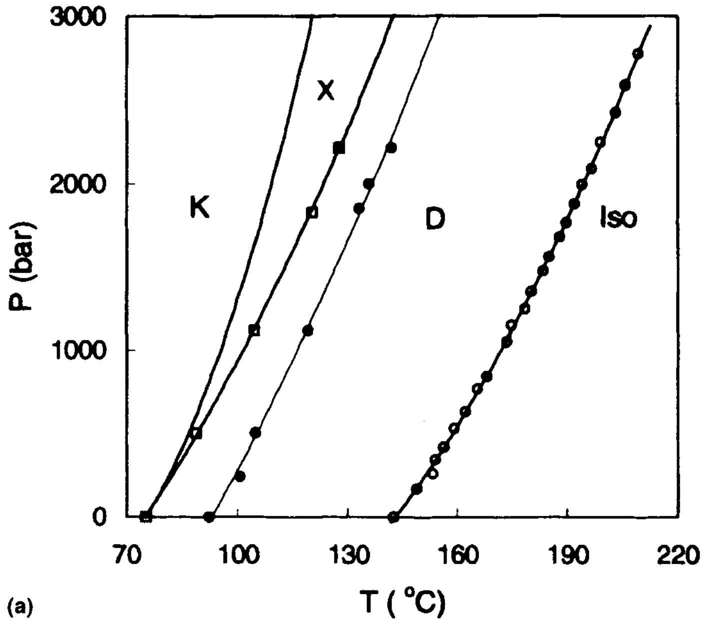
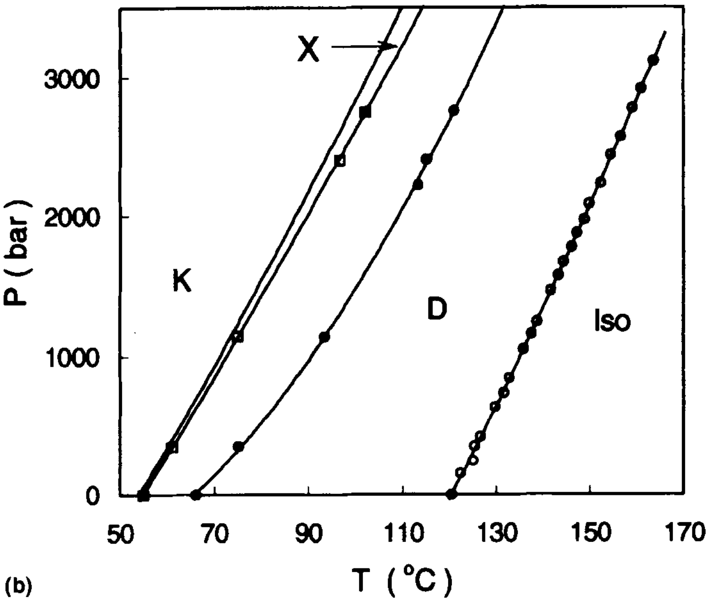


FIGURE 3 Pressure – temperature phase diagrams for the different homologues of HnTP observed in both heating and cooling modes. The lines are drawn as a guide to the eye. In all these diagrams the line joining the filled circles represents the melting (K-D) line. In both H4TP (Fig. 3a) and H5TP (Fig. 3b) the temperature range of the D phase remains almost the same till the highest pressure studied. The structure of the phase X observed just above crystallisation is not yet known (see Fig. 5 also). In contrast to the case of lower homologues the diagrams for H6TP (Fig. 3c), H7TP (Fig. 3d) and H8TP (Fig. 3e) show a drastic reduction in the range of the D phase with pressure resulting in K-D-Iso triple points (In this and subsequent diagrams the data for H8TP is taken from Ref. [6]).



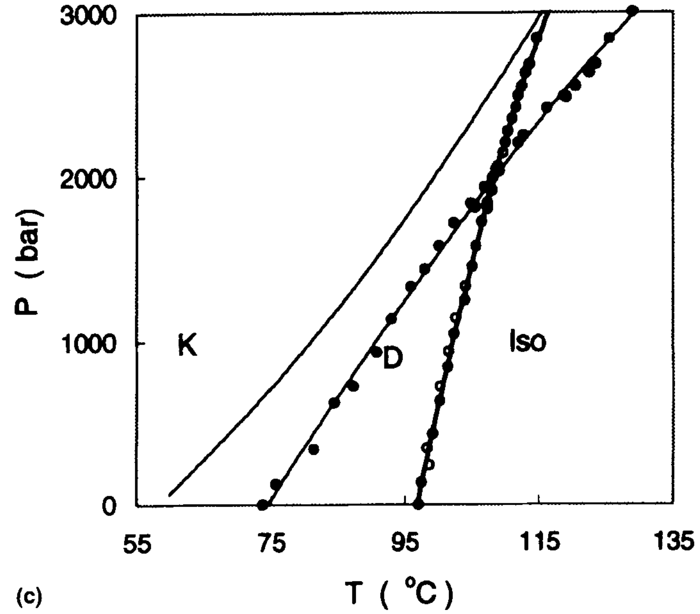


FIGURE 3 (Continued).

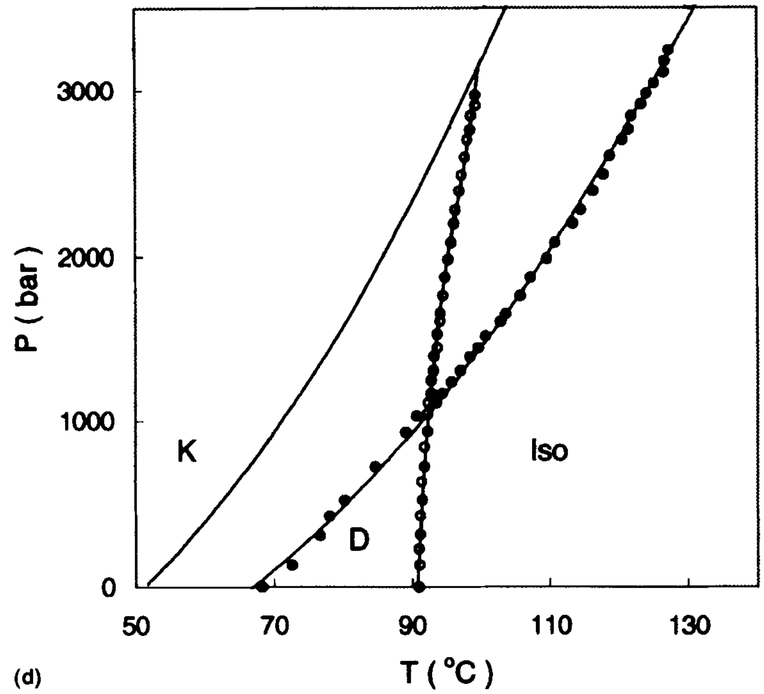


FIGURE 3 (Continued).

H6TP and H7TP so much so that the D-Iso transition becomes monotropic at higher pressures. For transitions recorded in the heating mode this results in a K-D-Iso triple point. The pressure at which the triple point occurs decreases with increasing chain length, ~ 2 kbar for H6TP and ~ 1 kbar for H7TP. In fact, Raja *et al.* [6] have done pressure studies on the eighth homologue of this series *i.e.*, H8TP, and their phase diagram (Fig. 3(e)) shows a similar feature, *viz.*, the D-Iso transition changes from enantiotropic to monotropic at high pressures. Further, the triple point pressure value (= 0.64 kbar) agrees with the trend for H6TP and H7TP.

Plotting the temperature range of the D phase in the heating mode (see Fig. 4) at room pressure and at a pressure of, say, 0.7 kbar, we observe that the behaviour is the same at both pressures, *i.e.*, the range decreases for increasing chain length, but the diminution is more rapid at the elevated pressure. Extrapolating the trend seen for 0.7 Kbar to $n = 8$ leads to the range to be zero at that pressure in agreement with the data shown in Figure 3(e). At much higher pressures, the D phase ceases to exist even in the cooling mode. Thus, increasing pressure is quite similar to increasing the

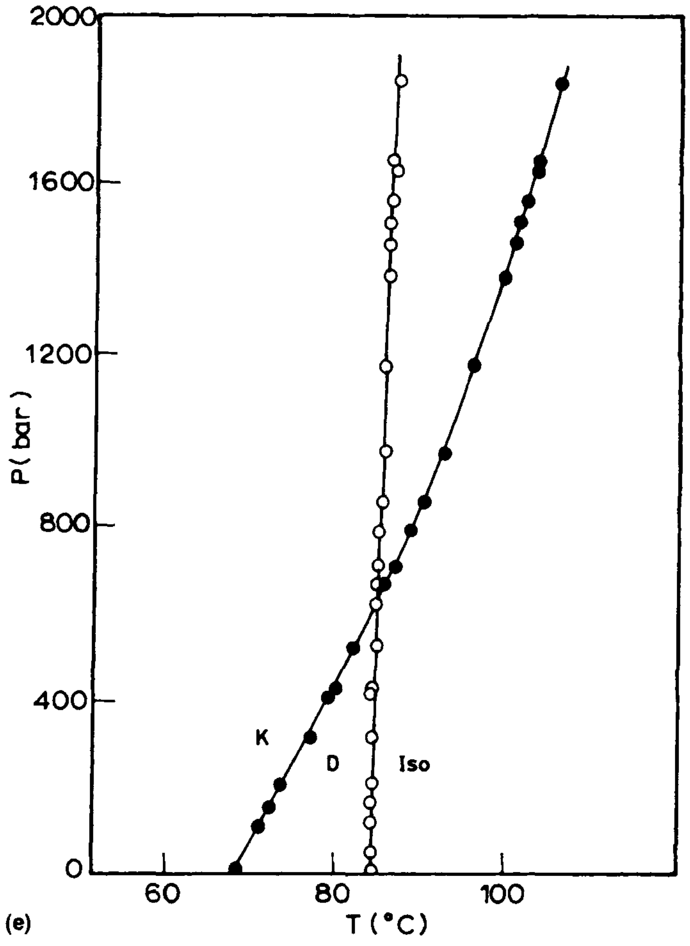


FIGURE 3 (Continued).

chain length. This phenomenon is quite well known in calamitic liquid crystals, an off-shoot of which is the observation of "pressure-induced mesomorphism" in non-mesogenic substances [7]. To check whether we can, in a similar fashion, induce the D phase in a non-mesogenic lower homologue, we investigated the compound H3TP [4, 8]. Unfortunately this compound was not thermally very stable and therefore the measurements were not very reliable.

Figure 5 shows raw scans of temperature *versus* intensity obtained in the cooling mode for H4TP, at room pressure, 0.5 kbar and 2.2 kbar. Notice that at room pressure there are only two transitions: Iso-D and D-K

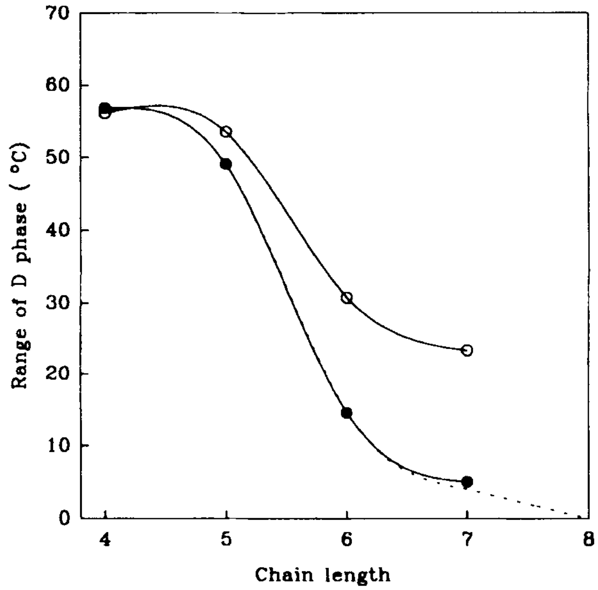


FIGURE 4 Comparison of the temperature range at 1 bar (o) and at 0.7 kbar (•) as a function of chain length *n*. The solid lines are only a guide to the eye. Extrapolating the data for 0.7 kbar to $n = 8$ (dashed line) shows that for this homologue the mesophase is monotropic at this pressure, in agreement with Figure 3(e).

(Crystal). But at higher pressure the D phase goes through another phase before crystallising. The range of this new phase, which we refer to as X, increases with increasing pressure. H5TP also shows this additional phase but right from room pressure. At room pressure its temperature range is only about 0.5°C but increases slightly with increasing pressure. We have not been able to perform any x-ray study in the X phase due to its proximity to crystallisation. Also no signature of this additional phase was seen in DSC scans. Thus the nature of the X phase is yet unknown, perhaps it is another type of plastic phase.

A remarkable feature to be noted in the phase diagrams is that with increasing *n*, the slope of the D-Iso phase boundary shows a drastic change. The dT/dP value calculated at room pressure $(dT/dP)_{1\,\mathrm{bar}}$ for both the D-Iso and K-D transitions are shown in Figure 6. For the sake of discussion we have also included the data for H8TP taken from Ref. [6]. The values for the D-Iso transition show a monotonic decrease becoming zero for $n > 6$. In contrast, the data for K-D line has an "odd-even" effect. Since both the transitions are known to be first order one can use the Clausius–Clapeyron

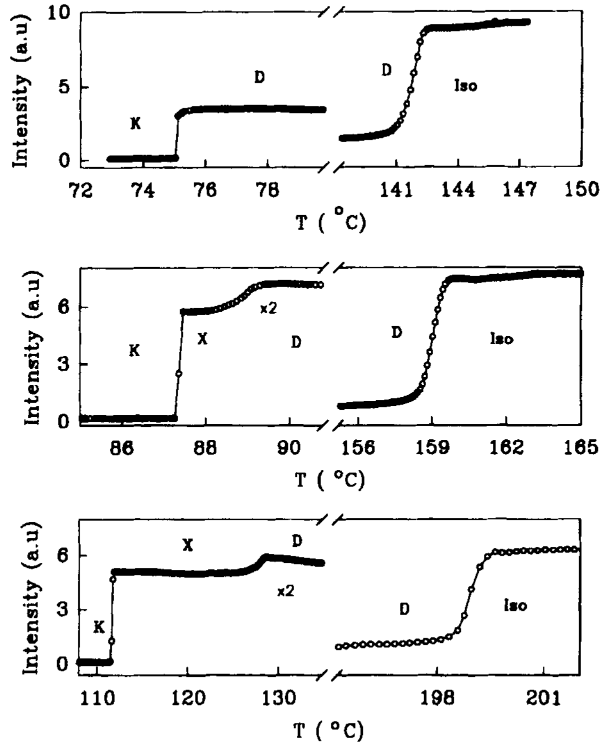


FIGURE 5 Raw intensity scans for H4TP in the cooling mode at 1 bar, 0.5 kbar and 2.2 kbar. While at 1 bar the D phase directly transforms to the crystalline (K) phase, the scan at 0.5 kbar shows the appearance of a new phase (X) whose temperature range increases with increasing pressure.

equation and with the knowledge of the transition entropy, ΔS ($= \Delta H/T$ with ΔH as the enthalpy and T, the transition temperature), the transition volume ΔV can be estimated. Figure 7 shows the transition entropy as a function of chain length for both the melting and the clearing (D-Iso) transitions. A similar plot of the transition volume is given in Figure 8. Note that both ΔV and ΔS increase with n for the melting transition but show a reverse trend for the D-Iso transition. Except in the case of H4TP, most of the volume and entropy changes occur at the melting transition, a feature typical of liquid crystals. In the case of H4TP, the volume change is much larger at the D-Iso transition than at the melting transition. This could be due to the "plastic" nature of the mesophase. Similar behaviour is observed *e.g.*, in long chain alkanes exhibiting the "rotator" phases and which undergo one or more "orientational disorder" transitions before transforming to an isotropic liquid [9]. Also mention may be made of the fact that the

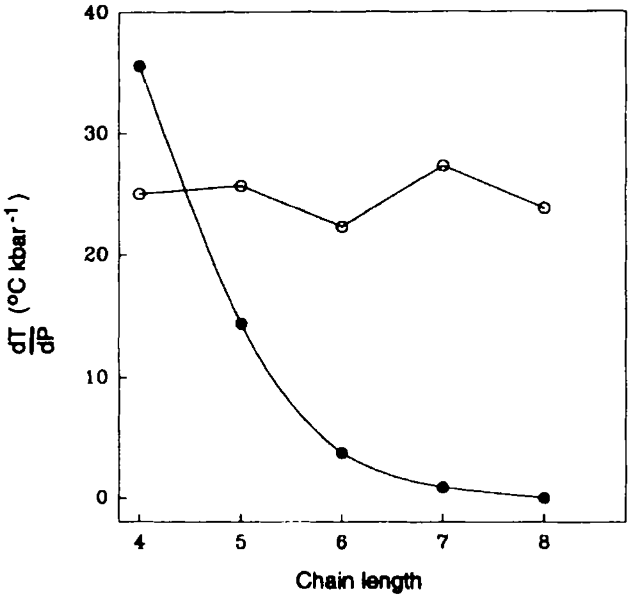


FIGURE 6 Chain length dependence of the slope (dT/dP) calculated at 1 bar for the melting (o) and D-Iso (•) transitions. In contrast to the slight odd even effect for the melting transition, the value drops drastically for the isotropic transition.

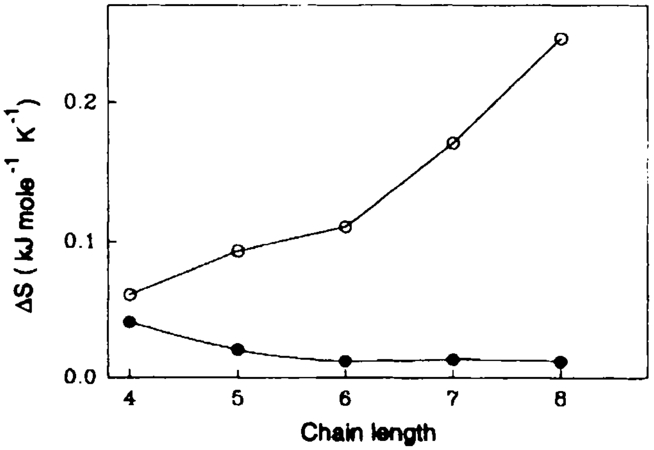


FIGURE 7 Transition entropy values for the different homologues at the K-D (o) and D-Iso (•) transitions. Notice the reverse in the trend for the two transitions.

combined enthalpy of K-D and D-Iso transitions is smaller compared to the melting enthalpy of the corresponding n-alkanes. This has been found to be true in the case of mesogenic phthalocyanines also [10].

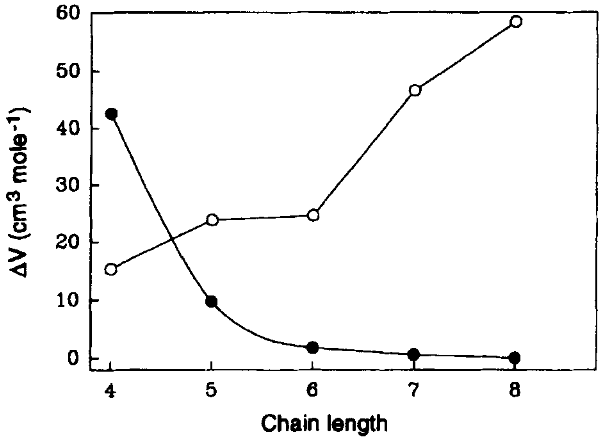


FIGURE 8 Transition volumes calculated using Clausius–Clapeyron equation showing monotonic increase for the melting (o) but a significant decrease for the D-Iso transition (•) as the chain length increases.

A feature that is quite puzzling is that the $(dT/dP)_{1\,\mathrm{bar}}$ and consequently the calculated ΔV values for D-Iso transition are practically zero for $n > 6$. This may be understood by considering the following argument. The alkoxy triphenylene molecule essentially contains two parts: the triphenylene core and six hydrocarbon tails. Here we take the oxygen atom of the alkoxy chain to belong to the core. At the transition from the solid to the mesophase the hydrocarbon tails melt and become liquid like. But the ordering of the core region stabilizes the mesophase; this ordering also gets lost at the mesophase-isotropic transition. To get an idea of the relative contributions of these two parts of the molecule to the thermodynamics of the transition, let us calculate the partial volumes occupied by the core and the tail regions. For this purpose we took x-ray diffractometer scans in the mesophase to measure intracolumnar and intercolumnar distances. Using these intercolumnar distances obtained from small-angle scans and approximating the disc to be a circle, the area (A) occupied by the molecule can be calculated. In the wide-angle region a broad diffuse reflection corresponding to the liquid-like order of the aliphatic chains and at least one sharp reflection (more in the case of H4TP which shows a "plastic" phase) corresponding to the intracolumnar stacking periodicity (C) of the triphenylene cores are seen. For such a case the volume of the entire molecule can be taken as $V_m = AC$. The calculated V_m turned out to be a linear function of the methylene (CH_2) groups in the aliphatic chain. Fitting the data to a straight line, we found the slope, which is nothing but the molar volume increment per CH_2 group, to be 20 Å^3. (A similar value is obtained from the data of Bengs *et al.* [11]). However, this value is smaller than those for simple alkanes (29.8 Å^3) [9], octa-*n*-alkoxy substituted phthalocyanines (29 Å^3) [10] and hexa-*n*-alkoxytruxenes (27.4 Å^3) [12], and perhaps suggests that the tails are slightly more ordered in the presently studied alkoxy triphenylenes.

As mentioned above, the aliphatic chains are already in a liquid-like arrangement even in the mesophase. Therefore, as far as the D-Iso transition is concerned the transition properties should essentially be dependent on the contribution from the core of the molecule. But as the length of the chain is increased the contribution of the core to the total area and thus to the total volume of the molecule decreases. For example, taking the diameter of triphenylene core to be 10.5 Å [13] and calculating the ratio of the volume of the core to the total volume we find that the ratio is only ~30% even in H4TP and decreases to ~22% for H7TP. Hence, it should not be surprising if this reduction in the ratio, as the chain length is increased, lowers the transition volume ΔV across the D-Iso transition which in turn decreases the (dT/dP) value.

Finally, we would like to comment on the shape of the D-Iso boundary for the different homologues. Notice that if ΔS and ΔV have zero or negligible pressure dependence, the Clausius–Clapeyron equation predicts a constant dT/dP or a linear phase boundary. Of course, non-linear cases can be analyzed provided information about the pressure dependence of ΔS and ΔV are known. In the absence of such information, different empirical relations are used. The simplest of these are higher degree polynomials. But they are not well suited for interpolations and extrapolations and depend on the data interval also. In a large number of cases including liquid crystals the Simon–Glatzel equation

$$\frac{P}{a} = \left(\frac{T}{T_0}\right)^b - 1 \tag{1}$$

(where T_0 is the transition temperature at room pressure and a, b are constants) has been found to be quite successful. We attempted to fit the D-Iso boundary to Eq. (1) and found that while the fit is good for H4TP and H5TP, the quality of fit was poor for H6TP and H7TP. Hence we used a modified form of this equation, recently proposed by Rein and Demus [14].

$$T = T_0\left(1 + \frac{P}{B}\right)^\alpha \exp(fP) \tag{2}$$

where α, B and f are constants. The fitting done to the data of all the four compounds are shown in Figure 9. Although in all the cases the value of f was found to be small, including it significantly improved the fit especially for H6TP and H7TP. The solid lines in the figure show that Eq. (2) describes the data very well for all the compounds, although there is a change in the sign of the curvature of the phase boundary on going from H4TP to H7TP. This supports the argument of Rein and Demus that Eq. (2), which assumes a pressure dependence for the $\Delta S/\Delta V$ ratio is a better equation to use to fit the P-T boundaries than higher degree polynominal expressions.

In summary, we have carried out high pressure investigations on four homologues of the hexa-*n*-alkoxy triphenylene series. The slope (dT/dP) of the mesophase-isotropic boundary has been observed to show a drastic decrease with increasing chain length. An attempt has been made to understand this behaviour with the change in the contribution of the fractional volume of the triphenylene core to the total volume.

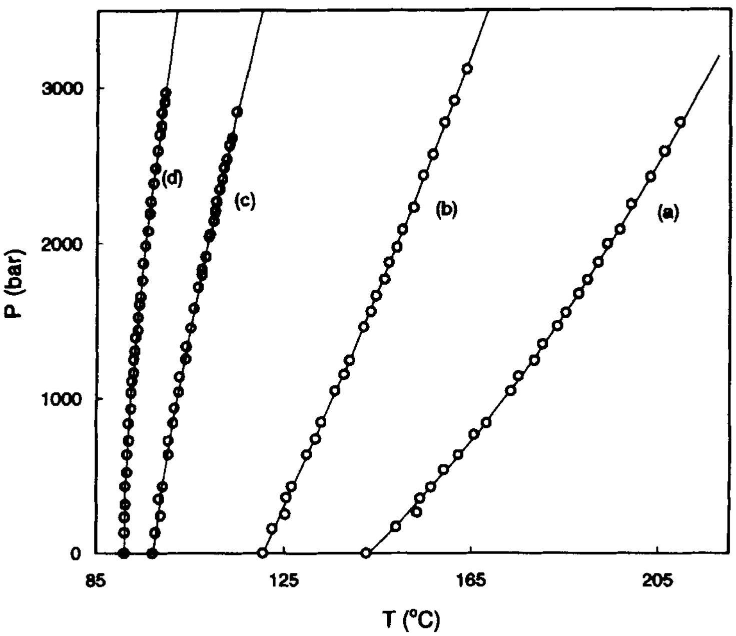


FIGURE 9 Plot showing the fitting of modified Simon – Glatz equation (Eq. (2)) to the Iso-D (cooling mode) transition of (a) H4TP, (b) H5TP, (c) H6TP and (d) H7TP.

Acknowledgements

We thank Prof. S. Chandrasekhar for his keen interest in this work and for many useful comments. A research grant from the U.S. Office of Naval Research (ONR Grant No. N00014-97-1-0904) is gratefully acknowledged. One of us (VKG) thanks Indian National Science Academy, New Delhi for a visiting fellowship.

References

[1] S. Chandrasekhar, B. K. Sadashiva, K. A. Suresh, N. V. Madhusudana, S. Kumar, R. Shashidhar and G. Venkatesh, *J. Phys.* (France), **40**, C3-120 (1979).

[2] S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, *Pramana*, **9**, 471 (1977).

[3] S. Kumar and M. Manickam, *Chem. Commun.*, 1615 (1997).

[4] C. Destrade, M. C. Mondon and J. Malthete, *J. Phys.* (France), **40**, C3-17 (1979).

[5] B. Glusen, W. Heitz, A. Kettner and J. H. Wendorff, *Liquid Crystals*, **20**, 627 (1996).

[6] V. N. Raja, R. Shasidhar, S. Chandrasekhar, R. E. Boehm and D. E. Martire, *Pramana*, **25**, L119 (1985).

[7] The first instance of pressure induced mesomorphism was reported by S. Chandrasekhar, S. Ramaseshan, A. S. Reshamwala, B. K. Sadashiva, R. Shashidhar and V. Surendranath, *Pramana Suppl.*, **1**, 117 (1975).

[8] L. Calucci, H. Zimmermann, E. J. Wachtel, R. Poupko and Z. Luz, *Liquid Crystals*, **22**, 621 (1997). It may be mentioned that the authors of this paper state that contrary to earlier reports H3TP also shows a D_h phase. In our optical microscopic studies we observed that on melting the substance shows a highly viscous phase with a texture similar to the D_h phase which at a higher temperature undergoes another transition to the isotropic phase. However, simple "coverslip shear test" leads us to conclude that this intermediate phase is probably be a more ordered phase than even the plastic D phase of H4TP.

[9] See *e.g.*, P. G. Schouten and J. M. Warman, G. H. Gelinck and M. J. Copyn, *J. Phys. Chem.*, **99**, 11780 (1995) and references therein.

[10] See *e.g.*, P. G. Schouten and J. M. Warman, G. H. Gelinck and M. J. Copyn, *J. Phys. Chem.*, **99**, 11780 (1995).

[11] H. Bengs, F. Closs, T. Frey, D. Funhoff, H. Ringsdorf and K. Siemensmeyer, *Liquid Crystals*, **15**, 565 (1993).

[12] J. F. Van der Pol, E. Neeleman, J. W. Zwikker, R. J. M. Nolte, W. Drenth, J. Aerts, R. Visser and S. J. Picken, *Liquid Crystals*, **6**, 577 (1989).

[13] S. Marguet, D. Markovitsi, P. Millie, H. Sigal and S. Kumar, *J. Phys. Chem.* (in press).

[14] C. Rein and D. Demus, *Cryst. Res. Technol.*, **28**, 273 (1993).