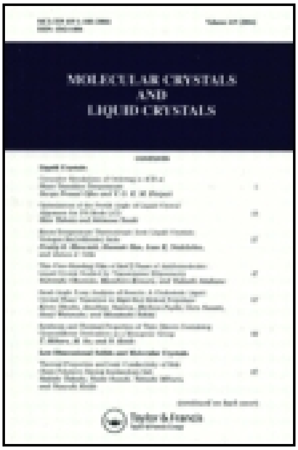

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High Pressure Investigations on the Phase Behaviour of Discotic Liquid Crystals

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HIGH PRESSURE INVESTIGATIONS ON THE PHASE BEHAVIOUR OF DISCOTIC LIQUID CRYSTALS

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Liquid crystals made of disc shaped molecules, now referred to as discotic liquid crystals, were discovered [1] in 1977 and represent a new class of thermotropic liquid crystals. Since the discovery, there are only a few studies [2–9] concerning the effect of pressure on these materials. Here we report high-pressure investigations on the columnar phase of several triphenylene compounds. We selected the compounds such that for one set of materials the number of peripheral substituents, x, was fixed and the length of the alkoxy chains, n, was varied, while for the second set n was fixed and x varied. We observe that with increase in either n or x, the slope of the pressure-temperature phase boundary, i.e., $(dT/dP)_{1bar}$ shows a strong decrease. The magnitude of the transition enthalpy and the calculated transition volume across the columnar-isotropic transition show a strong decrease with increasing n or x. To explain these features we propose an argument based on the ratio of the volume of the triphenylene core to the total volume of the molecule.

Keywords: high pressure; discotic liquid crystals; columnar phase; PT diagram

INTRODUCTION

Since the first observation [1] of thermotropic mesomorphism in disc shaped molecules a large number of compounds have been synthesized and a variety of mesophases have been identified. Among these the columnar mesophase is the one that has attracted lot of attention and widely investigated. In the

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*Permanent address: Department of Chemistry, University of Jammu, Jammu-180006, India simplest case, the columnar mesophase consists of discs stacked one on top of another aperiodically to form liquid-like columns, the different columns constituting a two-dimensional lattice. A number of variants of this structure have been identified, e.g., upright columns with hexagonal/rectangular lattice, tilted columns, an ordered arrangement of discs within the columns, etc.

In addition to yielding many interesting phase diagrams, pressure studies on the mesomorphic behaviour of liquid crystals are important because they reveal the structure-property relationship of the liquid crystalline molecule. There exists a large number of reports of high-pressure studies on calamitic systems [10], leading to many important observations like pressure induced mesomorphism, suppression of the mesophase at high pressure [11a], re-entrant phenomena [11b], multicritical phenomena [11c], triple reentrance [11d] etc. In contrast only a few studies have been done on the effect of pressure on the mesomorphic behaviour of discotic mesogens [2–9]. Here we report the effect of pressure on the mesomorphic behaviour of a number of compounds of the alkoxy triphenylene series.

EXPERIMENTAL

Figure 1 shows the generic structural formula and the transition temperature versus chain length phase diagram for the hexaalkoxy triphenylene series of compounds. High pressure experiments have been carried out on several of the compounds, viz., (i) by varying n the length of the alkoxy chains, keeping x, the number of substituents to the triphenylene core fixed, and (ii) with n fixed and varying x. All the compounds were found to show a columnar (Col) phase with a hexagonal arrangement of the lattice and having short-range intracolumnar order, except for the compound with $n = 4$ and $x = 6$, for which the columnar phase is plastic-like in nature.

The details of the high pressure optical cell are given in Ref. [8]. Essentially it consists of a sample sandwiched between optically polished sapphire cylinders enclosed in an elastomeric tube. A liquid with low viscosity and high flash point is used as the pressure transmitting medium. At different fixed pressures, the intensity of the He-Ne laser beam transmitted through the sample was monitored using a photodiode with a built-in amplifier, while the sample pressure was measured using a precision Heise gauge. A PC handled the data acquisition and control of the experiment.

RESULTS AND DISCUSSION

Figures 2(a)–2(e) show the pressure-temperature phase diagrams obtained both in the heating and cooling modes for the compounds of

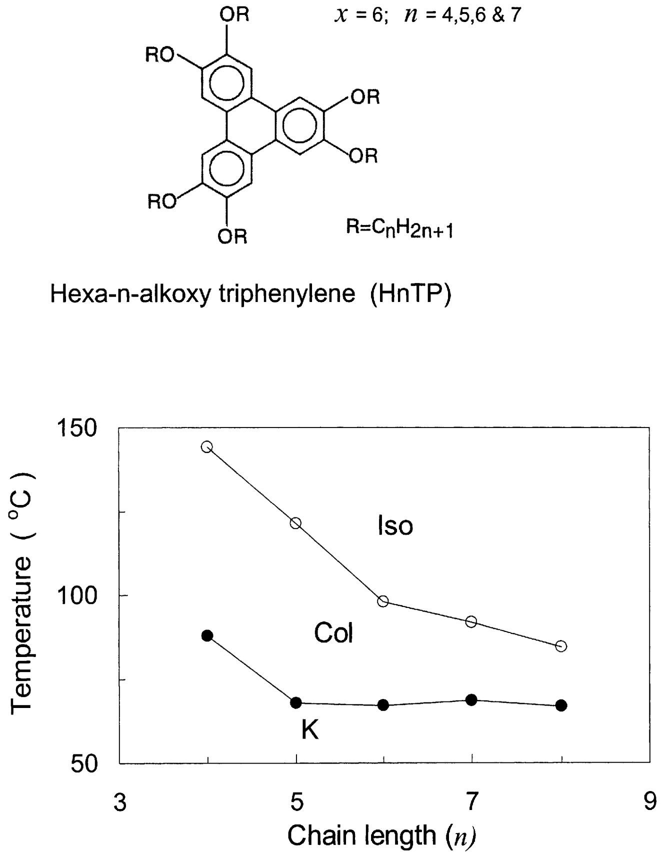


FIGURE 1 Temperature-chain length (n) phase diagram for the hexa substituted ($x = 6$) alkoxy triphenylene compounds. The top panel shows the generic structural formula of these compounds.

series (i) ($x = 6$, and n varied from 4 to 8). For the compound with $n = 4$ and 5, the crystal(K) to mesophase phase boundary remains almost parallel to the Columnar-isotropic (Col-Iso) phase boundary. With increase in pressure the transition remains enantiotropic and the temperature range of the Col phase remains unaltered. For the $n = 4$th member, the cooling mode shows pressure induced mesomorphism with a new phase(X) appearing below the Col phase. Similarly, for the $n = 5$th member the diagram shows the presence of this new phase(X) almost right from room pressure. The temperature range of this X phase is very small at room pressure but increases slightly with increasing pressure. We have not been able to perform any Xray studies in the X phase due to its proximity to

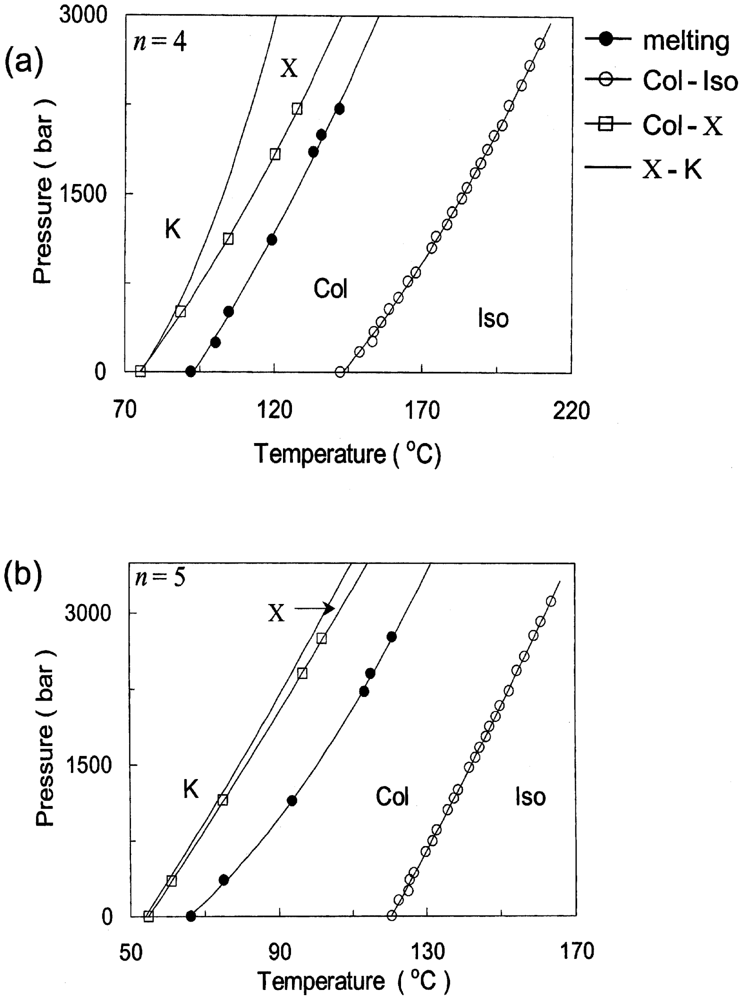


FIGURE 2 Pressure-temperature phase diagrams for different members of series (i) in both heating and cooling modes. The lines are drawn as guide to the eye. The data for $n = 8$ compound is taken from ref. 4. The temperature range of the Col phase remains same with increase in pressure for $n = 4$ and 5 (Panels a and b). Whereas for $n \geq 6$ the range decreases resulting in a K-Col-Iso triple point in the heating mode (Panels c–e). The transition which was enantiotropic below K-Col-Iso triple point becomes monotropic above this point. The triple point pressure is ~ 2 kbar for $n = 6$, ~ 1 kbar for $n = 7$ and 0.64 kbar for $n = 8$.

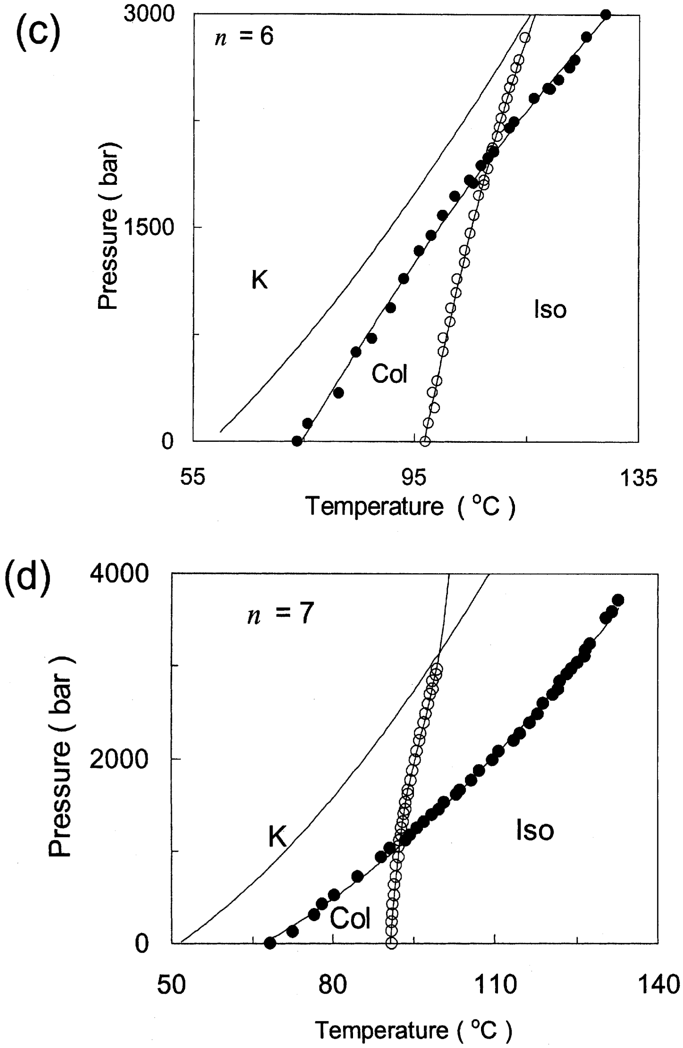


FIGURE 2 Continued.

crystallization. In contrast to the behaviour seen for $n = 4$ and 5 members the temperature range of the Col phase is found to decrease with increasing pressure for the 6th member and this decrease is appreciable for compounds as n is further increased. For each of these compounds the Col-Iso transition becomes monotropic at high pressure resulting in a K-Col-Iso triple point. The pressure at which this triple point occurs, decreases with increasing n, being ~2 kbar for $n = 6$, ~1 kbar for $n = 7$ and 0.64 kbar for

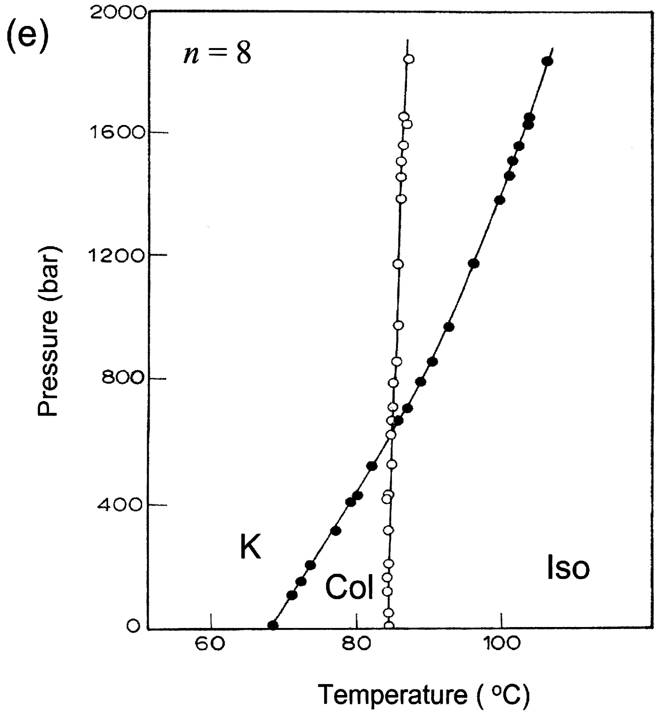


FIGURE 2 Continued.

$n = 8$. Beyond the triple point pressure, the compound transforms directly from the crystal to the isotropic state in the heating mode and the Col phase occurs only in the cooling mode. Further increase in pressure shows suppression of the mesophase even in the cooling mode. Figure 3 shows the temperature range of the mesophase at 1 bar, and at 0.7 kbar; the reduction in the range of the Col phase for higher n, is more drastic at 0.7 kbar.

Figure 4 shows the Iso-Col phase boundary for all the 5 homologues, i.e., the compounds with $n = 4$ to 8. It is evident that the phase boundary tilts more towards the y-axis with increase in n and for $n = 8$ becomes practically a vertical line or, in other words, the transition temperature becomes insensitive to the applied pressure! Figure 5 shows a plot of the slope calculated at atmospheric pressure $[(dT/dP)_{1bar}]$ versus n for both melting and Col-Iso phase boundary. While a small odd-even effect is seen for the melting line, the data for the Col-Iso boundary shows a continuous decrease with increasing n. Since both transitions are first order, using Clausius-Clapeyron equation and with the knowledge of the transition enthalpy ΔH, the transition entropy ΔS as well as the transition volume ΔV

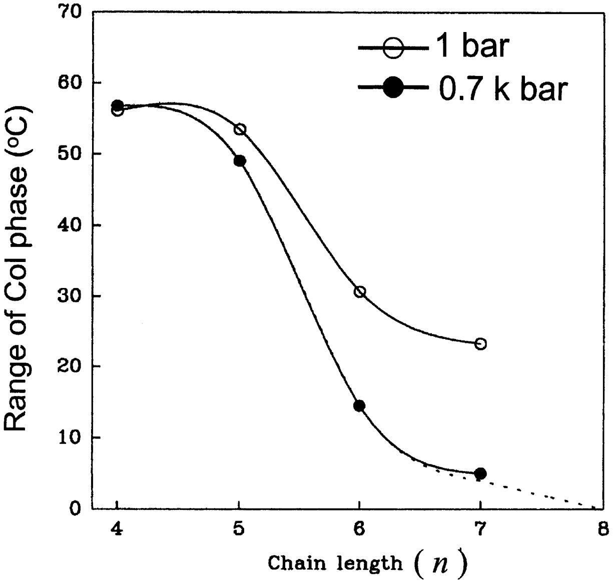


FIGURE 3 Plot showing the temperature range of the Col phase at 1 bar and at 0.7 kbar as a function of chain length n. Temperature range of the mesophase decreases in both the cases, the decrease being more rapid at 0.7 kbar.

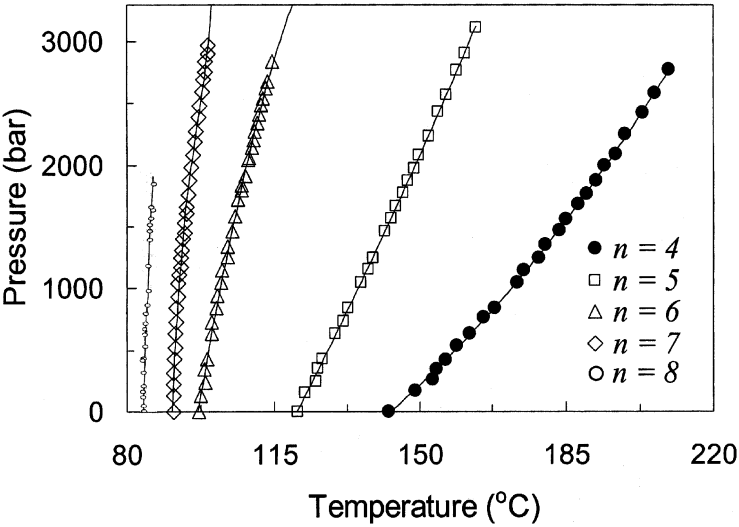


FIGURE 4 Col-Iso phase boundary as function of pressure for all members of the series (i). It can be seen clearly that for lower members, $(dT/dP)_{1bar}$ is large and finite, decreasing as n is increased. For $n = 8$ the boundary is almost vertical indicating $(dT/dP)_{1bar} \sim 0$.

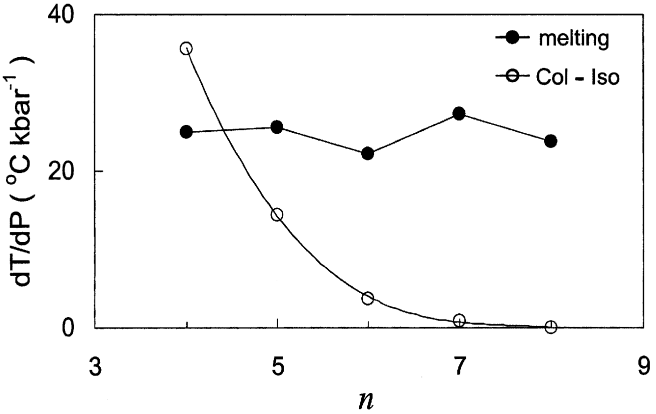


FIGURE 5 Plot of the slope $(dT/dP)_{1bar}$ versus chain length n for melting and the Col-Iso transitions. For the melting transition, the slope shows a slight odd-even effect whereas it drops monotonically and drastically for the Col-Iso transition.

can be calculated. Figures 6(a) and 6(b) show plots of ΔS and ΔV versus n for the K-Col and Col-Iso phase boundaries. Both ΔS and ΔV increase with increasing n for the melting line, but show a decrease for the Col-Iso phase boundary.

For the $n \geq 6$ members the slope $(dT/dP)_{1bar}$, the calculated transition entropy ΔS and the transition volume ΔV values are practically zero for the Col-Iso transition suggesting the transition to be a second order one. If it is indeed second order then it is somewhat puzzling since the two-dimensional lattice undergoes melting at the Col-Iso transition. It may be recalled that melting, in general, and the Col-Iso transition in particular, are well known to be first order [12–15]. A possible explanation is outlined in the following. The alkoxy triphenylene molecule consists of a central aromatic (triphenylene) core surrounded by six hydrocarbon tails. (Here we take the oxygen atom of the alkoxy chain to belong to the core). At the melting (K-Col) transition the hydrocarbon chains melt and become liquid-like, but the ordering of the core region stabilizes the mesophase. At the Col-Iso transition the ordering of the core region also gets lost and the system becomes truly isotropic. To get an idea of the relative contributions of these two parts of the molecule, it is necessary to calculate the partial volumes occupied by the core and the tail region. Approximating the disc to be a circle, the area A occupied by the molecule on the basal plane can be calculated by measuring the intercolumnar distance. The volume of the entire molecule $V_m = AC$, where C is the intracolumnar stacking periodicity of the triphenylene core. Taking the diameter of the triphenylene core to be 10.5 Å, the ratio of the volume of the core to the total volume is $\sim 30\%$ for $n = 4$

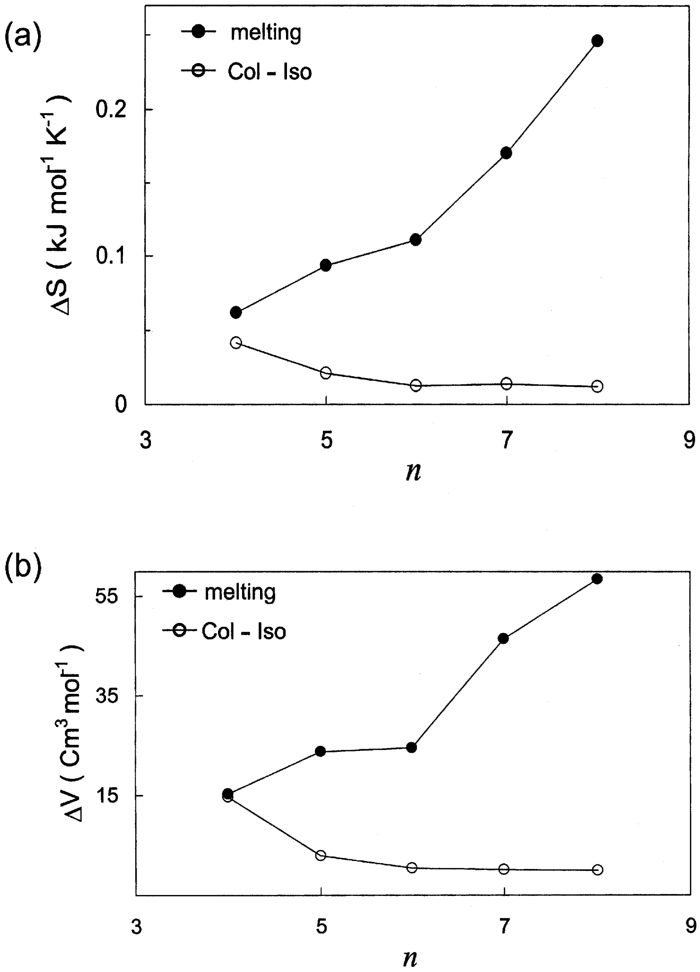


FIGURE 6 (a) Transition entropy ΔS versus *n* for the melting and the Col-Iso transitions (b) Transition volume ΔV versus *n* for the two transitions. Both ΔS and ΔV increase with increasing *n* for the melting transition while showing a significant drop for the Col-Iso transition.

and ~22% for $n = 7$. Figure 7 shows the plot of relative contribution of the core to the total volume (in terms of relative area on the basal plane) versus chain length *n*. This parameter is seen to decrease monotonically with increasing *n*. Further, X-ray measurements show (Fig. 8) that the core-core correlation length is larger for the lower members of the series but decreases as *n* is increased. In the light of these features, it is clear that an increase in the chain length *n* leads to a decrease in stability of the

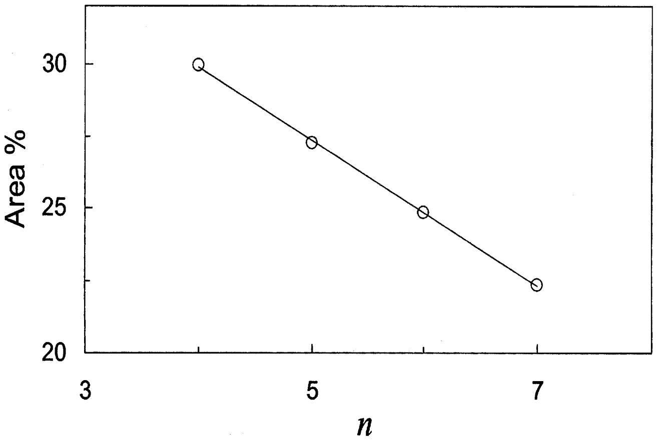


FIGURE 7 Plot of the relative contribution of the volume of the core to the total volume of the molecule versus n. The number is small (~30%) even for $n = 4$ showing further drop as n is increased.

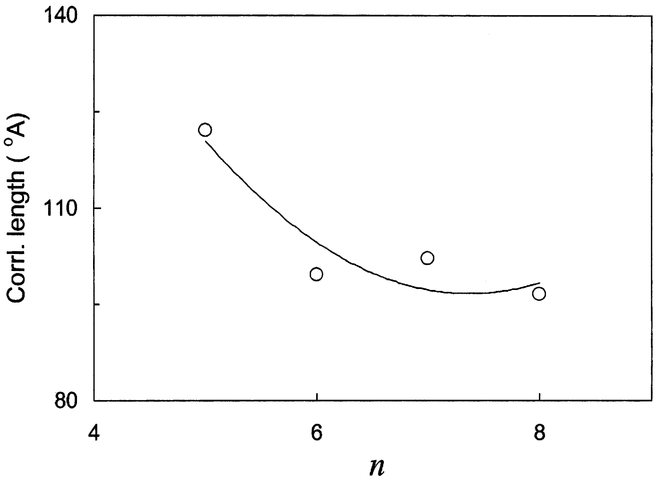


FIGURE 8 Plot of core-core correlation length versus n at a temperature ~22°C below the isotropic phase. The correlation length is large for $n = 5$ but decreases with increasing chain length suggesting that core-core packing weakens for larger n.

mesophase. Therefore it should not be surprising if this reduction in the ratio, arising due to a mere lengthening of the alkyl chain, lowers the transition volume ΔV and transition entropy ΔS at the Col-Iso transition.

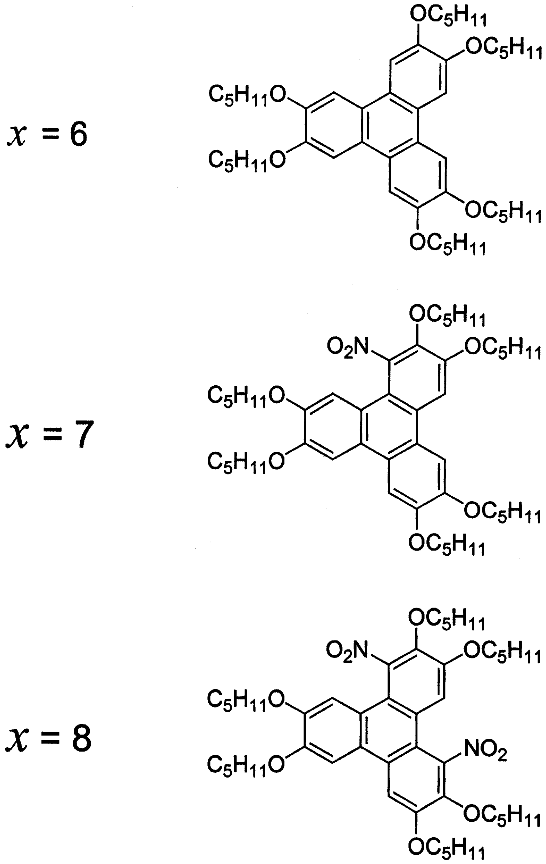


FIGURE 9 Structural formulae of compounds belonging to series (ii). *x* indicates the number of peripheral substituents to the core.

To study the effect of increasing the number of peripheral substituents to the core we have done experiments on compounds belonging to series (ii), i.e., keeping *n* fixed and *x* the number of peripheral substituents is varied. Even though the kind of substitution is different (viz., NO_2 group instead of an alkoxy chain) we consider it as just an increase in the number of peripheral substituents. The general structural formula of the compounds used is shown in Figure 9. In all these compounds the Col phase is stable even at room temperature. Figures 10a–c show the pressure-temperature phase diagrams obtained for these compounds. Since the compounds do not crystallize even under high pressure we have not plotted the melting/crystallization phase boundary. Figure 11 shows Iso-Col phase boundary on a reduced temperature ($T\text{-}T_{\text{Col-Iso}}$) [$T_{\text{Col-Iso}}$ being the Col-Iso transition temperature at room

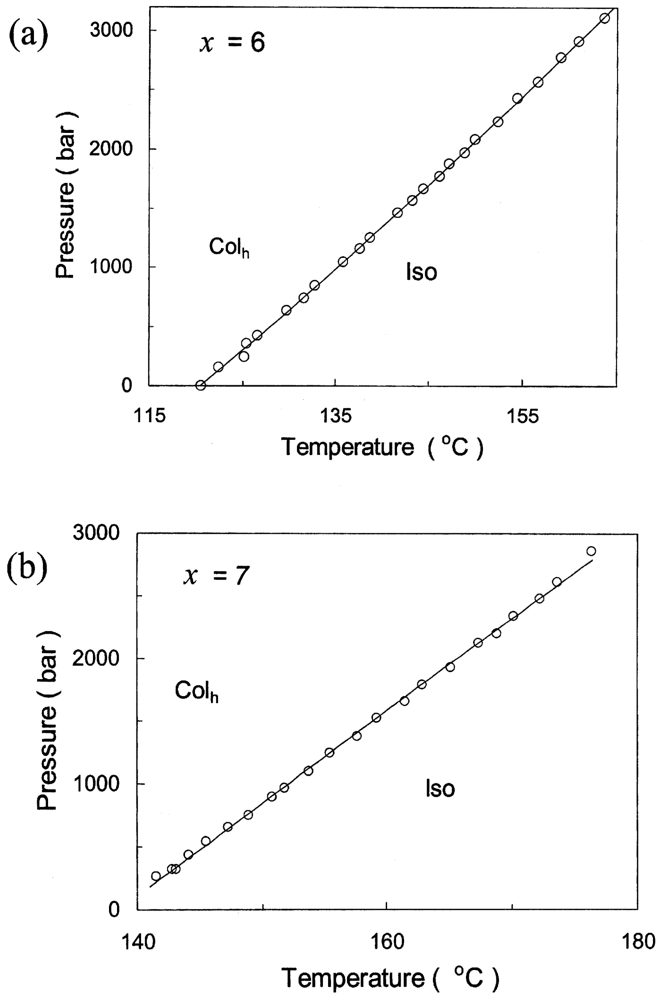


FIGURE 10 Pressure-temperature phase diagram for different members of the series (ii). Since these compounds stay in the mesophase till room temperature at all pressures the melting/crystallization have not been obtained.

pressure] scale for all the three compounds with $x = 6$, 7 and 8. For compounds with $x = 6$ and 7, the Iso-Col phase boundary falls one above another whereas for $x = 8$, the phase boundary is tilted more towards y-axis. Figure 12 shows a plot of slope $(dT/dP)_{1bar}$ as function of x. The slope value remains practically the same for $x = 6$ and 7, whereas for $x = 8$ there is a decrease in the value. The transition entropy ΔS and transition volume ΔV calculated

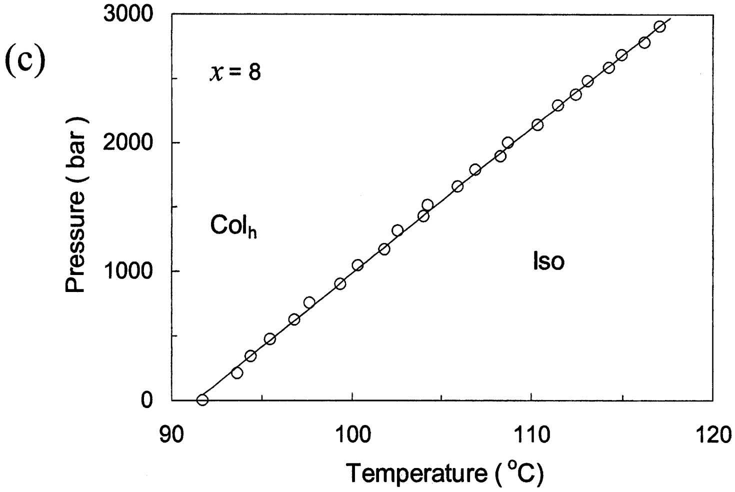


FIGURE 10 Continued.

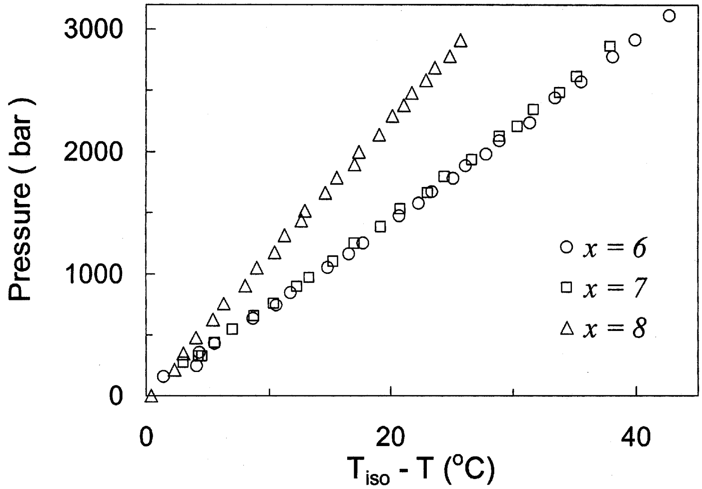


FIGURE 11 Col-Iso phase boundary on a reduced temperature scale ($T_{Col\text{-}Iso}$–T), $T_{Col\text{-}Iso}$ being the Col-Iso transition temperature at room pressure, as a function of pressure for all the members of the series(ii). For $x = 6$ and 7 the Col-Iso phase boundary overlaps at all pressures whereas for $x = 8$ there is significant decrease in the slope (dT/dP).

using the experimentally determined ΔH and the Clausius-Clapeyron equation show a decrease with increasing x (Fig. 13). Increase in x may be similar to increase in n like for the compounds of series (i). The ratio area % shows a

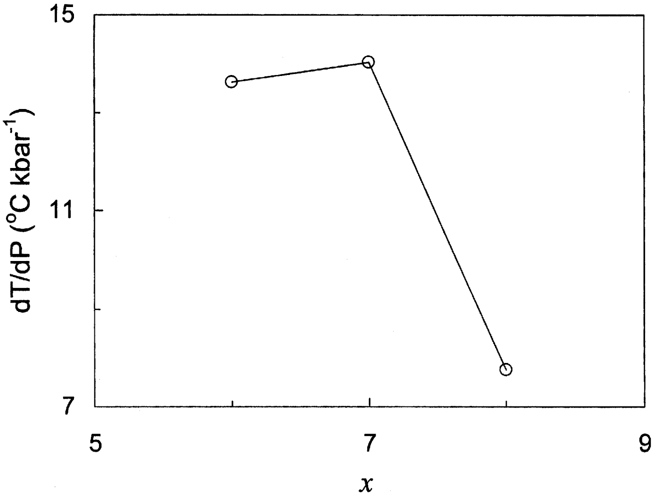


FIGURE 12 Plot of the slope $(dT/dP)_{1bar}$ versus number of peripheral substituents x, for the Col-Iso transition.

decrease (Fig. 14) with increasing x suggesting that increase in the number of peripheral substituents leads to decrease in the contribution to stabilization of cores, in other words the mesophase stabilization. Figure 15 shows a plot of core-core spacing versus $(T\text{-}T_{Col\text{-}Iso})$ for $x = 6,7$ and 8 member of the

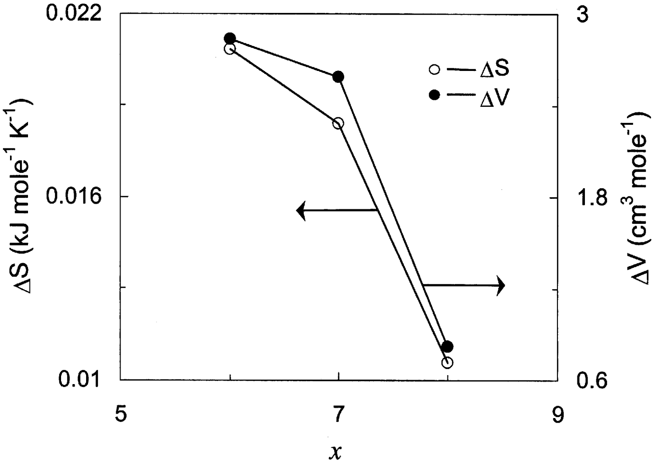


FIGURE 13 Plot of transition entropy ΔS and transition volume ΔV versus x for the Col-Iso transition. Both ΔS and ΔV show a significant drop with increase in x for the Col-Iso transition.

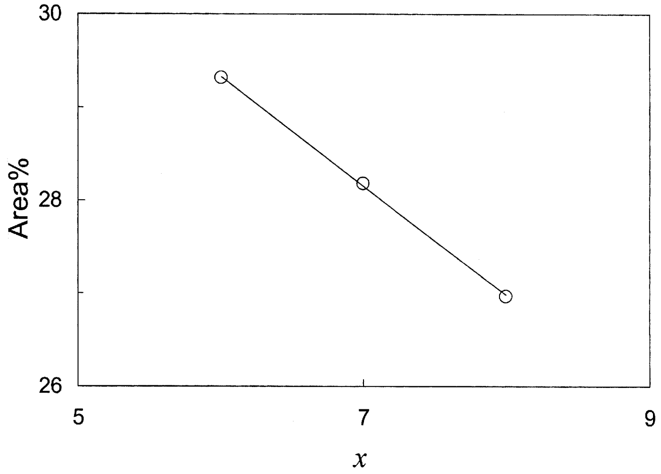


FIGURE 14 Plot of the relative contribution of the volume of the core to the total volume of the molecule versus x. The value drops appreciably with increase in x.

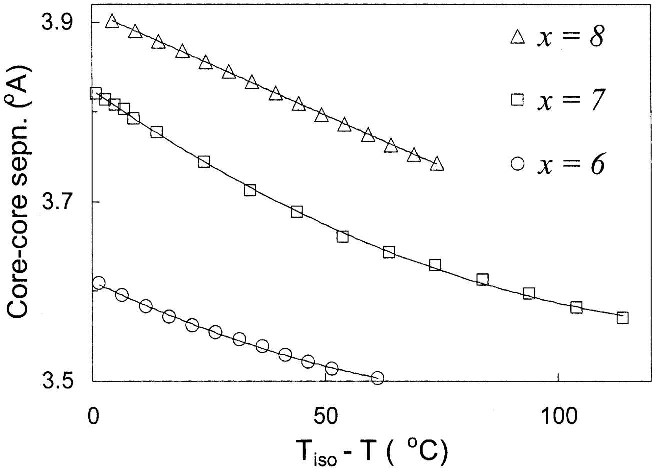
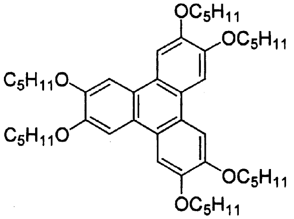


FIGURE 15 Plot of the core-core separation versus reduced temperature for compounds with $x = 6$, 7 and 8. The core-core separation is small for $x = 6$ but increases with increase in x.

series. The core-core spacing is small for the compound with lesser number of substituents viz., for $x = 6$ increases with increase in x. All these add up to the fact that smaller the peripheral substituent, more stable is the mesophase.

Table 1 compiles the structural formula and the experimental data at the Col-Iso phase transition for two compounds: one hexa substituted ($x = 6$) and another hepta substituted ($x = 7$), but both having five carbon atoms in each of the alkyl chains. In this case the difference is that all the peripheral substituents are alike for compounds with $x = 6$ and 7. Table 2 compiles the experimental data at the Col-Iso phase boundary for two hepta-substituted compounds, but two different n values, namely 5 and 7. In both the cases the slope $(dT/dP)_{1bar}$, the calculated transition entropy ΔS and the transition volume ΔV decreases with increase in either x or n.

$x = 6$



$x = 7$

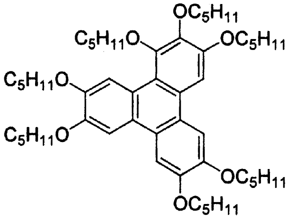
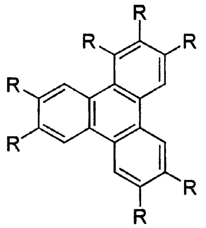


TABLE 1

x	$T_{Col\text{-}Iso}$(°C)	ΔH (kJ/mol)	$(dT/dP)_{1\ bar}$(°C/kbar)	ΔS (kJ mol^{-1} K^{-1})	ΔV (cc mol^{-1})
6	120.5	8.2	13.6	20.8×10^{-3}	2.8
7	73.1	6.0	10.0	17.3×10^{-3}	1.7



$R = OC_nH_{2n+1}$; $n = 5$ & 7

TABLE 2

n	$T_{Col\text{-}Iso}$(°C)	ΔH (kJ/mol)	$(dT/dP)_{1\ bar}$(°C/kbar)	ΔS (kJ mol^{-1} K^{-1})	ΔV (cc mol^{-1})
5	73.1	6.0	10.0	17.3×10^{-3}	1.7
7	69.3	5.5	5.1	16.1×10^{-3}	0.8

In conclusion we have studied the effect of high pressure on a number of triphenylene compounds with variation in either the chain length or the number of peripheral substituents. In both cases the temperature range of the mesophase was found to decrease with increase in pressure, which lead to a decrease in $(dT/dP)_{1bar}$, the calculated ΔS and ΔV at the Col-Iso phase transition. We have tried to explain this behaviour by considering the reduced contribution of the central core region to the total volume of the molecule.

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