CHAPTER VIII

HIGH PRESSURE STUDIES ON DISCOTIC LIQUID CRYSTALS

8.1 INTRODUCTION

Since Reinitzer's first observation of liquid crystallinity in 1888, the generally accepted rule has been that the molecule has to be long and 'rod-like' for mesomorphism to occur in thermotropic systems.[1] In 1977, mesophases built up of relatively simple disc-shaped molecules were discovered by Chandrasekhar et al.[2] This discovery has opened up a new field of activity. The compounds in which this new type of mesomorphism was observed were hexa-substituted esters of benzene. From thermodynamic, optical and X-ray studies it was concluded that these compounds form a new type of liquid crystal, quite unlike the classical nematic or smectic types. The model that was proposed is illustrated schematically in Fig. 8.1. The discs are stacked aperiodicaly one on top of the other to form liquid like columns, the different columns forming a hexagonal array.[2-5] This columnar structure has been confirmed by the X-ray studies of Levelut.[6-8] Thus the structure has translational order in two dimensions but not in the third, and is the first example to be discovered of a system "melted" in one dimension. This new type of thermotropic liquid crystal has been variously designated as canonic,[9] columnar[10,11] and discotic[12] (the last
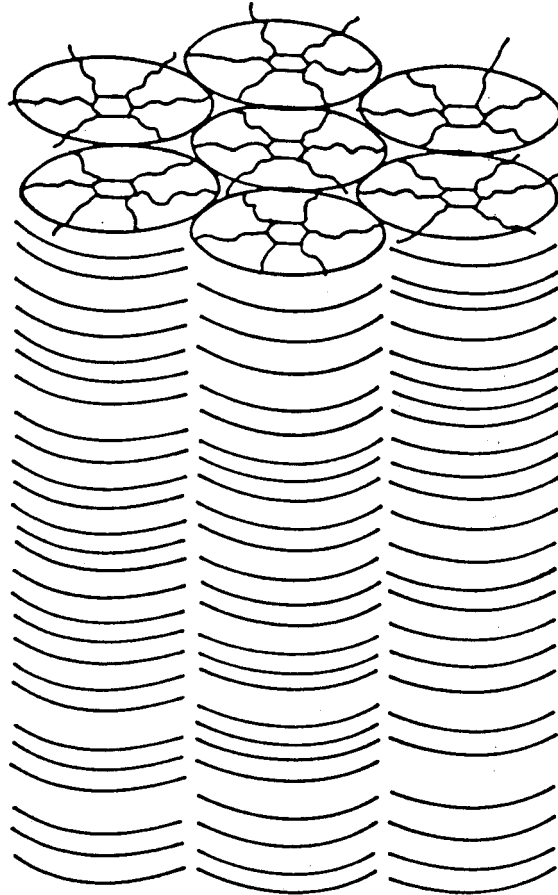
Schematic representation of *the columnar* structure of *the mesophase.* **The discs are** *spaced irregularly to form liquid-like columns.*

often being used to describe the molecules as well as the mesophases formed by them).

Since the discovery by Chandrasekhar et al.[2] a number of other **discotic** systems exhibiting the columnar phase were reported.[12-25] **It is** now known that **discotic** mesophases exhibit a rich polymorphism,[5] comparable to that observed in liquid crystals of rod-like molecules. In fact, a number of variants of this columnar structure have been found ⁻ upright columns with a hexagonal or rectangular lattice,[7,8] a tilted columnar arrangement[t8] (Fig. 8.2). Some differences have been found in th'e degree of order within the **columns.This** complex columnar polymorphism then raises further problems ,of nomenclature. Two alternate schemes have been proposed, one by the Paris group[2'] and the other by the Bordeaux group.[18] The former one **is** similar to the smectic classifications based on miscibility criteria: **it** consists of the **letter** D with other letters subscripted following generally in alphabetical order (D_A, D_B, D_C ..., etc.).[21,8,25] The other scheme proposed by Destrade et al.[18,26] is based on the crystallographic considerations; two simple crystallographic parameters are sufficient for the characterization of columnar arrangements,

(i)   the two dimensional lattice symmetry. **It** can be hexagonal, represented as D_h or rectangular represented as D_r or oblique, D_{ob},
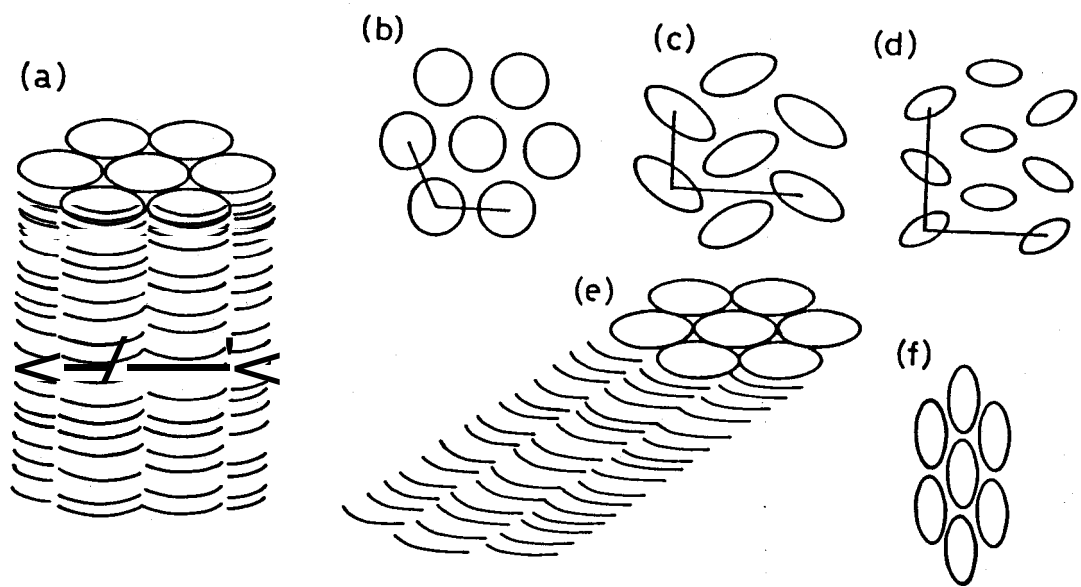
Figure 8.2

Columnar phanen of disc-like molecules: (a) upzight columnar ntzuctuze, (b) its hexagonal and (c),(d) Rectangulaz modifications, (e) Tilted columnaz ntzuctuze, (f) itn Qce-centzed rectangulaz lattice. (From Ref. 5).

(ii) the order or disorder of the molecular stacking in the columns.

Therefore, a hexagonal lattice of columns with ordered disc-like molecules is then represented as D_{ho}, then the notations D_{hd}, D_{rd} or D_{obd} are then clear.

It is of interest to study the effect of pressure on these phase transitions. The **first** high pressure studies on disc-like systems was conducted[3,27] on benzene-hexa-n-alkanoates - the effect of pressure on the phase transitions in the sixth to the ninth **homologs** was studied. The following interesting features were observed :

(i) The dT/dP for the solid-isotropic (or solid-mesophase) was found to be roughly the same for all the compounds about 8°C/kbar.

(ii) For compounds which exhibit mesophases even at atmospheric pressure, the dT/dP for the mesophase-isotropic transition is also the same, around 6-7 °C/kbar. This value is rather small compared to the dT/dP values that are normally observed for the mesophase-isotropic transitions in rod-like systems (where usually the values range between 35-45 °C/kbar).

(iii) However, when the mesophase is induced by pressure, the dT/dP values of the pressure induced phase-isotropic transition increrases considerably.

Since this early work, there have ,been several pressure studies on **discotic** substances.[28-31] In this chapter we shall present the pressure-temperature diagrams for two **discotic** compounds, hexa-n-octyloxytriphenylene and hexa-n-decanoyloxytriphenylene, both of which exhibit the columnar (D) phase at atmospheric pressure. The results of these studies will be presented in this chapter. One of the materials, namely, HOT, has in fact been studied earlier by Gasparoux et al.[28] though we were not aware of it when we undertook this study. We shall be comparing our results with theirs.

8.2   MATERIALS

We studied the eighth member of the hexa-alkoxy triphenylene series (hereafter abbreviated as HOT) and the ninth member of the hexaalcanyoloxy triphenylene series (hereafter abbreviated as HDOOT). The chemical.structure of HOT and HDOOT are shown in Fig. 8.3. Both these compounds show only one mesophase on heating from the solid phase before transforming into the isotropic phase. HOT exhibits a columnar phase denoted by D_{ho}[15,26] and HDOOT shows a columnar phase designated by D_{rd}.[15,16] The transition temperatures were determined optically using a polarizing microscope (**Leitz-Ortho**plan) and are listed in Table 8.1.

8.3   EXPERIMENTAL

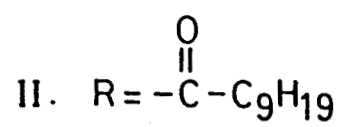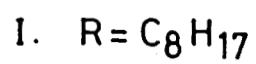The pressure studies were conducted using a high pressure

I.   R = C$_8$H$_{17}$
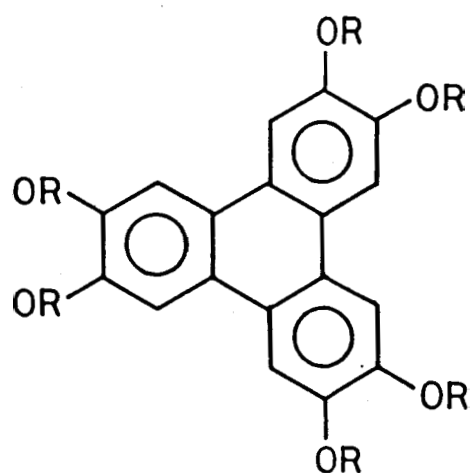
II. R = $-\overset{\overset{\displaystyle O}{\|}}{C}$-C$_9H_{19}$

Figure 8.3

Chemical *structures* **of** *the* **compounds.** *I. Hexa-n-octyloxy-*
triphenylene (HOT), **and** *11. Hexa-n-decanoyloxytriphenylene*
(HDOOT).

Table 8.1

Transition temperature of different transitions
exhibited by two discotic compounds

Compound	K – D (°C)	D – I (°C)
hexa–n–octyloxy triphenylene (HOT)	66.9	84.5
hexa–n–decanoyloxy triphenylene (HDOOT)	67.0	122.0

K : crystal   D : mesophase   I : isotropic

optical cell discussed in Chapter **II**. Transitions were detected by the optical transmission technique. The experiments were always conducted along isobars, **i.e.,** pressure was kept constant and the temperature of the sample varied at a controlled rate of about 1°C/min. The abrupt change in the intensity was taken as the signature of the phase transition. Pressure was measured (using a Heise gauge) to an accuracy of ±1.5 kbar and the temperature to ±0.1°C.

8.4   RESULTS AND DISCUSSION

HOT

The pressure–temperature diagram for the hexa–n–octyloxytriphenylene is shown in Fig. 8.4. **It** is seen that as the pressure is increased from atmospheric pressure, the solid–columnar (K–D), transition temperature varies at a rate of 23.75 °C/kbar while the columnar–isotropic **(D-I)** transition temperature does not have any pressure dependence ⁻ the D–I boundary is seen as a vertical line. Due to the wide disparity in the **dT/dP** values of the K–D and D–I phase boundaries, the range of the D phase (as measured on heating the solid) decreases with increasing pressure. This leads to bounding of the D–phase and a consequent solid–columnar–isotropic (K⁻D–I) triple point at 0.64 kbar, 84.5 °C. **It** should be mentioned that the D phase is bounded at this pressure only with respect to the heating mode ⁻ beyond 0.64 kbar the solid melts directly into the isotropic phase (see Fig. 8.4), but on cooling the isotropic–columnar transition is seen as a monotropic transi-
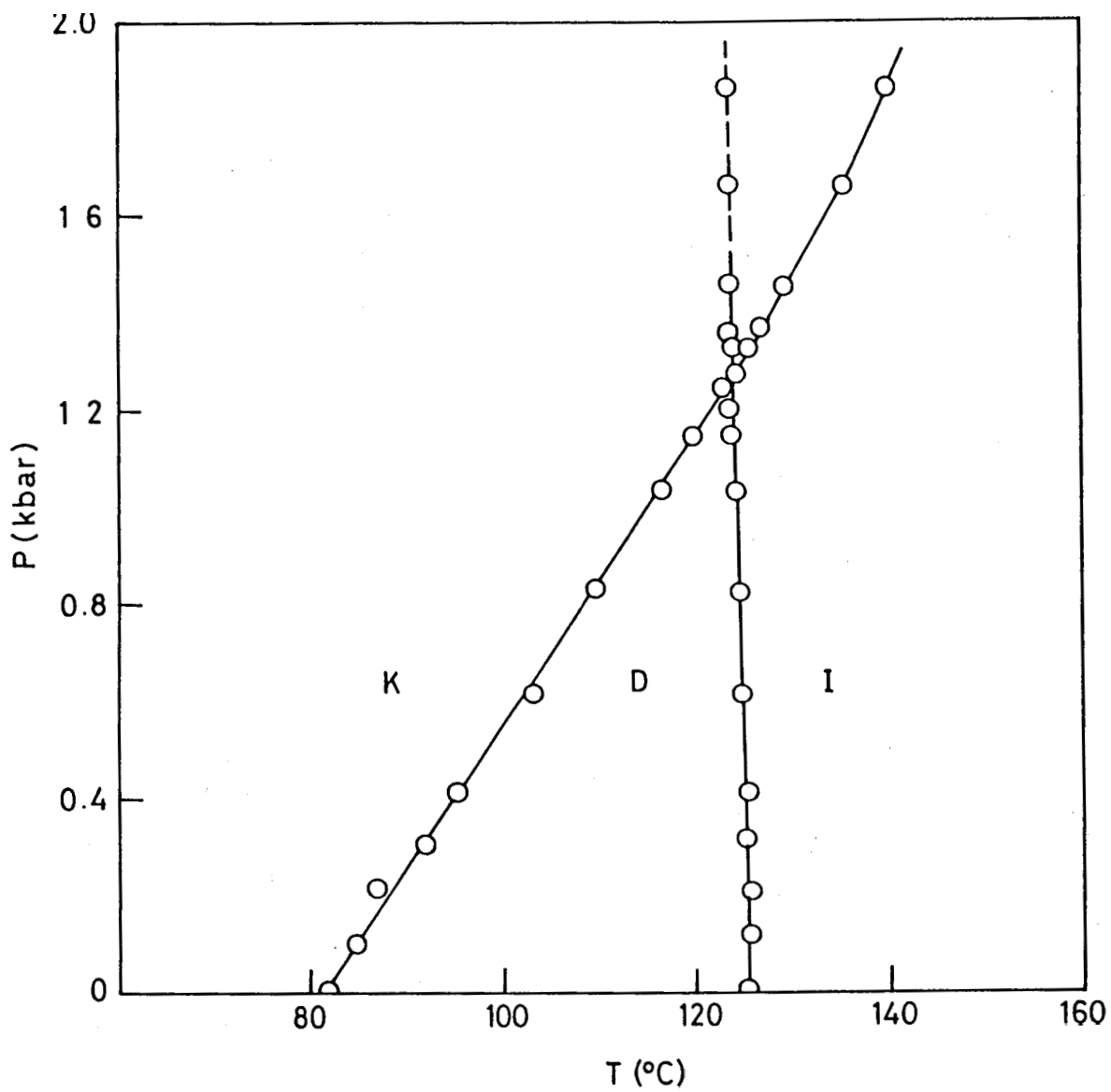
Figure 8.4

Pressure-temperature diagtam of hexa-n-octyloxytziphenylene. The dashed line denotes that the isotropic-columnar (D-I) in mono-ttopic.

tion. Thus at 0.64 kbar the D–I transition changes its character from enantriotropic to monotropic. Similar instances of pressure changing the character of the transition has been seen earlier in thermotropic liquid crystals of rod–like systems.[32,33] Finally, it is clear from the Fig. 8.4 that this monotropic I - D boundary is also vertical. Typical scans showing the different transitions (as a function of temperature) recorded at two different pressures on either side of the triple point are presented in Figs. 8.5 and 8.6.

After completion of this work, it was found that Gasparoux et al.[28] had in fact studied HOT earlier up to a pressure of about 2.7 kbar. The slopes of K - D and D - I phase boundaries obtained by them are similar to those shown by our data up to a pressure of about 0.6 kbar. However, they find that the D - I phase boundary, which is nearly vertical up to 0.6 kbar changes curvature suddenly and curls towards temperature axis beyond 0.6 kbar. Consequently, their K - D - I triple point occurs at a pressure of 1.7 kbar which is much higher than the value obtained by us, viz., 0.64 kbar. The reason for the discrepancy is not clear to us. It should be mentioned that we did not observe any qualitative change in the signal associated with the D - I phase transition in the entire pressure range of 0.1 kbar to 1.8 kbar. This indicates that we were in fact following the D - I transition as a function of pressure throughout.
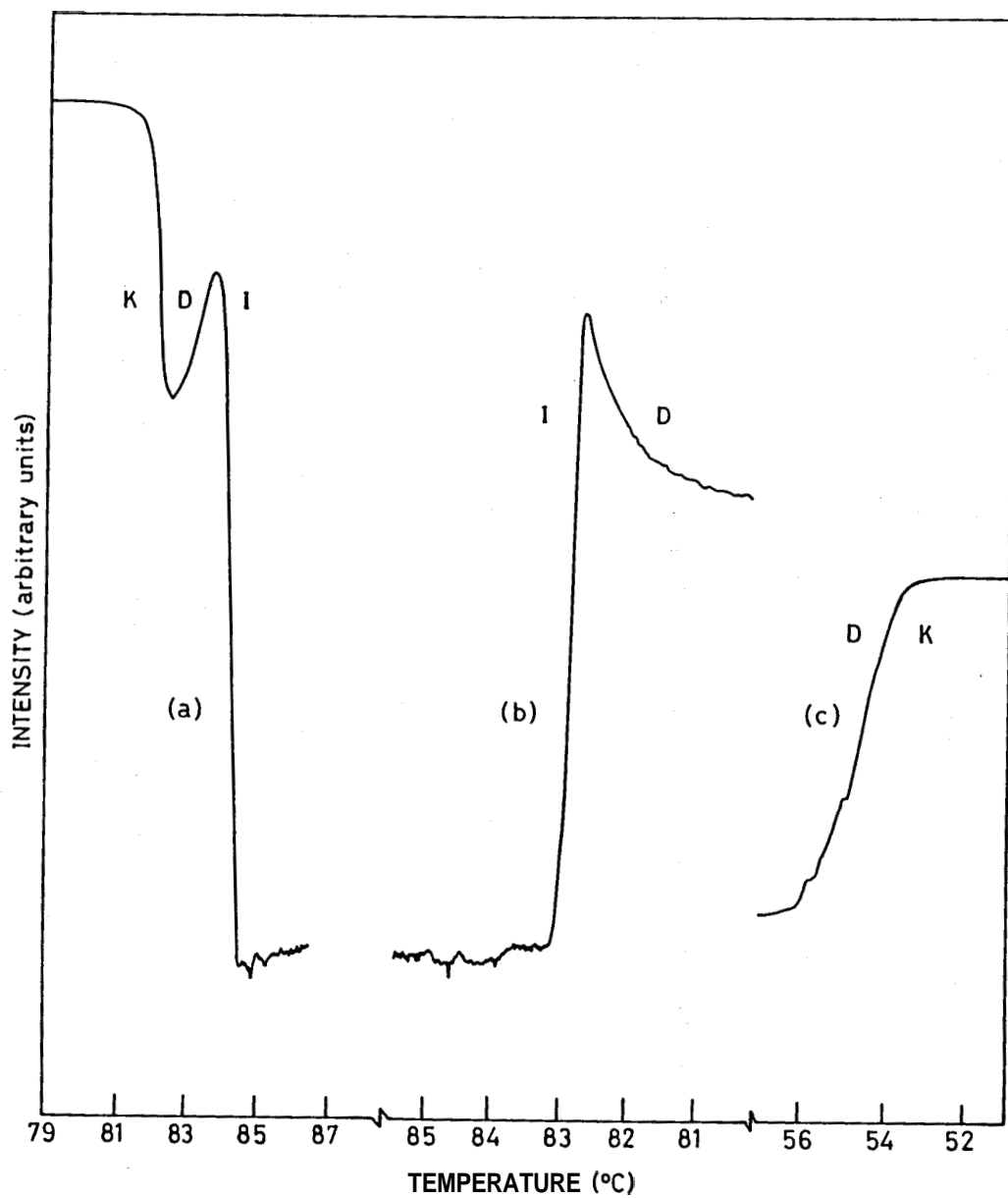
Figure 8.5

Raw traces showing the change in the transmitted light intensity in heating and cooling modes. (a) crystal-mesophase and mesophase-isotropic (heating), (b) isotropic-mesophase and mesophase-crystal (cooling). Pressure is the same for all these scans 10.6 kbar).
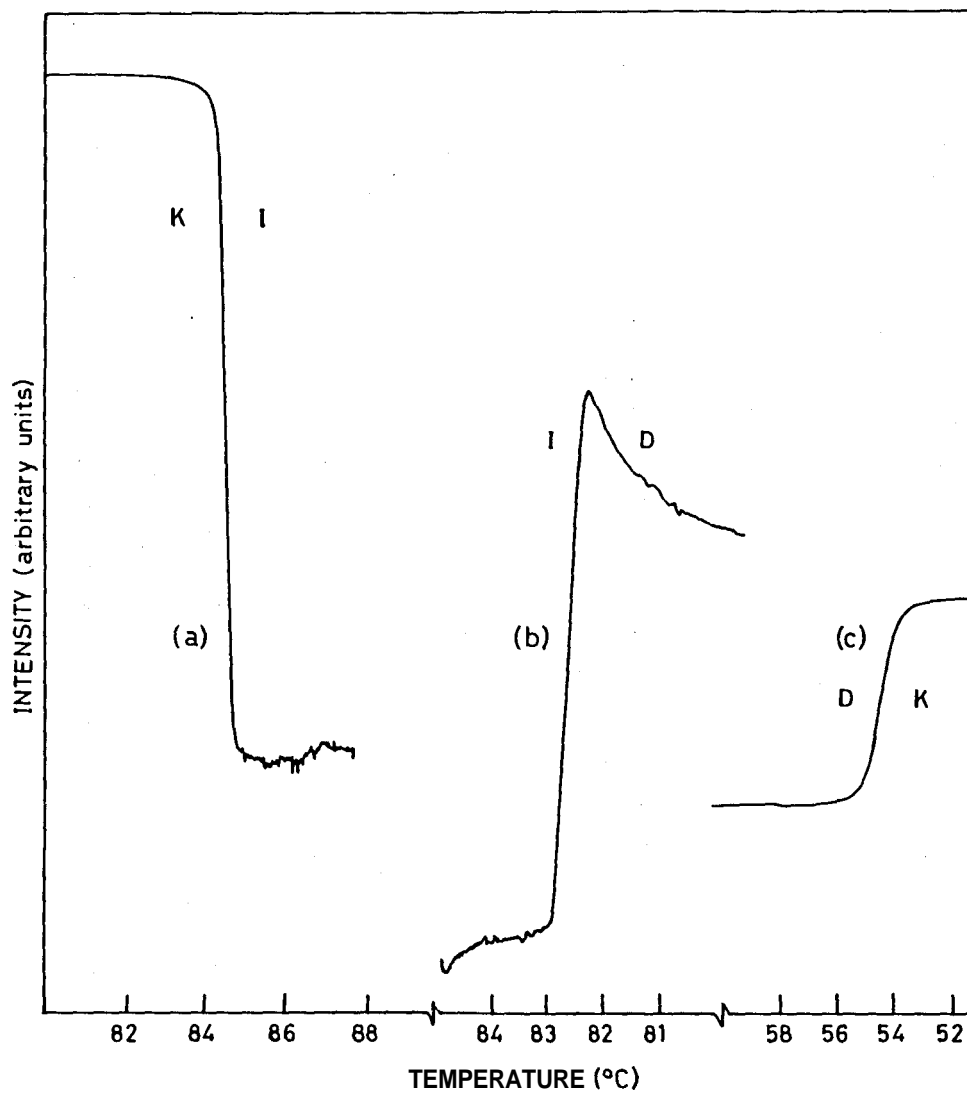
Figure 8.6

Raw traces showing the change in the transmitted light intensity in the heating and cooling modes. (a) crystal-isotropic transition, (b) isotropic-mesophase and mesophase-crystal. The pressure is the same for all thebe scans (0.7 kbar).

HDOOT

The P–T diagram of this compound exhibits essentially similar features as HOT and is shown in Fig. 8.7. The only difference is that the columnar phase is stable over a wider range of pressure and so the solid–columnar–isotropic triple point (observed in heating mode) is now at 1.25 kbar, the D–I transition being monotropic beyond this pressure. The D–I boundary is, as in HOT, a vertical line in the P–T plane. Table 8.2 gives the dT/dP values for the different transitions for the two compounds.

As mentioned earlier a noteworthy feature of both compounds is that the dT/dP for the D–I transition is nearly equal to zero over the entire range of pressure investigated. Cases are known in rod–like reentrant nematogenic systems wherein the slopes of the smectic A – nematic phase boundary is zero (but only over a very small pressure range) before becoming negative[32,33] leading to a reentrant nematic behaviour. However, as far as, we are aware, these appears to be the only instances of the slope of the mesophase-isotropic transition being zero and that too over such an extended pressure range. Considering that the heat of the D–I transition is quite large in both materials[15,26] – 1.04 kcal/mol for HOT and 0.69 kcal/mol for HDOOT, the the pressure independence of the D–I phase transition temperature implies that the volume change associated with this transition should be negligibly small. Accurate density measurements are needed to ascertain this point.
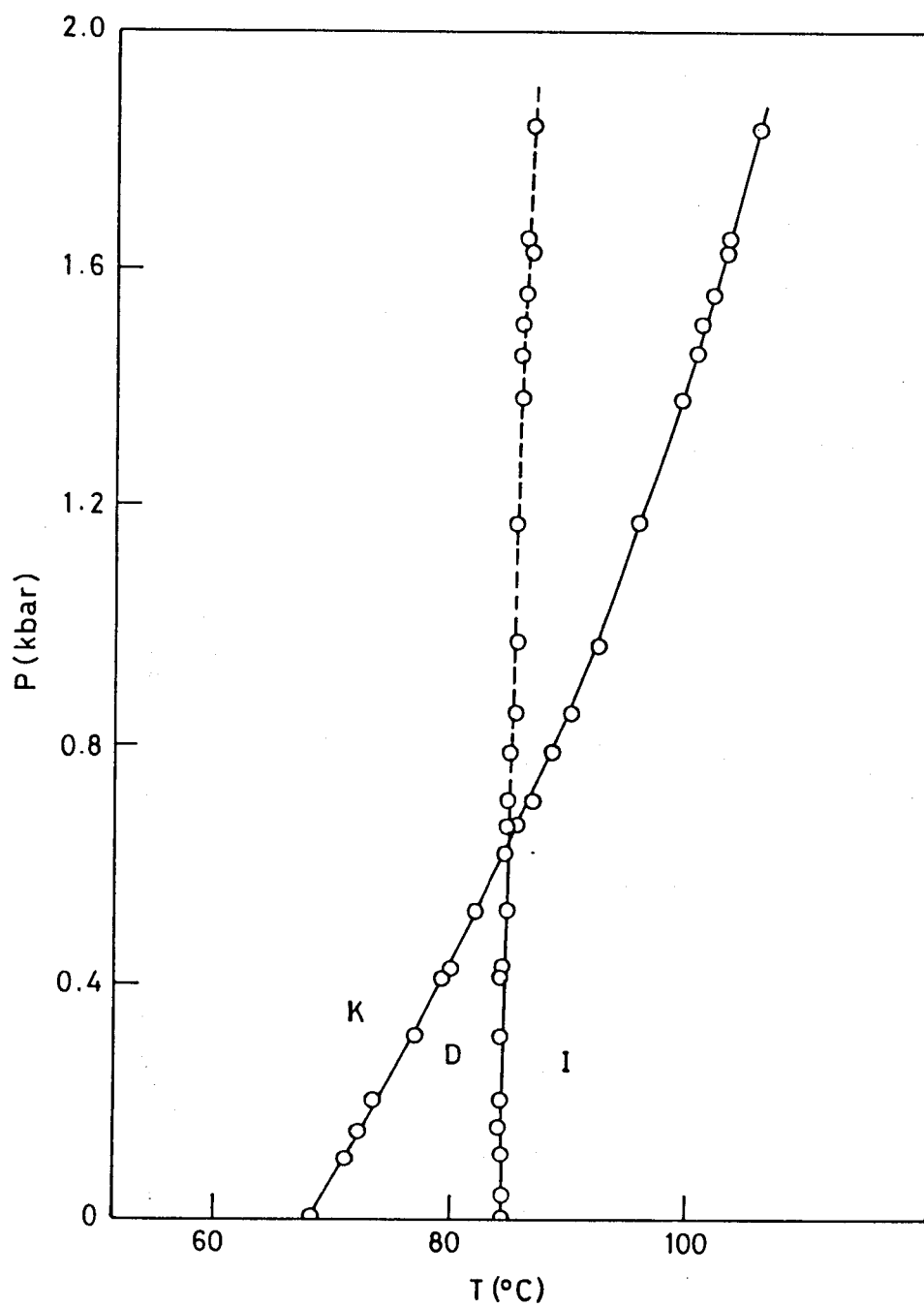
2.0

1.6

1.2

P (kbar)

0.8

0.4

0

K   D   I

60   80   100

T (°C)

Figure 8.7

P-T diagram for hexa-n-decanoyloxytriphenylene. The dashed line indicate4 that the D-1 transition is monotropic.

Table 8.2

dT/dP (in °C/kbar) values for different transitions

Compound	K – D	D – I
hexa–n–octyloxy triphenylene (HOT)	23.75	~ 0
hexa–n–decanoyloxy triphenylene (HDOOT)	33.75	~ 0

K : crystal   D : mesophase   I : isotropic

REFERENCES

1   S.Chandrasekhar, Liquid Crystals (Cambridge University Press, Cambridge, 1977)

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

3   S.Chandrasekhar, B.K.Sadashiva, K.A.Suresh, N.V.Madhusudana, S.Kumar, R.Shashidhar and G.Venkatesh, J. de Phys., 40, C3-120 (1979)

4   S.Chandrasekhar, Adv. Liq. Cryst., 5, 47 (1982).

5   S.Chandrasekhar, Phil. Trans. Roy. Soc., London, **A309,** 93 (1983).

6   A.M.Levelut, J. de Phys. Lett., 40, L-81 (1979)

7   A.M.Levelut, Proceedings of the International Liquid Crystals Conf., Bangalore, December 1979, Ed. S.Chandrasekhar (Heyden, London, 1980), p. 21

8   A.M.Levelut, J. Chim. Phys., 80, 149 (1983)

9   F.C.Frank and S.Chandrasekhar, J. de Phys., 41, 1285 (1980)

10   W.Helfrich, J. de Phys., 40, C3-105 (1979)

11   W.Helfrich, Proceedings of the International Liquid Crystals Conf., Bangalore, December 1979, Ed. S.Chandrasekhar (Heyden, London, 1980), p. 7

12   J.Billard, J.C.Dubois, Nguyen Huu Tinh and A.Zann, Nouv. J. de Chimie, 2, 535 (1978)

13   Nguyen Huu Tinh, J.C.Dubois, J.Malthete and C.Destrade, C. R. Acad. Sci. Paris, 286, 463 (1978)

14   J.C.Dubois, Ann. Phys., 3, 131 (1978)

15   C.Destrade, M.C.Mondon and J.Malthete, J. de Phys., 40, C3-17 (1979)

16   C.Destrade, M.C.Mondon and Nguyen Huu Tinh, Mol. Cryst. Liq. Cryst. Lett., 49, 169 (1979)

17   C. Destrade, J. Malthete, Nguyen Huu Tinh and H.Gasparoux, Phys. Lett., 78A, 82 (1980)

18   C.Destrade, M.C.Bernaud, H.Gasparoux, A.M.Levelut and Nguyen Huu Tinh, Proceedings of the International Liquid Crystal Conf., Bangalore, december 1979, Ed. S.Chandrasekhar (Heyden, London, 1980), p. 29.

19   Nguyen Huu Tinh, M.C.Bernaud, G.Sigaud and C.Destrade, Paper presented at the Third Liquid Crystals Conf. of Socialist Countries, Budapest, Hungary, August 1979.

20   Nguyen Huu Tinh, C. Destrade and H. Gasparoux, Phys. Lett. A, 72, 251 (1979)

21   A.Quiguiner, A.Zann, J.C.Dubois and J. Billard, Proceedings of the International Liquid Crystals Conf., Bangalore, December 1979, Ed. S.Chandrasekhar (Heyden, London, 1980), p. 35.

22   J.W.Goodby, P.S.Robinson, B.K.Teo and P.E.Cladis, Mol. Cryst. Liq. Cryst. Lett., 56, 303 (1980)

23   S.Chandrasekhar, Mol. Cryst. Liq. Cryst., 63, 171 (1981)

24   J.Malthete, C. Destrade, Nguyen Huu Tinh and J.Jacques, Mol. Cryst. Liq. Cryst. Lett., 64, 233 (1981)

25   J.Billard, in Liquid Crystals of One- and Two-Dimensional Order (Springer Series in Chemical Physics II, Berlin, 1980), p. 383

26   C.Destrade, Nguyen Huu Tinh, H.Gasparoux, J.Malthete and A.M.Levelut, Mol. Cryst. Liq. cryst., 71, 111 (1981); C. Destrade, H.Gasparoux, P.Foucher, Nguyen Huu Tinh, J. Malthete and J. Jacques, J.Chim. Phys., 80, 138 (1983)

27   G.Venkatesh, "High Pressure Studies of Liqwuid Crystals", Ph. D. Thesis, Bangalore University, India

28   H.Gasparoux, M.F.Achard, F.Hardouin and G.Sigaud, C. R. Acad. Sci., 293, Series II, 1029 (1981)

29   J.M.Buisine, J. Malthete, C. Destrde and Nguyen Huu Tinh, Physica, 139 & 140B, 631 (1986)

30   J.M.Buisine and M. Dornon, C. R. Acad. Sci. Series II, 1769 (1986)

31   J.M.Buisine, R.Cayeula, C. Destrade and Nguyen Huu Tinh, Mol. Cryst. Liq. Cryst., 144, 137 (1987)

32   P.E.Cladis, R.K.Bogardus and D.Aadson, Phys. Rev. A, **18,**
      2292 (1978)

33   A.N.Kalkura, R.Shashidhar and M.Subramanya Raj Urs, J. de
      Phys., **44,** 51 (1983)