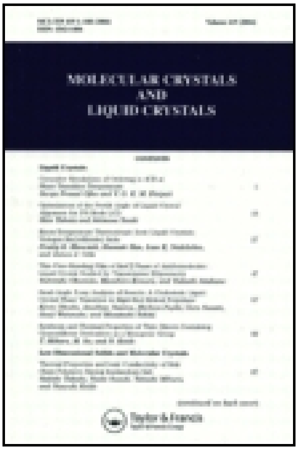


Molecular Crystals and Liquid Crystals

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

High Pressure Study of 4-n-Hexyloxyphenyl-4′-n - Decyloxybenzoate (6OPDOB)

R. Shashidhar [a] & H. D. Kleinhans [a]

[a] Department of Chemistry, Institute of Physical Chemistry, University of Bochum, 4630 Bochum 1, FRG

To cite this article: R. Shashidhar & H. D. Kleinhans (1981): High Pressure Study of 4-n-Hexyloxyphenyl-4′-n - Decyloxybenzoate (6OPDOB), Molecular Crystals and Liquid Crystals, 64:7-8, 217-223

To link to this article: http://dx.doi.org/10.1080/01406568108080168

Mol. Cryst. Liq. Cryst. Vol. 64 (Letters), pp. 217-223
0140-6566/81/6407-0217$06.50/0

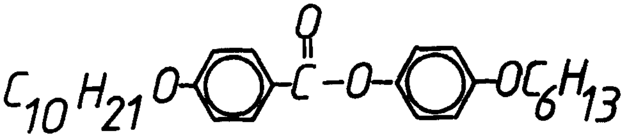
HIGH PRESSURE STUDY OF 4-n-HEXYLOXYPHENYL-4'-n-DECYLOXYBENZOATE (6OPDOB)

R. SHASHIDHAR* and H.D. KLEINHANS
Department of Chemistry, Institute of Physical
Chemistry, University of Bochum,
4630 Bochum 1, FRG

(Submitted for publication January 20, 1981)

Abstract. The effect of pressure on the various types of phase transitions in 6OPDOB has been studied. The smectic C phase is completely bounded with a resulting triple point at (2.22 ± 0.05) kbar, (374 ± 0.7)K. Two pressure induced phases are observed, one above 1.4 kbar and the other for pressures beyond 2.2 kbar. Also, this compound, which was hitherto believed to exhibit three smectic phases B, C and A, is found to exhibit an additional monotropic smectic E phase at atmospheric pressure.

Introduction. Most of the high pressure studies on liquid crystals have been mainly devoted to the study of nematics[1]. However, of late, there has been considerable interest in the study of polymorphic smectics[2-5]. We have under taken a pressure study of 4-n-hexyloxyphenyl-4'-n-decyloxybenzoate (hereafter abbreviated as 6OPDOB)



DSC and Textural Studies. Figure 1 gives raw DSC records of 6OPDOB. This compound which was first synthesized by Deutscher et al.[6], was initially reported to exhibit three smectic phases B, C and A,

---

[*] AvH Fellow, on leave of absence from the Raman Research Institute, Bangalore-560080, India

in addition to the nematic phase. However, it is clearly seen from the DSC runs that in the cooling mode an additional phase appears over a narrow range of temperature (~3.5K) before solidification takes place.

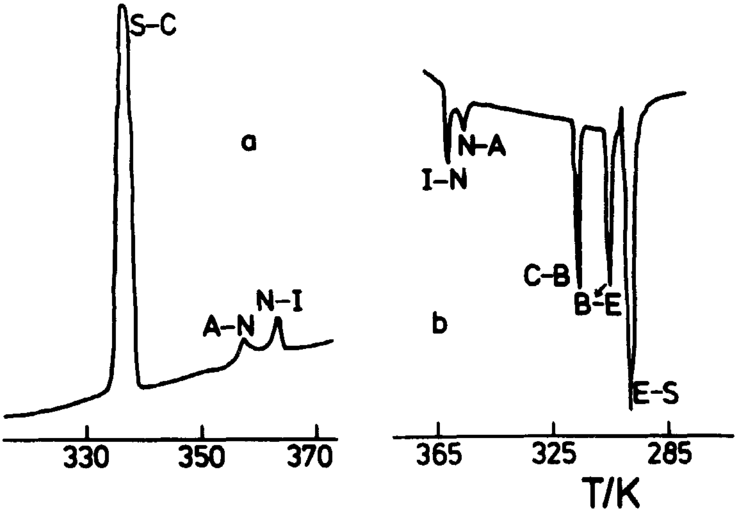


Figure 1: Raw DSC traces of 6OPDOB (a) on heating and (b) on cooling. The C-A transition is undetectable.

The textures of this new phase have been investigated by optical microscopy. The fan shaped textures of smectic B were found to develop concentric arcs characteristic of smectic E[7]. Also, the solid phase obtained by cooling of the mesophase exhibited strong paramorphic striated appearance as is normally seen in the solid resulting from the smectic E phase[8]. We therefore believe that this monotropic phase in 6OPDOB is the smectic E phase. Details of our textural studies as well as the results of our miscibility studies that are being taken up will be published separately.

Table 1 gives the transition temperatures (T_{tr}) as well as the heats of transition (ΔH) at atmospheric pressure as determined by the Perkin-Elmer DSC-2 differential scanning calorimeter equipped with a calculator interface and used in conjunction with an on-line computer (Tektronix 31) and a digital plotter (Textronix 4661).

TABLE 1: T_{tr} and ΔH Values for 6OPDOB

	T_{tr}/K	$\Delta H/kJ \cdot Mol^{-1}$
solid-smectic C (S-C)	334.2	45.32
smectic C-smectic A (C-A)	350.4*	~ 0
smectic A-nematic (A-N)	355.6	0.68
nematic-isotropic (N-I)	362.0	2.11
smectic C-smectic B (C-B)$^+$	(317.1)	4.70
smectic B-smectic E (B-E)$^+$	(307.3)	7.92

*determined by optical microscopy
$^+$monotropic transitions

Pressure studies

a) Phase diagram. All the transitions except the C-A transition were detected by using DTA as the probe while the C-A transition was detected by using diamond-anvil cell. (For a detailed description of the high pressure cells used see references 9 and 10). The complete p-T diagram for 6OPDOB is given in Figure 2. The range of the smectic C phase, which is about 16K at 1 bar, diminishes with increase of pressure, until at 2.2 kbar it disappears altogether resulting in a solid-smectic C-smectic A triple point at (2.22 ± 0.05) kbar, (374 ± 0.7) K. It may be recalled that a similar case of a bounded smectic C phase was observed before for 4-4'-di-n-heptyloxyazoxybenzene[11].

We have fitted the set of experimental data points for each transition to two forms of equations, viz., (i) $T/K = T_O/K + AP/bar - BP^2/bar^2$, the polynomial suggested by Horn[11] and (ii) $P/a = (T/T_O)^c - 1$, the modified form of the Simon-Glatzel equation as applied to liquid crystals by Feyz and Kuss[12]. The constants of these equations evaluated using a programmable calculator (Hewlett-Packard 9845B) are given below: (see Table 2)

b) Pressure-induced phases. Two pressure-induced phases are observed at higher pressures, one appears at 1.38 kbar and the other at 2.23 kbar. Figure 3 shows the raw DTA traces taken at three different pressures beyond 2.23 kbar. The three transitions are denoted by I , II and III , where in I and III are pressure-induced

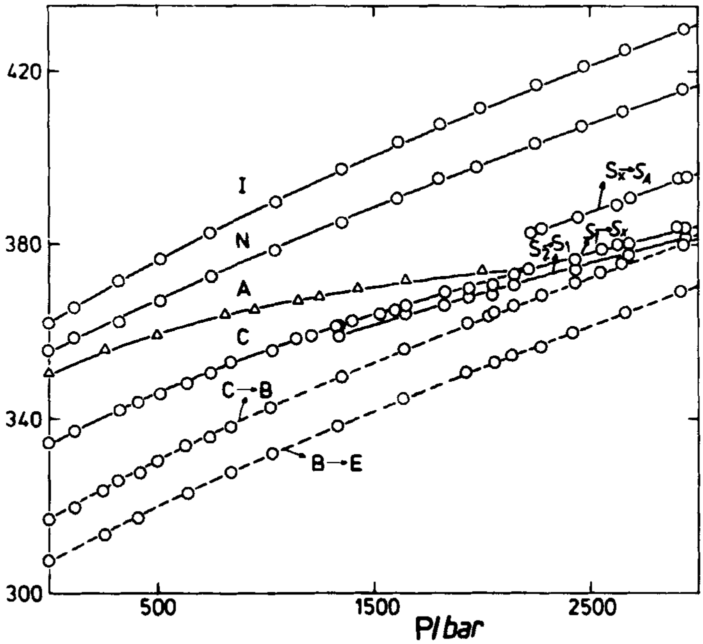


Figure 2: P-T diagram of 6OPDOB. The dashed lines indicate monotropic transitions. $S_2 - S_1$ transition is seen on heating only.

Table 2

	Constants (Polynominal)			Constants (SG equation)		
Transition	$A \cdot 10^3$	$B \cdot 10^6$	Mean error (bars)	$a \cdot 10^{-3}$ (bars)	c	Mean error (bars)
S-C*	23.3	2.2	±30	2.18	6.2	±45
C-A*	19.0	3.6	±21	0.71	20.5+	±17
A-N	23.2	1.0	±13	5.57	2.7	± 3
N-I	28.5	1.9	± 7	3.24	3.8	± 7
C-B	26.8	1.8	±11	3.23	3.6	±12
B-E	25.1	1.4	±16	4.08	2.9	±18

*indicates that the range of pressure over which the computations have been carried out is 0 to 2 kbar, this range being 0-3 kbar for all the other transitions.

+the implication of such a large value is still not clear

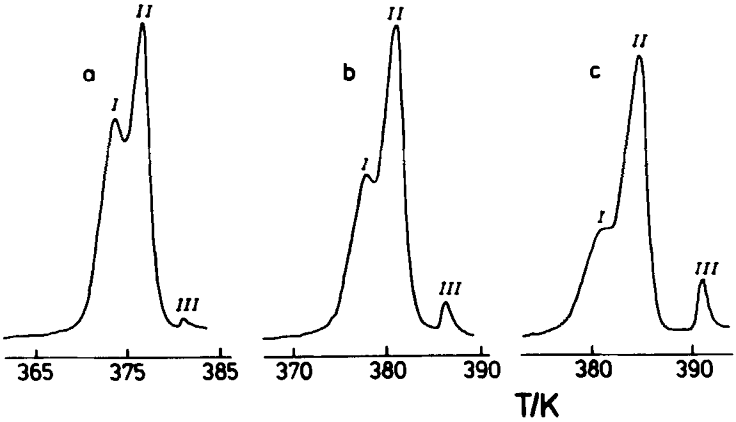


Figure 3: Raw DTA traces at three different pressures: (a) 2.25 kbar (b) 2.44 kbar and (c) 2.58 kbar. Heating rates 3-4K/minute.

transitions. The main peak (transition II) positions in these curves, when plotted in the P-T diagram, fall on a smooth curve which in fact is a continuation of what was designated as S-C phase boundary at lower pressures. The pressure-induced transitions (I & III), which appear on either side of II, exhibit distinctly different features. The transition I appears as a strong one at lower pressures, but becomes weaker as the pressure is increased. On the other hand, transition III begins practically as a second-order transition and gains rapidly in strength as the pressure is increased. In addition, the formation of transition I appears to be related to the tempering of the substance, ie, the rate of cooling and the temperature to which the substance is cooled below the smectic E phase. The occurence of transition III is however independent of the thermal history of the sample and occurs repeatedly (at any given pressure) at the same temperature on heating as well as on cooling. We therefore conjecture that I is a transition between two solid phases, one of them (S_1) being the pressure-induced solid phase, while transition III involves the smectic A phase and a pressure induced mesophase, say S_X. We have marked the corresponding phase boundaries in the phase diagram (Fig.2) accordingly.

The question may be asked as to what can be this S_X phase which occurs below the A phase in the P-T plane. It is interesting to note that the S_X phase starts appearing just after the C phase has disappeared. It is of course not possible to say much on the nature of the S_X phase by DTA experiments alone. However, we suggest tentatively that the S_X phase could be a tilted form of smectic A[13] which may have a different degree of rotational freedom than the original smectic A phase which exists at a higher temperature. Evidently x-ray high pressure studies are needed to be conducted to verify this point.

Acknowledgements. The authors are highly indebted to Prof. G.M. Schneider for his encouragement and for several interesting discussions. Thanks are due to Dr. U. Deiters for his help in computations, to Dr. H. Arntz for DSC runs and to Dr. B.R. Ratna for some useful discussions. One of us (R.S.) is grateful to Alexander-von-Humboldt-Stiftung for a fellowship.

REFERENCES

1. See eg. S. Chandrasekhar and R. Shashidhar, Advances in Liquid Crystals, 4,83(1979)
2. W. Spratte and G.M. Schneider, Mol.Cryst.Liquid Cryst., 51,101(1979)
3. J. Herrmann, J. Quednau and G.M. Schneider, Mol. Cryst.Liquid Cryst., (in Press)
4. R. Shashidhar, A.N. Kalkura and S. Chandrasekhar, Mol.Cryst.Liquid Cryst.Letters (to be published)
5. R. Shashidhar, A.N. Kalkura and G. Venkatesh, Presented at the 8th International Liquid Crystals Conference, Kyoto, June-July 1980
6. H.J. Deutscher, W. Weissflog, D. Demus and G. Pelzl, DDR-WP 86269 (1970)
7. A. Biering, D. Demus, G.W. Gray and H. Sackmann, Mol.Cryst.Liquid Cryst., 28,273(1974)
8. D. Demus and L. Richter, Textures of Liquid Crystals (Verlag Chemie, Weinheim-New York, 1978)
9. W. Spratte, Dissertation, University of Bochum (1978)
10. R. Shashidhar and K.V. Rao, Liquid Crystals, Proc.Int.Liquid Cryst.Conf., Bangalore, December 1979. Ed: S. Chandrasekhar, Heyden (London), p.115

11. R.G. Horn, J.Phys. (Paris), 39,167(1978)
12. M. Feyz and E. Kuss, Ber.Bunsenges.Phys.Chem., 78,834(1974)
13. A. de Vries, in Liquid crystals (Ed: F.D. Saeva): (Marcel Dekker, New York and Basel, 1979), p.1