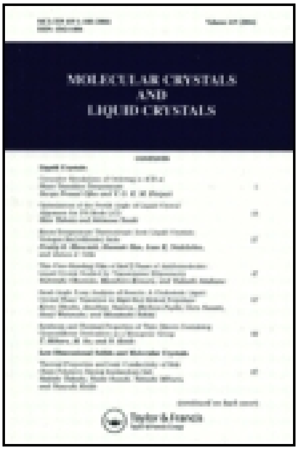

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

High Pressure Studies on Polymorphic Liquid Crystals

A. N. Kalkura [a], R. Shashidhar [b], G. Venkatesh [a], D. Demus [c] & W. Weissflog [d]

[a] Raman Research Institute, Bangalore, 560080, India

[b] Presently on leave of absence at Physikalische Chemie II, Ruhr Universität, Postfach 102148, 4630 Bochum 1, West, Germany.

[c] Sektion Chemie, Martin Luther Universität, Halle (Saale), Mühlpforte 1, G.D.R.

[d] VEB Spezialchemie, Leipzig, G.D.R.

Version of record first published: 14 Oct 2011.

To cite this article: A. N. Kalkura, R. Shashidhar, G. Venkatesh, D. Demus & W. Weissflog (1982): High Pressure Studies on Polymorphic Liquid Crystals, Molecular Crystals and Liquid Crystals, 84:1, 275-284

To link to this article: http://dx.doi.org/10.1080/00268948208072147

Mol. Cryst. Liq. Cryst., 1982, Vol. 84, pp. 275–284
0026-8941/82/8401-0275 $06.50/0

Printed in the United States of America

High Pressure Studies on Polymorphic Liquid Crystals

A. N. KALKURA, R. SHASHIDHAR† and G. VENKATESH
Raman Research Institute, Bangalore 560080, India

D. DEMUS
Sektion Chemie, Martin Luther Universität, Halle (Saale), Mühlpforte 1, G.D.R.

and

W. WEISSFLOG
VEB Spezialchemie, Leipzig, G.D.R.

(*Received July 27, 1981; in final form November 2, 1981*)

The effect of pressure on phase transitions has been studied for four compounds, viz., di-ethyl-p-azoxybenzoate, 4-nitrophenyl-4′-octyloxybenzoate, 4-*n*-pentyloxyphenyl-4′-*n*-decyloxybenzoate and 4-*n*-heptyloxyphenyl-4′-*n*-decyloxybenzoate, which exhibit different types of mesophases at atmospheric pressure. The experimental phase diagrams are presented and the *dT/dP* values of the various transitions as well as the volume change at these transitions are evaluated.

1 INTRODUCTION

Most of the high pressure experiments on liquid crystals have been mainly devoted to the study of nematics,[1] although, of late, there have been some studies on polymorphic smectics.[2–4] We have undertaken a high pressure investigation of four compounds exhibiting a variety of mesophases with a view to study the influence of pressure on different mesophase structures.

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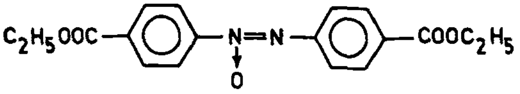
† Presently on leave of absence at Physikalische Chemie II, Ruhr Universität, Postfach 102148, 4630 Bochum 1, West Germany.

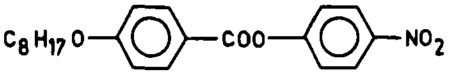
2 COMPOUNDS

The compounds studied are given below along with their structural formulae.

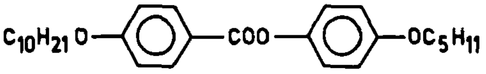
di-ethyl-*p*-azoxybenzoate (EPAB)[5]



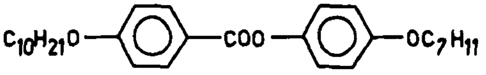
4-nitrophenyl-4′-octyloxybenzoate (NPOOB)[6]



4-*n*-pentyloxyphenyl-4′-*n*-decyloxybenzoate (50 PDOB)[7]



4-*n*-heptyloxyphenyl-4′-*n*-decyloxybenzoate (70 PDOB)[7]



The sample of EPAB obtained from Eastman Kodak, USA, was recrystallized several times from benzene till the smectic A-isotropic transition temperature was constant. The other three substances have all been synthesized according to the procedures given in Refs. (8) and (9). The transition temperatures as well as the heats of transition (ΔH), as determined by differential scanning calorimetry (Perkin Elmer DSC-2), are given in Table I. The observed transition temperatures and heats are in reasonable agreement with the literature data.[5-7]

3 EXPERIMENTAL

All the phase transitions except the smectic C—smectic A (or C—A) transition were detected using differential thermal analysis as the probe. The C—A transition was determined using the opposed diamond Anvil cell. The constructional details of the cells used have already been described elsewhere[10,11] and will not be repeated here. We shall only mention the accuracy of pressure and temperature measurements.

All transitions were recorded in the heating mode only, the rate of heating being typically 1-2 K/minute. In the DTA cell, the relative variation of pressure could be controlled to an accuracy of ±5 bar while the absolute accuracy

TABLE I

Transition temperatures (T_c) and heats of transitions (ΔH) at atmospheric pressure

Compound	Transition	T_c(°C)	ΔH(kJ/mol)
EPAB	solid—smectic A (S—A)	114.0	19.67
	smectic A—isotropic (A—I)	122.5	4.78
NPOOB	solid 2—solid 1 (s_2—s_1)	47.6[a]	32.37[b]
	solid 1—smectic A (S—A)	49.8[a]	
	smectic A—nematic (A—N)	61.2	0.14
	nematic—isotropic (N—I)	67.5	0.47
50 PDOB	solid—smectic C (S—C)	64.0	46.03
	smectic C—smectic A (C—A)	68.3[a]	~0
	smectic A—nematic (A—N)	79.9	1.13
	nematic—isotropic (N—I)	84.6	1.80
70 PDOB	solid—smectic C (S—C)	70.3	50.56
	smectic C—smectic A (C—A)	80.5[a]	~0
	smectic A—nematic (A—N)	84.5	1.06
	nematic—isotropic (N—I)	87.8	2.62

[a] Determined by optical microscopy.

[b] The two solid phases could not be resolved in the DSC experiments. The heat given is the combined heat for the two transitions.

was ±2%. The transition temperature determination was accurate to ±1°C. In the diamond anvil cell the pressure could be estimated (see Ref. 8 for details of the procedure used for pressure determination) to ±15 bar while the transition temperature was reproducible to an accuracy of ±0.25°C.

4 RESULTS AND DISCUSSION

The experimental P—T diagrams for EPAB, NPOOB, 50 PDOB and 70 PDOB are given in Figures 1-4 respectively. The phase diagram of EPAB (Figure 1) is a "typical" one in that the range of smectic A phase increases with increasing pressure.

NPOOB, which has a nitro end group, is known to have an "incommensurate" smectic A phase, the layer spacing as determined by x-ray study is 3.14 nm[12] while that evaluated from a molecular model is about 2.74 nm.[13] Experiments were therefore undertaken on this bilayer compound to see if it exhibits a re-entrant behavior under pressure. However, the smectic A—nematic (or A—N) phase boundary does not curve towards the pressure axis (see Figure 2) even up to 4 kbar. On the other hand, the solid—smectic A phase boundary

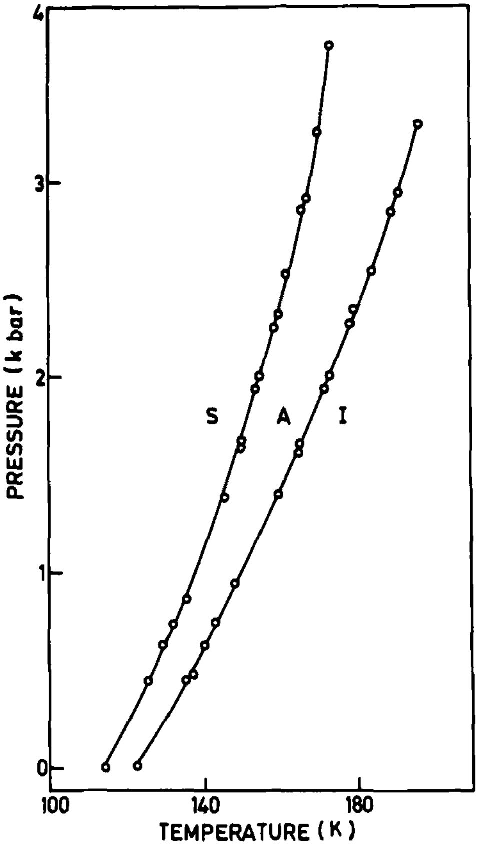


FIGURE 1 P—T diagram of EPAB.

shows an interesting behavior. For pressures beyond about 2.3 kbar a pressure induced (still unidentified) phase is observed, the triple point being at (2.35 ± 0.05) kbar, (70.3 ± 1)°C. After completion of these experiments, it was learned that Cladis *et al.*[14] have also studied this compound as a function of pressure. Their values of *dT/dP* for the A—N and N—I transitions (12.2 K/kbar and 25.0 K/kbar) are in good agreement with our values (13.2 K/kbar and 26.0 K/kbar). However, there is a marked difference as regards the smectic A—solid phase boundary. Firstly, the *dT/dP* obtained by Cladis *et al.* is 22.0 K/kbar while our value is 10.0 K/kbar. This difference is perhaps attributable to the large discrepancy in the ΔH values at atmospheric pressure. The ΔH reported by Cladis *et al.* is 15.67 kJ/mol while for our sample it is 27.96 kJ/mol, although the transition temperatures are practically the same in both

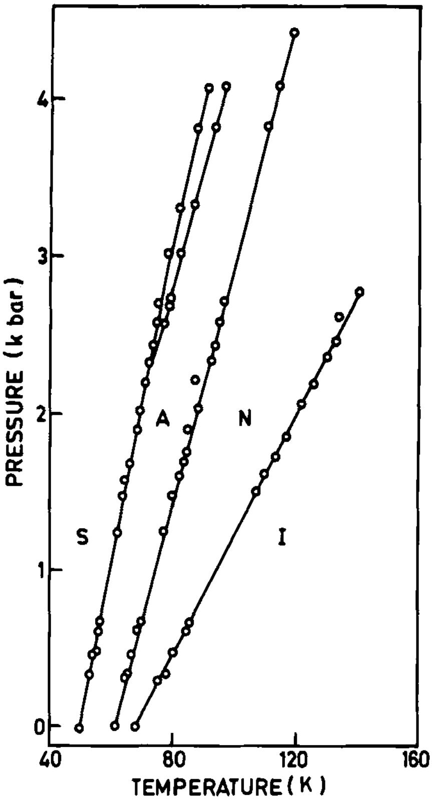


FIGURE 2 P—T diagram of NPOOB.

cases. Secondly, Cladis *et al.* do not observe any pressure induced phase even up to 4 kbar.

Experiments were undertaken on 50 PDOB and 70 PDOB with a view to observing at high pressure the "Lifshitz Point" in a single component system.[15] However, for both substances, the smectic A phase is found to be stable over the entire range whereas the smectic C phase decreases with increase of pressure until it is completely bounded and the solid transforms directly into the smectic A phase. The resulting solid—smectic C—smectic A triple points occur at (1.32 ± 0.05) kbar, (76.8 ± 0.7)°C for 50 PDOB and (3.40 ± 0.05) kbar, (103.0 ± 0.7)°C for 70 PDOB. It may be recalled that a similar case of bounded smectic C was observed earlier.[16] It therefore appears that a tilted structure is somehow not favored at high pressures. Detailed high pressure x-ray studies have to be conducted to understand the reason for such a suppression of the smectic C phase.

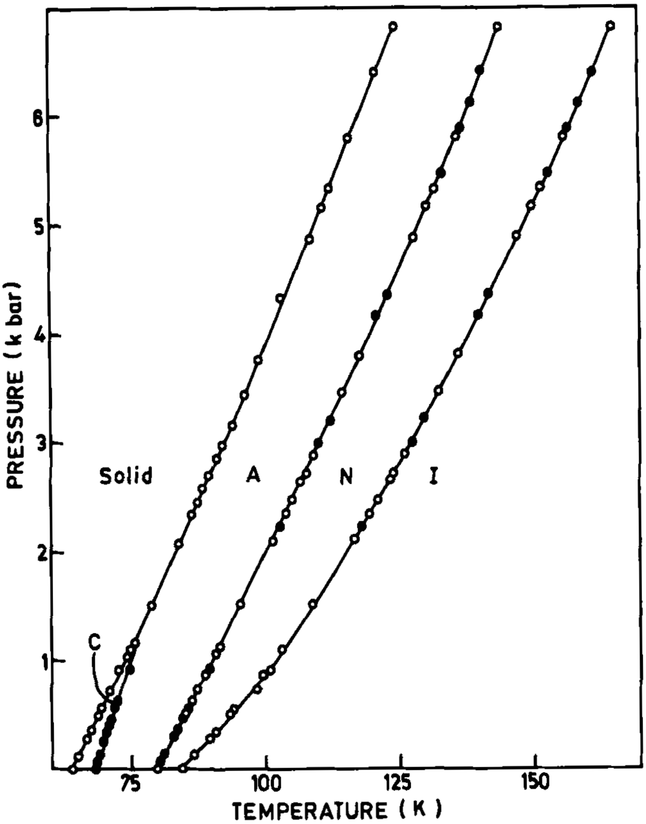


FIGURE 3 P—T diagram of 50 PDOB. O—data from DTA, ●—data from diamond anvil cell.

We have fitted the set of experimental data points for each transition and for each substance to two forms of equations, viz.

$$T/K = T_0/K + AP/\text{bar} - BP^2/\text{bar}^2, \tag{1}$$

the polynomial suggested by Horn,[17] and

$$P/a = (T/T_0)^c - 1, \tag{2}$$

the modified form of the Simon-Glatzel equation as applied to liquid crystals by Feyz and Kuss.[18] The constants of Eqs. (1) and (2) evaluated using a programmable calculator (Hewlett-Packard 9845B) are given in Tables II and III respectively. The fits appear to be equally good for both the equations.

The available experimental data on the volume change (ΔV) at transition involving different kinds of liquid crystalline phases are rather sparse. Hence

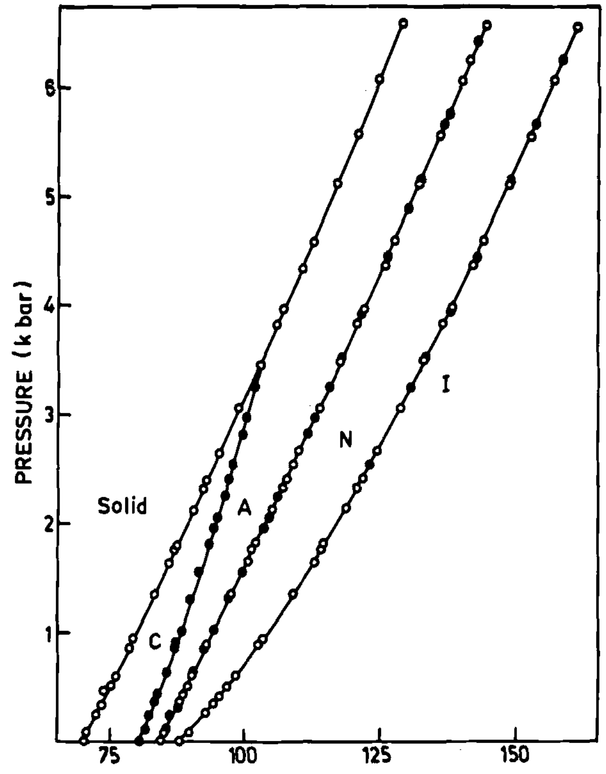


FIGURE 4 P—T diagram of 70 PDOB. O—data from DTA, ●—data from diamond anvil cell.

it is of interest to calculate ΔV for the substances studied. From the initial linear portions of the P—T diagrams dT/dP for the various transitions have been evaluated. Using these values and the ΔH values given in Table I, ΔV at 1 bar has been calculated (Table IV). A comparison is also made in this table between the calculated and the known experimental values[6,19] of ΔV for two cases. The agreement is reasonably good.

5 CONCLUSION

The shape of the P—T boundaries as well as the dT/dP values appear to be strongly dependent upon the nature of the mesophases exhibited by the com-

TABLE II

Constants evaluated from Eq. (1)

Substance	Transition[a]	$A \cdot 10^3$	$B \cdot 10^6$	Mean error (bar)
EPAB	S—A	25.7	2.74	±16
	A—I	28.6	2.00	±12
NPOOB	S—A	9.9	0.25	±19
	A—N	12.8	0.01	±26
	N—I	26.9	0.51	±26
50 PDOB	S—C	10.0	0.17	±14
	C—A	7.2	0.87	±16
	A—N	10.7	0.19	±29
	N—I	16.4	0.07	±49
70 PDOB	S—C	9.9	0.14	±21
	C—A	7.9	0.40	±7
	A—N	10.1	0.15	±19
	N—I	15.7	0.73	±44

[a] See Table I for the notations used.

TABLE III

Constants *a* and *c* evaluated from Eq. (2)

Substance	Transition[a]	$a \cdot 10^{-3}$ (bar)	c	Mean error (bar)
EPAB	S—A	1.324	9.36	±43
	A—I	3.026	4.34	±17
NPOOB	S—A	11.702	2.78	±21
	A—N	26.385	0.99	±26
	N—I	8.385	1.51	±29
50 PDOB	S—C	13.250	2.51	±15
	C—A	3.067	1.54	±19
	A—N	12.514	2.60	±39
	N—I	4.135	4.82	±45
70 PDOB	S—C	15.394	2.24	±24
	C—A	13.254	2.51	±8
	A—N	14.776	2.37	±24
	N—I	3.905	5.35	±21

[a] See Table I for the notations used.

TABLE IV

dT/dP and volume change (ΔV) at transition at 1 bar

Compound	Transition[a]	dT/dP (K/kbar)	$10^4\ \Delta V$ (cm^3/g) Calculated	Experimental
EPAB	S—A	25.39	377.3	
	A—I	29.18	103.1	174.0[19]
NPOOB	S—A	10.0	270.3	
	A—N	13.19	1.5	1.35[6]
	N—I	25.95	9.7	7.17[6]
50 PDOB	S—C	10.06	312.3	
	C—A	6.78	0	
	A—N	10.5	7.6	
	N—I	18.48	21.1	
70 PDOB	S—C	10.15	319.4	
	C—A	8.42	0	
	A—N	9.84	6.2	
	N—I	18.42	28.6	

[a] See Table I for the notations used.

pounds. Further studies are in progress involving different kinds of C—A transitions in order to see the effect of pressure in such cases.

Acknowledgment

The authors are indebted to Professor S. Chandrasekhar for his keen interest in this work.

References

1. See e.g., 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. J. Herrmann, H. D. Kleinhans, J. Quednau and G. M. Schneider, *Mol. Cryst. Liquid Cryst. Lett.*, **64**, 109 (1980).
5. H. Arnold and P. Roediger, *Z. Phys. Chem.* (*Leipzig*), **231**, 407 (1966).
6. "Forschungen über Flüssige Kristalle 1: 4-*n*-octyloxy-benzoesaure-4-nitrophenyl ester" (Ed. D. Demus), Martin Luther Universität Halle, Wissenschaftliche Beiträge, 1978.
7. D. Demus, H. J. Deutscher, D. Marzotko, H. Kress and A. Wiegeleben, Proc. Int. Liquid Cryst. Conf., Bangalore, 1979 (Ed. S. Chandrasekhar), Heyden, London, p. 97 (1980).
8. H. J. Deutscher, W. Weissflog, D. Demus and G. Pelzl, DDR-WP 86269 (1970).
9. R. Steinstrasser, *Z. Naturforsch.*, **27b**, 774 (1972).
10. A. S. Reshamwala and R. Shashidhar, *J. Phys. E.*, **10**, 183 (1977).

11. R. Shashidhar and K. V. Rao, Proc. Int. Liquid Cryst. Conf., Bangalore, 1979, (Ed. S. Chandrasekhar) Heyden, London, p. 115 (1980).
12. A. C. Griffin, and J. F. Johnson, *J. Amer. Chem. Soc.*, **99**, 4859 (1977).
13. A. C. Griffin, T. R. Britt, N. W. Buckley, R. F. Fisher, S. J. Havens and D. W. Goodman, in "Liquid Crystals and Ordered Fluids," Vol. 3, Eds. J. F. Johnson and R. S. Porter, Plenum Press, New York, London (1977) p. 61.
14. P. E. Cladis, D. Guillon, W. B. Daniels and A. C. Griffin, *Mol. Cryst. Liquid Cryst. Lett.*, **56**, 89 (1979).
15. R. Shashidhar, A. N. Kalkura and S. Chandrasekhar, *Mol. Cryst. Liquid Cryst. Lett.*, **64**, 101 (1980).
16. R. Shashidhar and S. Chandrasekhar, *J. Phys* (*Paris*), C1-36 (1975).
17. R. G. Horn, *J. Phys.* (*Paris*), **39**, 167 (1978).
18. M. Feyz and E. Kuss, *Ber. Bunsenges. Phys. Chem.*, **78**, 834 (1974).
19. L. E. Hajdo, A. C. Eringen and A. E. Lord, *Appl. Eng Sci.*, **2**, 367 (1974).