

HIGH PRESSURE STUDIES ON 4'-*n*-ALKYL-4-CYANOBIPHENYLS

R. SHASHIDHAR and G. VENKATESH

Raman Research Institute, Bangalore 560006, India

**Résumé.** — On étudie l'effet de la pression sur les transitions de phase dans les composés 4'-*n*-alkyl-4-cyanobiphényl. La courbe  $dT/dP$  pour la transition nématique isotrope oscille avec le nombre d'atomes de carbone dans la chaîne tandis que pour la transition solide nématique (ou smectique) on n'observe pas ce phénomène. La transition smectique A-nématique dans le 4'-*n*-octyl-4-cyanobiphényl, qui est du premier ordre à la pression atmosphérique, devient du second ordre à haute pression. Le point critique se situe à  $2,68 \pm 0,08$  hbar,  $92,5 \pm 1,5$  °C. Le rapport des températures de transition smectique A-nématique, nématique-isotrope au point critique est égal à 0,90 ce qui est en bon accord avec la théorie du champ moyen.

**Abstract.** — The effect of pressure on the phase transitions in the pentyl to octyl homologues of 4'-*n*-alkyl-4-cyanobiphenyls has been studied. The slope  $dT/dP$  for the nematic-isotropic transition shows an alternation with the number of carbon atoms in the alkyl chain, while that for the solid-nematic (or smectic) transition does not show such a behaviour. The smectic A-nematic transition in 4'-*n*-octyl-4-cyanobiphenyl, which is first order at atmospheric pressure, becomes second order at high pressures, the tricritical point occurring at  $2.68 \pm 0.08$  kbar,  $92.5 \pm 1.5$  °C. The ratio of the smectic A-nematic transition temperature to the nematic-isotropic transition temperature at the tricritical point is 0.90, in reasonable agreement with the prediction of the mean field theory.

1. **Introduction.** — The first attempt to study the effect of pressure on the phase transition temperatures of successive members belonging to a homologous series was by Feyz and Kuss [1]. They found the interesting result that  $dT/dP$  for the nematic-isotropic (N-I) transition alternates with the number of carbon atoms in the alkyl end chain. On the other hand they did not see such alternation for the solid-nematic (S-N) transition. We have carried out high pressure studies on the fifth to eighth derivatives of 4'-*n*-alkyl-4-cyanobiphenyl (nCB) series. Ever since the synthesis of these compounds by Gray *et al.* [2], and the realization of their suitability for electro-optic display devices they have been the subject matter of a variety of experimental studies [3-6]. A study of nCB under pressure is therefore of considerable interest.

2. **Experimental.** — The experiments were carried out using a 200-ton hydraulic press which incorporates a piston-cylinder device and which has been recently fabricated in our laboratory. A special feature of this press is that both the end load ram and master ram pressures and hence the cell pressure are controlled minutely by two adjustable relief valves used in conjunction with hydraulic pumps made by Whitney, USA. The constructional as well as the working details of this press will be published elsewhere [7]. Line pressures were measured using a calibrated pressure transducer (type PT 21UA made by ISRO) reading to

an accuracy of  $\pm 0.2$  %. The true pressure as seen by the sample was computed by measuring the resistance of a standard manganin gauge [8, 9] which was immersed in silicone oil filled in the sample capsule [10]. Although variations in the cell pressures could be measured to an accuracy of  $\pm 4$  bar, the absolute accuracy of the pressure measurement is reckoned to be about  $\pm 2$  %. The phase transition temperatures were determined by using differential thermal analysis (DTA) as the probe. A detailed description of the cell as also the details of the experimental set up have already been given [11, 12] and will not be repeated here. The transition temperatures could be reproduced to an accuracy of about  $\pm 1.5$  °C for the N-I and smectic A-nematic (A-N) transitions although the error was found to be greater for the solid-mesophase transitions, perhaps because of the broader nature of these transitions. Since the sample was completely enclosed by teflon, there was no probability of its getting contaminated from the pressure transmitting medium. Also, these compounds are highly chemically stable. Nevertheless, after completion of each set of experiments a small quantity of the sample was removed from the sealed teflon capsule and its transition temperatures were redetermined on the hot stage microscope. These values agreed to within 0.2 °C of the values determined before the commencement of the experiments thereby showing clearly that the sample was completely free of contamination.

All the compounds studied except 8 CB were synthesized in our chemistry laboratory. 8 CB was obtained from BDH, England. Their transition temperatures at atmospheric pressure as measured by a hot stage microscope are listed in table I. They compare well

TABLE I

Transition temperatures (at atmospheric pressure)  
in °C of nCB

	Solid-nematic (or smectic)	Smectic- nematic	Nematic- isotropic
5 CB	22.5	—	35.0
6 CB	13.0	—	28.0
7 CB	28.5	—	41.5
8 CB	21.0	32.5	40.0

with the values of Gray *et al.* [2]. For 5 CB which was the first compound to be studied experiments were carried out using 3 different cells and the data from the three independent set of measurements were self-consistent confirming the reproducibility of the measurements. It was therefore thought sufficient to carry out only one set of experiments each for both 6 CB and 7 CB. For 8 CB, however, since our interest was to investigate the possibility of its A-N transition showing tricritical behaviour, the experiments were done in a more elaborate manner. From two initial experiments it was ascertained that the A-N transition does become weak beyond about 2.5 kbar while a third experiment, in which pressure was varied by very small intervals, pin-pointed the tricritical point.

3. Results and discussion. — 3.1 PHASE DIAGRAMS. — The pressure-temperature diagrams of 5 CB-8 CB are presented in figures 1-4.

For 5 CB, 6 CB, and 7 CB which show only the nematic phase, the phase diagrams look essentially alike. All the transition temperatures were recorded in the heating mode only. A common problem which was encountered for all the three compounds was that the sample in the nematic phase supercooled considerably making the determination of the solid-nematic transition temperature at lower pressures rather difficult. The increase of the nematic range with pressure is more pronounced in the case of 5 CB and 7 CB than in 6 CB. In the case of 8 CB, which has a smectic A phase in addition to the nematic phase, the range of the smectic phase decreases for pressures beyond 1 kbar. But the smectic A-nematic phase boundary has a positive slope throughout in contrast to CBOOA [13, 14] for which this boundary has a negative slope. After completion of these experiments we learnt that Leibert and Daniels [15] have also studied this compound. They have found that the smectic A phase disappears with a solid-smectic A-nematic triple point at ~ 3 kbar and 94 °C. We could not confirm this since it was not possible to detect the A-N transition

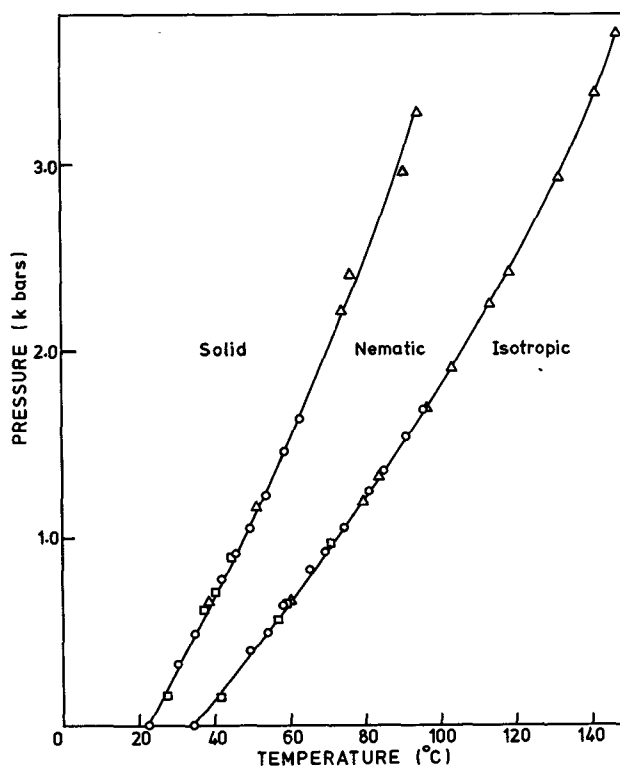


FIG. 1. — P-T diagram of 5 CB. □, Δ and ○ represent three independent sets of measurements.

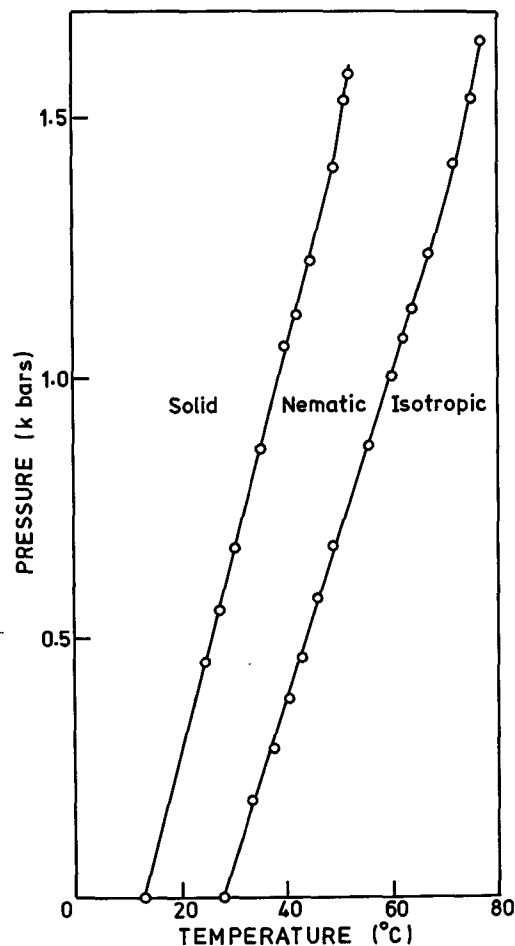


FIG. 2. — P-T diagram of 6 CB.

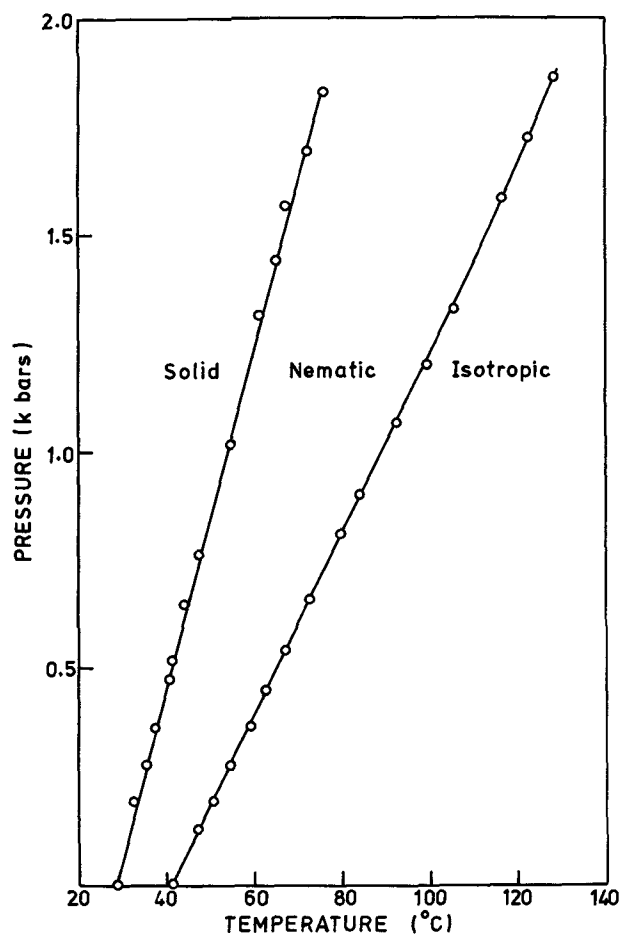
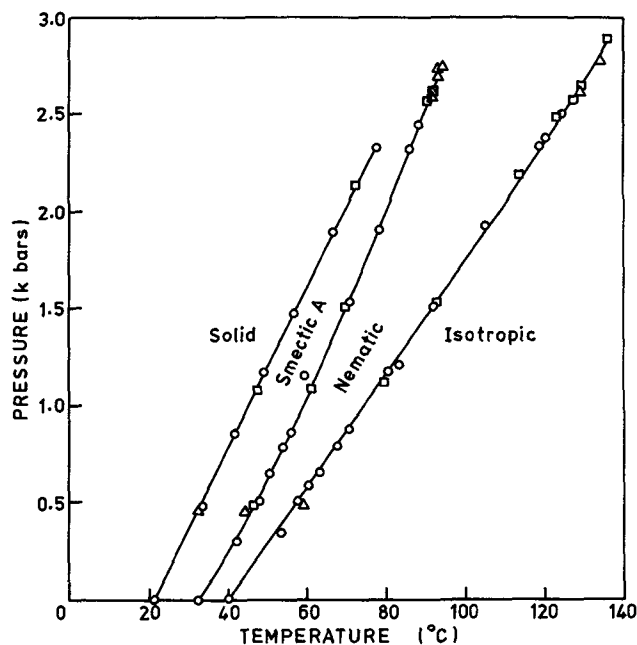


FIG. 3. — P-T diagram of 7 CB.

FIG. 4. — P-T diagram of 8 CB. O,  $\Delta$  and  $\square$  represent three independent sets of measurements.

for pressures beyond 2.78 kbar, the transition having become second order. We shall discuss this aspect of our experiments later. In the range of pressure that

has been studied by us, our data agree very well with those of Liebert and Daniels.

3.2 BEHAVIOUR OF  $dT/dP$  FOR THE SUCCESSIVE HOMOLOGUES. — The slopes ( $dT/dP$ ) for the N-I transition of the four successive homologues show an alternation with increasing chain length (Fig. 5), simi-

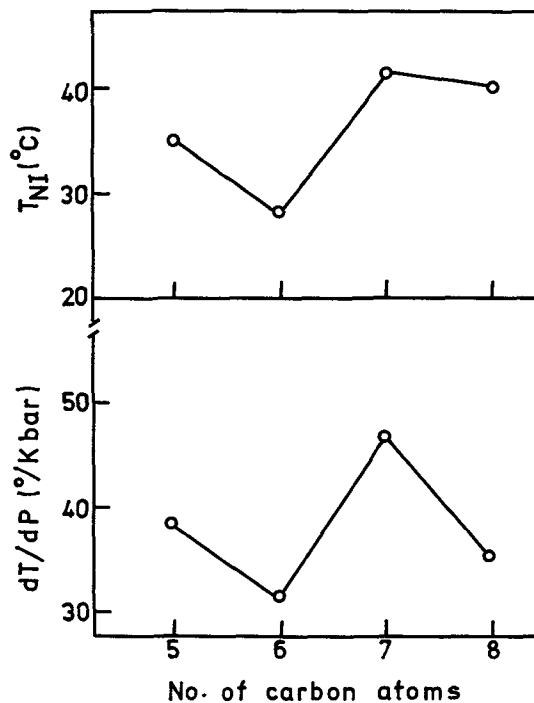


FIG. 5. — Variation of (a) the nematic-isotropic transition temperature ( $T_{NI}$ ) at atmospheric pressure, and (b)  $dT/dP$  for the nematic-isotropic transition as functions of the number of carbon atoms in the alkyl chain length.

lar to that exhibited by  $T_{NI}$  at atmospheric pressure (see table I). However,  $dT/dP$  for the solid-mesophase transition is roughly the same, viz.,  $25.5 \pm 1.0^\circ/\text{kbar}$  for all the four compounds, although the transition temperatures themselves at atmospheric pressure show an alternation. Similar results have been obtained by Feyz and Kuss [1] for other homologous series. The reason for such a difference in behaviour of  $dT/dP$  for the two transitions is not clear to us. Accurate quantitative  $PVT$  measurements would be needed to throw more light on this. It may also be mentioned that our values of  $dT/dP$  for 5 CB and 8 CB agree very well with those obtained by Horn for 5 CB [16] and by Liebert and Daniels for 8 CB [15].

Since data on both volume change at transition ( $\Delta V$ ) and the heat of transition ( $\Delta H$ ) are available for 8 CB, we shall compare the experimental  $dT/dP$  values with those evaluated from the Clausius-Clapeyron equation. So far, there have been three measurements of  $\Delta H$  for 8 CB. These are due to Karat [17], Leadbetter *et al.* [18] and Liebert and Daniels [15]. Their values agree with one another fairly well. Taking the average of these three  $\Delta H$  measurements and the  $\Delta V$  values of Leadbetter *et al.* [18], we get the slopes

for the A-N and N-I transitions to be 28.1 °/kbar and 38.2 °/kbar. (No calculation could be made for the solid-smectic transition since  $\Delta V$  for this transition is not given.) These values compare reasonably well with the measured values of 30.4 °/kbar and 36.0 °/kbar respectively.

The variation of transition temperature with pressure may be expressed by the relation

$$T_P = T_0 + AP - BP^2$$

where  $T_P$  and  $T_0$  are the transition temperatures measured at a pressure  $P$  and at atmospheric pressure respectively,  $A$  and  $B$  are empirical constants [16]. The negative sign for the term involving  $P^2$  has been chosen considering that P-T curves of most liquid crystals show, at higher pressures, a curvature towards the pressure axis. For each compound and for each transition, a least squares fit to (the collection of) the measured data points was carried out and the constants  $A$  and  $B$  determined using a Hewlett-Packard 9821-A programmable calculator. The values of  $A$  and  $B$  obtained in this manner are given in table II. It is seen from this table that the constants  $A$  for the two-transitions also reflect the behaviour of  $dT/dP$ .

**3.3 TRICRITICAL BEHAVIOUR IN 8 CB.** — Of late, the study of tricritical behaviour in liquid crystals using high pressure technique has been of considerable interest [19-22]. Owing to its low A-N transition temperature and due to its high chemical stability, 8 CB was chosen to study a possible tricritical behaviour. As mentioned earlier, a few initial experiments gave the clue that the tricritical point might exist beyond about 2.5 kbar. To exactly locate this point very careful experiments were carried out by taking

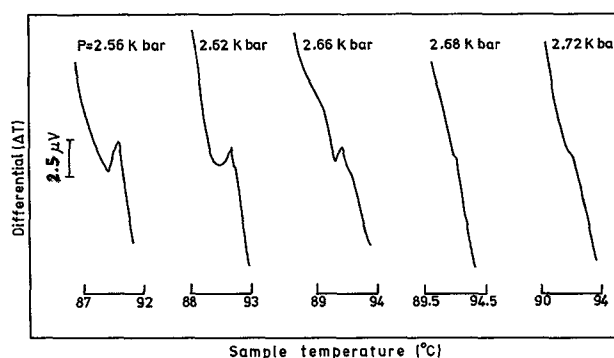


FIG. 6. — Raw DTA traces obtained for the smectic A-nematic transition in 8 CB at 5 different pressures, heating rate  $\sim 4$  °C/min.

DTA runs under identical rates of heating at very small intervals of pressure starting from 2.56 kbar. Figure 6 shows raw DTA records taken at 5 different pressures. It is seen that the strength of the DTA signal, which is about 2.5  $\mu\text{V}$  at 2.56 kbar progressively decreases with increase of pressure until at 2.68 kbar it is less than 0.25  $\mu\text{V}$ , the resolution of our experimental set up. Thus we can ascribe a tricritical point at  $2.68 \pm 0.08$  kbar and  $92.5 \pm 1.5$  °C. The ratio of the A-N to the N-I transition temperature at the tricritical point is 0.90 which is in good agreement with McMillan's theory [23].

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TABLE II

Constants  $A$  and  $B$  for nCB

	Solid-nematic (or smectic)			Smectic-nematic			Nematic-isotropic		
	$A$	$B$	RMS error	$A$	$B$	RMS error	$A$	$B$	RMS error
5 CB	26.4	1.29	1.06	—	—	—	40.3	2.64	0.82
6 CB	26.4	0.92	0.37	—	—	—	33.7	2.10	0.49
7 CB	24.6	0.98	0.52	—	—	—	47.9	0.54	0.46
8 CB	24.4	0.09	0.38	30.4	3.04	1.38	36.0	0.94	0.67

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