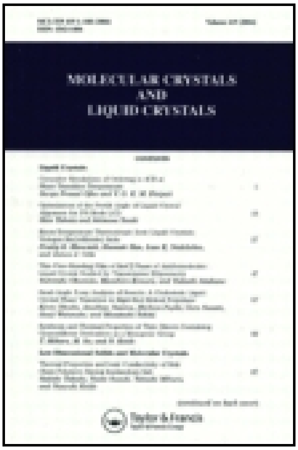

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The Search for a Lifshitz Point in a Single-Component Liquid Crystalline System: A High Pressure Study of 50.6

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THE SEARCH FOR A LIFSHITZ POINT IN A SINGLE-COMPONENT LIQUID CRYSTALLINE SYSTEM: A HIGH PRESSURE STUDY OF 50.6

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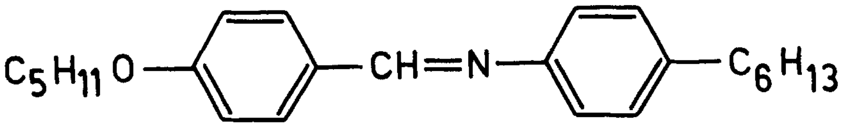
ABSTRACT. The pressure-temperature diagram of N-(4-n-pentyloxybenzylidene)-4'-n-hexylaniline has been investigated up to 8 kbar. The smectic C-smectic A and smectic A-nematic phase boundaries converge and nearly meet, indicating that a Lifshitz point is likely to occur at a higher pressure.

The intersection of the smectic C-smectic A (CA), smectic A-nematic (AN) and smectic C-nematic (CN) transition lines in a phase diagram has been called a Lifshitz point.[1-4] Such an intersection has been observed in the composition-temperature diagrams of certain mixtures.[5,6] We have undertaken pressure studies of some pure compounds with a view to locating a Lifshitz point in a single component system. We present here the results on N-(4-n-pentyloxybenzylidene)-4'-n-hexylaniline (hereafter abbreviated to 50.6[7,8]):



The compound was kindly given to us by Dr.D.Demus. At atmospheric pressure it exhibits 5 smectic phases and a nematic phase, but we shall be concerned here only with the B,C,A and

N phases. The temperatures and heats of transition (ΔH) at atmospheric pressure, as determined by a Perkin Elmer DSC-2 differential scanning calorimeter, are given below.

	Temperature (°C)	ΔH (kJ/mole)
smectic B-smectic C	51.3	2.45
smectic C-smectic A	52.7*	∿ 0
smectic A-nematic	61.6	0.80
nematic-isotropic	72.6	1.03

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*Determined by thermal microscopy.

The P-T diagram was obtained by using an opposed diamond anvil cell constructed in this laboratory for high pressure optical (and X-ray) studies of liquid crystals. The constructional details of the cell as well as its working have been described before[10,11] and will not be repeated here. With this cell, even a second order transition (in particular, the CA transition) could be precisely determined. The data were brought to an absolute scale by conducting a calibration experiment using a differential thermal analysis (DTA) cell[12] (see ref.10 and 11). The transition temperatures could be measured to a relative accuracy of ±0.1°C and the pressure to ±15 bars; the absolute accuracies are reckoned to be about ±1°C and ±2% respectively.

In all, six different sets of measurements were carried out (each time using a fresh sample), one set with the DTA cell and the rest with the diamond anvil cell. First the DTA cell was used to obtain the BC and AN phase boundaries up to 8 kbar.

Then the diamond cell was used to record all the transitions - BC, CA, AN and NI. The BC phase boundary determined with the DTA cell was used to bring the diamond cell data to an absolute scale. To check the reliability of the calibration, the data points (on an absolute scale) for the AN boundary as determined by the two cells were compared; these are shown in Fig. 1. It can be seen from the figure that there is excellent accord between the data obtained with the two cells, and further that the five independent sets of measurements using the diamond cell agree well with each other. After completion of each set of measurements, the sample in the gasket was removed and its transition temperatures (at atmospheric pressure) were re-determined. They were found to be exactly the same as before the commencement of the experiment, thus confirming that the material did not suffer any decomposition.

Special care was taken to see from the DTA experiment if the AN transition line shows a tricritical point (see ref. 13 and 14). It was observed that the first order character of this transition diminishes with increasing pressure up to about 4 kbar, but beyond this pressure the change is hardly detectable and the transition remains first order, though weakly so, right up to about 8 kbar.

The complete P-T diagram of 50.6 is shown in two parts for convenience of presentation of the data; the measurements up to 4 kbar are shown in Fig. 2, while those for pressures between 4 kbar and 8 kbar are shown on an enlarged temperature scale in Fig. 3. The temperature range of the smectic A phase diminishes with increasing pressure, becoming as small as about 0.7°C at 4 kbar (Fig. 2). At higher pressures the range of the A phase decreases still further, but the rate of decrease is very slow; at 8 kbar, the maximum pressure attainable with our

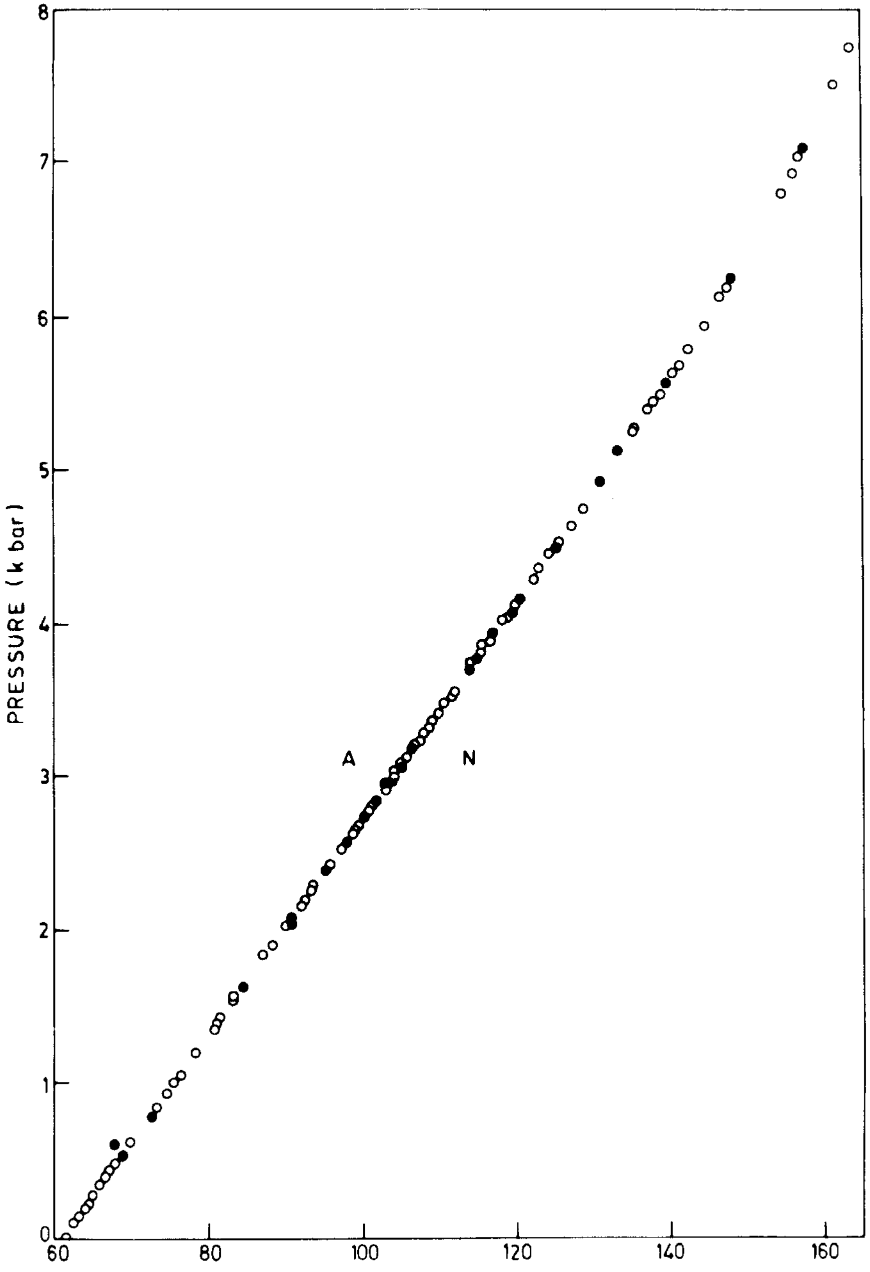

FIGURE 1: The AN phase boundary of 50.6; ● data points using the DTA cell; ○ data points (representing five independent sets of measurements) using the diamond anvil cell.

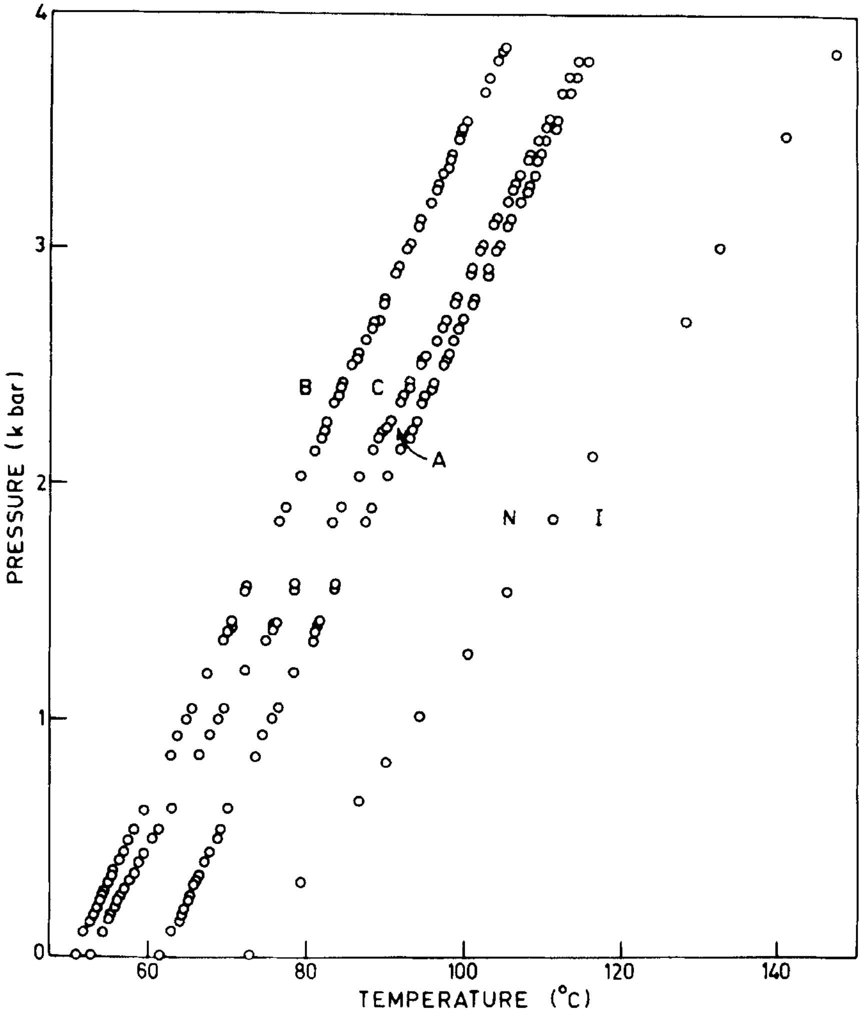

FIGURE 2: P-T diagram of 50.6 up to 4 kbar.

diamond cell, the range is about 0.4°C (Fig. 3). Had the resolution of our experimental set up been less than what it is at present, we might have concluded that the CA and AN phase boundaries intersect at about 4 kbar. However, the precision of our data shows that this is not in fact the case

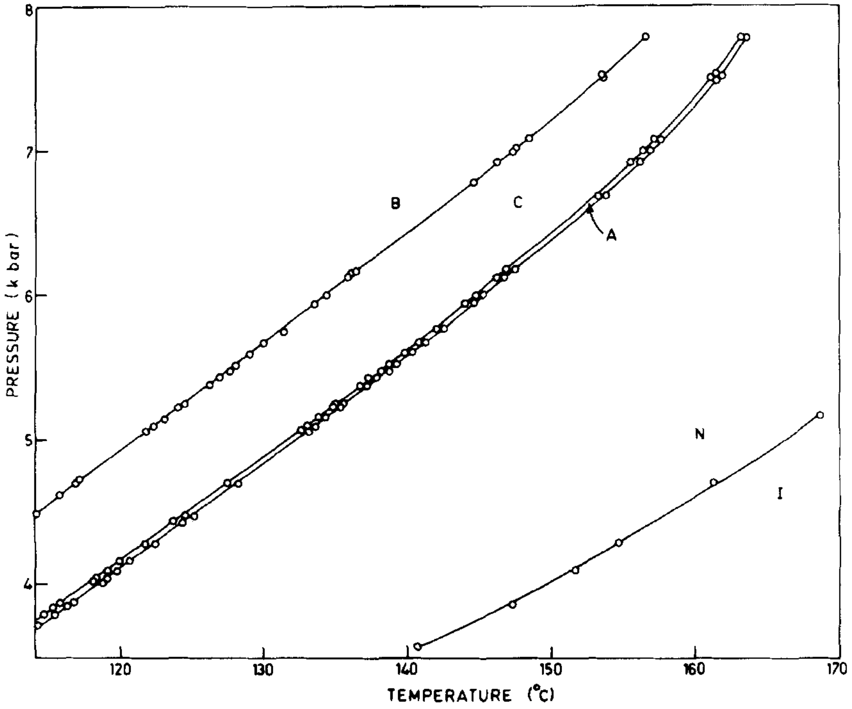

FIGURE 3: P-T diagram of 50.6 from 4-8 kbar.

and we can only infer that a Lifshitz point will probably occur at a pressure higher than 8 kbar.

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