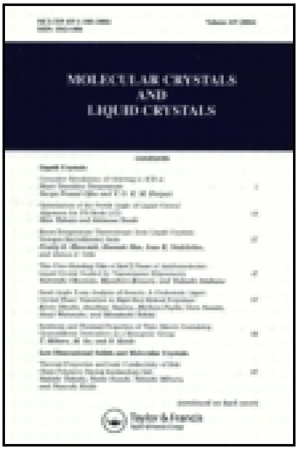

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The Metabolemeter II-Detection of Mesogenic Polymorphism under Pressure Using Small Quantities

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The Metabolemeter II–Detection of Mesogenic Polymorphism under Pressure Using Small Quantities[†]

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Every first order phase transition for mesogens can be detected by the continuous recording, as a function of temperature, of the pressure of the sample enclosed in a metallic cell. Studies of a compound (octylcyanobiphenyl) exibiting several transformations (crystal–smectic A, smectic A–nematic, nematic–liquid) show that this barometric method is convenient to detect polymorphism from one thermobarogram, and to draw the Clapeyron phase diagram; the smectic A-nematic transition involving small enthalpy and volume changes is clearly observable and this method is very sensitive. Moreover, the enthalpies and volumes of transition can be deduced from the pressure changes. Lastly, pressure and temperature are intensive data, and very little sample (1.3 mm^3) may be used.

INTRODUCTION

Several processes can be used to detect mesogenic polymorphism under pressure:[1] isothermal or isobaric volumetric studies,[2] optical observations of a mesogenic sample enclosed in a pressure chamber,[3] differential ther-

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mal analysis,[4] Raman scattering,[5] nuclear magnetic resonance,[6] measurements of the refractive index[7] or of the wavelength of the maximum reflection.[8] These methods allow one to measure the transition temperatures under different pressures and then to plot the Clapeyron phase diagram. In a preceding paper,[9] we have proposed a new barometric method to record, in a continuous way, the pressure dependence of the transition temperature for each individually studied transformation; the entire thermobarogram obtained for all the transitions of a compound permit one to draw the complete Clapeyron diagram and to observe polymorphism under pressure. In this method, only intensive data occur, so we predicted that miniaturization was possible.

We describe here experiments performed on 4-n-octyl-4′-cyanobiphenyl (8CB) and studies of the phase transitions showing that polymorphism under pressure can be detected from only one thermobarogram and the Clapeyron phase diagram deduced from it. The results show that this barometric method is very sensitive, that it allows one to obtain the enthalpy and relative volume changes at the transformations, and lastly that it requires very little sample to be used.

METHOD AND EXPERIMENTS

(a) Method and apparatus

The barometric method used and the working apparatus (metabolemeter) are described elsewhere.[9] The principle consists in the measurement, as a function of the temperature, of the pressure of a mesogenic sample enclosed in a dilatable cell. The thermobarogram, obtained by recording simultaneously both data, give, for each studied transition, the temperature pressure/dependence (Clapeyron slope). Pressure and temperature are intensive data and miniaturization is then possible. Perturbations revealed by the pressure detection were studied and allow us to predict that transformations will be observable for a 1 mg sample.

(b) Experimental procedure

For a compound exibiting polymorphism, the observation on the same thermobarogram of two successive phases, is only possible for a pressure increment arising from the first transformation detected that is lower than the leak pressure of the cell (here 1.4 kbars at maximum). For melting transitions, the experimental pressure change is generally so big (the calculated value is greater than 1.5 kbars[9]) that leaks appear before the next transition occurs. Then, part of the mesogen is ejected from the chamber, the pressure decreases (generally less than 0.1 kbars), and then stabilizes. When the temperature is further increased, the pressure stays practically stable, and mesogen is regularly leaving the cell. If the temperature reaches a sufficiently high value, the next transition occurs under high pressure without being detected. However, after cooling and on reheating, both transitions will now be observable. This procedure is used, in our experiments, to detect successively three transitions.

For experiments on small samples involving transitions between two fluid phases or a crystalline and a fluid phase, the experimental procedures previously employed on 6 mm^3 samples,[9] are still convenient; the only change necessary is in the volume of the cell enclosing the mesogen.

(c) Substances

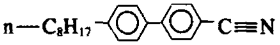
To test that the metabolemeter is convenient to detect polymorphism with only one thermobarogram, we used a compound exibiting three transformations involving clearly different volume changes; this was 4-n-octyl-4'-cyanobiphenyl (8CB) for which transition data are given in the Table I.

TABLE I

Literature data for the temperature, Clapeyron slope, enthalpy, volume and relative volume changes for the three transitions of 8CB.*

Transitions	K		S_A		N		I	References
Temperature (°C)	·	21	·	32	·	40	·	10
Enthalpy change (kcal. mole^{-1})		6.05		0.030		0.21		10
		6.05		0.031		0.23		11
		6.0		0.044		0.20		12
		6.0302		0.0729		0.2944		13
Clapeyron slope (bars K^{-1})		36.4		40		25.6		14
		40		39.7		25.8		10
		41.7		31.7		26.9		15
				39.84		28.73		16
Volume change (cm^3 mole^{-1})				0.098		0.5		17
				0.14		0.95		18
Relative volume change (%)				0.03		0.17		17
				0.05		0.35		18

*8CB:



The studies of the influence of the quantity of matter used were performed on an easily detectable transition, for which the pressure increment can be recorded without any leaks; our previous studies[9] showed that the clearing transition of 8CB is convenient.

RESULTS

The thermobarogram shown in Figure 1 gives, for a sample of 8CB enclosed in a 6 mm^3 cell, the successive recording, on heating, of the crystal–smectic A (K–S_A), smectic A–nematic (S_A–N) and nematic–isotropic phase (N–I) transitions. The transformations occur respectively at 20°C

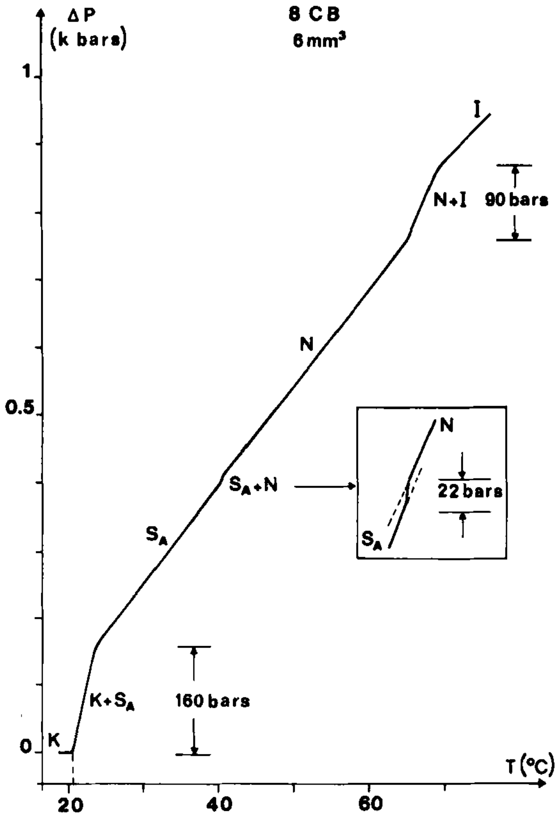
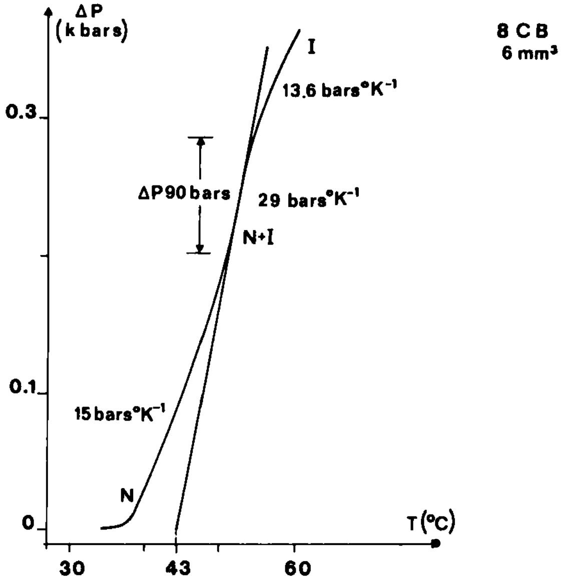


FIGURE 1 Experimental thermobarogram showing the successive recording of the melting, smectic A–nematic and clearing transitions for 8CB.

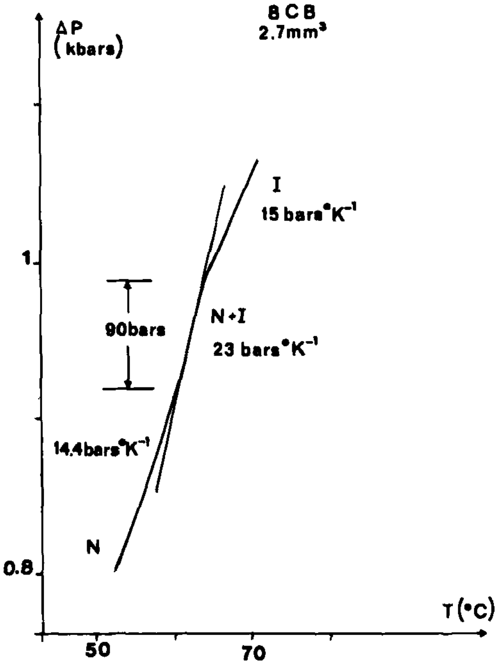
under 0 bar, 40°C 390 bars, and 65°C under 760 bars; they are attended respectively by 160 bars, 22 bars and 90 bars of pressure change. The slopes at the K–S_A and N–I transitions (Clapeyron slope) are 49 bars K^{-1} and 23.2 bars K^{-1}. The clearing temperature extrapolated at atmospheric pressure is 36°C. On the curved portion relating to the S_A–N transition, no straight line exists and the Clapeyron slope cannot be measured. The slopes away from the transitions are respectively, in smectic A, nematic and isotropic phases, 14.5 bars K^{-1}, 14.9 bars K^{-1} and 11.3 bars K^{-1}.

The thermobarograms shown in Figure 2 illustrate the influence of the quantity of tested matter on the pressure increment at the clearing transition of 8CB. For 6 mm^3 (Figure 2a) and 2.7 mm^3 (Figure 2b) chamber volume, the transition, that occurs respectively under 0.2 kbars and 0.94 kbars pressure, is attended by a 90 bars pressure change; for a 1.3 mm^3 volume (Figure 2c), the pressure change is 80 bars under about 1 kbar pressure. The slopes of these three thermobarograms are respectively, at the transition 29 bars K^{-1}, 23 bars K^{-1}, and 15 bars K^{-1}, in the nematic phase 15.9 bars K^{-1}, 14.4 bars K^{-1}, and 8.9 bars K^{-1}, and in the isotopic phase 13.6 bars K^{-1}, 15 bars K^{-1}, and 7 bars K^{-1}. In Figure 2, the clearing temperature is extrapolated at atmospheric pressure and then is 43°C.



(*a*)

FIGURE 2 Experimental thermobarogram of the clearing transition for a 8CB sample enclosed in a (*a*) 6 mm^3, (*b*) 2.7 mm^3, (*c*) 1.3 mm^3 cell.



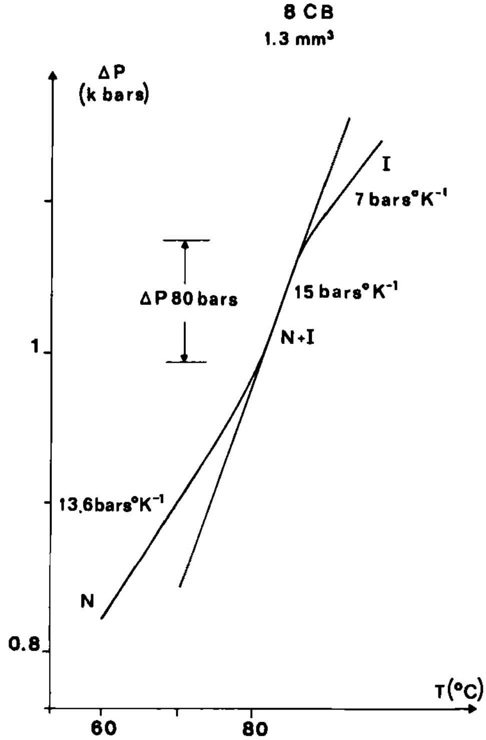
(*b*)

DISCUSSION

Explanations relative to the curves are given elsewhere.[9] The observations recorded in Figure 1 show that the metabolemeter allows one to detect polymorphism on using one thermobarogram. The Clapeyron phase diagram can be deduced from the Clapeyron slopes, eventually extrapolated at atmospheric pressure (melting and clearing), and when this is not possible (S_A–N transition), by joining with a straight line the transition point at atmospheric pressure and the middle of the transition curve under pressure. Figure 3 illustrates the agreement between our results and those of different authors.

A value of the maximum pressure change at a transition can be calculated from the relation[9]

$$(\Delta p)_T = \frac{\Delta V}{V}\left(\chi - \frac{T\Delta V}{\Delta H}\alpha\right)^{-1}$$



(*c*)

with α and χ respectively the thermal expansion and isothermal compressibility of the phase previous to the transition. For the K–S_A transition (Figure 1) no comparison between the experimental and calculated pressure changes is possible (the compound does not fill up the cell when the transition occurs.[9] For numerical calculations of $(\Delta p)_T$ at the S_A–N and N–I transformation, we used mean values for the transition data (Table I) and for α and χ (no numerical data are known) mean values for the mesomorphic phases respectively: 8.3 10^{-4} K^{-1} and 5.75 10^{-10} m^2 N^{-1}; then the calculated pressure increments are respectively 11.3 bars and 98 bars. Pressure change calculations at the transitions as a cavity volume function let us predict that the effects are a maximum for a 6 mm³ sample and decrease less than 5% for a 1.3 mm³ sample[9] (nearly 93 bars for the N–I transformation). The experimental results (Figures 2a, b and c) are in good

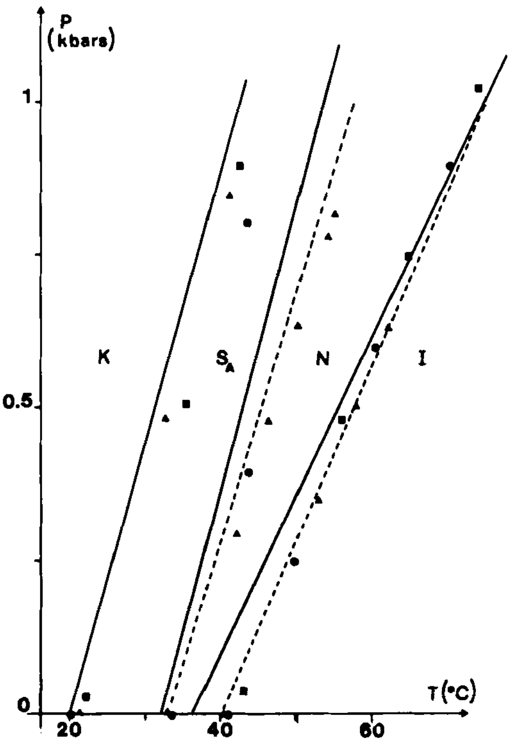


FIGURE 3 Clapeyron phase diagram; full curves: present work; ●Liebert and Daniels;[10] ■Cladis, Bogardus and Aadsen;[14] ▲Shashidhar and Venkatesh;[15] broken curves: Wallis and Roy.[16]

agreement with that prediction and clearly illustrate that miniaturization is possible. For $(\Delta p)_T$, the differences between the experimental (Figures 1 and 2) and calculated data can be understood in terms of uncertainties relating to the transition and phase data. For the S_A–N transformation, although the relative volume change is very small (Table I), the pressure increment is big, and this proves that the barometric method is very sensitive.

From the $(\Delta p)_T$ expression, the enthalpy (ΔH) and the relative volume $(\Delta V/V)$ changes can be expressed as a thermobarogram data function (Clapeyron slope, $p_c = \Delta H/T \cdot \Delta V$, slope previous to the transition $p_v = \alpha/\chi$[9], transition temperature T and, of course, pressure increment $(\Delta p)_T$):

$$\Delta H = (\Delta p)_{\mathrm{T}} \cdot T \cdot \alpha \cdot \nu \left[\frac{p_{\mathrm{e}}}{p_{\mathrm{v}}} - 1\right]$$

$$\frac{\Delta V}{V} = (\Delta p)_{\mathrm{T}} \cdot \alpha \cdot \left[\frac{1}{p_{\mathrm{v}}} - \frac{1}{p_{\mathrm{c}}}\right]$$

with $\nu = \mu/\rho$ where μ is the molar mass (0.291 kg mole^{-1} for 8CB) and ρ the specific volume in the phase previous to the transition. For the melting transition in Figure 2a (optimal cavity volume), all the thermobarogram data can be measured; in a first approximation, we choose for α and ρ 8.3 10^{-4} $°\mathrm{C}^{-1}$ (see above) and 1 g cm^{-3} respectively.[17,18] The relative volume change is then 0.22% and agrees with the average of both data in Table I (0.26%). The enthalpy change is 0.135 kcal mole^{-1}; although this value is a little lower than the literature values (Table I), a good order of magnitude is given.

In our experiments, we detect the temperature of the oven,[9] and then, between the cell and the temperature sensor, there exists a temperature gradient, a positive function of the speed of heating. The latter has been chosen for the thermobarograms of Figures 2a, b and c respectively to be low, medium, and high. For a low speed of heating, the experimental Clapeyron slope (29 bars K^{-1}) agrees with the literature data (Table I) and the extrapolation at atmospheric pressure of the transition temperature gives a good result (43°C); for medium and high speeds, the Clapeyron slope decreases and the extrapolated temperature is then too low. However, the full effects are still the same and qualitative studies are possible.

CONCLUSION

The different methods used to detect polymorphism under pressure consist in measuring, under different pressures, the transition temperature. Another barometric method we have presented previously concerns the continuous recording, as a function of the temperature, of the pressure of a sample enclosed in a metallic cell. We give here results obtained on 4-n-octyl-4′-cyanobiphenyl showing that this method allows us to detect polymorphism using only one thermobarogram, and to deduce the Clapeyron phase diagrams. Temperature and pressure are intensive data and let us predict that miniaturization is possible. The results on the clearing transition for 6, 2.7, and 1.3 mm^3 samples confirm our predictions. The experimental pressure increments at the smectic A–nematic or nematic–isotropic phase transitions are in good agreement with those calculated. For the clearing transition, orders of magnitude of the enthalpy and relative volume changes are deduced from the pressure increment; moreover, the smectic A–nematic transformation that is accompanied by a small volume change is clearly observable. This barometric method is therefore very sensitive. Lastly, when the speed of heating of the aparatus is low, there is good agreement between the experimental and literature data for both the Clapeyron slope and the transition temperature at atmospheric pressure.

We think this method will be convenient to study compounds exibiting a rich polymorphism, weakly first order and/or high temperature phase transitions; both are currently under study.

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