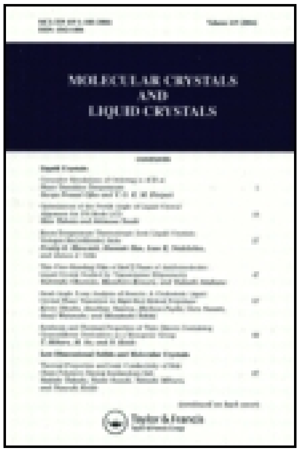

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Metabolemeter III: Phase Behaviour Under Pressure of bis-(4-4′-n-Heptyloxybenzylidene)- 1, 4-Phenylenediamine and Terephthalylidene-bis-(4-n-Decylaniline)

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Version of record first published: 20 Apr 2011.

To cite this article: J. M. Buisine (1984): The Metabolemeter III: Phase Behaviour Under Pressure of bis-(4-4′-n-Heptyloxybenzylidene)- 1, 4-Phenylenediamine and Terephthalylidene-bis-(4-n-Decylaniline), Molecular Crystals and Liquid Crystals, 109:2-4, 143-157

To link to this article: http://dx.doi.org/10.1080/00268948408078702

Mol. Cryst. Liq. Cryst., 1984, Vol. 109, pp. 143–157
0026-8941/84/1094-0143/\$18.50/0

The Metabolemeter III: Phase Behaviour Under Pressure of bis-(4-4′-*n*-Heptyloxybenzylidene)-1,4-Phenylenediamine and Terephthalylidene-bis-(4-*n*-Decylaniline)

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(*Received September 15, 1983*)

By using a metabolemeter, the phase transitions of *bis*-[4,4′-*n*-heptyloxybenzylidene]-1,4 phenylenediamine (HBPD) and terephthalylidene-*bis*-[4-*n*-decylaniline} (TBDA) have been studied. The weakly first order phase transitions (S_G–S_F and S_F–S_I) and the narrowly separated phase transitions (S_C–S_A and S_A–I) of TBDA are detectable. For HBPD, both transitions S_G–S_I and S_I–S_C are individually observed and the enthalpy changes are deduced from pressure increments at the transformations; two triple points are detected, one directly by a change of slope in the drawing of the equilibrium curves. The pressure-temperature phase diagrams are given; for each transition, the volume increases on increasing the temperature.

INTRODUCTION

Previously,[1,2] with compounds exhibiting successively three first order phase transitions, it has been shown that the metabolemeter, using only small quantities, is convenient for detecting polymorphism under pressure, establishing pressure-temperature phase diagrams, and de-

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ducing enthalpy and volume changes from experimental thermobarograms. Now we use this process to study mesogens exhibiting a rich polymorphism including weakly first order and high temperature phase transitions.

METHOD AND EXPERIMENTS

a) Method and apparatus

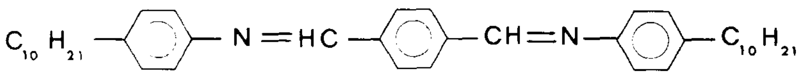
Details of the method and of the experimental set up (metabolemeter) are described elsewhere.[1] The principle consists in measuring the pressure of a small sample of mesogen enclosed in a cell as a function of temperature.

b) Experimental procedure

The experimental procedure (e.g., filling of the cell, individual or successive recording of several transitions) is treated elsewhere.[1,2] To detect a transition under two (or several) different pressures, the method previously explained,[2] is used twice (or several times), and this involves leaving a small part of the compound out of the cell at high pressure, so that after cooling, the sample can be heated again. Heating rates were about 5°C $\min^{-1}$, and cooling rates about 1°C $\min^{-1}$.

c) Substances

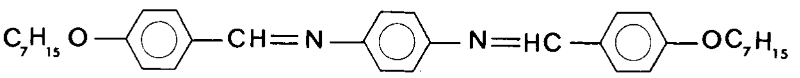
The compounds used were terephthalylidene-*bis*-[4-*n*-decylaniline] (TBDA) and *bis*-[4-4′-*n*-heptyloxybenzylidene]-1,4-phenylenediamine (HBPD). In TBDA



synthesized by Neubert and Maurer,[3] smectic G, F, C and A phases have been identified by isomorphy. The mesophase now inserted between the smectic F and C phases is named smectic I;[4] the phase structures have been studied by X-ray.[5] The phase sequence under atmospheric pressure is:

$$\mathrm{K}\ 72\ \mathrm{S_G}\ 115\ \mathrm{S_F}\ 149\ \mathrm{S_I}\ 155\ \mathrm{S_C}\ 189\ \mathrm{S_A}\ 191\ \mathrm{I}.$$

In the first study of HBPD



only two mesophases are described.[6] Later DTA and microscopic studies revealed five different smectic mesophases, and the smectic C phase was identified; at this time S_G was, of course, described as S_B and evidence was given that S_I was different from S_A, S_B and S_C.[7] Three years later the volume changes at the phase transitions were measured and the crystalline nature of the previously described smectic phase stable at lower temperature was established.[8] Consecutive DSC and microscopical studies later gave six smectic phases.[9] By X-ray studies the following phase sequence has been established:

$$K_1\ 127\ K_2\ 130\ K_3\ 146\ S\ 154\ S_G\ 157\ S_I\ 164\ S_C\ 197\ N\ 241\ I$$

and S has the same structure as the monotropic mesophase of TBBA (the butyl homologue of TBDA);[10] consequently, S is S_H.[11]

The transition data for both compounds are given in the Table I. For TBDA, there occur at atmospheric pressure two weakly first order phase transitions (S_G–S_F and S_F–S_I),[12,13] and at higher temperatures, two narrowly separated phase transformations (S_C–S_A and S_A–I). For HBPD, calorimetric measurements were performed under pressure by Spratte *et al.*;[14] however, for the S_G–S_I and S_I–S_C transitions, the enthalpy changes could not individually be measured. Moreover, for the volume change at the S_G–S_I transition, Spratte's results are in disagreement with Demus's results[8] (obtained by density measurements).

The quantity of tested matter was about 6 mm^3 for the S_F–S_I, S_I–S_C, S_C–S_A and S_A–I transition studies of TBDA and about 2.5 mm^3 for the other studies.

RESULTS

If not specified, explanations relating to the interpretation and the exploitation of thermobarograms to obtain ($P - T$) phase diagrams are given elsewhere.[1,2]

TBDA

For TBDA, three characteristic thermobarograms obtained experimentally are presented in Figures 1 to 3. They exhibit at the K–S_G,

TABLE 1

Experimental and literature data for transition temperature, molar enthalpy change, Clapeyron slope, volume change at the transitions, and slope out of the transitions from experimental thermobarograms for the compounds studied.

		K_1		K_2		K_3		S_H		S_G		S_I		S_C		N		I	Ref.
HBPD	Temperature (°C)	·	127	·	130	·	146	·	154	·	157	·	164	·	197	·	241	·	9
		·	112	·	125.4	·	148.7	·	155.9	·	162.7	·	168.2	·	198	·	240.4	·	14
		·	110.7	·	124.3	·	147.3	·	153.8	·	162.4	·	168.6	·					
	Molar enthalpy change (kcal/mole)						2.68		0.51		0.12		0.77		0.86		0.51		9
							1.63		0.36			0.76[a]			0.65		0.26		14
											0.191		0.473						
	Clapeyron slope (Bars/K)		30		14.5		24.1		29.1		23		24.3		28.7		19.4		14
			27.2		15		29.7		22		18.8		21.2						
	Volume change (cm^3/mole)		11		9		6.7		1.2			3[a]			2		1.6		14
									0.99		−1.52		3						8
											0.80		1.85						
	Slope out of the transition (Bars/K)	16.7				12.4		13.7		9.6		11.9		8.6					
		K		S_G		S_F		S_I		S_C		S_A		I					
TBDA	Temperature (°C)	·	72	·	115	·	149	·	155	·	189	·	191	·					4
		·	72	·	115	·	149	·	154	·	189	·	190	·					12
		·	72.5	·	105	·	147	·	155	·	195	·	197	·					
	Molar enthalpy change (kcal/mole)		11.96		0.0005		0.004		1.55		0.179		1.75						12
			11.74		0		0.001		1.33		0.115		1.52						13
	Clapeyron slope (Bars/K)		36		65		25		23		14		18						
	Volume change (cm^3/mole)		40.25		8.10^{-4}		0.016		6.6		1.16		8.72						
	Slope out of the transition (Bars/K)		7.6			8.8		7.3		7		10.8		10.8					

a S_G–S_C transition

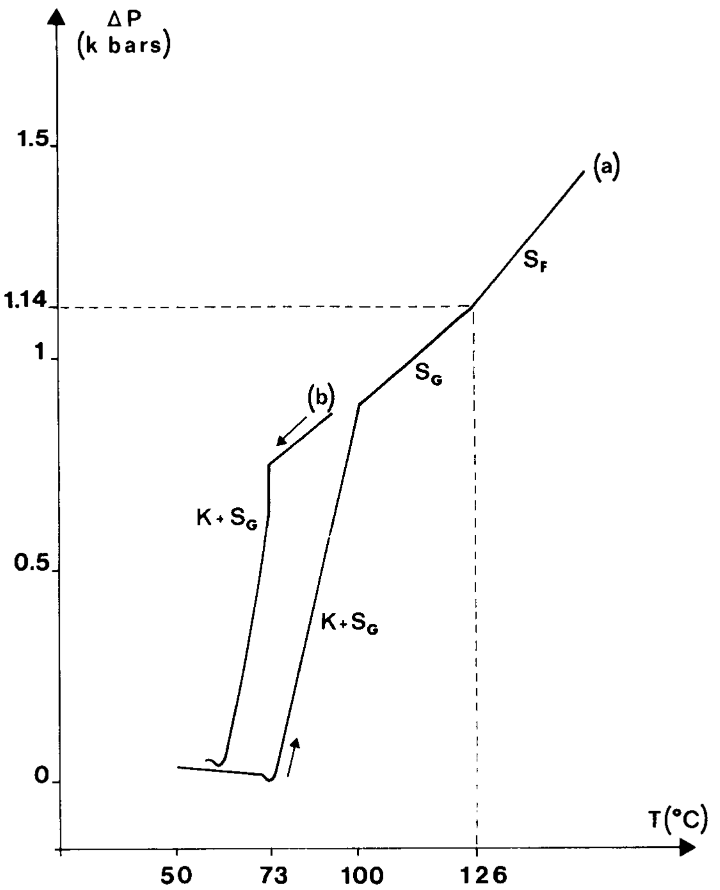


FIGURE 1 Experimental thermobarogram showing (for TBDA) (*a*) the K–S_G and S_G–S_F transitions on heating; (*b*) the K–S_G transition on cooling.

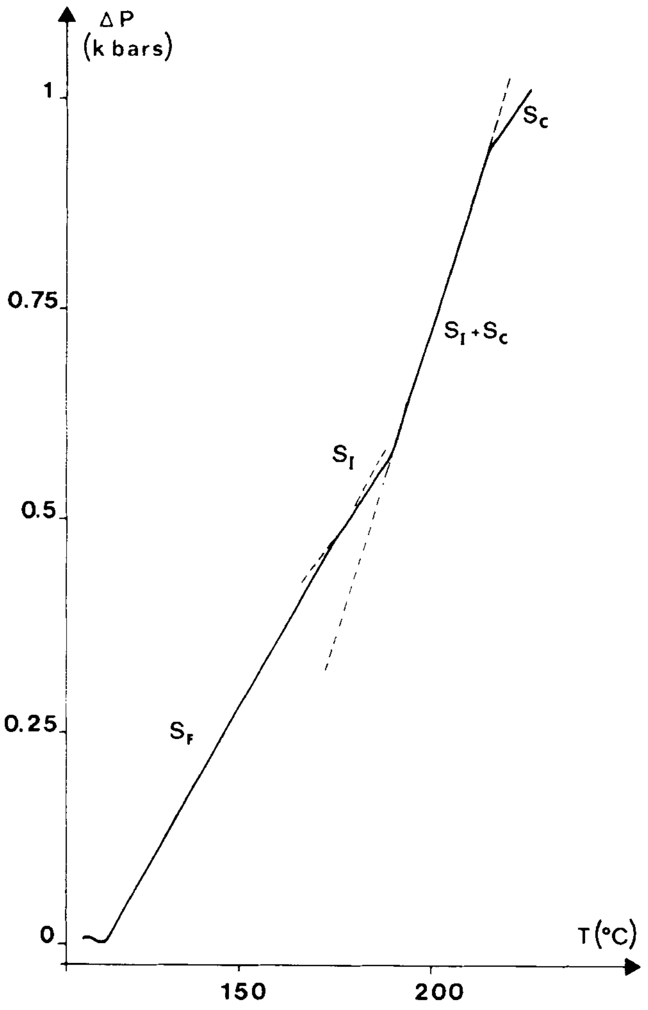


FIGURE 2 Experimental thermobarogram showing for TBDA the S_F–S_I and S_I–S_C transition on heating.

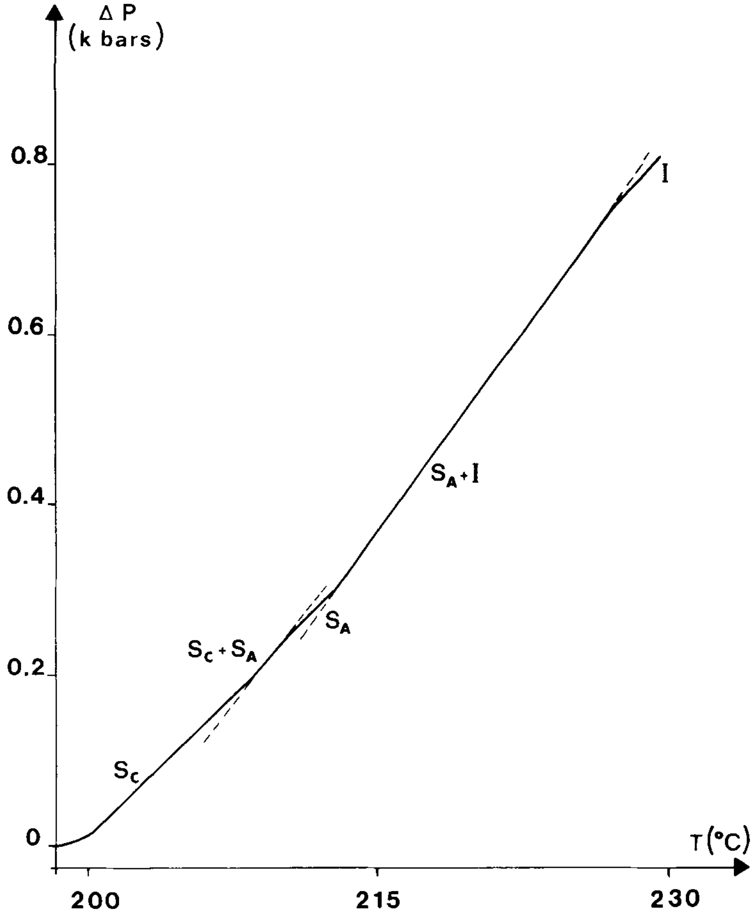


FIGURE 3 Experimental thermobarogram showing for TBDA the S_C–S_A and S_A–I transition on heating.

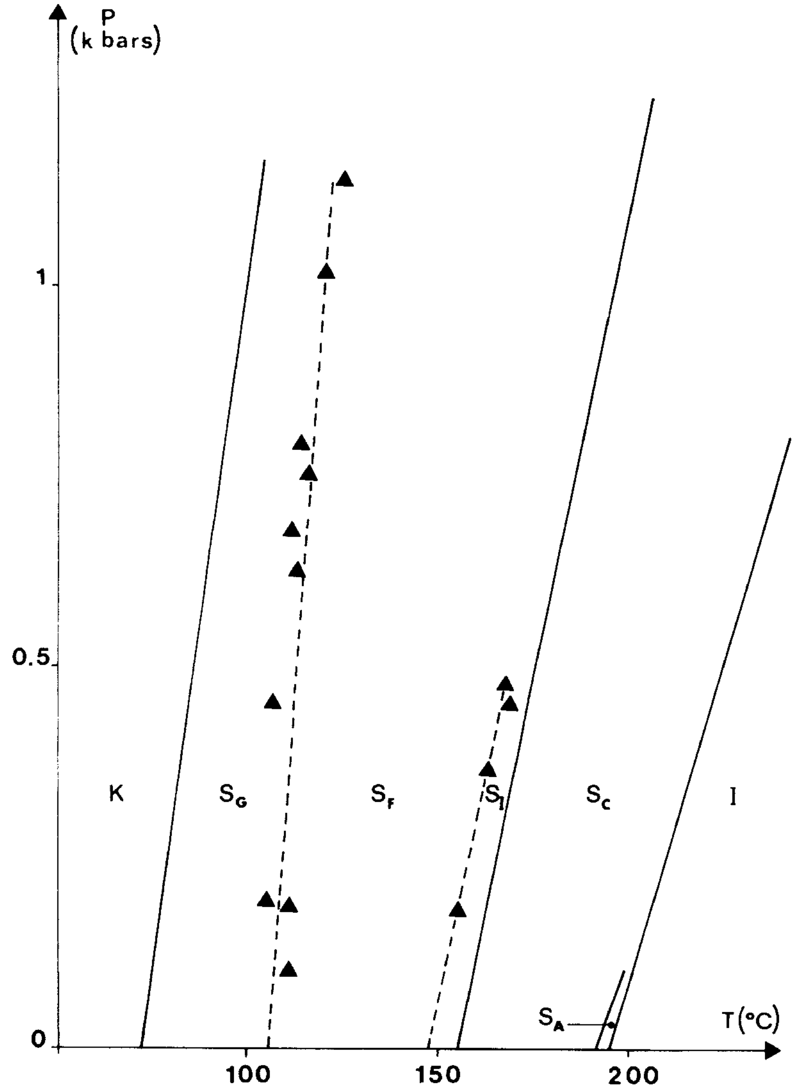


FIGURE 4 Pressure-Temperature phase diagram for TBDA: full lines: equilibrium curves plotted on using mean values from several thermobarograms for the Clapeyron slopes and for the transition temperatures at atmospheric pressure. ▲ transition temperatures under pressure (measured at the changes of slope on thermobarograms).

S_I–S_C, S_C–S_A and S_A–S_I transitions, a very clear pressure increment (characteristic of first order phrase transitions). But such an increment is not detected at the S_G–S_F and S_F–S_I transformations; there occurs only a weak change of slope, relative to the different values of the thermal expansion and of the isothermal compressibility, on both side of the transition. For these transitions, the relative volume changes are lower than $10^{-2}\%$, which is beyond the sensitivity of the metabolemeter; these transformations are either second order (as proposed by Benatter *et al.*[15] for S_G–S_F transitions) or weakly first order.[12] The thermobarogram in Figure 3 shows the S_C–S_A and S_A–I transitions; although only very narrowly separated, they are easily observable. In Figure 1b, supercooling of the S_G phase is observable; then crystallization occurs, first of all very rapidly (the pressure decreases by 150 bars in 0.1°C), then more slowly. The crystallization temperature at atmospheric pressure is about 61°C. The $(P - T)$ phase diagram is given in Figure 4; for the first order phase transitions, the equilibrium curves supposedly rectilinear, are plotted by using mean values from several thermobarograms for the Clapeyron slopes and for the transitions temperature at atmospheric pressure.[2] For the other transitions

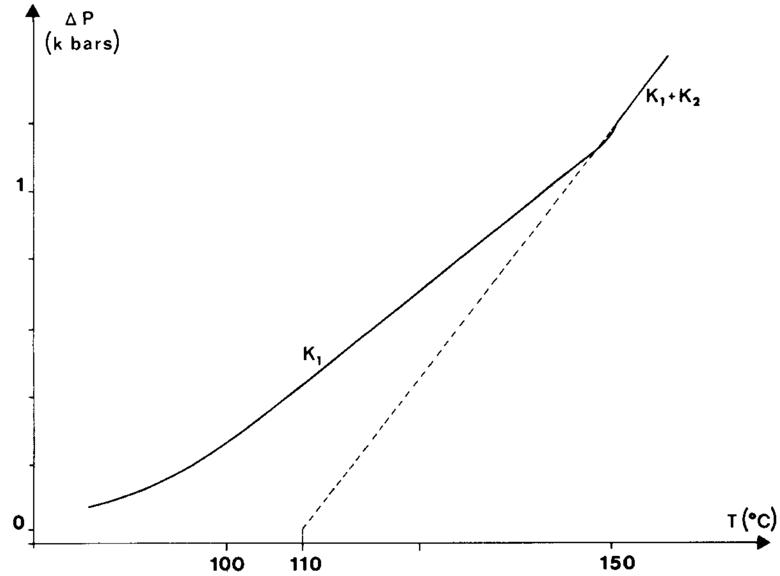


FIGURE 5 Experimental thermobarogram showing for HBPD the K_1–K_2 transition on heating.

we used the transition temperatures under different pressures (measured at the slope changes) given by several thermobarograms. The thermal stability of the S_G and S_A phases decreases with increasing pressure, but the existence of triple points is uncertain because of the uncertainty about the Clapeyron slopes. For all transformations, the transition temperatures, the slopes of the equilibrium curves from Figure 4, and the volume changes, calculated with the Clapeyron relation on using Wiegeleben data,[12] are reported in the table. Data relating to the slopes out of the transition α/χ^1 (where α and χ are respectively the thermal expansion and isothermal compressibility) are also reported in the Table.

HBPD

Figures 5 to 7 present three experimental thermobarograms showing the K_1–K_2, K_2–K_3, K_3–S_H, S_H–S_G, S_G–S_I and S_I–S_C transitions of HBPD; the two last transitions have not been studied because their observation under pressure involves temperatures too near to or higher

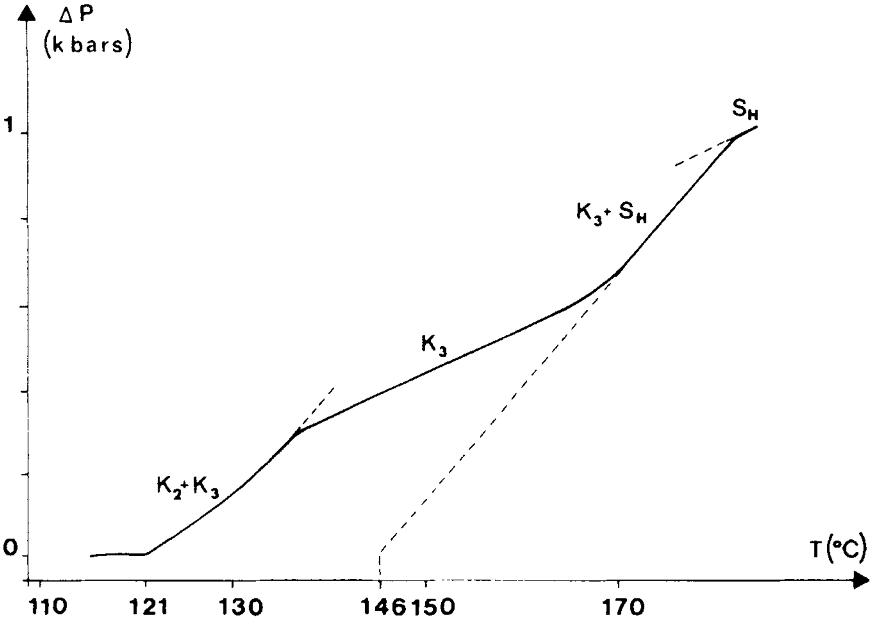


FIGURE 6 Experimental thermobarogram showing for HBPD the K_2–K_3 and K_3–S_H transitions on heating.

than the maximum working temperature of the metabolemeter (240°C, melting temperature of the tin joint). On the thermobarogram of Figure 5, the dilatation of the K_1 phase can be observed until 1,15 kbars; the slope of the thermobarogram for the K_1 phase is about 16.7 bars/K. Thus, the metabolemeter allows us to measure the ratio α/χ, not only for fluid phases,[1,2] but also for crystalline phases. On Figure 7, both transitions S_G–S_I and S_I–S_C, not detected under pressure by Spratte,[14] are here clearly observable; an order of magnitude of the molar enthalpy changes at atmospheric pressure can be deduced from the pressure increments[2] which occur at the transitions, and this is reported in the table. The whole enthalpy change for the two transitions is 0.664 kcal/mole, close to Spratte's result (0.76 kcal/mole). For both transitions, the volume changes, calculated from the Clapeyron relation by using Spratte's data for the transition temperature and Clapeyron slope are reported in the table. In Figure 8 are reported several recordings obtained under different pressures for the K_3, S_H and S_G phases. On the curves *a*, *b*, *c* and *d*, three changes of

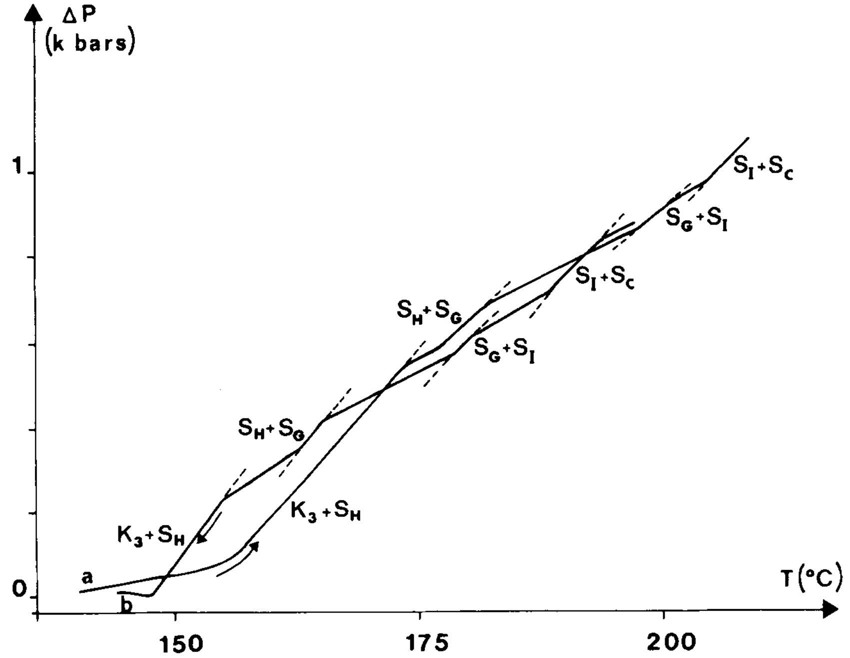


FIGURE 7 Experimental thermobarogram showing for HBPD the K_3–S_H, S_H–S_G, S_G–S_I and S_I–S_C, transitions (*a*) on heating (*b*) on cooling.

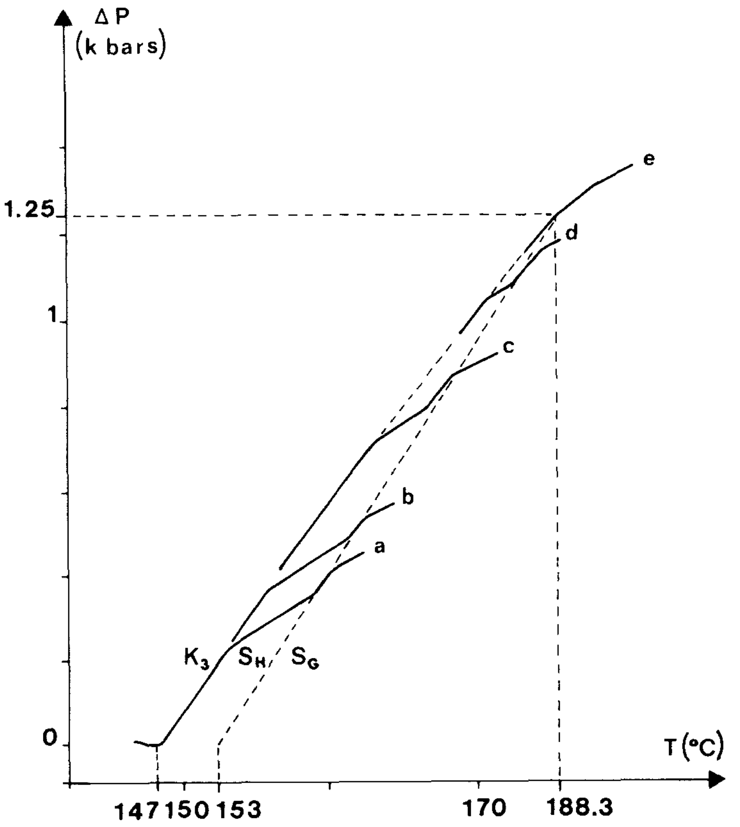


FIGURE 8 Experimental curves showing for HBPD: *a*, *b*, *c*, *d*, the K_3–S_H and S_H–S_G transitions under pressure, and *e* the triple point K_2–K_3–S_G.

slopes are observable corresponding to the two successive transitions K_3–S_H and S_H–S_G. The temperature existence domain of the S_H phase disappears under pressure. On curve *e*, only two changes of slope are detectable; the report on the (P, T) diagram (Figure 9) permits us to interpret the first change of slope to the presence of a triple point (K_2–K_3–S_G) at 188°C and 1250 bars. The second triple point (K_3–S_H–S_G equilibrium) is detectable, at a pressure and temperature slightly lower than the first one. The whole $(P - T)$ diagram is in perfect agreement with Spratte;[14] especially, Spratte detects the (K_2–K_3–S_G) triple point at 1140 bars and 188°C and the (K_3–S_H–S_G) triple point a bit lower. Data for the slopes of the equilibrium curves and the transition temperature at atmospheric pressure from Figure 9 and of the slopes out of the transitions are reported in the Table.

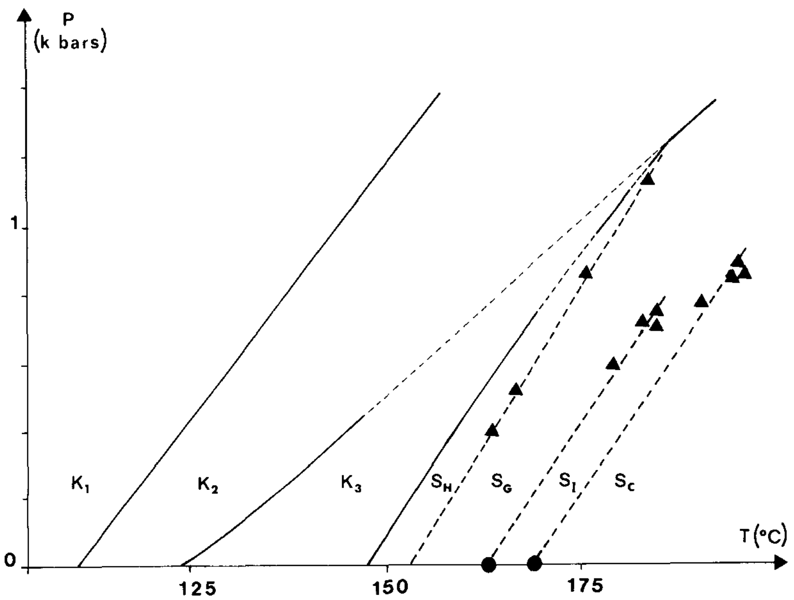


FIGURE 9 Pressure-Temperature phase diagram for HBPD: full lines: equilibrium curves plotted on using mean values from several thermobarograms for the Clapeyron slopes and for the transition temperatures at atmospheric pressure. ▲ Transition temperatures under pressure taken at the middle of the experimental equilibrium curves.[2]

● Wiegeleben temperature data.

DISCUSSION

In Figure 7, differences exist between the data obtained on heating and on cooling for the transition temperatures and for the Clapeyron slopes; this is due to the temperature gradient between the cell and the temperature sensor[2] which is not the same on heating and on cooling. We also note that the transformations are more clearly detectable on cooling than on heating because the speed of cooling is lower (about 1°C min^{-1}), than the speed of heating (about 5°C min^{-1}). The influence of heating and cooling rates have been studied only in the case of HBPD. Except for the crystallisation, no thermobarograms were recorded on cooling for TBDA. Observation of the thermobarograms in Figures 3 and 7 shows the efficiency of the metabolemeter for detecting under pressure phase transitions occurring at high temperature at atmospheric pressure. The actual maximum working temperature of the apparatus will be increased to 270°C (maximum work temperature of the pressure transducer) on using a gold joint.

Some results are in disagreement with those of Demus *et al.*;[8] from densities measurements, they obtain, on heating, a negative volume change (-1.5 cm^3/mole) for the S_G–S_I transition of HBPD. Outside of reentrant mesomorphism, another transition with a negative volume change on heating has been observed by Demus:[8] -2.9 cm^3/mole for the S_2–S_B transition of *bis*-[4′-*n*-octyloxybenzylidene]-1-4-phenylenediamine, but Spratte[14] observed an increement of volume (0.35 cm^3/mole). Thus it seems that for mesogens, outside the reentrant phenomenon, no transition with a decrease of volume on heating is yet known.

CONCLUSION

The metabolemeter is convenient for detecting mesogenic polymorphism under pressure with small samples; it was used here to study two compounds exhibiting a rich polymorphism: terephthalylidene-*bis*-(4-*n*-decylaniline) and the *bis*-(4-4′-*n*-heptyloxybenzylidene)-1,4-phenylenediamine. For both compounds, high temperature phase transitions occurring at atmospheric pressure have been detected under pressure. For the first compound, the S_G–S_F and S_F–S_I transitions, which are weakly first order (or second order) phase transitions, and the S_C–S_A and S_A–I transitions, which are separated only by two degrees, are easily detectable with this apparatus. For the second compound, both transitions S_G–S_I and S_I–S_C, not individually observed under pressure by calorimetric measurements are here separately observable. The enthalpy changes are deduced from pressure increments at the transformations; the ratio α/χ of the crystalline phase K_1 has been measured. Two triple points (K_2–K_3–S_G and K_3–S_H–S_G) are detectable, the first directly by a change of slope on the drawing of the equilibrium curve. For both compounds, $(P - T)$ phase diagrams are given. For each transition, the volume increases on increasing the temperature.

Now we plan to use the metabolemeter for studies of binary mixtures.

Acknowledgments

The author is grateful to Dr. L. Liebert and Dr. C. Germain for the synthesis of the compounds used, Dr. J. J. Benattar who encouraged this study, and Professor J. Billard for his fruitful collaboration.

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