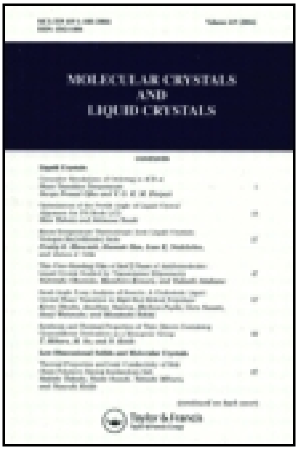

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Thermo-Barometric Analysis of some Pyramidic Mesogens

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THERMO-BAROMETRIC ANALYSIS OF SOME PYRAMIDIC MESOGENS

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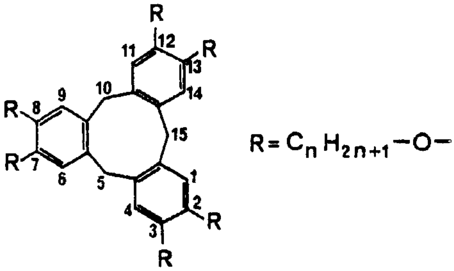
Abstract The phase behaviour under pressure of four members (n = 7, 9, 10 and 11) of the hexaalkyloxytribenzocyclononene homologous series have been investigated by thermo-barometric analysis. The pressure - temperature phase diagrams are determined. For n = 7, 9 and 10 a new stable phase is detected ; it seems it is a P_B phase. For n = 7 that phase is monotropic under atmospheric pressure ; two virtual transitions are deduced by extrapolation. Volume changes for the transitions and ratio of the expansion and isothermal compressibility coefficients for the phases are given.

INTRODUCTION

Compounds consisting of a rigid pyramidic shaped central core and six equal flexible side chains can exhibit pyramidic mesophases [1-3]. For such compounds no results relating to the volume changes under atmospheric pressure and pressure - temperature dependance of the phase transitions are known. More microscopical and calorimetric measurements performed on ten members of the hexaalkyloxytribenzocyclononene homologous series have shown the existence of a pyramidic B mesophase for an intermediate term of the series that is not observed for the other ones [1]. Following the thermo-barometric analysis of calamitic [4] and discotic [5-6] mesogens, we have investigated four members of the previous series of pyramidic (so called bowl-like or cone shaped) mesogens and studied their phase sequences under various pressures.

I. SUBSTANCES

The studied compounds are members of the hexaalkyloxytribenzocyclononene homologous series (C_nHTBCN) [1] :



Under atmospheric pressure, a pyramidic P_A mesophase is observed for n = 4 to 12 (monotropic phase for n = 4 and 5). For n = 11, an enantiotropic pyramidic P_B phase appears at lower temperature than P_A [1]. Thermo-barometric measurements have been performed on derivatives with n = 7, 9 to 11 from recently synthesized samples.

II. THERMO-BAROMETRIC ANALYSIS

The thermo-barometric measurements have been performed with a scanning numerical metabolemeter [7]. Details relating to the method, interpretation and exploitation of thermobarograms are given elsewhere [8].

Figure 1 gives a thermobarogram obtained on heating for n = 11 and showing the melting ($K + P_B$) and $P_B - P_A$ transition ($P_B + P_A$). The $P_B - P_A$ transformation exhibits an important pretransitional behaviour (progressive change of slope at the beginning of the transformation) that can result from conformational changes for the molecules. For n = 7 (Figure 2) a change of slope for the melting curve occurs at 36.5°C under 300 bar ; more a transformation ($M + P_A$) not previously detected under atmospheric pressure is observed under pressure. For n = 9 and 10 the thermobaro-

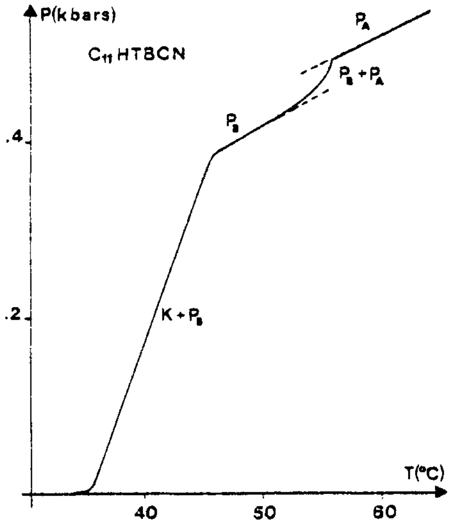


FIGURE 1. Thermobarogram obtained on heating for C_{11}HTBCN.

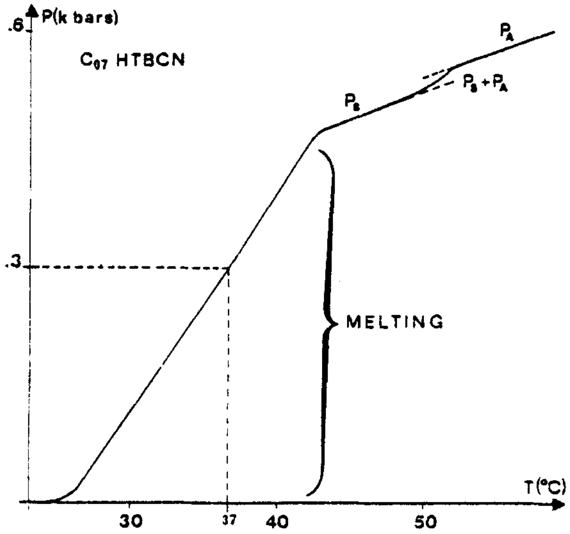


FIGURE 2. Thermobarogram obtained on heating for C_{07}HTBCN.

grams have the same general shape as Figure 1.

The pressure - temperature phase diagrams for the studied compounds are plotted Figure 3 a to d. Data that can be deduced from P-T phase diagrams (i.e. transition temperatures under atmosphere pressure, slopes of the equilibrium curves, volumes changes for the transitions) and thermograms (i.e. ratio thermal expansion/isothermal compressibility) are reported in the Table.

III. DISCUSSIONS

Comparison between the four P-T phase diagrams (Figure 3) let predict the phase stable at lower temperature than P_A for n = 7, 9 and 10 is a P_B phase (see also Figure 4). Cause our experiments have been performed on new resynthesized samples, it is on surprising that a P_B phase - not previously observed - is now detected for n = 7, 9 and 10 ; this is confirmed by higher data obtained for n = 9 and 10 by thermo-barometric analysis for the melting temperatures than those obtained by initial microcopical observations [1] (Table). By increasing pressure the temperature range for the stability of P_B increases for n = 7 and 9 and decreases for n = 10 and 11.

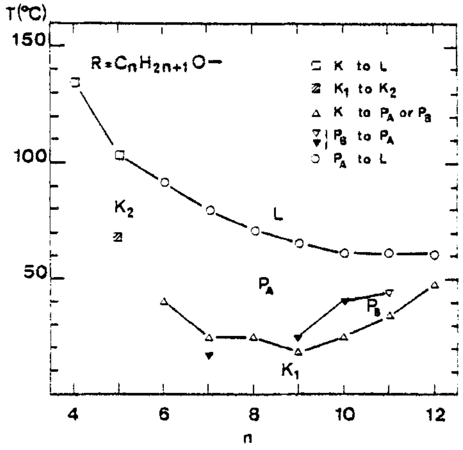


FIGURE 7. Schematic representation of the phase transition temperatures for C_nHTBCN ;
▼ : this work.

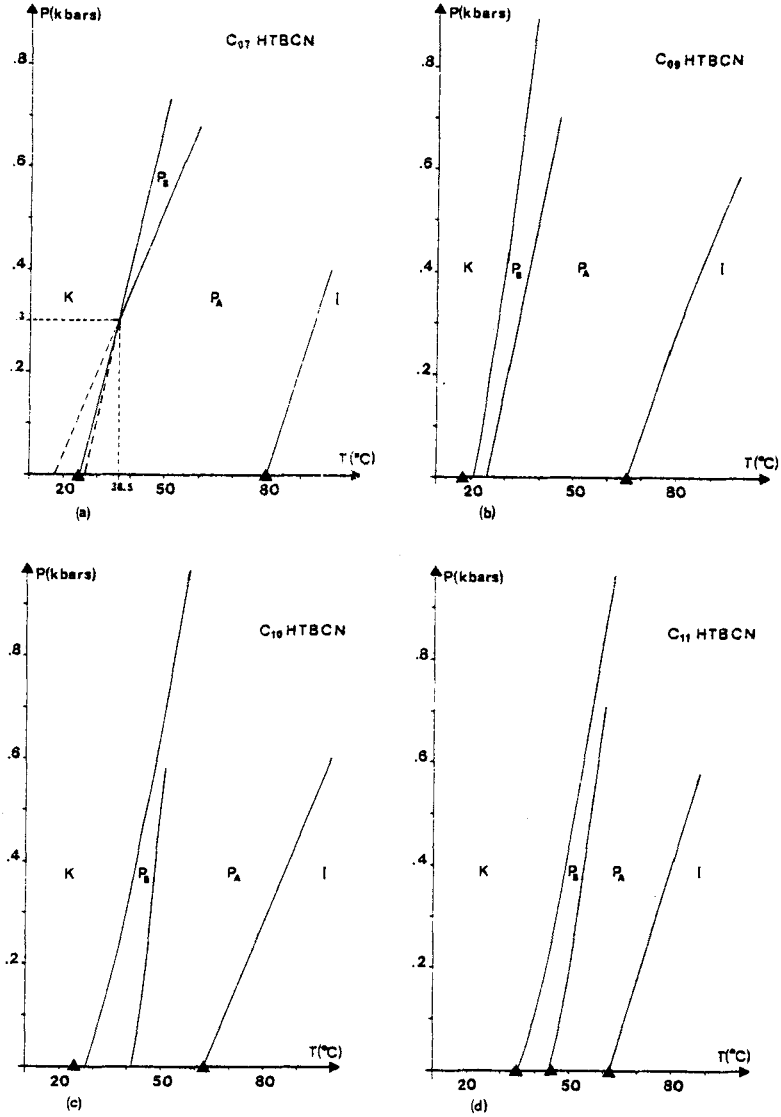


FIGURE 3. Pressure-Temperature phase diagram for a : C_{07}HTBCN, b : C_{09}HTBCN, c : C_{10}HTBCN and d : C_{11}HTBCN ;

▲ : Literature data .

TABLE

Literature, experimental and calculated data for the transitions of C_nHTBCN :

T : Transition temperature (°C),
ΔH : Enthalpy changes (kcal.Mole^{-1}),
$(\frac{dP}{dT})^E$: Slope of the equilibrium curves (bar.K^{-1}),
ΔV : Volume changes (cm^3.mole^{-1}),

and experimental data for the phases

$(\frac{dP}{dT})_V = \frac{\alpha}{\chi}$: Slope of the thermobarograms (bar K^{-1}) ;

(i) monotropic, (ii) virtual transitions.

	K		P_B		P_A		I	ref
n = 7 T	.	25	—		.	79.9	.	1
			.	$[17.5]^{i}$	.			
ΔH		5.05				2.22		1
$(\frac{dP}{dT})^E$		26		15.9		22		
ΔV		27.2		9.4		12		
T	.	$(27)^{ii}$	.					
ΔH		4.01						
$(\frac{dP}{dT})^E$		30						
ΔV		18.6						
$(\frac{dP}{dT})_V$	8.5		7.2		6.4		12.5	
n = 9 T	.	18.6	—		.	66.1	.	1
ΔH		6.84				1.65		1
T	.	21	.	25	.			
$(\frac{dP}{dT})^E$		41.4		33		22		
ΔV						9.25		
$(\frac{dP}{dT})_V$	14.9		10		8.6		9.5	
n = 10 T	.	25.5	—		.	63.2	.	1
ΔH		9.66	.			1.6		1
T	.	28	.	41.5	.			
$(\frac{dP}{dT})^E$		25		36.4		26		
ΔV						7.6		
$(\frac{dP}{dT})_V$	10.1		8.2		7.9		8.4	
n = 11 T	.	34.8	.	44.2	.	62	.	1
ΔH		13.4		1.72		1.36		1
$(\frac{dP}{dT})^E$		24.6		25.8		22		
ΔV		74		8.8		7.7		
$(\frac{dP}{dT})_V$	11		9.9		7.9		9.1	

For n = 7, the P-T phase diagram (Figure 3 a) exhibits a triple point K - P_A - P_B at 36.5°C under 300 bar that corresponds to the change of slope of the melting curve in Figure 2. Two virtual transitions K - P_B and P_B - P_A can be deduced by extrapolation under atmospheric pressure. The P_B - P_A transition corresponds with a monotropic transition. For both transformations the enthalpy changes can be calculated from the relations of entropy and enthalpy changes conservation :

$$\Delta S^{K-P_A} = \Delta S^{K-P_B} + \Delta S^{P_B-P_A}$$

$$\Delta H^{K-P_A} = \Delta H^{K-P_B} + \Delta H^{P_B-P_A}$$

The volume changes are calculated (Table) from the Clapeyron's relation :

$$\frac{dP}{dT} = \frac{\Delta H}{T.\Delta V} .$$

CONCLUSION

Thermo-barometric measurements have been performed on four members (n = 7,9, 10 and 11) of the hexaalkyloxytribenzocyclononene homologous series. The pressure-temperature phase diagrams have been determined. For n = 7, 9 and 10, a phase stable at lower temperature that P_A is observed ; it seems it is a P_B phase. For n = 7, that P_B phase is monotropic under atmospheric pressure ; a virtual transition between the crystalline and P_B phase is detected under atmospheric pressure ; the enthalpy changes for both K - P_B and P_A - P_B transitions are determined. For all the transformations when the enthalpy changes are known, the volume changes are given.

Note

The scanning numerical metabolemeter is now manufactured and distributed under the reference MAB 02 by Micro Technique Métropole LEADER, Moulin 1, 2 Rue de la Créativité
59650 Villeneuve d'Ascq - FRANCE.

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