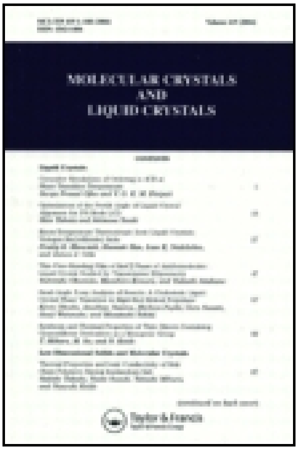

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Calorimetric Study of NPOB

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Calorimetric Study of NPOB

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In the case of NPOB two solid modifications, stable and metastable, were found. Thermodynamic parameters were determined for the solid–smectic A, smectic A–nematic and nematic–isotropic liquid phase transitions. The nature of these transitions is analyzed. Special attention was paid to the kinetics of the metastable-to-stable phase transition.

1 INTRODUCTION

The investigated 4-nitrophenyl 4′-octyloxybenzoate (NPOB) (Figure 1) is a liquid-crystalline compound with two mesomorphic phases: the smectic S_A phase and the nematic phase. The transition temperatures obtained by scanning calorimetry[1] are as follows:

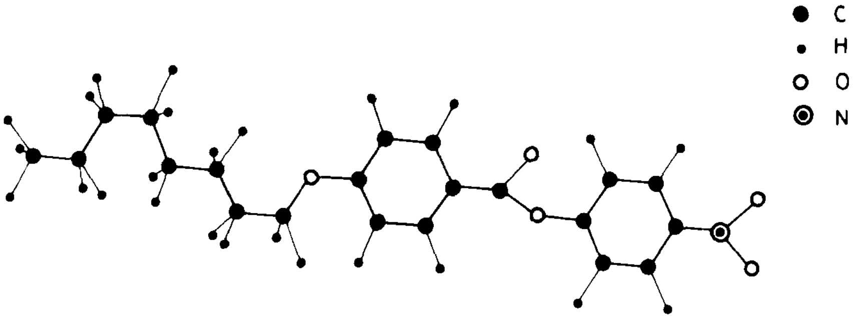

FIGURE 1 NPOB molecule structure.

Solid K → Smectic S_A → Nematic N → Isotropic I
T[K]: 323.6 ± 0.2 334.6 ± 0.2 341.3 ± 0.2

An adiabatic calorimetric measurement of NPOB has been undertaken in order to find the thermodynamic parameters and to recognize the nature of the phase transitions, and to investigate possible near-transitional effects specific of liquid crystals. Moreover, it was interesting to know if the solid phase of NPOB features two modifications as in the case of MBBA[2] and HOAB (4,4′-di-heptyloxyazoxybenzene)[3]—previously examined in our laboratory.

The NPOB sample for our investigation was synthesized in the Chemical Department of the Martin-Luther University in Halle (GDR) and used without further purification.

2 CALORIMETRIC INVESTIGATIONS

2.1 Experimental

Specific heat c_s mesurements for NPOB were made in the 100 K–356 K range by means of the adiabatic calorimeter described in detail in [4]. The mass of the sample was 52.06 g (i.e. 0.1402 mole).

All series of measurements were performed while the sample was heated: eight series in the temperature range over 298 K and four series for each stable and metastable solid phase. The reproducibility of the results obtained in different c_s measurement series was excellent: the average scattering of experimental points at low temperatures was about 1.3% and increased to about 1.7% at the higher temperatures.

2.2 Results and discussion

2.2.1 Phase situation. Figure 2 shows the temperature dependence of the specific heat of NPOB. Three phase transitions at the following temperatures are evident:

$$T_{K-S_A} = (323.70 \pm 0.03)\ \mathrm{K}$$
$$T_{S_A-N} = (334.9 \pm 0.3)\ \mathrm{K}$$
$$T_{N-I} = (341.2 \pm 0.5)\ \mathrm{K}$$

These values do not differ much from these of a DSC method (Table II).

The most interesting outcome of the present calorimetric study is the discovery of two solid phases with different thermodynamic properties, viz., a stable phase (lower curve) and a metastable phase (upper curve). The metastable phase was obtained always when the sample was rather quickly cooled (with mean rate about 2.5 K/min) from the isotropic phase to about 100 K. At

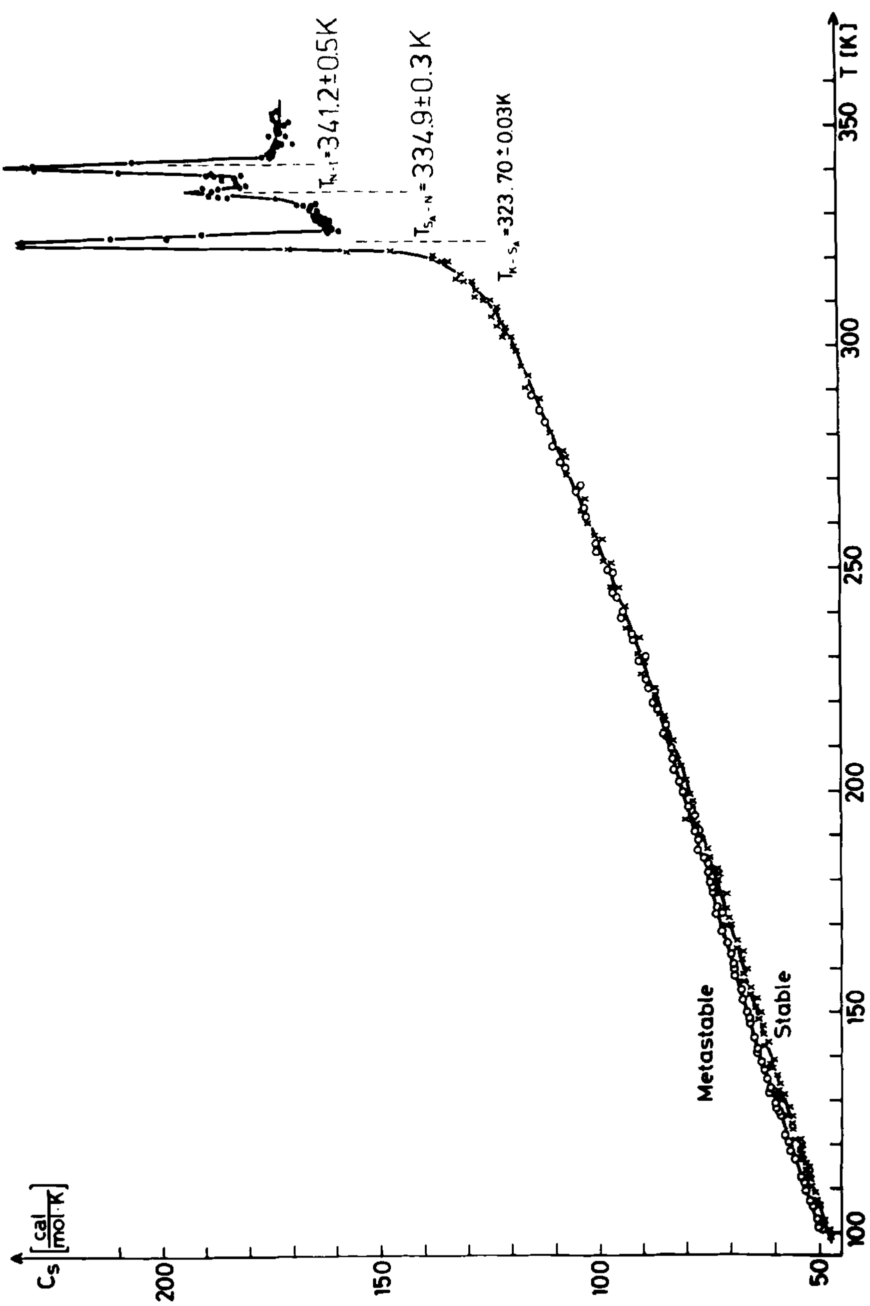

FIGURE 2 The specific heat of NPOB vs temperature.

cooling temperature the sample was kept several hours. The c_s measurement series were performed while the sample was heated. Both phases stable and metastable have the same values of the specific heat over 200 K up to about room temperature when the metastable modification transforms irreversibly and spontaneously by an exothermal process to the stable modification. The increase of sample temperature was about 1.96 K, which gives an enthalpy change between the metastable and stable phases of about 229 ± 6 cal/mole.

Typically for liquid crystals the transition from the metastable to the stable phase is the relaxation phenomenon depending on the thermal history of the sample, i.e. on the cooling rate, on the size of the sample[5,6] on the cooling temperature and on the time the sample is maintained at this temperature. Some of the observed results of this experiment are presented in Table I. It is clear that the total time of the transition depends strongly on cooling temperature and rather weakly on the time the sample is kept at this temperature. Moreover, it has been established that the metastable-to-stable phase transition can occur also at a temperature below 295.14 K. In such cases the rate of the transition is much smaller: at a temperature of 290.85 K this rate (after 30 min) is about seven times smaller.

2.2.2 Thermodynamic parameters To recognize the nature of the transitions between respective phases of NPOB a plot of the calorimeter-sample system temperature against the total amount of heat supplied was taken into consideration (see Figure 3). A detailed description of the procedure to analyze the data is presented in Ref. 4.

A glance at the c_s vs T and T vs ΣQ curves makes it clear that: 1) the K $-$ S_A transition is distinctly of the first order with an infinite specific heat value and with a distinct pre-transitional effect; a similar effect observed for HOAB[3] was explained on the basis of the results of Ref. 7 as being due to the occurrence of nuclei of the new phase already in the solid, 2) the N $-$ I transition also seems

TABLE I

The time of the metastable-to-stable phase transition (at 295.14 K) as a function of the thermal history of the sample

Cooling temperature [K]	105		150	
Time sample was maintained at the cooling temperature, [h]	23	1	23	1
Time of the transition	5 h 20 min	6 h 10 min	8 h 20 min	8 h 40 min

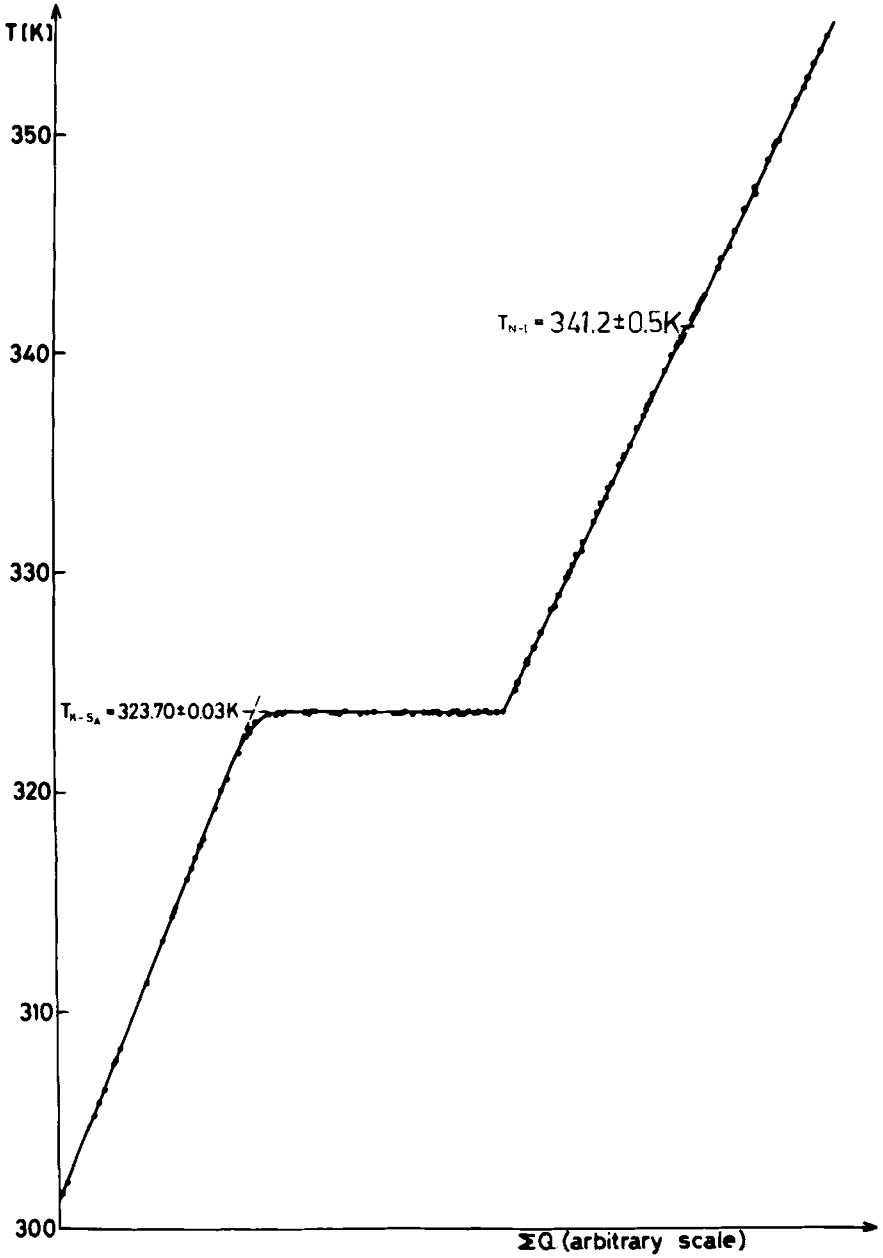

FIGURE 3 T vs ΣQ dependence for NPOB in the phase transitions region.

to be of the first order but with a much smaller thermal effect than melting; this shows up as a distinct plateau at the transition temperature T_{N-I} which is however, much shorter than for melting (Figure 3).

For both these transitions the enthalpy change ΔH was estimated as the length of the corresponding plateau. ΔS was calculated as $\Delta H/T$. The error in ΔH is associated with some arbitrariness in estimating the length of the plateau. The thermodynamic parameters are collected in Table II.

Some difficulties arise when identifying the $S_A - N$ transition in the same way. At the temperature T_{S_A-N} no inflection point of the T vs ΣQ curve was observed because the thermal effect connected with the transition was very small. Basing on existing theories[8,9] the nature of the $S_A - N$ transition may be said to be of the first order because the ration T_{S_A-N}/T_{N-I} is equal to 0.98 (this is higher than the limiting value of 0.7 corresponding to the transition of the second order). For this transition ΔH and ΔS were estimated by integrating c_s vs T and c_s/T vs T curves, respectively (Table II). In both cases the deviations of the experimental points from the "mean curve" constituted a measure of the error.

2.2.3 Comparison of the results presented in this work and in [*1*], [*5*], [*6*] The investigations[5,6] of the phase situation of NPOB also gave the evidence of more than one solid modification in that compound. The cooling rate used in [5] (about 15 degree/min) was very much different from that used in this work. This fact seems to be related to different stability of the metastable phase obtained in this work and in [5]. And so in results presented here during measurements the metastable phase existed in all temperature regions (from liquid nitrogen temperature to about room temperature) (about 60 hours) and started to transform to the stable phase at about +17.7°C. On the other hand in [5] we find that for example at −4°C the existence time of metastable phase is 1 h. In [5] the transition from the metastable to stable phase was observed at −2°C which was lower by 19.7°C from our results here. The heat of transition from metastable to stable modification calculated in [5] is 0.45 kcal/mole.

TABLE II

The thermodynamic parameters of phase transitions in NPOB

$K - S_A$	$S_A - N$	$N - I$
$T = 323.70 \pm 0.03$ K 323.6 ± 0.2 K[a]	$T = 334.9 \pm 0.3$ K 334.6 ± 0.2[a]	$T = 341.2 \pm 0.5$ K 341.3 ± 0.2[a]
$\Delta H = 8228 \pm 72$ cal/mol 7600[a]	$\Delta H = 51 \pm 12$ cal/mol 50[a]	$\Delta H = 107 \pm 36$ cal/mol 130[a]
$\Delta S = 25.42 \pm 0.22$ cal/mol K	$\Delta S = 0.14 \pm 0.03$ cal/mol K	$\Delta S = 0.31 \pm 0.10$ cal/mol K

[a] Scanning calorimetric results[1]

Thus the heat is about 2 times larger than that estimated in our work. On the other hand we should add that we have compared ΔH values for various temperatures of transition. There also is no correspondence between our observations and [5] where the cooling rate lower than 5 degree/min. (which corresponds to the rate used in this work) results in a very unstable mixture of the metastable and stable phases, transforming rapidly to the stable phase.

We should also add that results presented in [5], [6] obtained with use of the same technique are incoherent. In [6] for example, the phase transition from metastable to stable phase was observed at temperatures 227, 246, 266 K. In [6] the cooling rate was 500 degree/min., which was very different from those used in our work and in [5]. At such cooling rate the evidence of several metastable phases was probably discovered. The transition from one to the second and from the second to the third can take place at 227, 246, 266 K. It seems that in investigations presented here various numbers of metastable phases were observed: one in [5] and in this work and three in [6]. Although our comparison was made for various temperatures of the transition, we may presume that the metastable phases observed in [5] and in this work probably were various phases, because they differ from one another by the value of liberated heat.

3 CONCLUSIONS

This paper presents the results of calorimetric measurements for NPOB

1) In the specific heat c_s vs temperature curve there are three anomalies associated with the following phase transitions: melting (at 323.7 K), the $S_A - N$ transition (at 334.9 K) and the $N - I$ transition (at 341.2 K).

2) Two solid phases—stable and metastable—featuring different thermodynamical properties have been detected. The metastable phase transforms spontaneously at about room temperature into the stable one.

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