Vol. A55 (1979) ACTA PHYSICA POLONICA No 1

AN ADIABATIC CALORIMETRIC STUDY OF PHASE SITUATION IN HOAB (4,4′-di-n-HEPTYLOXYAZOXYBENZENE)*, **

By M. Rachwalska

Institute of Chemistry of the Jagellonian University, Cracow**

and Nguyen Xuan Phuc

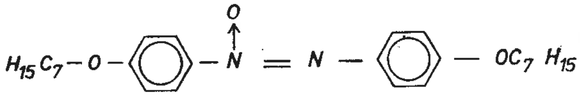
Institute of Physics of the Jagellonian University, Cracow***

(Received February 1, 1978; final version received April 21, 1978)

The results of specific heat measurements of 4–4′-di-heptyloxyazoxybenzene in the temperature range from approximately 90 K to 420 K are presented. Measurements were carried out by means of an adiabatic calorimeter. Three anomalies were observed on the specific heat vs temperature curve. They were identified as being due to melting, the smectic *C*-nematic transition and the nematic-isotropic liquid transition. Two modifications of the solid were found to exist: a stable one and a metastable one. In the temperature range comprizing the nematic phase no cybotactic anomaly was in evidence. In the melting region of the solid phase a distinct pre-melting effect was found to appear. On the basis of Landau's theory the coefficient of nematic order was estimated, use being made of the specific heat vs temperature relationship. Changes in enthalpy and entropy were estimated for all of the phase transitions.

1. *Introduction*

The substance chosen for this study was 4,4′-di-heptyloxyazoxybenzene (HOAB) having the chemical formula



---

* Presented at the Second Liquid Crystal Conference of Socialist Countries, Sunny Beach, Bulgaria, September 27–30, 1977.

** This work was partially supported by American-Polish M. Curie-Skłodowska Found under Grant No INT-76-01318.

*** Address: Instytut Chemii UJ, Krupnicza 41, 30-060 Kraków, Poland.

**** Address: Instytut Fizyki UJ, Reymonta 4, 30-059 Kraków, Poland.

One of the goals of this study was to examine the modifications of the solid phase resulting from different cooling rates. Similar studies were previously made for another liquid-crystalline substance, namely, MBBA [1]. Moreover, since HOAB in the low-temperature range of the nematic phase is known [2,3] as exhibiting cybotactic smectic structure, precise calorimetric experiments may either support or refute the hypothesis suggesting the existence of cybotactic nematic phase as a separate thermodynamical phase [4]. Finally, it is very important to recognize as well as possible the character of the various phase transitions and to analyze any possible pre-transitional effects.

Up to now, specific heat measurements for this substance have been made by Arnold [5], whose only heat treatment of the sample was heating it from 323 K to 433 K.

Some preliminary results of the present calorimetric investigations have been presented in Ref. [6].

2. *Results of measurements*

Specific heat measurements for HOAB were made in the 92.5 to 419.5 K range by means of the adiabatic calorimeter described in detail in Ref. [7]. The mass of the substance was 50.76 g i. e. 0.1191 mole. The specific heat measurements were preceded by a calibration procedure of the calorimetric vessel of mass 213.94 g. The mean scattering of experimental points for the calibration curve was approximately 0.3 per cent at low temperatures, rising to approximately 0.6 per cent at temperatures exceeding room temperature.

Figure 1 shows the temperature dependence of the specific heat of HOAB. Three phase transitions are evident at the points: $T_{K-S_C} = 347.75 \pm 0.05$ K, $T_{S_C-N} = 368.2 \pm 0.30$ K, $T_{N-I} = 397.25 \pm 0.05$ K. The reproducibility of the results obtained in different measurement series was excellent. The measurements consisted of five series for the stable solid phase, two series for the metastable solid phase, eight for the smectic C phase, eight for the nematic phase and seven series for the isotropic phase.

3. *Method of analyzing the results*

In order to be able to determine accurately the phase transitions temperatures in HOAB plots of a calorimeter-sample system temperature against the total amount of heat supplied were made (Figs 2a, b, c). The phase transition temperatures were read at the inflexion points of these curves.

Near the phase transition temperatures in the T vs $\sum Q$ curves (Figs 2a, b, c) the experimental points deviate from the straight lines led through points lying far from the inflextion points. This is evidence of some effects accompanying phase transitions. Distinct pre-transitional effects are seen to occur before melting and at the nematic isotropic transition. For the remaining transitions, i. e. S_C-K, S_C-N, $N-S_C$ and $I-N$ these effects are weaker. Apart from these near-transitional effects, however, the T vs $\sum Q$ curves reveal the existence of an isothermal part for the $K-S_C$ and $N-I$ transitions (as segments parallel to the $\sum Q$ axis).

Taking into account the fact that near-transitional effects occur, the changes in enthalpy and entropy at the phase transitions were determined as follows:

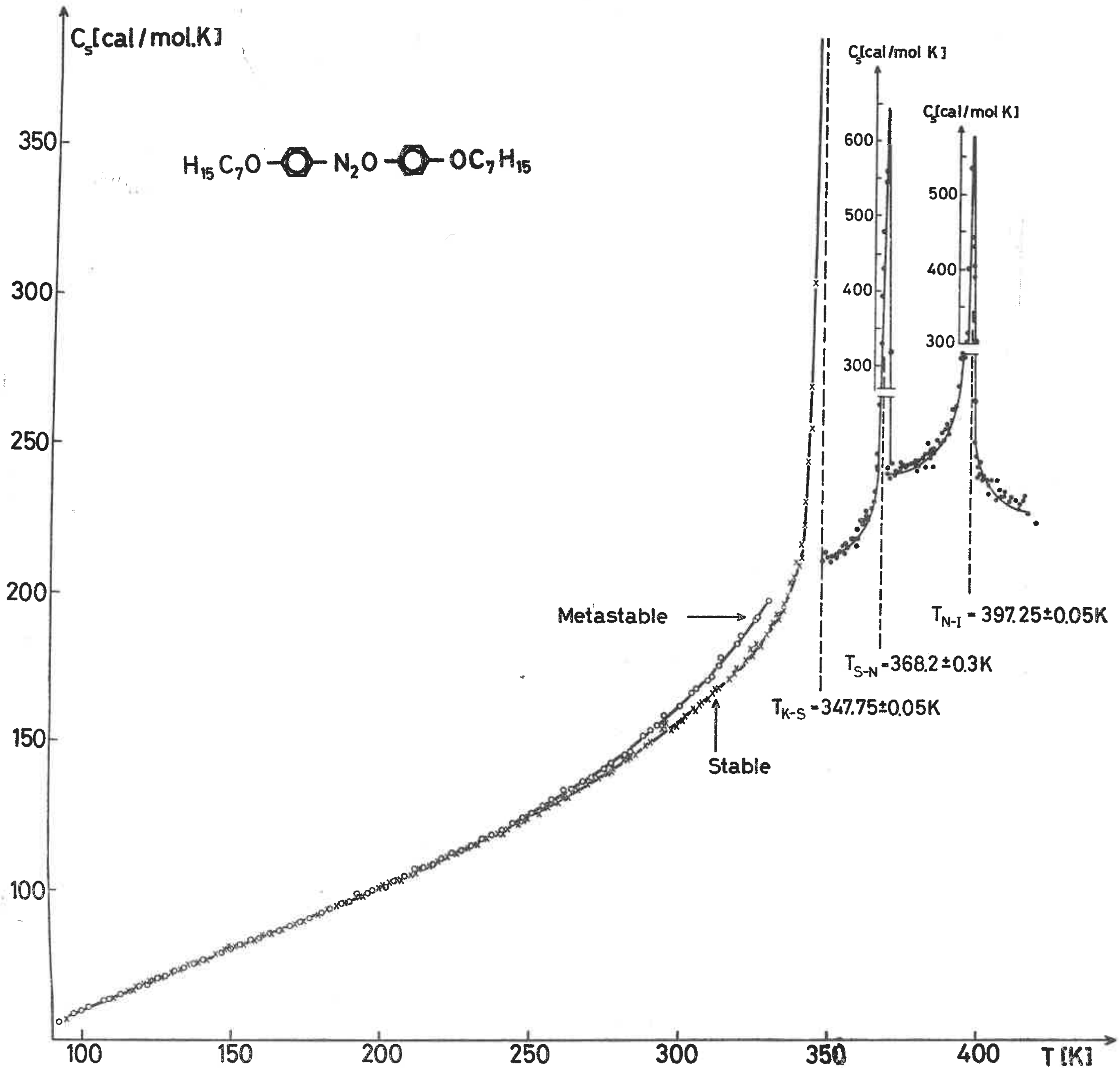


Fig. 1. Specific heat vs temperature for HOAB

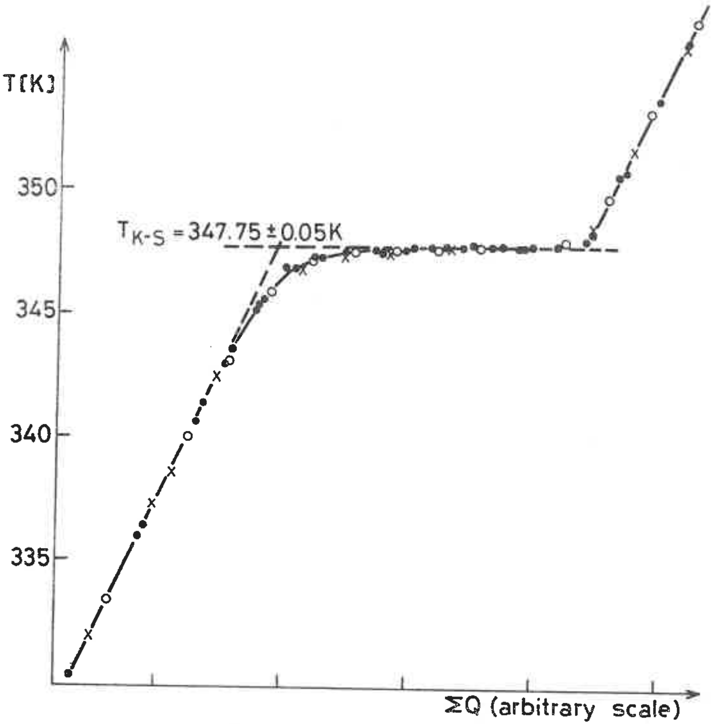


Fig. 2a. T vs $\sum Q$ for K—S_C phase transition in HOAB

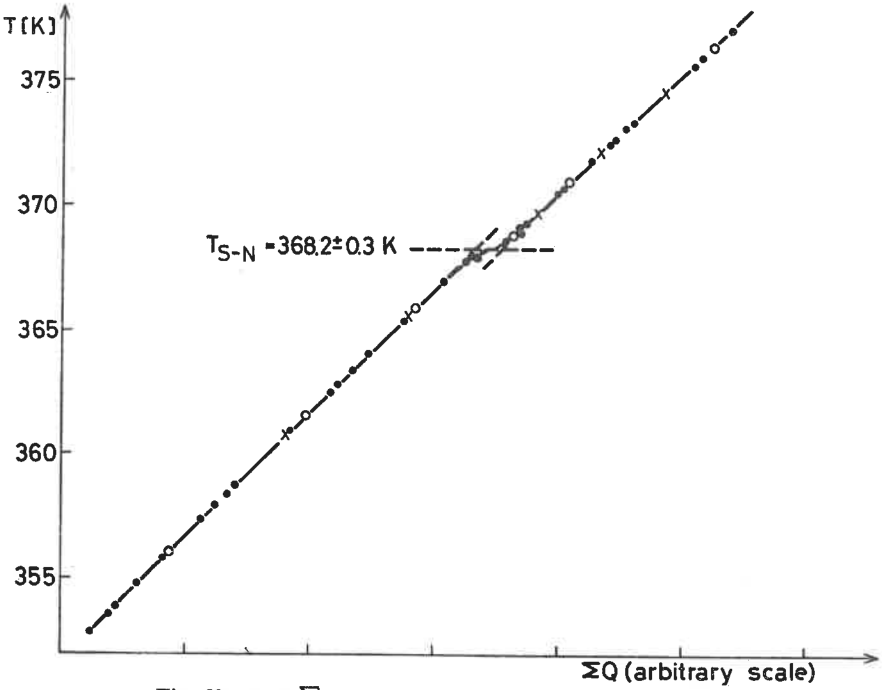


Fig. 2b. T vs $\sum Q$ for S_C—N phase transition in HOAB

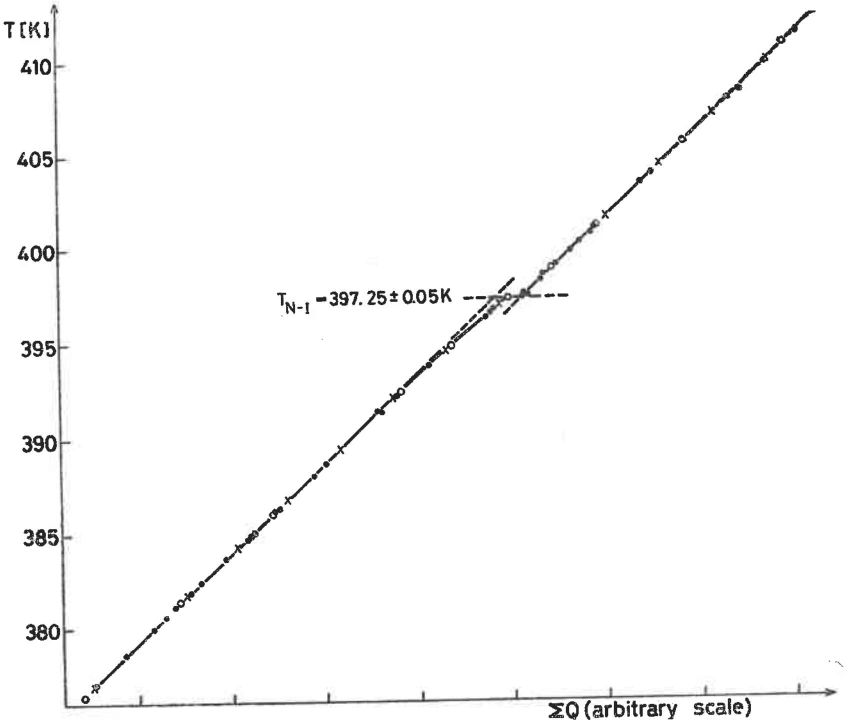


Fig. 2c. T vs $\sum Q$ for N–I phase transition in HOAB

In the T vs $\sum Q$ plots the experimental curves were extrapolated to the phase transition temperatures in order to estimate the so-called isothermal part ($\Delta Q_{\text{isothermal}}$) of the total transition heat. Using various possible ways of carrying out the extrapolation yielded the error $\Delta Q_{\text{isothermal}}$.

In the phase transition regions outlined in Fig. 2 by the dashed line the contributions to ΔH and ΔS associated with the pre, and post-transitional effects were calculated by integrating C_s over T in the case of ΔH and C_s/T over T in the case of ΔS.

4. *Discussion*

This Section deals with the matter of the existence of the metastable and stable phases in solid HOAB (Subsection 4.1), an analysis of the nature of the various phase transitions in HOAB (4.2), the problem of the smectic cybotactic structure in HOAB's nematic phase (4.3) and a comparison of the results of this study with those obtained earlier by Arnold (4.4).

4.1. Characteristics of the two solid state phases: stable and metastable

The most interesting outcome of this study is the discovery of two phases of the solid state featuring different thermodynamical properties. The lower curve in Fig. 1 corresponds to the stable modification and the upper curve to the metastable one. The metastable modification goes irreversibly and spontaneously by an exothermal process to the stable modification.

The metastable and stable phases have the same specific heat in the temperature range from 92.5 to 235 K. Beginning with 235 K the curves distinctly start to spread apart, the separation being much greater than the mean error of the experimental points. Attempts to melt the metastable phase were unsuccessful. Its specific heat curve terminates at 330 K. The stable phase melts at 347.75 K, as had already been mentioned.

The metastable phase was obtained during relatively quick cooling from the isotropic phase to liquid nitrogen temperature. The mean cooling rate was about 2.5 K/min. The transition of the metastable form to the stable one occurred at about 340 K and exhibited itself as a rise in the temperature of the calorimetric vessel. This transition proceeded in two evident stages: one at about 335 K and the other at 343 K. After their conclusion the stable phase was obtained. Hence, one cannot exclude the existence of yet another metastable intermediate phase (not marked in Fig. 1), the specific heat values of which are between the curves for the metastable and stable phases.

The total time of transition from the metastable to stable phase (including both stages) exceeded 10 hours. It has been shown that time may be considerably decreased by applying "thermal pulses", e. g. a one-minute period of heating, then 30 minutes of temperature stabilization, repeated over and over.

4.2. Analysis of the character of phase transitions in HOAB

A glance at the C_s vs T and T vs $\sum Q$ curves makes it clear that a much greater thermal effect is associated with melting than with the other phase transitions. It also becomes evident that the melting, with very high specific heat values (5×10^5 cal/mole K) and distinct hysteresis (determined by DSC and dielectric measurements [8, 6], is a transition of the first order according to Ehrenfest's classification and a transition of the 2I type inMcCullough's classification [9].

As is seen in Fig. 2b, the $S_C - N$ transition features a heat of transition much smaller than the heat of melting. Fig. 2b does show a distinct plateau which makes this transition classifiable as one of the first order. On the other hand, a look at the shape of the C_s vs T curve would give preference to classifying this transition as of the 2N type (according to McCullough's rules).

Similar conclusions may be also drawn for the N$-$I transition, except that from the point of view of McCullough's classification it rather resembles a 3N type transition.

It may, perhaps, be controversial to take the isothermal part of the $S_C - N$ transition into account. The existing theories [10, 11] do not designate the type of the $S_C - N$ transition. In theory, the $S_C - S_A$ transition is of the second order, whereas the nature of the $S_A - N$ transition may be defined when the ratio

$$\frac{T_{S_A-N}}{T_{N-I}}$$

is known, where T_{S_A-N} and T_{N-I} are the temperatures of the $S_A - N$ and $N - I$ transitions. If this ratio is smaller or equal to 0.7, then $S_A - N$ is a transition of the second order. Basing on these facts, it is not excluded that also our $S_C - N$ transition in HOAB is of the second order; if so our method of segregrating the isothermal part would be incrorrect.

4.2.1. Determination of the nematic order parameter η

The N–I and S–N phase transitions seem to reflect the change in the order parameter η [10]. A comparison of the ΔS values (Table I) for the S_C–N and N–I transitions shows, in qualitative terms, that the order parameter undergoes a smaller change at the S_C–N transition than at the N–I transition. This conforms with the change of order parameter η determined in other measurements, which give for the S_C–N transition 0.31 and for the N–I transition 0.34 [12, 13].

Calculations of the change in the parameter η with temperature for the nematic phase on the basis of our calorimetric C_S data were made with the help of the assumptions of the thermodynamical theory of phase transitions developed by Landau [14]. According to this theory, in the phase transition region the thermodynamical potential can be expanded into a series,

$$G(p, T, \eta(p, T)) = G_0+\alpha\eta+\tfrac{1}{2}A\eta^2-\tfrac{1}{3}B\eta^3+\tfrac{1}{4}C\eta^4+\dots \tag{1}$$

It can be shown [14] if states with $\eta = 0$ and $\eta \neq 0$ differ in symmetry, as assumed here, then $\alpha = 0$. If a phase transition is considered at a fixed of pressure, then in a near enough vicinity of the transition point it may be assumed that

$$A = a(T-T^*), \tag{2}$$

where a is a constant parameter, T^* is a temperature equal to or slightly lower than the phase transition temperature. The thermodynamical potential then takes the form

$$G(T, \eta(T)) = G_0+\tfrac{1}{2}a(T-T^*)\eta^2-\tfrac{1}{3}B\eta^3+\tfrac{1}{4}C\eta^4. \tag{3}$$

The expansion coefficients a, B, C and T^* take on constant values. Making use of the thermodynamical relations yields an expression for the specific heat surplus over the normal run in the vicinity of the phase transition temperature. Furthermore, using Eq. (1) and the equation for η (acquired from (1) and from the condition of thermodynamical potential G minimalization) we obtain

$$\frac{C_p}{T} = [a(T-T^*)-2B\eta+3C\eta^2]\,\frac{a^2}{B^2-4aC(T-T^*)}. \tag{4}$$

In order to be able to determine η as a function of temperature for HOAB according to the equation

$$\eta = \frac{B+\sqrt{B^2-4aC(T-T^*)}}{2C} \tag{5}$$

the four expansion coefficients of Eq. (1), a, B, C, and T^*, must be found. For this purpose the three relations acquired from the condition of equality of the thermodynamical potential of the two phases at $T_k = T_{\mathrm{N-I}}$ are used, viz.

$$T_k-T^* = 2B^2/9aC, \tag{6}$$

$$\eta_k = \tfrac{2}{3}\,B/C, \tag{7}$$

$$\Delta S = \tfrac{1}{4}\,a. \tag{8}$$

Here, η_k is the change in the order parameter at temperature T_k. The latter was obtained from (1) and the expression $S = -(\partial G/\partial T)_p$ via $S = -\frac{1}{2}a\eta^2$, assuming that the parameter η varies from 0.7 at temperature T_{S_C-N} to zero. Experimental values were put in the formulae for $T_k = T_{N-I}$ and ΔS. Expressing parameters B and C as functions of η_k and T^* and then in Eq. (5) η also as a function of η_k and T^* alters Eq. (4) to the form

$$\frac{C_p}{T} = \left[4\Delta S(T-T^*) - 6\Delta S(T_k-T^*)\left(3+\sqrt{9-8\frac{T-T^*}{T_k-T^*}}\right)\right.$$

$$\left.+\tfrac{3}{2}\,\Delta S(T_k-T^*)\left(3+\sqrt{9-8\,\frac{T-T^*}{T_k-T^*}}\right)^2\right]\frac{\eta_k^2}{9(T_k-T^*)^2-8(T_k-T^*)\,(T-T^*)}\,. \qquad (9)$$

The least squares method was used for choosing the best parameters T^* and η_k, i. e. those for which the fit of the theoretical C_p/T curve to the experimental curve was closest.

Knowledge of T^*, η_k, and ΔS and T_k unambiguously defines the parameters a, B and C. Subsequently $\eta = \eta(T)$ values were calculated from Eq. (5), the results being depicted in Fig. 3. This figure also carries the results of other studies [12, 13]. It is seen here that

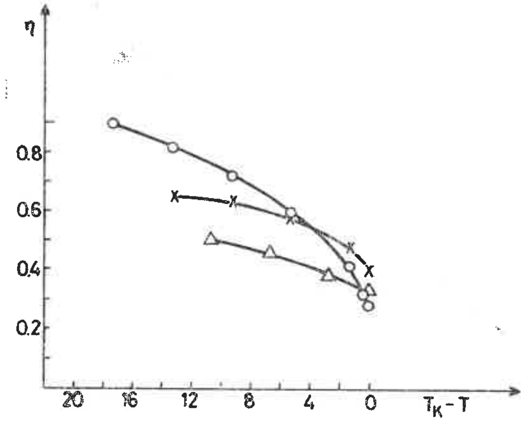


Fig. 3. η vs $T_{k_i}-T$, T_{k_i} being the clearing temperature for HOAB determined by the NMR (T_{k_1}) [12] and IR(T_{k_2}) [13] methods, and in this study (T_{k_3}); ○ — our results, × — IR results, Δ — NMR results

the changes in η at T_k are consistent in the three methods. It is also evident, however, that our values are greater than those obtained by other techniques for the nematic phase, especially in the temperature range far from the clearing point. This can be associated with the invalidity of the Landau theory in temperatures ranges far from T_k, as had already been observed in [15]. Moreover, in the temperature region near T_k there was also obtained a large discrepancy between the theoretical C_p/T curve and the experimental curve, which seems to suggest a limited validity for the Landau theory to the N−I transition for HOAB.

4.2.2. Determination of the amount of liquid clusters in the solid substance

Special notice should be given to the shape of the melting peak which features distinct pretransitional effect from the low temperature side, in a range of several Kelvins. At present, there are two points of view which explain this phenomenon:

a. the pre-transitional effect mentioned earlier is due to the presence of impurities in the substance, and

b. the effect is caused by the occurrence of nuclei of the new phase already in the solid and which becomes fully developed when the substance melts [16, 17].

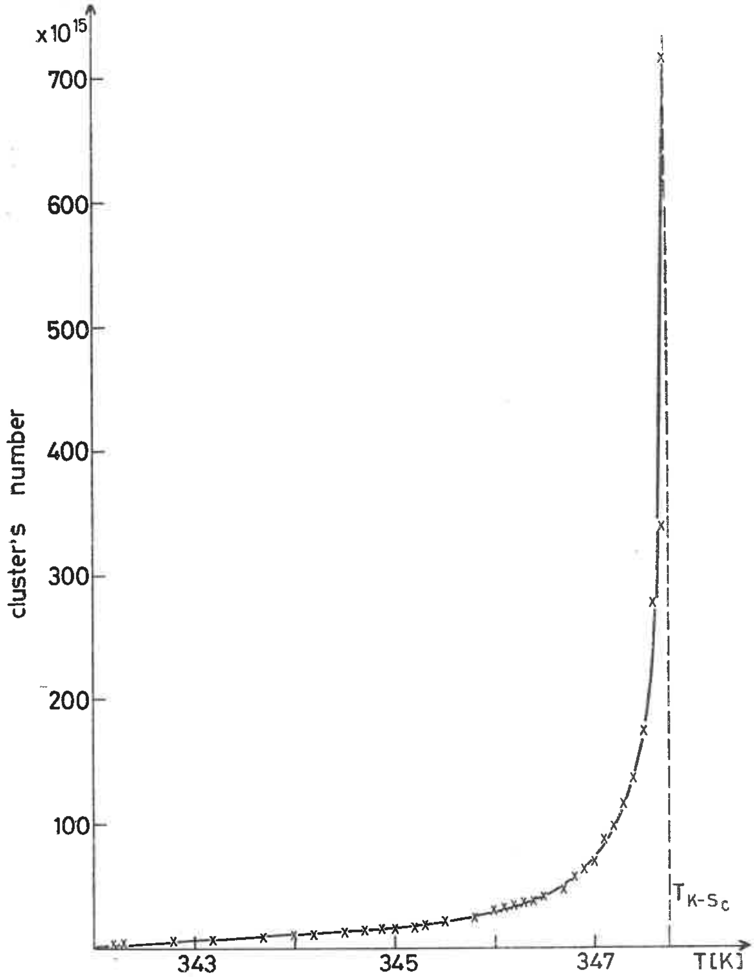


Fig. 4. Temperature dependence of the number of liquid-crystalline clusters in the premelting region

Assuming that the pre-transitional effect observed at melting is associated only with the presence of impurities in the sample, their content was assessed by Stone's method [9] to be 0.35%. On the other hand, a similar estimate for the other phase transition gave impurity contents of 0.07% (S_C-N) and 0.03% ($N-I$). Owing to the large scatter of these values and the very improbable value of 0.35% (the sample was a spectropically pure sample manufactured by Merck), we rather tend to suppose that the pre-transitional effect is primarily caused by the mechanism stated in b.

By calculating the fraction of the melted substance at successive temperatures within the range from 342.0 K (at which a distinct bend is seen to appear in the T vs $\sum Q$ plot of Fig. 2a) to 347.75 K, the number of liquid-crystalline clusters which occur at temperatures just below the melting point could be estimated. The ratio of segments, parallel to the $\sum Q$ axis, to the segment, parallel to the ordinate axis, at the melting point T_{melt}, gives the melted substance fractions at various temperatures. Knowing the total mass of the sample, 0.1191 mol, and assuming the number of molecules in a liquid-crystalline cluster as of the order of 10^5 [18] allowed the number of liquid-crystalline clusters to be found as a function of temperature (Fig. 4). It is seen in this figure that very near to T_{melt} (approximately 3 K below T_{melt}) the fraction of liquid-crystalline clusters was only approximately 1%. This is in agreement with the value estimated for various liquid-crystalline substances by the nuclear magnetic resonance method [16], .i e. 2.5% at a temperature approximately 3 K below the melting point T_{melt}. At temperatures only 0.05 K below the melting point T_{melt} clusters constitute about 50% of the whole sample mass, after which it grows jumpwise to 100% for T_{melt}.

4.3. Cybotactic smectic structure in calorimetric investigations

In both: the dielectric measurements made at radio frequencies for the same HOAB sample [6] and the diffusion coefficient measurements [3] a quite clear jumpwise change of these physical quantities at a certain temperature in the nematic phase was seen. This anomaly could have been associated with the cabotactic nematic phase-to-classical nematic phase transition. However, in the specific heat vs temperature curve no anomaly was obtained in the nematic phase region, which is evidence that we are not dealing here with different thermodynamical phases.

4.4. Comparison of results of this study with Arnold's

We can compare our results for HOAB with the calorimetric results of Arnold [5] for the same substance. This comparison is depicted in Table I. Our values of specific heat (approximately 400 experimental points) are much more accurate than Arnold's corresponding ones (approximately 50 experimental points). It should also be emphasized that our calorimetric measurements were made in the 92.5–419.5 K temperature range, whereas his only in the 323–433 K range. Taking into account the difference in measurement accuracy, our specific heat values conform rather well to the corresponding values of Arnold. There is no mention of the solid's polymorphism in his work.

The phase transition temperatures for HOAB agree with the corresponding values quoted by Arnold. He does not give entropy changes for the various phase transitions among the quoted thermodynamical parameters. It is difficult to compare our thermodynamical parameters with Arnold's because he does not give error values which should be taken into account. The values of enthalpy changes at the melting point (ΔH_{K-S_C}) agree

TABLE I

Temperatures, enthalpies and entropies of phase transitions in HOAB

Temperatures [K]	ΔH total [cal/mole]	Enthalpies		Entropies		ΔS near-transit. [cal/mole · K]
		ΔH isothermal [cal/mole]	ΔH near-transit. [cal/mole]	ΔS total [cal/mole · K]	ΔS isothermal [cal/mole · K]	
$T_{C-S_C} = 347.75$ ± 0.05 $T^*_{C-S_C} = 347.55$	9860 ± 830 9780*	6560 ± 475	3300 ± 355	30.3 ± 4.63	18.86 ± 1.37	11.44 ± 3.26
$T_{S_C-N} = 368.2$ ± 0.3 $T^*_{S_C-N} = 368.55$	650 ± 150 380*	130 ± 50	520 ± 100	1.68 ± 0.45	0.36 ± 0.14	1.32 ± 0.30
$T_{N-I} = 397.25$ ± 0.05 $T^*_{N-I} = 397.35$	770 ± 100 243.3 (451.1)*	198 ± 30	572 ± 70	2.1 ± 0.3	0.49 ± 0.009	1.57 ± 0.21

* Arnold's results.

quite well. The discrepancy in the values of enthalpy of the S_C-N and $N-I$ transitions presumably stems from our use of different methods of calculating this quantity. Calculations made now were based on the procedure described in the preceding section, which takes the isothermality contribution into account. On the other hand, in his paper, Arnold did not consider this contribution at all, which is equivalent to assuming that the transition is not of the first order. It seems that this kind of assumption is incorrect, for the $N-I$ transition at least, since it is seen in Fig. 2c that the T vs $\sum Q$ curve for this transition has a distinctly isothermal character. Apart from this, the way in which the "background" was determined when calculating the other terms of Eq. (1) seems to be arbitrary and rather unjustified in Arnold's paper.

5. *Conclusions*

This paper presents the results of calorimetric measurements for HOAB.

a. In the specific heat vs temperature curve there are three anomalies. They are associated with the phase transitions: melting at 347.75 K, the S_C-N transition at 368.2 K and the $N-I$ transition at 397.25 K.

b. Two phases for the solid state—stable and metastable — having different thermodynamical properties were detected.

c. The stable phase melts at 347.75 K, whereas attempts to melt the metastable phase were unsuccessful. Its specific heat curve ends at 330 K.

d. At about 335 K the metastable phase spontaneously transforms into the stable phase. The second stage of this transformation takes place at approx. 343 K.

e. The distinct pre-transition effect at melting was explained as being due to the occurrence of the new phase's nuclei already in the solid; this new phase becomes developed fully once the substance is melted.

f. The shape of the peak associated with the N – I transition was analyzed and on the basis of Landau's theory; the temperature dependence of the order parameter η was found to agree fairly well with the results of other methods.

g. In the nematic phase region no cybotactic anomaly was obtained, which proves that we are not dealing here with various thermodynamic phases.

We wish to thank Professor J. A. Janik and Doc. J. M. Janik for their interest and many helpful discussions. We also thank Mr. R. Zach for his help in specific heat measurements.

REFERENCES

[1] J. Mayer, T. Waluga, J. A. Janik, *Phys. Lett.* **41A**, 102 (1972).
[2] F. Rondelez, *Solid State Commun.* **11**, 1675 (1972).
[3] J. A. Murphy, J. W. Doane, *Liq. Cryst. Orded Fluids* **2**, 63 (1974).
[4] A. De Vries, *Proc. Int. Conf. Liq. Cryst.*, Bangalore 1973.
[5] H. Arnold, *Z. Phys. Chem.* **226**, 146 (1964).
[6] J. Mościcki, X. P. Nguyen, S. Urban, S. Wróbel, M. Rachwalska, J. A. Janik, *Mol. Cryst. Liq. Cryst.* **40**, 177 (1977).
[7] J. Mayer, T. Waluga, Report No 750/PL, IFJ, Kraków 1971.
[8] X. P. Nguyen, *Thesis*, Institute of Physics of the Jagellonian University, Kraków 1977.
[9] *Physics and Chemistry of the Organic Solid State*, Editors: D. Fox, M. Labes, A. Weissberger, New York–London 1965.
[10] G. W. Smith, *Advances in Liquid Crystals*, G. H. Brown, edt., vol. 1, Academic Press, New York–San Francisco–London 1975.
[11] D. Johnson, D. Allender, R. de Haff, to be published.
[12] K. H. Weber, *Z. Naturforsch.* **14A**, 112 (1959).
[13] W. Maier, G. Englert, *Z. Phys. Chem.* **19**, 168 (1959).
[14] L. D. Landau, E. M. Lifshits, *Statisticheskaya fizika*, Izd. 2, Nauka, Moskva 1964.
[15] Y. Poggi, P. Atten, J. C. Filippini, *Mol. Cryst. Liq. Cryst.* **37**, 1 (1976).
[16] S. Limmer, *Thesis*, Karl Marx University, Section of Physics, Leipzig 1976.
[17] N. I. Afanasjeva, V. M. Burlakov, G. N. Shishin, *JETP Lett.* **23**, 506 (1976).
[18] G. W. Gray, *Molecular Structure and Properties of Liquid Crystals*, Academic Press 1962.