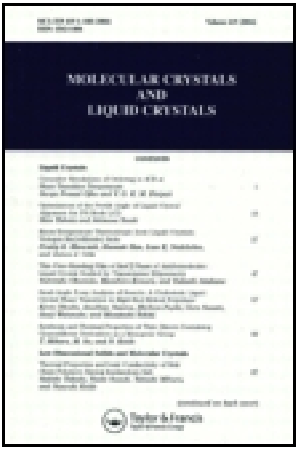

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Study of the Phase Situation in 4-n-pentylphenyl-4′-n-heptyloxythiobenzoate (7S5)

J. Chruściel [a], L. Richter [b] & M. Rachwalska [c]

[a] Institute of Chemistry, Agricultural and Pedagogical University, 3-go Maja 54, 08-110, Siedlice, Poland

[b] Martin-Luther Uniaversität, Sektion, Chemie, Múhlpforte 1, DDR-402, Halle

[c] Institute of Chemistry, Jagiellonian University, ul. M. Karasia 3, 30-060, Kraków, Poland

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Study of the Phase Situation in 4-n-pentylphenyl-4′-n-heptyloxythiobenzoate ($\bar{7}$S5)

J. CHRUŚCIEL
Institute of Chemistry, Agricultural and Pedagogical University, 3-go Maja 54, 08-110 Siedlce, Poland

and

L. RICHTER
Martin-Luther Universität, Sektion Chemie, Mühlpforte 1, DDR-402 Halle

and

M. RACHWALSKA
Institute of Chemistry, Jagiellonian University, ul. M. Karasia 3, 30-060 Kraków, Poland

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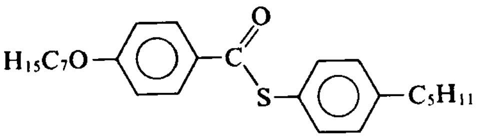
Results of measurements of the specific heat of 4-*n*-pentylphenyl-4′-*n*-heptyloxythiobenzoate in the temperature range from about 90 K to about 370 K are presented. They were carried out with an adiabatic calorimeter, a differential scanning calorimeter and a polarizing microscope. Adiabatic calorimetry revealed four anomalies in the specific heat vs. temperature curve viz., two associated with transitions in the solid phase, one with melting and one with the liquid-crystalline nematic-to-isotropic phase transition. Also, two modifications of the solid, stable and metastable, were found to exist. In addition, the DSC method applied in the 285 K to 370 K range revealed a smectic *C* phase, but only when the sample is being cooled. The polarizing microscope showed the structural polymorphism of the solid phase in the 297 K to 327 K range to be more complex than would stem from adiabatic calorimetry and DSC measurements alone. It also confirmed the occurence of the S_C phase on cooling as ascertained by the DSC method.

1 INTRODUCTION

The substance examined was 4-*n*-pentylphenyl-4′-*n*-heptyloxythiobenzoate ($\bar{7}$S5) of the chemical formula



In order to diagnose the phase situation of $\bar{7}$S5, specific heat measurements were carried out and values of enthalpy and entropy changes associated with the phase transitions were determined. Attempts were also made to acquire the smectic *C* phase revealed earlier by the DSC method and polarizing microscopy. The question of whether the solid phase exists as a single modification or as several also had to be answered. That the phase situation of the solid phase may be complicated was expected beforehand on the basis of calorimetric studies of other liquid-crystalline substances performed earlier. For instance MBBA[2] was found to have a stable and metastable phase. The latter phase after some thermal history of the sample, was melted. Experiments with some other liquid crystals, such as NPOB and HOAB, also achieved a metastable modification as well as the stable one,[3,4] but attempts to melt it were unsuccessful.

2 RESULTS OF MEASUREMENTS

The $\bar{7}$S5 used in the study was obtained by condensing heptyloxybenzoic acid chloride and penthylthiophenol.[5,6] The substance was recrystalized threefold from absolute ethyl alcohol.

Measurements of the phase situation of $\bar{7}$S5 were carried out by three techniques: DSC†, polarizing microscopy† an adiabatic calorimetry. The results obtained by the various methods will now be presented.

II.1. DSC MEASUREMENTS

The phase situation of $\bar{7}$S5 was examined in the temperature range from 285 to 370 K by means of a Perkin Elmer DSC-model 2 differential scanning calorimeter. The mass of the sample was 2.39 mg. The upper "endo" curve in Figure 1, obtained when the sample was heated at a rate of 5 deg/min, has two anomalies corresponding to the existence of three phases, viz., the solid crystalline *K* phase, the nematic *N* phase and the liquid isotropic *I* phase. The phase transition points are $T_{K\text{-}N} = 327.7 \pm 3$ K and $T_{N\text{-}I}$ 354.7 ± 3 K,

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†Measurements carried out at the Section of Chemistry of the Martin Luther University in Halle (GDR)

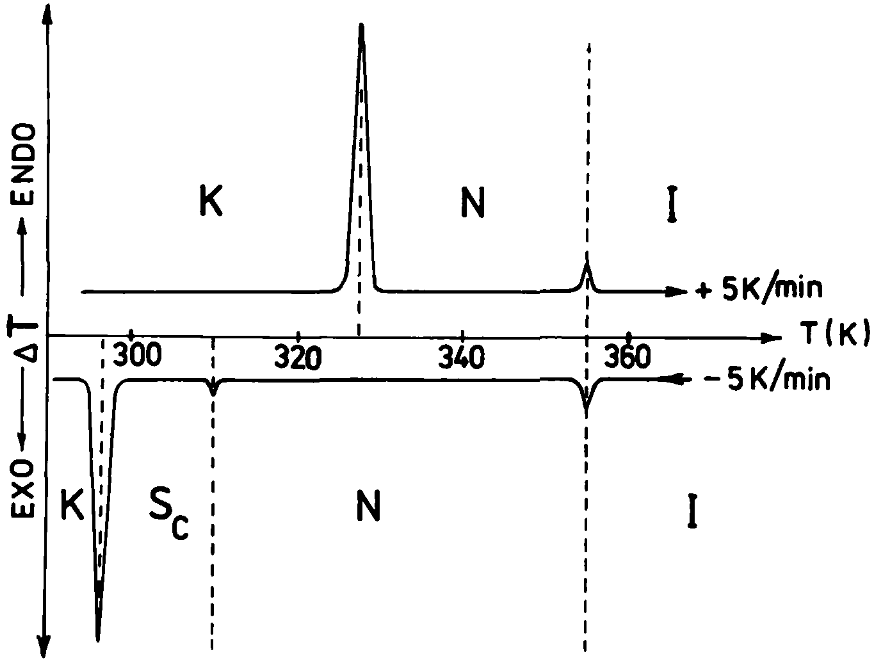

FIGURE 1 "Exo" and "endo" curves found for $\bar{7}$S5 by the DSC method.

respectively. The lower "exo" curve obtained when the sample was cooled at a rate of 5 deg/min features not two anomalies, as in the "endo" curve, but three, associated with the existence of four phases, i.e. the isotropic *I*, nematic *N*, smectic *C* (which was absent in the "endo" curve) and solid *K* phases. The phase transition temperatures recorded during the cooling process are $T_{N\text{-}S_c} = 309.2 \pm 3$ K and $T_{S_c\text{-}K} = 296.0 \pm 3$ K.

The diagram below depicts the number and type of phases "seen" by the DSC method in the examined temperature range. Corresponding ΔH values are also given.

$$\begin{tikzcd}
 & & N \arrow[r, "354.7 \pm 3\ \mathrm{K}", "300\ \mathrm{cal/mol}"'] \arrow[dl, "309.2 \pm 3\ \mathrm{K}", "54\ \mathrm{cal/mol}"'] & I \\
K \arrow[urr, "327.7 \pm 3\ \mathrm{K}", "7100\ \mathrm{cal/mol}"'] & S_c \arrow[l, "296.0 \pm 3\ \mathrm{K}"'] & &
\end{tikzcd}$$

It should be noted that the transition from the smectic *C* phase to the crystal is a monotropic one. On the other hand, the $S_c - N$ transition takes place in both directions. The existence of the S_c phase had been suggested earlier by

Reynolds.[7] The shape of the $S_c - N$ anomaly obtained by DSC is analogous to the one observed in the study,[1] for there are no near-transition effects in it from the nematic phase side.

II. 2. Optical microscopy

Observations of the phase situation in $\bar{7}$S5 in the temperature range from 290 to 370 K were carried out with a Carl Zeiss-Jena microscope during heating and cooling of the substance at the rate of 0.5 deg/min. Results are shown in Figure 2. It is seen that the phase transition points are identical or very near the values found by the DSC method. However, three rather unexpected structures of solid $\bar{7}$S5 were revealed; they are donated K_1, K_2, K_3, respectively (K_1—needle texture, K_2—gravel texture, K_3—plain texture).

In these measurements cooling of the isotropic phase resulted in the appearance of the nematic phase, then the smectic *C* phase and finally the solid phase. When heated, the latter began to melt at 323.5 ± 0.3 K. During fusion the structural pattern of this solid phase became altered (from K_3 to K_2). The obtained K_2 solid phase began to melt at 325.9 ± 0.3 K. With this process the structure was seen to change from K_2 to K_1. The latter melted at 326.9 ± 0.3 K to the nematic phase.

II. 3. Specific heat measurements by adiabatic calorimetry

The specific heat of $\bar{7}$S5 was measured in the 90 K to 370 K range by means of a adiabatic calorimeter described in detail in Ref. (8). The mass of the examined substance was 54.15 g, which is equivalent to 0.136 mol of $C_{25}H_{34}O_2S$. Specific heat measurements of $\bar{7}$S5 were preceded by calibration of the calorimeter

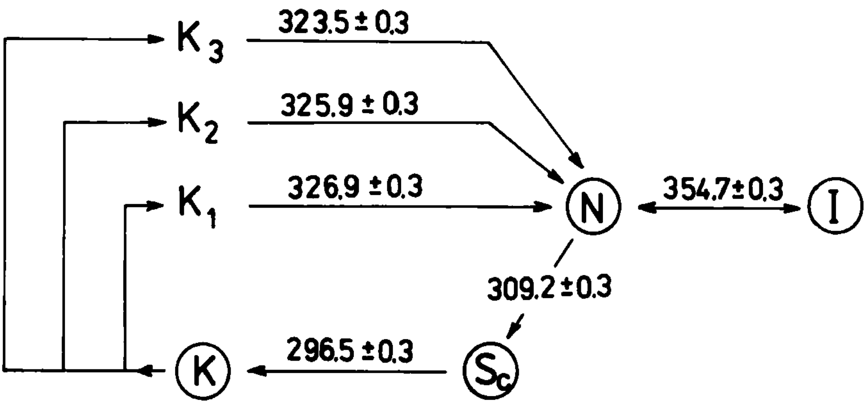

FIGURE 2 Phase situation of $\bar{7}$S5 as seen by thermal microscopy.

vessel of mass 213.94 g. The mean scatter of experimental points on the calibration curve was about 0.3 per cent at the low temperatures and about 0.6 per cent at the higher ones. The maximum departure of the experimental points from the smooth c_s vs. T curve for the sample was less than 2 percent. Figure 3 depicts the found temperature dependence of the specific heat of $\bar{7}$S5. The phase transition points are: $T_{KIII\text{-}KII} = 183.53 \pm 0.09$ K; $T_{KII\text{-}KI} = 272 \pm 0.4$ K, $T_{KI\text{-}N} = 325.87 \pm 0.04$ K and $T_{N\text{-}I} = 352.2 \pm 0.4$ K.

The measurements consisted of three series for the stable phase of the

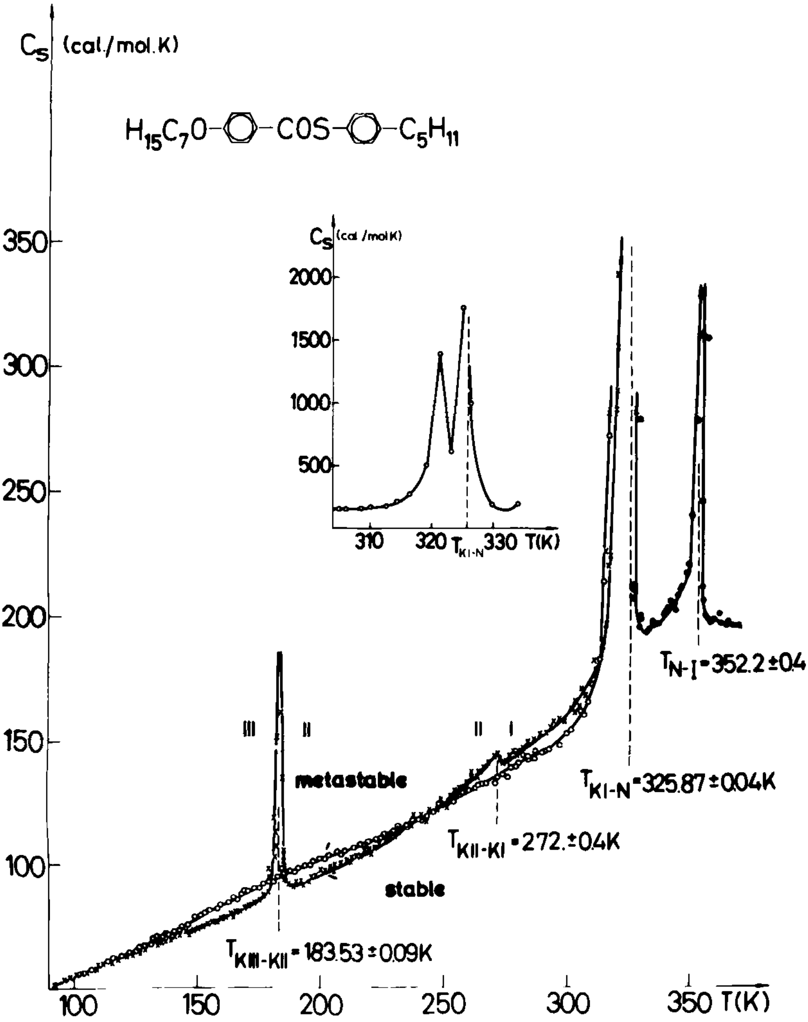

FIGURE 3 Specific heat vs. temperature dependence obtained by adiabatic calorimetry.

sample as prepared virgin fresh for the experiment, three series for the stable phase obtained from the metastable phase after the sample was melted, three series for the metastable phase, four series for the nematic phase and four for the isotropic phase. In all, this gave 427 experimental points. The reproducibility of results in the various series was very good.

It should be noted here that the results of the first series of measurements differ somewhat from those of all subsequent series. This concerns only the peak corresponding to the nematic-to-isotropic phase transition. The temperature at which this transition occurs determined from the first series is 354.81 K and, as is seen, this value is in excellent agreement with that determined by the DSC method. It is different, however, than the value determined from subsequent measurements series cited in Figure 3, where the reproducibility was very good. The ΔS value for this transition found for the first series was 1.07, whereas for the subsequent series it was 1.28 e.u., as given in Table 1. This distinct broadening of the peak of this phase transition once the first series of measurement had been carried out and the lowering of the transition temperature may be due to the appearance of impurities in the examined substance, presumably from the surface of the copper calorimetric vessel.

III ELABORATION OF RESULTS OBTAINED WITH THE ADIABATIC CALORIMETER

The exact phase transition temperatures for $\bar{7}S5$ were found as the points of intersection on the plots of temperature versus total quantity of heat supplied to the sample (Figures 4a, b). This procedure could not be used in the case of the *II-I* transition because there is no inflexion in the T vs. $\Sigma\ Q$ curves owing to the small thermal effect associated with this transition. In this case the transition point was taken as the mean value of abscissae corresponding to the experimental points lying within the area of the peak.

The deviation of experimental points from the dashed straight lines seen in the T vs. $\Sigma\ Q$ plots is evidence of the existence of near-transition effects accompanying the phase transitions of $\bar{7}S5$. They are smaller for the *III-II* and *N-I* transitions and much larger for fusion.

Owing to the existence of these near-transition effects, the ΔH and ΔS values were found by the method outlined in Ref. (4). Enthalpy and entropy changes were divided into a so-called isothermal part and a part associated with the appearance of these effects (Table 1). Of the three phase transitions which should be treated in this way, the ΔH and ΔS values could not be successfully divided into two parts for the *III-II* transition because of the low "density" of experimental points in the specific heat peak region.

TABLE I

Thermodynamical parameters of phase transitions in $\bar{7}$S5

Temperature (K)	Enthalpy change [cal/mol]			Entropy change [cal/mol · K]		
	ΔH overall	ΔH isothermal	ΔH near-transitional	ΔS overall	ΔS isothermal	ΔS near-transitional
$T_{KIII\text{-}KII} = 183.53 \pm 0.09$	279 ± 79			1.44 ± 0.38		
$T_{KII\text{-}KI} = 272.0 \pm 0.4$	54.4 ± 14.0			0.21 ± 0.10		
$T_{KI\text{-}N} = 325.87 \pm 0.04$	6815 ± 1101	6080 ± 1061	735 ± 40	21.14 ± 3.43	18.8 ± 3.28	2.35 ± 0.15
$T_{N\text{-}I} = 352.2 \pm 0.4$	610 ± 65	201 ± 25	409 ± 40	1.28 ± 0.16	0.52 ± 0.07	0.76 ± 0.09

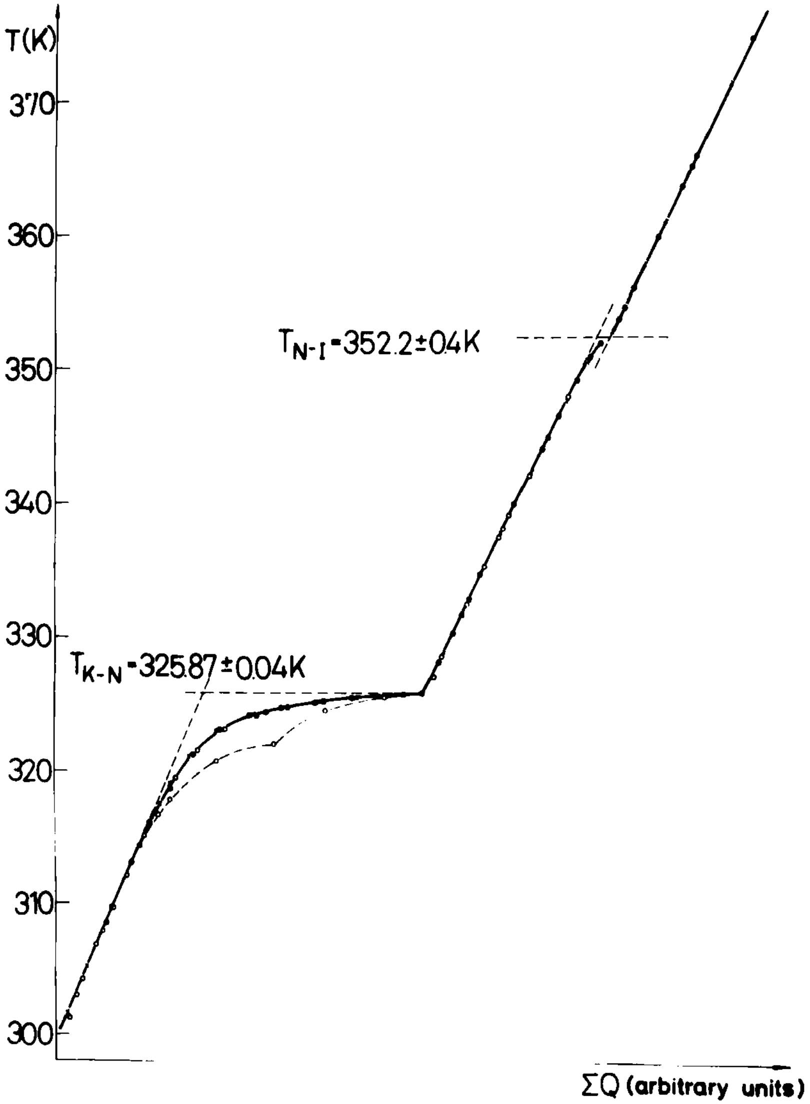

FIGURE 4 Temperature vs. total heat supplied for melting point and clearing point.

IV DISCUSSION

This section deals with the results concerning the metastable and stable phases of solid $\bar{7}S5$ (Subsec. IV.1), gives an analysis of the character of the phase transitions (Subsec. IV.2), describes the characteristic features of the smectic phase (Subsec. IV.3) and presents the enthalpy and entropy values of phase transitions in $\bar{7}S5$ (Subsec. IV.4).

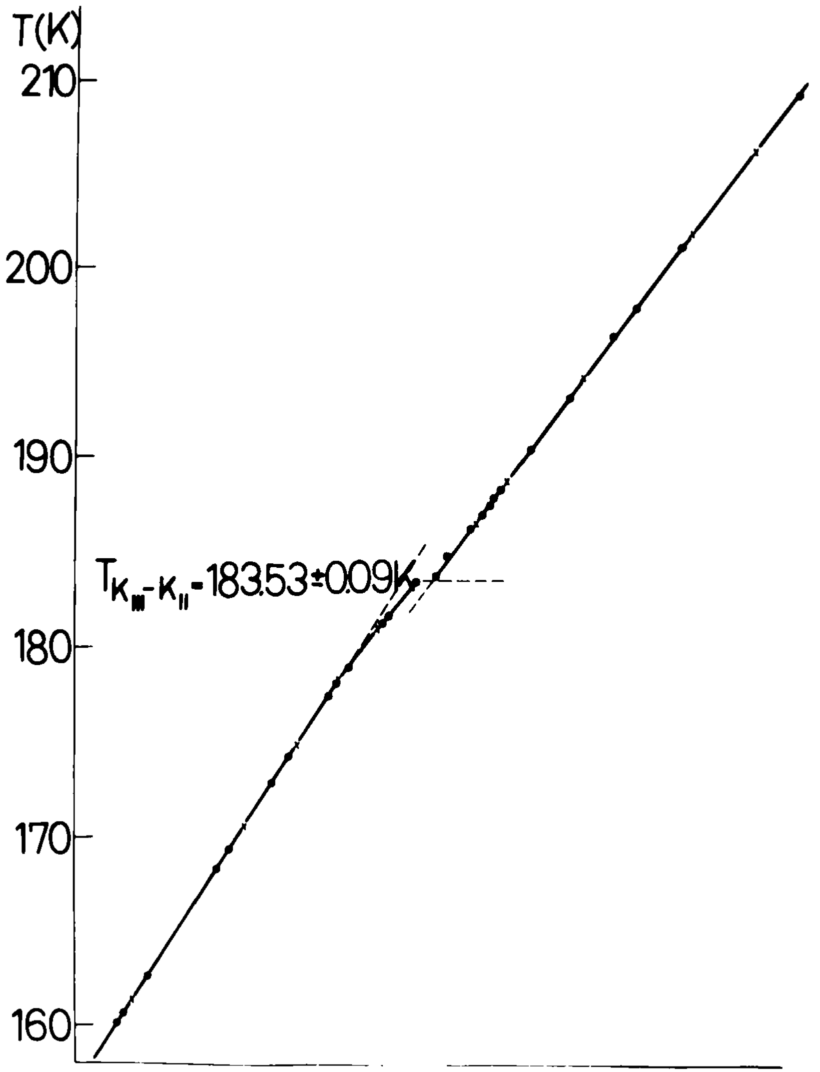

FIGURE 4b Temperature vs. total heat supplied for low-temperature phase transition in the stable modification of $\bar{7}$S5.

IV.1. Characteristics of the two, stable and metastable, solid phases

Measurements of the specific heat of $\bar{7}$S5 show that this substance can occur in two monotropic solid modifications: stable and metastable. This is quite evident in Figure 3. The thermodynamic differences between the stable and metastable modifications are well defined, as two different specific heat curves are seen to exist. In one of them—that for the stable phase marked by the crosses in Figure 3—there are two anomalies, a very distinct one at 183.53 K and a smaller one at 272.0 K. On the other hand, no such anomalies appear in the metastable curve, marked by the open circles in Figure 3.

Both modifications possess identical values of specific heat in the temperature range from 108 K to 115 K. From 115 K upwards the metastable modification curve lies above that of the stable modification. The difference between them at 150 K already reaches 5.4 percent (relative to the stable phase curve), hence, it is much greater than the maximum scatter of experimental points. Further on the metastable curve "intersects" the 183.53 K anomaly of the stable modification curve and then from about 250 K onwards proceeds below it.

The method of obtaining the stable and metastable modifications of solid $\bar{7}$S5 depends on the heat treatment of the sample and is similar to that applied for MBBA,[2] HOAB[4] and NPOB.[3] When cooling proceeds at an average rate of 2 deg/min from the isotropic phase to liquid nitrogen temperature the metastable modification is obtained. On the other hand, the stable modification is obtained by a spontaneous transformation from the metastable phase. It should be emphasized that the virgin sample placed in the calorimetric vessel was in the stable phase, which for other liquid-crystalline samples is not always the case. The transition from the metastable to stable modification was observed as a spontaneous rise of the temperature of the sample + calorimetric vessel system which is associated with the exothermal process taking place in the sample. This spontaneous transition occured at 297.62 K at a rising temperature rate of about 0.23 deg/h, at 294.16 K at a rate of about 0.06 deg/h, whereas at 302.15 K at a rate of 0.12 deg/h. Hence, it depended on sample temperature, but also on its thermal history.

When the substance is cooled quickly from the istotropic phase, not to a point near that of liquid nitrogen but to within 287.6–296.5 K, the metastable $\bar{7}$S5 modification became "fixed" to such an extent that the spontaneous transition to the stable modification occured down at a temperature of 322 K. This was observed as a splitting of the fusion peak for the metastable modification (this is evident in Figure 3 where the c_s vs. T dependence for the metastable modification in the 305 K to 335 K range is plotted above the basic curve). Ultimately, as is seen in Figure 4a, the metastable phase could not be melted. The dashed curve running through the open circles corresponding to the metastable phase has an inflexion at exactly the same temperature as the continuous curve corresponding to the stable phase.

It should be emphasized that as there are two anomalies in the specific heat curve for the stable modification of solid $\bar{7}$S5 a low-temperature solid phase, denotated *KIII*, is distinguished in the range from about 90 K to 183.53 K, an intermediate phase *KII* in the 183.53 K to 272.0 K range and a high-temperature phase *KI* in the 272.0 K to 325.87 K range.

A comparison of the transition points obtained for $\bar{7}$S5 by adiabatic calorimetry, thermal polarizing microscopy and DSC shows that

1) the stable phase *KI* corresponds to the K_2 phase, for the value $T_{KI\text{-}N} = 325.87$ K is in excellent agreement with $T_{K_2\text{-}N} = 325.9$ K,
2) it appears that the phase obtained in DSC measurements during sample heating corresponds with the K_1 phase ($T_{K_1\text{-}N} = 326.9$ K and $T_{K\text{-}N} = 327.7$ K),
3) the metastable phase seems to correspond to the K_3 phase because the melting point of the latter is lower than that of the other solid modifications.

IV.2. Analysis of the character of the phase transitions in $\bar{7}$S5

The c_s vs. T and T vs. $\Sigma\ Q$ plots show that a much greater thermal effect is associated with fusion than with the other phase transitions. For fusion, high values of specific heat were obtained (ca 6×10^3 cal/mol K). In addition to this, DSC and dielectric[9] measurements revealed distinct hysteresis. This is a phase transition of the first king according to the Ehrenfest classification and type 2*I* according to the McCullogh classification.[10]

As is seen in Figure 4a the *N-I* phase transition poccesses a very small heat of transition as compared with fusion. This figure implies that this transition can be classified as one of the first kind (a distinct plateau is evident), whereas the McCullogh classification principles would place it as a 3*N* type transition.

Of the remaining two transitions in the stable phase of $\bar{7}$S5, the *KIII-KII* transition can be said to be of the 3*N* type while the *KII-KI* transition of an *H* type. In the Ehrenfest classification the former would be of the first kind and the latter of the second kind.

IV.3. The smectic *C* phase

The smectic *C* phase was obtained in DSC and microscopic measurements by cooling the sample from the isotropic phase. The S_C phase formed from the supercooled nematic phase.

Attempts to achieve the S_C phase of $\bar{7}$S5 in adiabatic calorimetry were unsuccessful. Implementation of an average cooling rate of 0.2 deg/min for the 374 K–313.5 K range and 0.02 deg/min for the 313.5 K–298 K range led to the acquisition of a curve corresponding to melting of the stable phase. The failure to establish conditions in the adiabatic calorimetric methods which earlier led to the acquisition of the S_C phase (in the DSC method) may be due to the effect of such factors on the generation of this phase as sample size or temperature gradient. It should be emphasized that these factors differed (by orders of magnitude) in the two studies.

Studies of dielectric relaxation in $\bar{7}$S5[11] in the 280–370 K range have shown that the S_C phase transforms spontaneously to the solid phase both in the megahertz and gigahertz range. This is proof of the instability of the smectic *C* phase in $\bar{7}$S5.

That the S_C phase appears only when the substance is being cooled was also ascertained in the case of the 4-*n*-alcylophenyl-4'-*n*-alcoxythiobenzoate homologue next in succession after $\bar{7}$S5, i.e., $\bar{8}$S5.[12] The S_C phase exists here within an approximate 25 degree range.

IV.4. Thermodynamic parameters of phase transitions in $\bar{7}$S5

Changes of enthalpy and entropy of the phase transitions of $\bar{7}$S5 were calculated by the method outlined in Sec. III. These values are tabulated together with the phase transition temperatures in Table 1.

The *KI-N* and *N-I* phase transitions at 325.87 K and 352.2 K are associated with fusion and the clearing point, respectively. The other two transitions in the stable solid phase deserve a closer look. For the *KIII-KII* transition at 183.53 K the entropy of the transition $\Delta S_{KIII\text{-}KII} = 1.44$ cal/mol K is equal within error limits to the value $\Delta S = R \ln 2$, which rather implies that this is a configuration type transition. This value rather implies that above $T = 183.53$ K the molecule can appear in two equi-energy configurations. They may, for example, be associated with the rotation of two parts of the molecule about the C—S bond, which is quite feasible because this bond is a single one.

The next transition from phase *II* to phase *I* at $T_{KII\text{-}KI} = 272.0$ K can be linked up with some small distortion of the crystal lattice owing to the very low value of entropy change of transition. These hypothetical ascertainments for the *KIII-KII* and *KII-KI* transitions may be corroborated by structural studies in a broad temperature range.

V CONCLUSIONS

The studies of the phase situation of $\bar{7}$S5 by adiabatic calorimetry, DSC and polarizing microscopy presented here allow the following conclusions to be reached.

a) Four anomalies appear in the specific heat vs. temperature curve. They are associated with the phase transitions:
solid phase *III* - solid phase *II* at 183.53 K,
solid phase *II* - solid phase *I* at 272.0 K,
melting (*KI-N*) at 325.87 K and
N-I at 352.2 K.

b) Two modifications, stable and metastable with distinctly different thermodynamical properties occur in the solid.

c) The metastable phase spontaneously transforms into the stable modification in the 294.2 K to 302.2 K range if previously cooled to liquid nitrogen temperature.

d) The metastable phase can be "fixed" so that it transforms into the stable modification only when cooled to about 3.9 deg below the melting point of the stable phase.

e) Near-transition effects appear distinctly for the *KI-N, N-I* and *KIII-KII* transitions.

f) The smectic *C* phase is found to exist. However, evidence of this phase by adiabatic calorimetry was unachievable.

g) The most abundant information about the structural polymorphism of the solid in the range from room temperature to about 327 K was acquired by polarizing microscopy (three phases) whereas adiabatic calorimetry revealed two phases and the DSC technique only one. The phases as detected by the different methods were found to be correlated.

Acknowledgments

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