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New Intermediate Phases in Di-(4-N-Butyloxyphenyl)-Trans-Cyclohexane-1,4-Dicarboxylate

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NEW INTERMEDIATE PHASES IN DI-(4-N-BUTYLOXYPHENYL)-TRANS-CYCLOHEXANE-1,4-DICARBOXYLATE

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ABSTRACT

Thermal and dynamical properties of TCDCBPh : $H_9C_4O-C_6H_4-OOC-C_6H_8-COO-C_6H_4-OC_4H_9$,which forms liquid crystal phases : Cr 107 S_A 156 N 209 I, were studied by means of quasielastic neutron scattering (QNS), differential scanning calorimetry (DSC) and polarizing microscopy. Temperature dependencies of parameters of different models fitted to experimental QNS data suggest the existence of another liquid crystalline or soft solid phase with orientational disorder in the temperature range ca. 103 - 106 °C. Precise DSC studies confirmed this hypothesis. Two additional phases below smectic A phase with temperature range 95 - 93 °C and 93 - 86 °C were detected on cooling in DSC experiments. This behavior was also confirmed with the polarizing microscope.

keywords : quasielastic neutron scattering, differential scanning calorimetry, polarizing microscopy .

1. INTRODUCTION

Thermotropic liquid crystalline di-(4-n-butyloxyphenyl) *trans*-cyclohexane-1,4-dicarboxylate $C_4H_9O\cdot C_6H_4\cdot O(O)C\cdot C_6H_{10}\cdot \cdot C(O)O\cdot C_6H_4\cdot OC_4H_9$ (TCDCBPh) forms smectic A and nematic

phases. The temperatures of phase transitions were already established : Cr 107 S_A 156 N 209 I.[1] The TCDCBPh molecule consists of a cyclohexane ring (see Fig.1) which can influence dynamical properties of TCDCBPh. These properties were studied by means of quasielastic neutron scattering method (QNS), with the energy resolution 137 μeV.[2] The experiments were performed in the Institute of Energy Technology at Kjeller, Norway.

Experimental spectra were fitted with a function :

$$I_{exp} \sim [\ p \cdot \delta(\omega) + (1-p) \cdot S(\vec{\kappa},\omega)\ ] \odot G(\omega) \qquad (1)$$

where $S(\vec{\kappa},\omega)$ is the scattering law depending on assumed model of molecular motions, $G(\omega)$ is the instrumental function and $\odot$ means the convolution operation. "p" is the phenomenological parameter called "excess of elasticity" with the following physical meaning [3,4]:

p >0 means that too many motions were accepted in the model

p <0 means that too few motions were accepted in the model

p =0 means that there is a *formal* adequacy of the model.

This parameter "p" and the correlation time (parameter of the scattering law) were fitted to experimental data. Eleven different models of reorientations were proposed.[2] The analysis of the QNS results suggested the reorientational motions of cyclohexane ring already in the solid phase (below 105°C). At the temperature ca. 103°C values of "p" parameter were drastically reduced (for all considered models). It suggests the increase of molecular mobility. Later on, the increase of temperature generates further decrease of p values at ca. 106°C, however, not so rapid as the former one. In differential scanning calorimeter (DSC) experiments[1] the temperature of Cr → S_A phase transition was measured as 107°C. Taking into account the accuracy of DSC and QNS experiments the discrepancy between 103 and 107 °C is too big. This leads to hypothesis that at 103°C there is a transition to another phase formerly not detected, whereas the further decrease of QNS

fitted parameter "p" is connected with the phase transition of this new phase into smectic A.

The polarizing microscopy observations have also detected the new phase, but only on cooling, yet there was no new phase on heating.[2] These results required further explanation. Therefore the new analysis of QNS data as well as new calorimetric and microscopic experiments were performed.

2. NEW ANALYSIS OF THE QUASIELASTIC NEUTRON SCATTERING (QNS) DATA

Model fitting (eq.1) to the experimental data was repeated. The model was taken into consideration in which cyclohexane ring in the TCDCBPh molecule reoriented around its flat part (in fact, it is a fictitious reorientation due to an assumption that chemical bonds between the cyclohexane ring and remaining parts of the molecule are broken, see Ref. 2) and the rest of the molecule reoriented around *para*-axes of benzene rings (Fig.1). It was assumed that these fragments of the molecule were rigid and their motions were occurring with one effective correlation time (cf. with model 2 in Ref. 2).

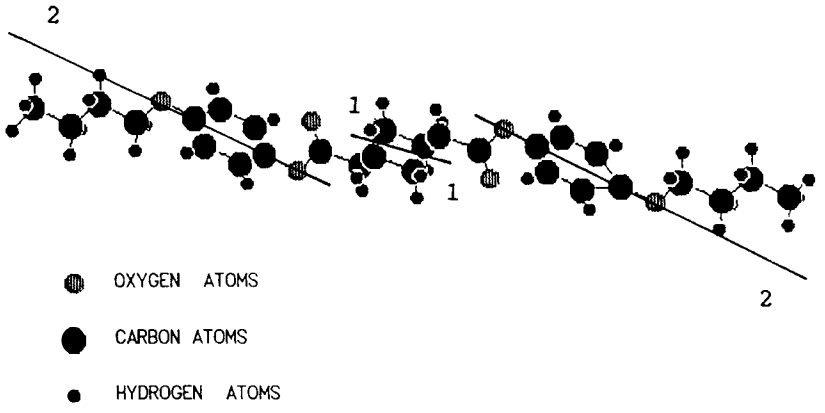

Figure 1. TCDCBPh molecule model.
The reorientational axes of the cyclohexane ring (symmetry axis of the flat part of the ring (1)) and the remaining parts of the molecule (2) are shown (model No 2 in Ref.2).

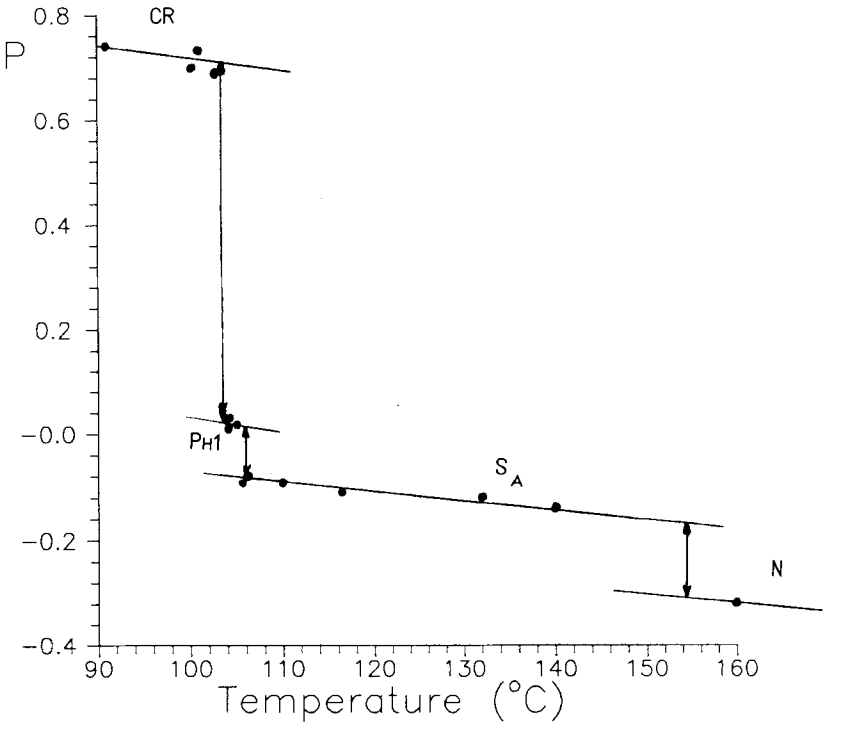

Figure 2. Temperature dependence of " p" parameter for the model of reorientation as in Fig.1.
Arrows mark three sudden falls of the p value.

Figure 2 shows results of calculations as the temperature dependence of the "elasticity excess" parameter "p". One can see a sudden decrease of p value from ca. +0.6 to ca. -0.02 between 103°C and 104°C. This is due to increase of rotational mobility of formerly frozen motions which can be connected with phase transition in the sample. Between the temperature 105°C and 106°C there is another, but smaller change of p value. It is comparable with the p value change between 140 and 160 °C (phase transition from smectic A to nematic phase). Thus the hypothesis can be suggested that besides transition to S_A phase, there appears transition to the new phase Ph1. This hypothesis can be verified using DSC and polarizing microscopy observations.

3. DIFFERENTIAL SCANNING CALORIMETRY (DSC) AND POLARIZING MICROSCOPY EXPERIMENTS

DSC measurements were performed using Perkin - Elmer DSC-7 for two samples (2.17 mg and 12.72 mg of TCDCBPh) with various rates of heating and cooling (from 0.2°C/min to 10°C/min) in the temperature range from 20 to 250 °C covering the phases from crystal one to isotropic phase.

The polarizing microscope observations were carried out with Biolar PI microscope (PZO, Warsaw, Poland) equipped with Linkam THM 600 heating stage, TMS 90 programmer and CCD video camera recorder. Observations were performed from 20 to 250 °C with different rates of the temperature changes.

4. RESULTS AND DISCUSSION

In the DSC experiment performed by heating from the room temperature up to 250°C all phase transitions reported before [1] were reproduced with good agreement. Since the QNS data analysis suggests the existence of the new phase in the vicinity of transition to S_A phase, special attention was paid to this temperature range. The example of this transition is presented in Figure 3 (upper curve). Although at first glance the melting peak (at 106°C) looks as the single one, the detailed study performed at the heating rate of 1°C/min shows clearly the new phase transition (Figure 4). Namely, the single peak observed at 106°C in Figure 3 is separated into two peaks corresponding to two phase transitions Cr → Ph1 (small effect at 104°C) and Ph1 → S_A (large effect at 106°C). Moreover, in Figure 5 results of another experiment confirming the existence of the phase Ph1 are shown. In this experiment heating was finished at 104.5°C just before transition to S_A phase (in Ph1 phase) and then the sample was cooled. The inverse transition was observed. Thus this transition is reversible. These results fully support the hypothesis

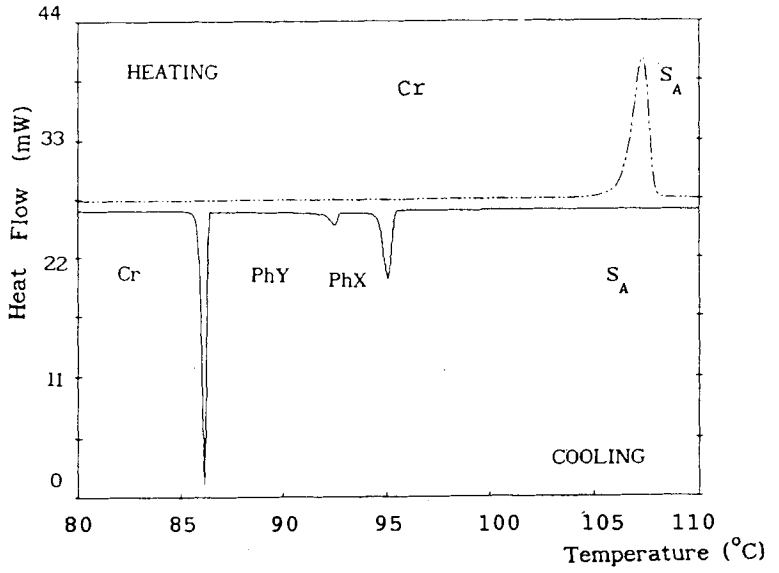

Figure 3. DSC thermogram in the range 80 - 110 °C obtained by sample heating (upper curve) and cooling (lower curve) at the rate 5°C/min.

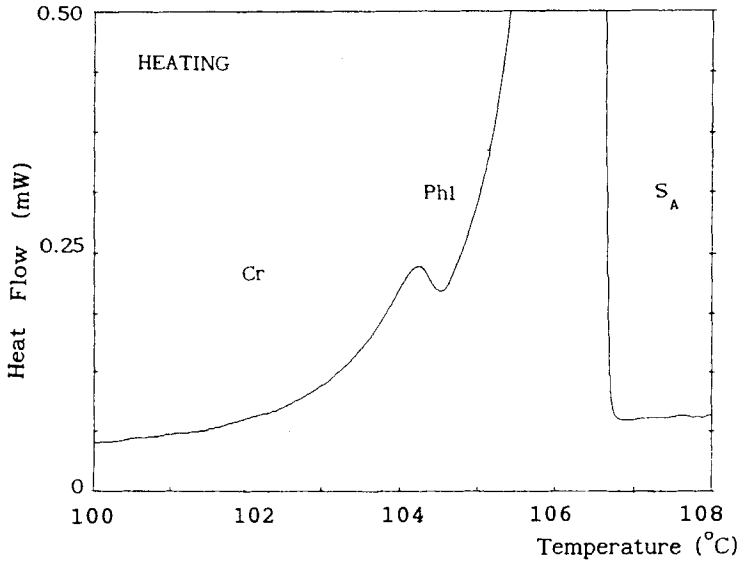

Figure 4. DSC thermogram obtained by sample heating from 100 to 108 °C with the rate 1°C/min. One can see phase transition Cr → Ph1 at 104 °C.

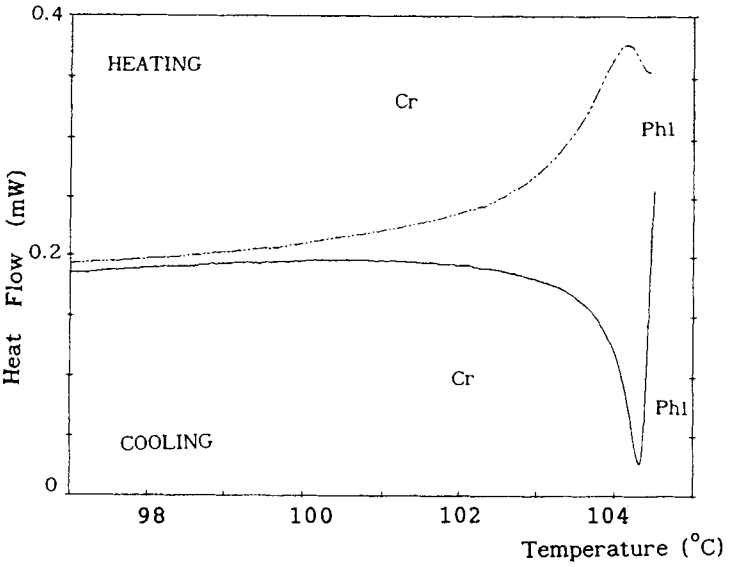

Figure 5. DSC thermogram obtained by sample heating from 97 to 104.5 °C (upper curve) and by cooling from 104.5 to 97 °C (lower curve) at the rate 1°C/min. As can be seen, thermal effect of this phase transition (Cr → Phl) is reversible.

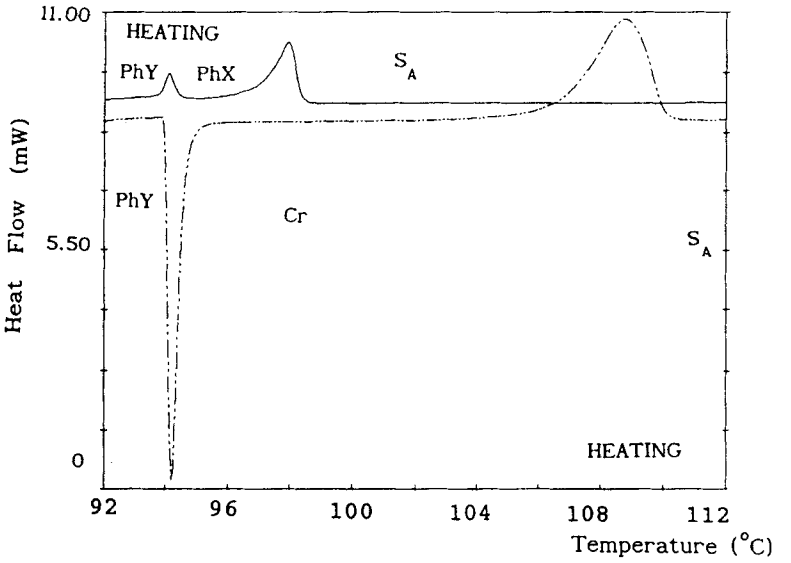

Figure 6. The comparison of two DSC experiments :
Solid line - sample heated to 112°C (S_A phase) immediately after cooling to 92 °C (phase PhY),
Dashed line - sample kept at 92°C (in phase PhY) for 20 minutes and later heated to 112°C (S_A phase).

derived from QNS data analysis described above.

The cooling from isotropic phase (250°C) confirms the appearance of nematic and smectic A phases as was reported in Ref.1. But the transition to crystal phase is not passing directly from smectic A phase. As it is seen from Figure 3 (lower curve) there are two additional phases between smectic A and the crystal one. These phases exist in narrow temperature range 95 - 93 °C (phase PhX) and 93 - - 86 °C (phase PhY). Below 86°C the crystal phase is formed (Figure 3). The appearance of new phase on cooling was already reported in Ref.2. However, the polarizing microscope experiments described there suggested only one phase between smectic A and the crystal phase. These experiments were repeated.

On cooling from isotropic phase the transitions to the nematic and smectic A phases were observed. On further cooling the smectic A phase was undercooled to 97°C when the transition to phase PhX was observed (Figure 7). Unfortunately, the texture of this phase is unknown. It does not exist in any catalogue.[5,6] While cooling this phase PhX transforms to crystal phase at 89°C. On heating the phase PhX melts to smectic A at 99°C. Unfortunately, no texture change connected with the transition to the phase PhY was observed. But the peculiar properties of phase PhY were studied in another experiment. The sample was kept for some time in chosen temperature between 90 and 97 °C. Then it was heated. For upper part of the mentioned range of temperatures (above 93°C) the phase PhX transformed into smectic A directly. Whereas, after keeping the sample at 91 - 92 °C for ca. 10 minutes on further heating the observed texture changed into another one, isomorphic with the texture of crystal phase (Figures 8,9). Moreover, it changes to smectic A texture at 107°C. Similar experiment was performed with DSC confirming these observations (Figure 6).

In this experiment at first the sample was cooled from 112°C (S_A phase) to 92°C (phase PhY) and next immediately

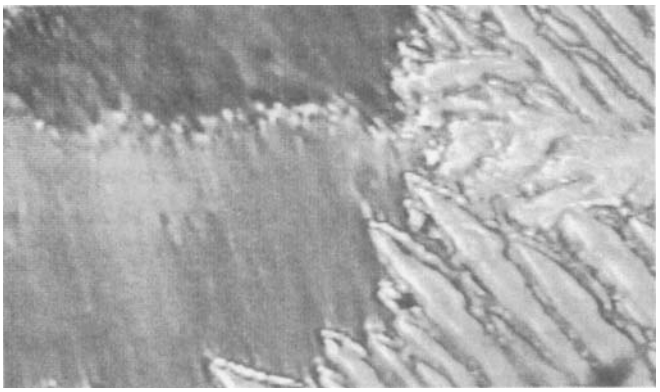

Figure 7. Smectic A to phase PhX transition in the polarizing microscope. See Color Plate XVII.

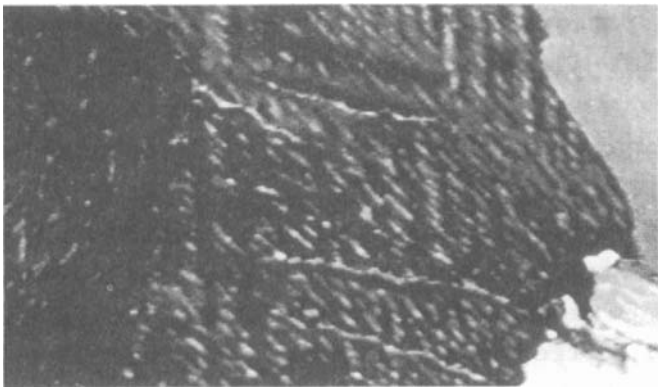

Figure 8. Formation of the crystal phase (from the right - side). See Color Plate XVIII.

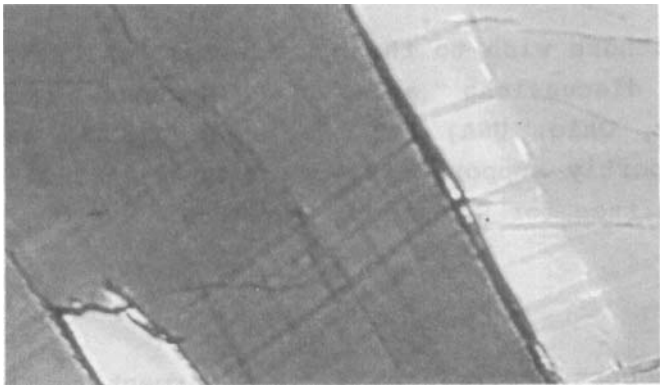

Figure 9. The texture of the crystal phase. *See Color Plate XIX.*

heated to 112°C. As is well seen in Figure 6 (solid line) the thermal history of the sample is restored (i.e. PhY 94 PhX 97.5 S_A). Later after cooling from 112°C sample was kept at 92°C (in phase PhY) for 20 minutes. Then it was heated to 112°C (dashed line in Figure 6). At 94°C one can observe large exothermic effect connected with the transition to crystal phase and then at 107.5°C endothermic effect connected with the melting of the crystal phase to the smectic A.

This behavior is analogous to that observed in the polarized microscope.

5. CONCLUSIONS

The hypothesis based upon the analysis of QNS data stating that there is one new phase (Ph1) occurring on heating between crystal and smectic A was confirmed. Additionally the DSC experiments discovered two other phases (PhX and PhY).

Some of these results were also confirmed in polarizing microscopy studies, however even precise observations did not allow to register all transitions. It is very likely that small differences in phase structures do have not resemblance in their textures.

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