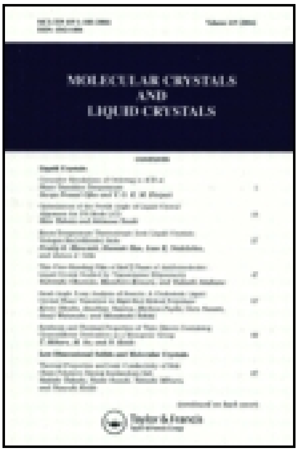

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High-Pressure Phase Studies of Some 4,4′-Disubstituted Phenylcyclohexanes (PCHs) and Bicyclohexanes (CCHs) by DTA

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High-Pressure Phase Studies of Some 4,4′-Disubstituted Phenylcyclohexanes (PCHs) and Bicyclohexanes (CCHs) by DTA

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T-p phase diagrams of the mesogenic compounds *trans*-4-*n*-dodecyl(4-cyanophenyl)cyclohexane (12PCH), *trans*-4-*n*-propyl(4-*n*-alkoxyphenyl)cyclohexanes (alkoxy = ethoxy (302PCH) and butoxy (304PCH)), and *trans,trans*-4-*n*-propyl(4-cyanocyclohexyl)cyclohexane (3CCH) are presented. The investigations were performed with new high-pressure computer-assisted DTA equipment in the temperature range 300 to 500 K up to a maximum pressure of 7 kbar. Several high-pressure effects typical for liquid crystals could be observed, e.g., pressure-induced phases (nematic and smectic), the occurrence of triple points, complex solid state polymorphism, changes in the nature of phase transitions from monotropic to enantiotropic etc. The *T-p* phase diagrams are discussed with regard to the influence of pressure on the stability of the different phases and of systematic changes in molecular structure.

Keywords: cyclohexane systems, interdigitated smB phase, phase diagrams, differential thermal analysis (DTA), high pressures, pressure-induced phases

INTRODUCTION

The pressure dependence of phase transitions makes evident the influence of density on the formation and stability of mesophases. Thus, high-pressure studies make a valuable contribution to knowledge of thermodynamic properties and the understanding of the phase behaviour of liquid crystals. In order to achieve information about the correlation between pressure effects and the influence of structural features, we earlier performed high-pressure investigations on different homologous series. One important result of this work was the demonstration of the opposite effect of enhanced pressure and increasing chain-length on mesophase stability.[1,2]

The interpretation of the relationship between molecular structure and mesomorphic properties has changed since the discovery of nematic mesogens with only partially aromatic or non-aromatic rigid cores by Eidenschink *et al.*[3,4] With regard to such molecular systems, Osman[5] has emphasized the dominance of steric conditions, like molecular packing, as distinct from the effect of conjugated π-electron systems (i.e., anisotropy of polarizability), for mesophase formation and stability.

In this context, high-pressure studies on substances containing non-aromatic ring systems seemed to be worthwhile. In the present paper recent investigations of *trans*-1,4-disubstituted cyclohexane ring systems are presented and discussed.

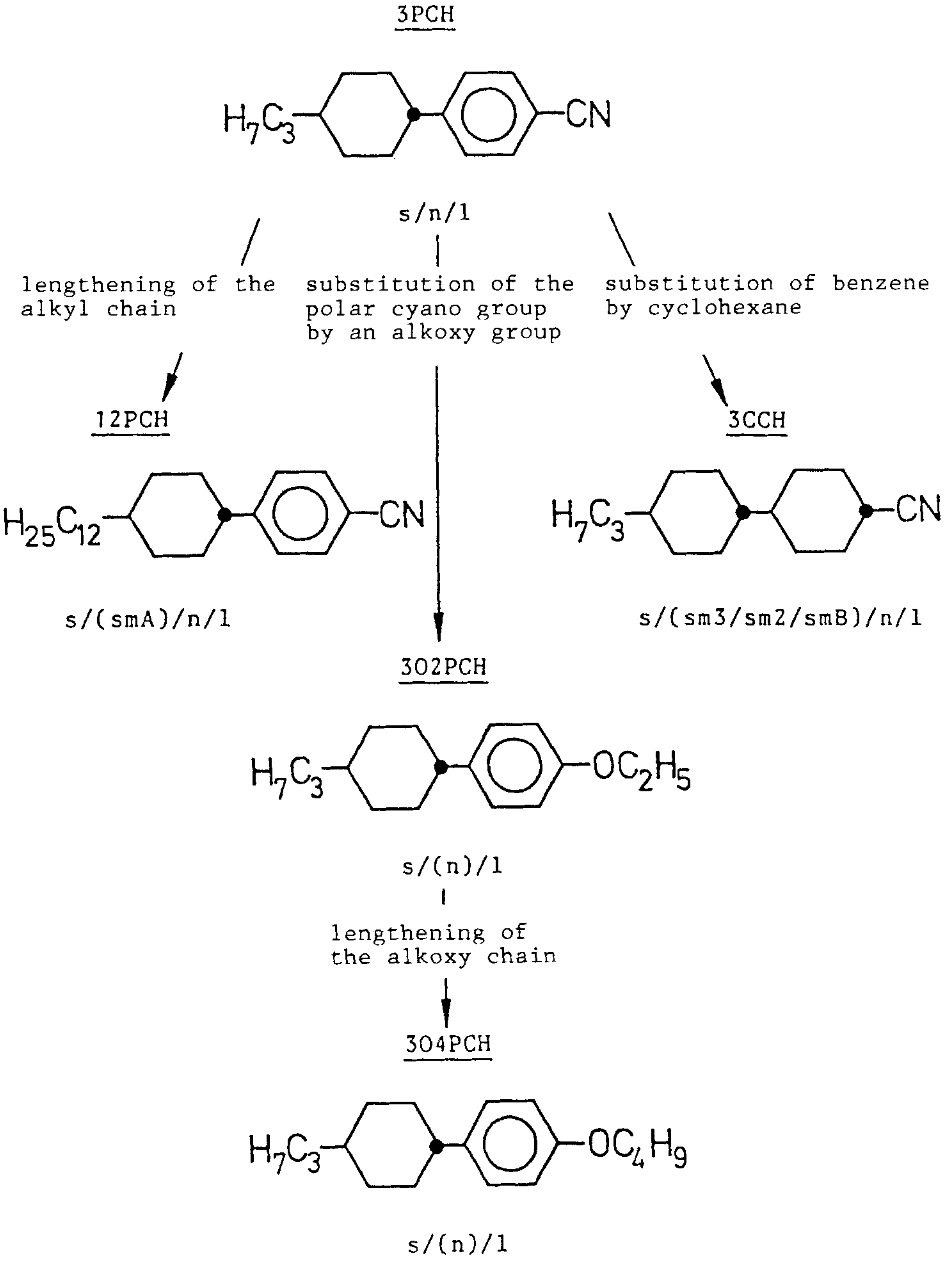

FIGURE 1 Samples under test.

EXPERIMENTAL

Computer-assisted DTA equipment recently developed for a maximum pressure of 7 kbar was used for the present measurements.[6,7]

The pressure transmitting medium was compressed argon gas. Chromel-alumel thermocouples were used for temperature measurement. The samples were enclosed in gas-tight cells made of lead which were mounted on to the thermocouple junctions; a typical sample quantity was 20 mg. Transition temperatures were determined from heating runs with rates of 1 K/min. The accuracy of the temperature measurements varied from ± 0.2 K for sharp signals to about ± 0.4 K for broad peaks normally associated with melting transformations. For the pressure measurements the accuracy was ± 5 bar.

Materials

Liquid crystalline substances exhibiting systematic changes in molecular structure were chosen for the experiments; they are compiled in Figure 1, and start from 3PCH as the basic compound. Some comments concerning the structural differences between the substances under test are also given in Figure 1. The *T-p* phase diagram for 3PCH was determined in our earlier studies.[11,2]

Below the graphic formulae in Figure 1, the phase sequences at atmospheric pressure are given, as found by other authors (3PCH,[3] 12PCH,[8] 3CCH,[4,10] 302PCH and 304PCH[9]). As phase symbols we use *s* for solid, sm for smectic, *n* for nematic, and *l* for isotropic liquid; metastable phases are given in brackets. The assignment of the mesomorphic phase types to different areas of the phase diagrams above the melting pressure curves (see Figures 2, 3, 4 and 8) is justified, since according

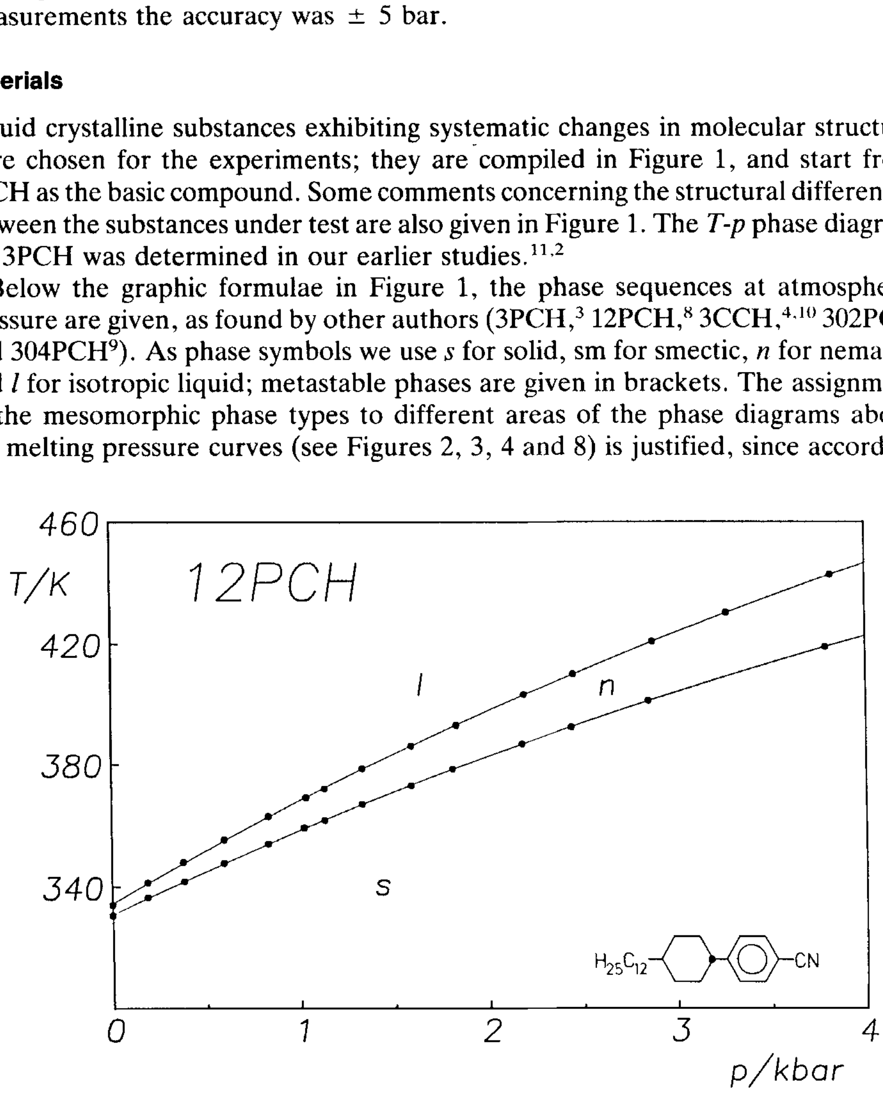

FIGURE 2 *T-p* phase diagram for 12PCH.

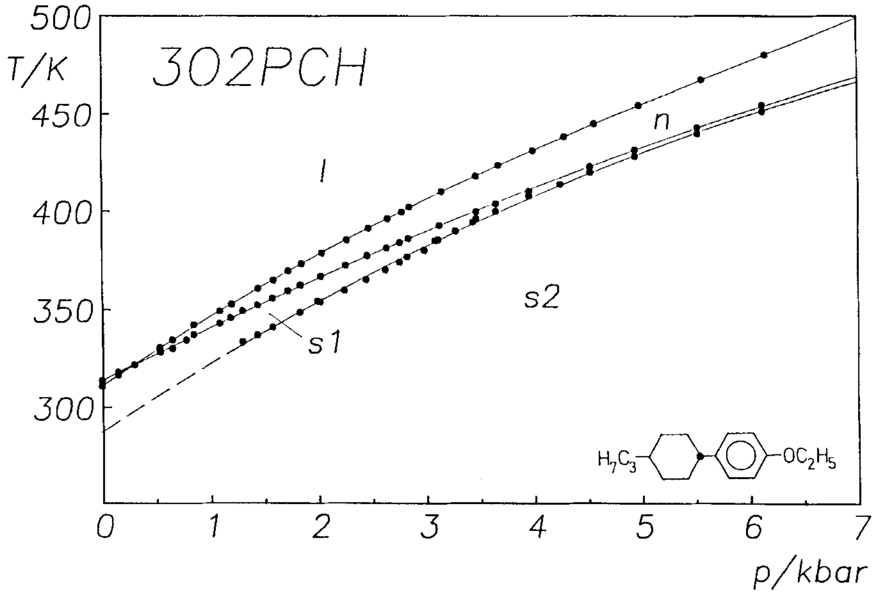

FIGURE 3 T-p phase diagram for 302PCH (---: extrapolated curve).

to normal pressure measurements, low enthalpy transitions that cannot be detected by DTA are only found in the metastable ranges, below the melting pressure lines of the substances investigated.

All compounds were obtained from E. Merck (Darmstadt) and used without further purification.

RESULTS AND DISCUSSION

12PCH

In continuation of our earlier investigations concerning the homologous series of *trans*-4-*n*-alkyl(4-cyanophenyl)cyclohexanes (PCHs),[11,2] the phase behaviour of the dodecyl-compound (12PCH) was studied. The T-p diagram of 12PCH which is shown in Figure 2 indicates a distinct increase in the nematic range with increasing pressure. The same behaviour has already been observed for 3PCH, 4PCH and 7PCH[11,2] and is typical for the high-pressure behaviour of a nematic phase. The smA/*n*-transition with a ΔH-value of about 0.08 $J \cdot g^{-1}$ at one bar, as published by Eidenschink *et al.*[8] could not be detected in our experiments at normal and high pressures because of insufficient resolution of the measuring equipment.

302PCH and 304PCH

Figures 3 and 4 show the T-p phase diagrams for 302PCH and 304PCH, respectively. Each compound exhibits a pressure-induced nematic phase. The corresponding

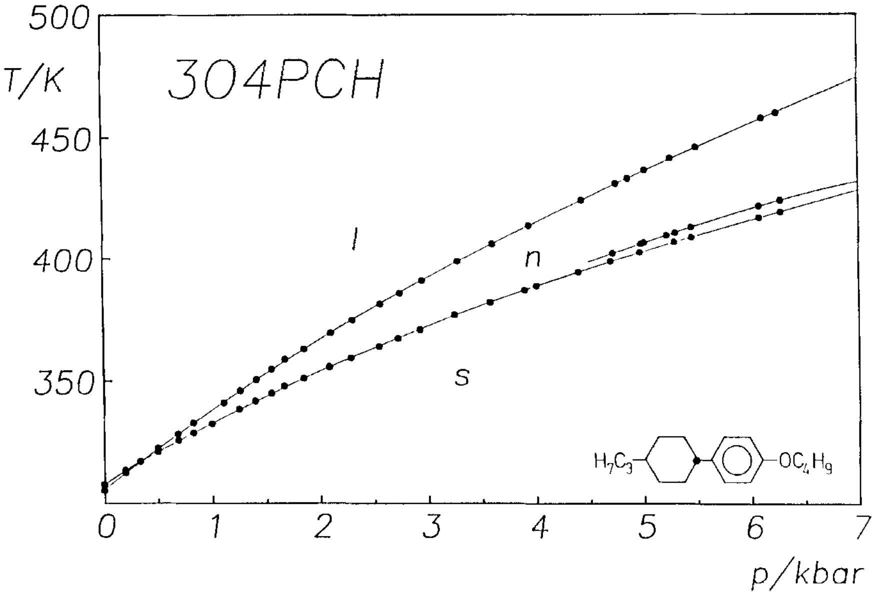

FIGURE 4 *T-p* phase diagram for 304PCH.

s/*n*/*l*-triple points were determined at about 300 bar and 322 K for 302PCH and at 335 bar and 317.5 K for 304PCH.

Because of the marked supercooling of the melting transitions, the *n*/*l*-transitions could be detected in heating runs at pressures below the triple point pressure. Figure 5 illustrates the determination of the triple point for 302PCH. Curve 1 shows the peak for the melting process, while curve 2 represents the clearing transition obtained on a heating run which was started before solidification of the sample had occurred. At 300 bar, the starting points of the linear slopes of both signals *s*/*l* and *n*/*l* are situated at the same temperature, so that this point simply represents the *s*/*n*/*l*-triple point for the sample under test.

Figure 6 shows typical DTA traces for 302PCH obtained at 3280 bar by heating and cooling. Besides the melting (*s*1/*n*) and the clearing (*n*/*l*) transitions, an additional signal indicated by *s*2/*s*1 is found which presumably belongs to a transition between two solid modifications. Because of the marked supercooling of this transition, it could not be observed at low pressures; the extrapolated part of the *s*2/*s*1-transition curve is given in the *T-p* phase diagrams as a dotted line (Figure 3).

Above about 5 kbar, the *T-p* diagram for 304PCH (Figure 4) shows an additional transition whose appearance in the thermograms is demonstrated in Figure 7: Near the melting peak, a very small signal is found which considerably increases with increasing pressure. A similar increase in the area of this peak could be induced by annealing experiments. These observations suggest the existence of an additional metastable solid modification at pressures above about 5 kbar whose formation at low pressures is probably hindered kinetically.

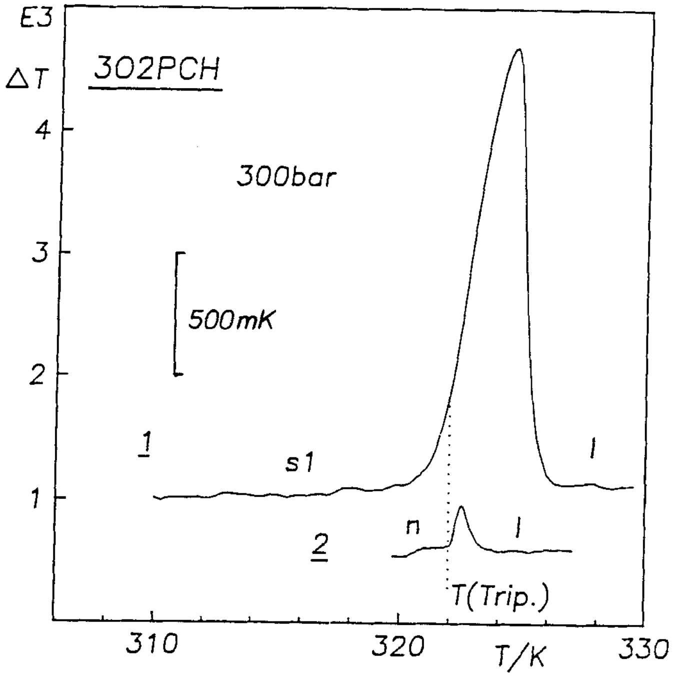

FIGURE 5 Original DTA traces for 302PCH; determination of the *s*/*n*/*l* -triple point.

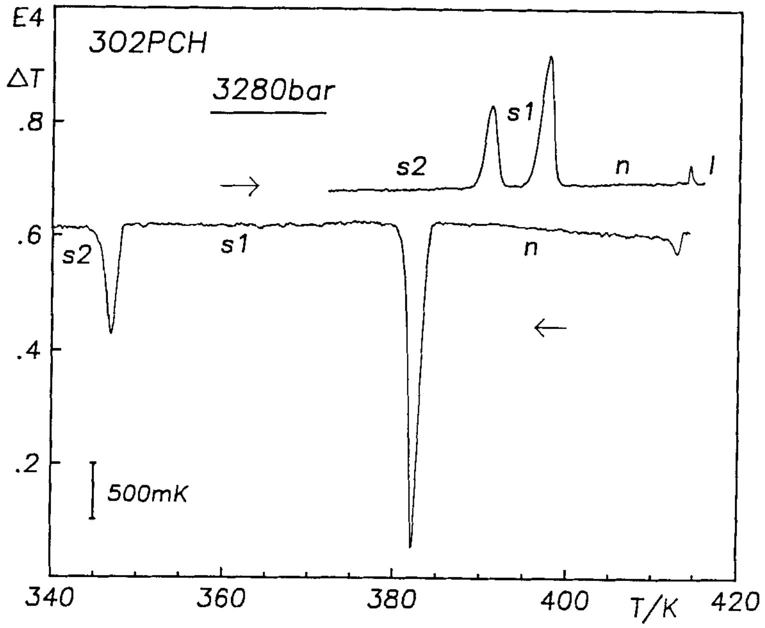

FIGURE 6 Original DTA traces for 302PCH obtained at 3280 bar by heating and cooling.

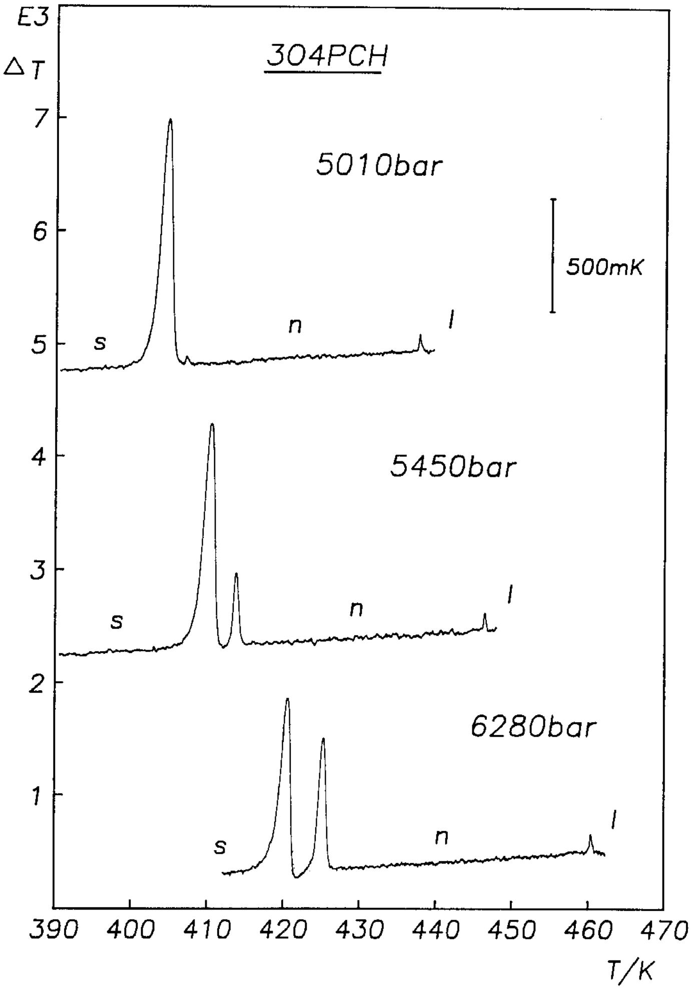

FIGURE 7 Original DTA traces for 304PCH obtained at different pressures by heating.

A comparison of the phase behaviour of the alkoxyphenylcyclohexanes 302PCH and 304PCH with the analogous cyanophenylcyclohexane 3PCH at normal pressure manifests a stable nematic phase for 3PCH, whereas for 302PCH and 304PCH the nematic phase exists in the metastable region only. The greater mesomorphic stability of cyano-substituted compounds can be explained by the tendency to molecular pairing already discussed e.g., by Gray[12] and Osman.[13] Due to the strong electron-withdrawing group, a charge distribution is created which results in a molecular association with opposite charges at minimal distance. This arrangement produces an enhanced geometrical anisotropy which is probably responsible for the mesomorphic stability of cyano-substituted compounds.

For the alkoxyphenylcyclohexanes, this stabilizing effect is absent, and therefore the nematic phase occurs at normal pressure in the thermodynamically metastable region only. But for both compounds, the nematic phase is pressure-induced and, as the *T-p* phase diagrams demonstrate (Figures 3 and 4), a distinct increase in the nematic stability range is found for increasing pressures. Here, pressure causes an approach of the molecules which evidently changes the molecular packing in a manner such that the formation of nematic order becomes possible. These considerations make it evident that external pressure and terminal polar groups have an analogous effect on the intermolecular distances and therefore on the formation and stability of the nematic phase.

3CCH

Figure 8 shows the *T-p* phase diagram for 3CCH. At atmospheric pressure, we observed the phase sequence *s*/*n*/*I* on heating and *I*/*n*/smB/sm2/*s* on cooling, demonstrating the existence of two additional smectic phases in the supercooled region. The high-temperature smectic phase was identified as an interdigitated smB phase by Brownsey and Leadbetter;[10] in this phase the molecules are hexagonally close-packed with interdigitated propyl and cyano-end groups.

Because of the marked supercooling of the appearance of the solid phase, the detection of the *n*/smB-transition was possible in the metastable region. This is shown in Figure 9: For curve 1 the run was started in the crystalline region, and therefore only melting and clearing signals respectively are exhibited. Curve 2, however, starts in the supercooled range before solidification of the sample had occurred, and consequently, this allows the detection of the smB/*n* as well as the *n*/*I* transition. The very slow onset of the smB/*n*-transition peak is unusual for a

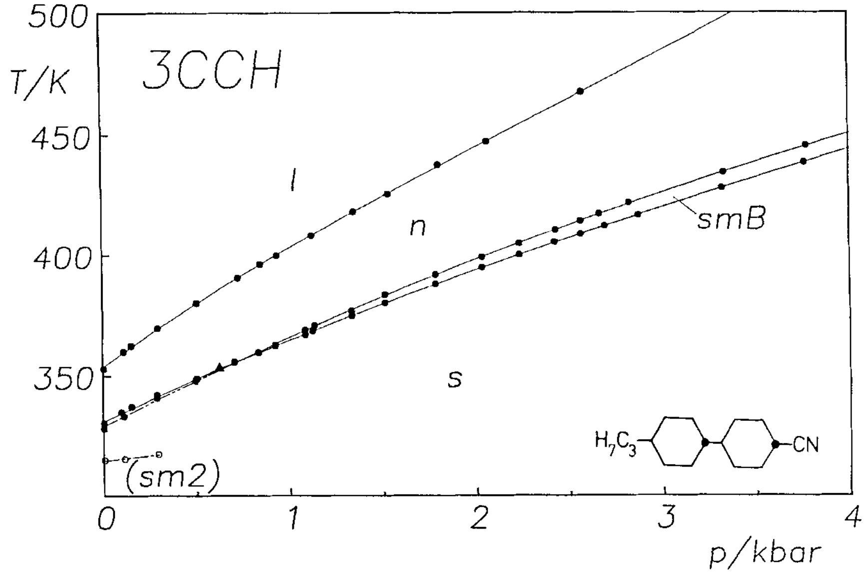

FIGURE 8 *T-p* phase diagram for 3CCH. (●: by heating; ○: by cooling; ▲: triple point *s*/smB/*n*; ---: in supercooled region).

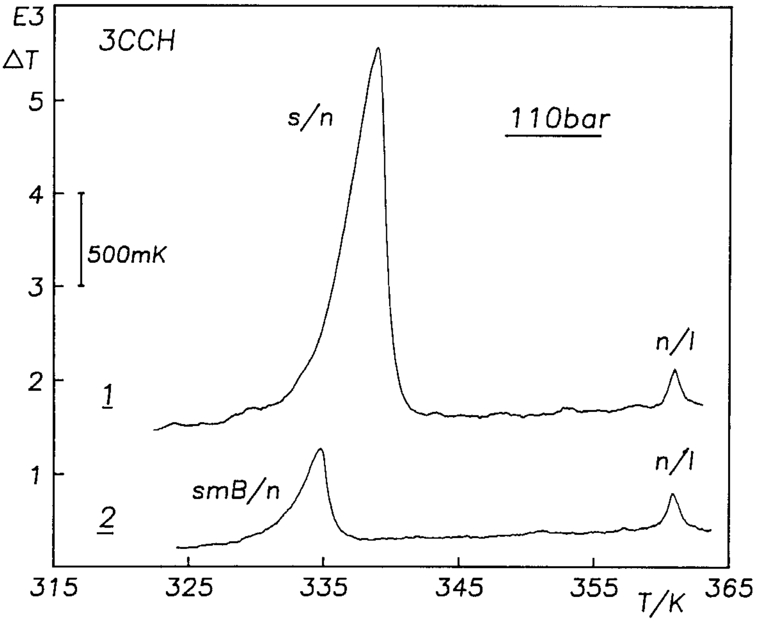

FIGURE 9 Original DTA traces for 3CCH obtained at 110 bar by heating.

transformation between two liquid crystalline phases. This behaviour, that is in principle typical for a melting transition, might be a consequence of the highly ordered nature of the smB-phase.

Figure 10 demonstrates the stabilizing effect of increasing pressure on the smB-phase resulting in a *s*/smB/*n*-triple point at 620 bar and 353 K. Here a thermogram is shown that is typical for a constant pressure run above the triple point. To our knowledge, the present study is the first one in which a pressure-induced smB-phase has been detected. The second smectic phase, indicated as sm2, could not be observed at pressures above 300 bar, because solidification of the sample occurred before this phase appears.

The dimerisation of 3CCH results in a higher geometrical anisotropy in comparison with 3PCH.[12] This explains the appearance of a stable nematic phase for 3CCH at atmospheric pressure compared with 3PCH. Evidently the favourable combination of dipolar interactions and steric factors is responsible for the formation of the smB-phase.

For additional data and a more detailed description and discussion of the results, see Reference 6.

Acknowledgment

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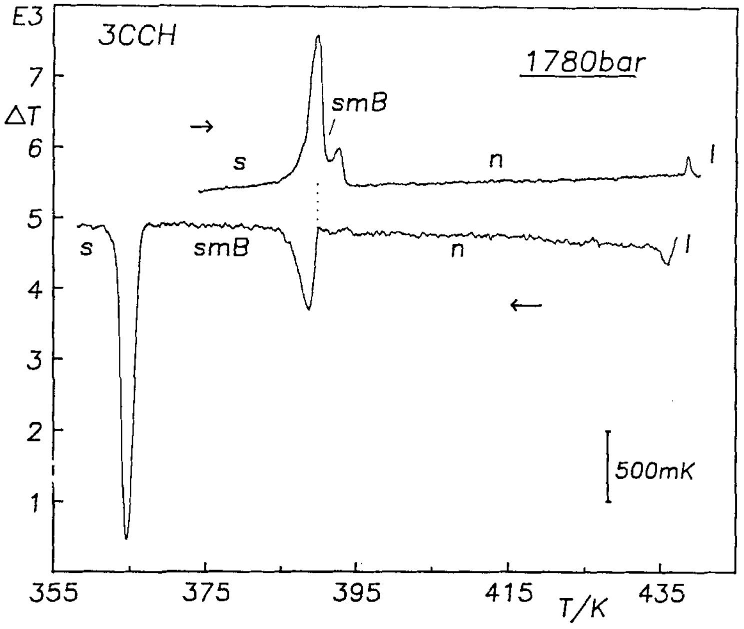

FIGURE 10 Original DTA traces for 3CCH obtained at 1780 bar by heating and cooling.

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