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Miscibility studies of the smectic phases of *trans,trans*-4′-alkylbicyclohexyl-4-carbonitrile (CCH) liquid crystals

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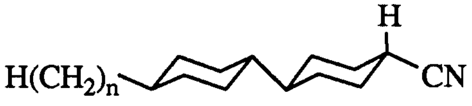
Complete temperature-composition phase diagrams for binary mixtures of 4′-ethyl-, 4′-propyl-, and 4′-butylbicyclohexyl-4-carbonitrile (CCH-2, CCH-3, and CCH-4, respectively) in each of the three possible combinations have been constructed from differential scanning calorimetry and thermal microscopy data. The highest temperature smectic phases of each of the pure mesogens are immiscible with one another, even though CCH-3 and CCH-4 have both been previously assigned the bilayer crystal-B structure on the basis of X-ray diffraction studies. The present studies indicate that the enantiotropic smectic phase of CCH-4 is slightly higher-ordered than is the monotropic smectic phase of CCH-3. The smectic phase of CCH-2, which previously has been found to be characterized by rhombohedral packing on the basis of X-ray diffraction data, is miscible with the second, previously uncharacterized (monotropic) smectic phase (S_2) of CCH-3. Photographs illustrating the subtle differences in the microscopic textures of these smectic phases are also presented.

1. Introduction

The series of *trans,trans*-4′-alkylbicyclohexyl-4-carbonitrile liquid crystals (CCH-*n*; $n = 2$–7) [1, 2] comprise a particularly interesting and useful family of mesogens. The lower members of the family ($n = 2$–5) are polymorphic, exhibiting nematic phases as well as one or more highly-ordered smectic phases. The *n*-propyl (CCH-3) and *n*-pentyl (CCH-5) derivatives form a series of monotropic smectic phases [1], of which the high temperature ones have been classified as crystalline, bilayer S_B phases (crystal-B) on the basis of X-ray diffraction studies [3]. The ethyl (CCH-2) and *n*-butyl (CCH-4) derivatives, on the other hand, have each been reported to form single enantiotropic smectic phases [2]. These have also recently been examined by X-ray diffraction techniques [4], which show that the smectic phase structure of CCH-4 is very similar to that of the *n*-propyl and *n*-pentyl homologs (bilayer crystal-B), while the smectic phase of CCH-2 is an even higher-ordered type characterized by rhombohedral packing and threefold symmetry [4].



CCH-*n*

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The highly-ordered, enantiotropic nature of the smectic phases of CCH-2 and CCH-4, the convenient temperature ranges over which they exist (29–44°C and 28–54°C, respectively [2]), and the fact that their nematic and isotropic phases are also accessible at reasonably low temperatures render these two mesogens particularly attractive for studies of solute conformational mobility and chemical reactivity in liquid crystalline media [5–12]. Furthermore, the transparency of these compounds in the mid- and near-U.V. spectral range (> 210 nm) make them (and the ternary eutectic mixture of CCH-3, 5, and 7: ZLI 1167) particularly useful as solvents for U.V. absorption [13–15] and fluorescence [5] spectroscopy, and their negative diamagnetic anisotropy renders them extremely useful as solvents in N.M.R. structural studies of dissolved solutes [16–19].

We wish to report the results of an investigation of the miscibility relationships between the $n = 2$–4 members of the CCH-*n* series. This study was originally undertaken in an effort to identify the smectic phase structures of CCH-2 and CCH-4 by comparison with the previously characterized [3] CCH-3 derivative. While it has been reported that the (high temperature) S_1 phase of the latter compound is immiscible with a variety of other known S_B liquid crystals [3], it appeared reasonable to assume that the miscibility rule [20] should hold within the homologous CCH-*n* series. We have thus employed differential scanning calorimetry (D.S.C.) and thermal microscopy (TM) to construct complete temperature-composition phase diagrams for the three binary combinations of these three compounds. The results of this study are reported below.

2. Results

Figures 1, 3, and 5 show representative D.S.C. heating and cooling traces, recorded with a 2°/min temperature program in each case, for series of CCH-2/CCH-3, CCH-2/CCH-4, and CCH-3/CCH-4 mixtures, respectively. Almost complete enantiotropic behaviour was observed for all mixtures in the CCH-2/CCH-4 series, and for all those containing $\leqslant 70$–80 mol % CCH-3 in the other two. Binary phase diagrams were constructed from each set of data are shown in figures 2, 4, and 6, respectively. Because the smectic phases exhibited by the CCH-3 mixtures containing $\geqslant 70$ mol % CCH-3 are monotropic, the phase diagrams constructed from heating and cooling data differ considerably (see figures 2 and 6). In general, the phase boundaries defined by the I–N, N–S, and S–S transitions are considered to be much more reliable than those involving K–S or K–K transitions at the lower temperatures, because the latter are subject to substantial supercooling. In the CCH-2/CCH-3 series in particular (figure 1), this resulted in particularly poor reproducibility in the D.S.C. heating scans.

Transition enthalpies for the various phase transitions in the pure and mixed mesogens are collected in the table. Since these quantities varied somewhat depending on sample composition, they are reported in the table as enthalpy ranges. Individual values are estimated to be accurate to ± 10 per cent.

3. Discussion

No less than four different types of highly-ordered smectic phases are exhibited by these three mesogens and their binary mixtures. For the purposes of discussion, these are labelled in the phase diagrams shown in figures 2, 4, and 6 as S(I), S(II), etc., in order of increasing enthalpy content. It is clear, first of all, that the high temperature

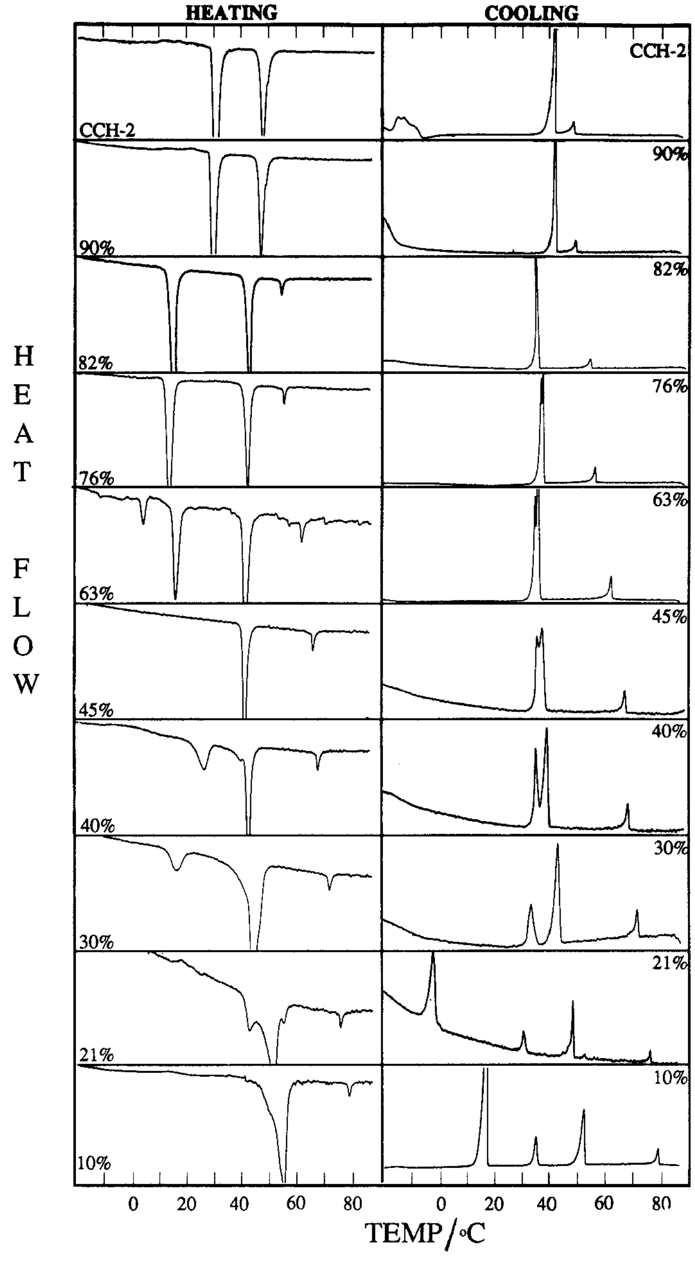


Figure 1. Representative D.S.C. traces obtained for CCH-2/CCH-3 mixtures, recorded with a 2°/min temperature programme. (*a*) Heating; (*b*) Cooling.

smectic phases of each of these three CCH derivatives are different, with the relative degree of smectic phase order decreasing in the sequence CCH-2 > CCH-4 > CCH-3. Such a dramatic variation in mesomorphic behaviour within the homologous series might not be unexpected, considering that these compounds have such short alkyl chains and their smectic phases are very highly ordered. Similar variations in mesomorphic behaviour within homologous series have been observed previously for *n*O.*m* liquid crystals [21].

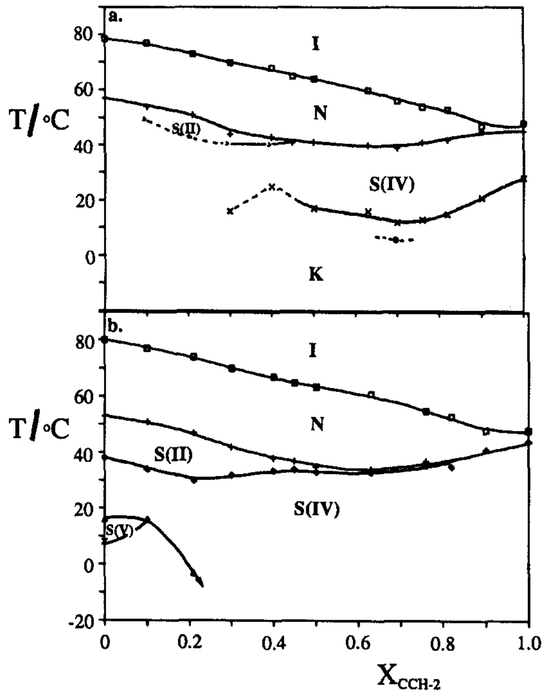


Figure 2. Binary phase diagrams for the CCH-2/CCH-3 system, measured by differential scanning calorimetry. (*a*) Heating; (*b*) Cooling.

Transition enthalpies for K–S, S–S, S–N, and N–I phase transitions in pure and mixed CCH-*n* liquid crystals†

Transition type	ΔH/kcal/mol	Example
N–I	0·16–0·25	All
S(I)–N	0·58–0·86	CCH-2/CCH-4 (20–70 per cent)
S(II)–N	0·90–1·21	CCH-3
S(III)–N	1·06–1·24	CCH-4
S(IV)–N	1·38–1·82	CCH-2
S(I)–S(III)	0·09–0·12	CCH-2/CCH-4 (20–65 per cent)
S(I)–S(IV)	0·31–0·41	CCH-2/CCH-4 (65–70 per cent)
S(II)–S(III)	0·12–0·20	CCH-3/CCH-4 (20–65 per cent)
S(II)–S(IV)	0·33–0·49	CCH-2/CCH-3 (0–55 per cent) CCH-3/CCH-4 (65–100 per cent)
S(III)–S(IV)	0·04–0·25	CCH-3/CCH-4 (0–65 per cent)
S(IV)–S(V)	0·29–0·32	CCH-3‡
K–S(III)	2·84–3·26	CCH-4
K–S(IV)	2·18–3·21	CCH-2
K–S(V)	2·60–3·40	CCH-3‡

† Calculated from D.S.C. cooling and/or heating scans. 1 = isotropic; N = nematic; S = smectic; K = solid.

‡ Cooling only.

As figures 5 and 6 show, the single, enantiotropic smectic phase of pure CCH-4 (S(III)) and the (monotropic) S_1 phase of pure CCH-3 (S(II)) are immiscible. The enthalpy difference between the two phases is *c*. 0·2 kcal/mol, with the latter being the less-ordered of the two. This result is particularly significant, since reported X-ray

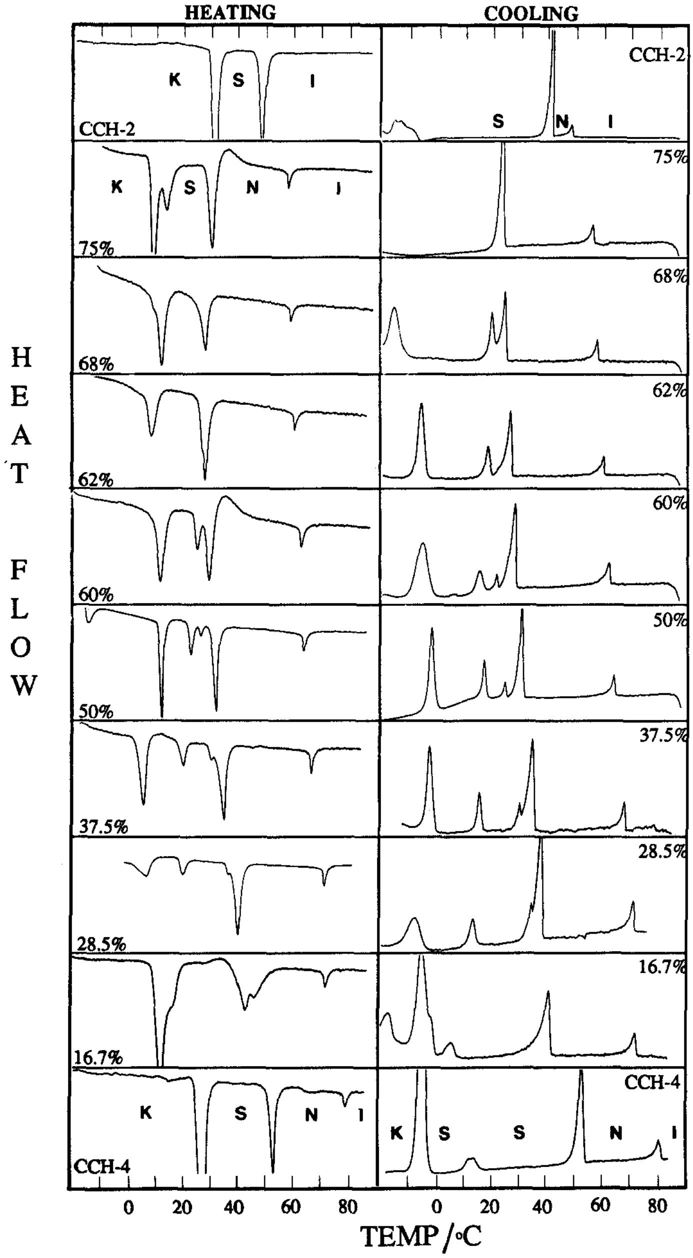


Figure 3. Representative D.S.C. traces obtained for CCH-2/CCH-4 mixtures, recorded with a 2°/min temperature programme. (*a*) Heating; (*b*) Cooling. Phase identities have been labelled in representative mixtures: I, isotropic; N, nematic; S, smectic; K, crystalline.

diffraction data indicate that the two phases are very similar [3, 4]; both phases reportedly possess an interdigitated, bilayer structure with hexagonal packing within the bilayers. It was concluded that the molecular orientation within the layers is perpendicular to the layer plane in the case of the S(II) phase of pure CCH-3 [3]. In the case of S(III) (of pure CCH-4), the data reported evidently do not allow one to distinguish between a perpendicular or a slightly tilted intralayer orientation in this phase [4].

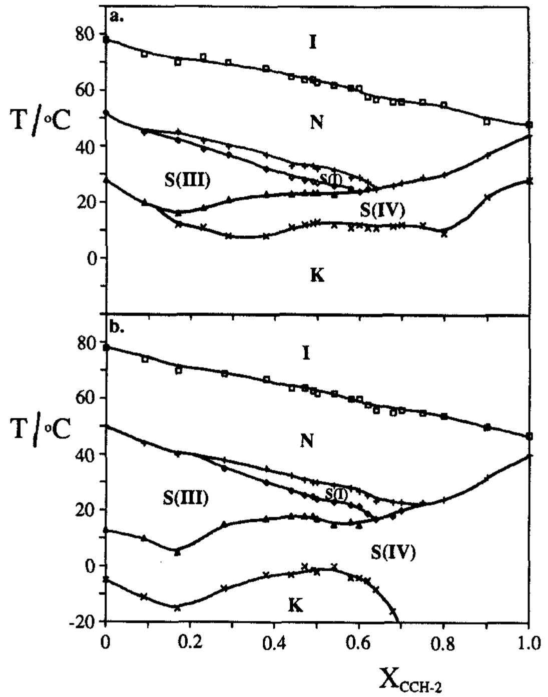


Figure 4. Binary phase diagrams for the CCH-2/CCH-4 system, measured by differential scanning calorimetry. (*a*) Heating; (*b*) Cooling.

Brownsey and Leadbetter have provided a rather detailed description of the smectic phase structure of S(II) in pure CCH-3 [3]. The packing in this phase is characterized by *ABAB* . . . type packing of equivalent half-layers, and the interdigitated bilayer structure has been proposed to be the result of steric, layer packing factors as opposed to polar ordering effects [3]. The interdigitation results in a bilayer thickness that is somewhat less (5·7 Å) than twice the molecular length of the mesogen. A similar difference between bilayer thickness and two molecular lengths (5·8 Å) was found for the smectic phase of CCH-5, leading to the conclusion that the high temperature smectic phases of these two homologs are identical [3].

This differs somewhat from the analogous parameter obtained from the X-ray data for the smectic (S(III)) phase of pure CCH-4 [4]; in this case, the difference between the observed bilayer thickness and two molecular lengths is 4·0 Å [4]. While this corroborates our own conclusion that the two smectic phases are slightly different, it presumably indicates that half-layer interdigitation is slightly *less*-pronounced in S(III) relative to that in S(II). If this is the case, then some other factor must overshadow half-layer interdigitation in contributing to the overall higher degree of order possessed by S(III) compared to S(II).

Another feature that should be noted is that the single smectic phase of pure CCH-2 (S(IV)) appears to be miscible with the monotropic, previously unidentified S_2 phase of CCH-3 (figures 1 (*b*), 2 (*b*)). While this phase has been found to possess a rhombohedral structure by X-ray diffraction studies on pure CCH-2 [4], X-ray data for this phase in pure CCH-3 cannot be obtained because of its propensity to crystallize [3]. In CCH-2/CCH-3 mixtures, this propensity exists only for those rich

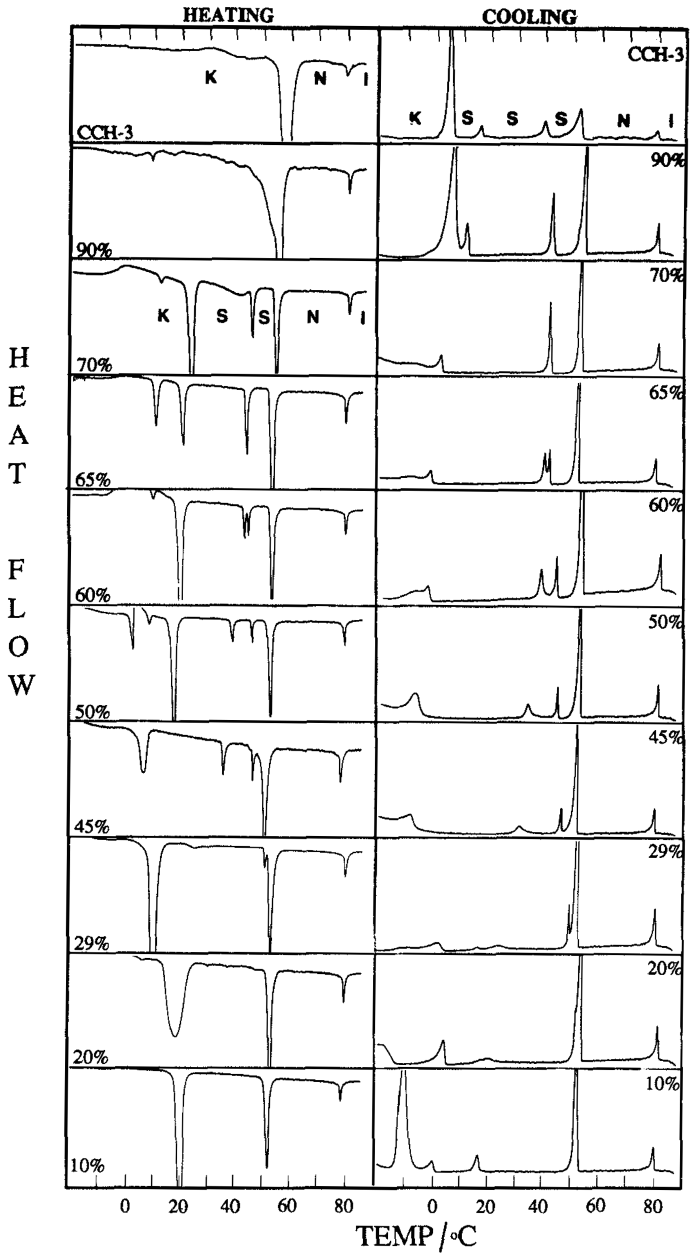


Figure 5. Representative D.S.C. traces obtained for CCH-3/CCH-4 mixtures, recorded with a 2°/min temperature programme. (*a*) Heating; (*b*) Cooling. Phase identities have been labelled in representative mixtures: I, isotropic; N, nematic; S, smectic; K, crystalline.

(> 70 mol %) in CCH-3. It is due to the monotropic behaviour of these mixtures that the D.S.C. heating and cooling traces (figure 1), and the resulting phase diagrams (figure 2), differ so dramatically.

The D.S.C. cooling data for CCH-4 provides evidence that an additional, monotropic smectic phase is formed by this compound at 10–12°C (see figure 3). This

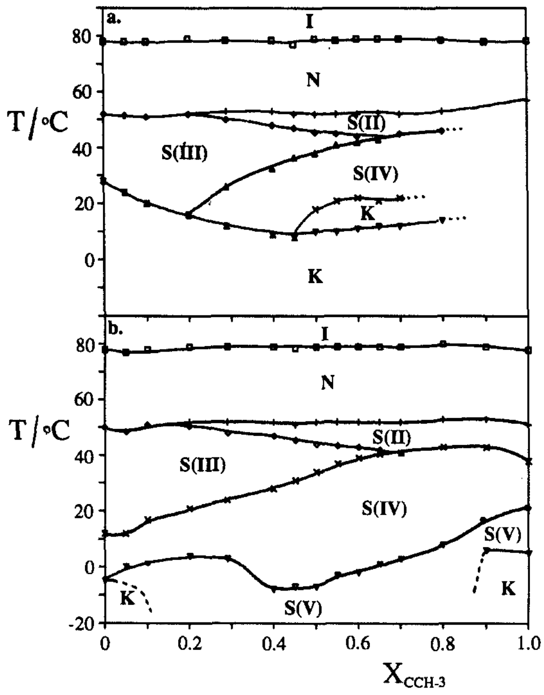


Figure 6. Binary phase diagrams for the CCH-3/CCH-4 system, measured by differential scanning calorimetry. (*a*) Heating; (*b*) Cooling.

monotropic phase is miscible with the enantiotropic S phase of CCH-2 and the second monotropic Sm phase of CCH-3, and can thus be assigned the S(IV) phase structure.

Mixtures of CCH-2 and CCH-4 in the 0·2–0·7 mol % composition range afford a high temperature, injected smectic phase (S(I)) that is common to neither of the pure mesogens. While we have labelled it differently than the high temperature S(II) phase associated with the CCH-2/CCH-3 and CCH-3/CCH-4 mixtures (the S_1 phase of pure CCH-3), there is some possibility that the two are in fact identical. Texture comparisons (*vide infra*) are largely inconclusive, and transition enthalpy comparisons lead to somewhat conflicting conclusions. If S(I) is a less-ordered smectic phase than S(II), then one would expect this to be reflected in several of the transition enthalpies shown in the table. The S(I)–N transition enthalpies are significantly lower than those for the S(II)–N transitions, which provides the strongest evidence that S(I) is less-ordered than S(II) and forms the basis for our labelling the two as different. The S–S transition enthalpies lead to the opposite conclusion, although with considerably less certainty; those for the S(I)–S(III) and S(I)–S(IV) transitions are both slightly *lower* (or perhaps the same within experimental error) than those for the S(II)–S(III) and S(II)–S(IV) transitions, respectively.

We also note that the 65 per cent CCH-2/CCH-4 mixture forms a nematic phase between 25°C and 54°C, and thus affords a potentially useful room-temperature nematic solvent for spectroscopic and photochemical studies [10]. This mixture is a useful alternative to the ternary eutectic mixture of CCH-3/CCH-5/CCH-7 (ZLI-1167).

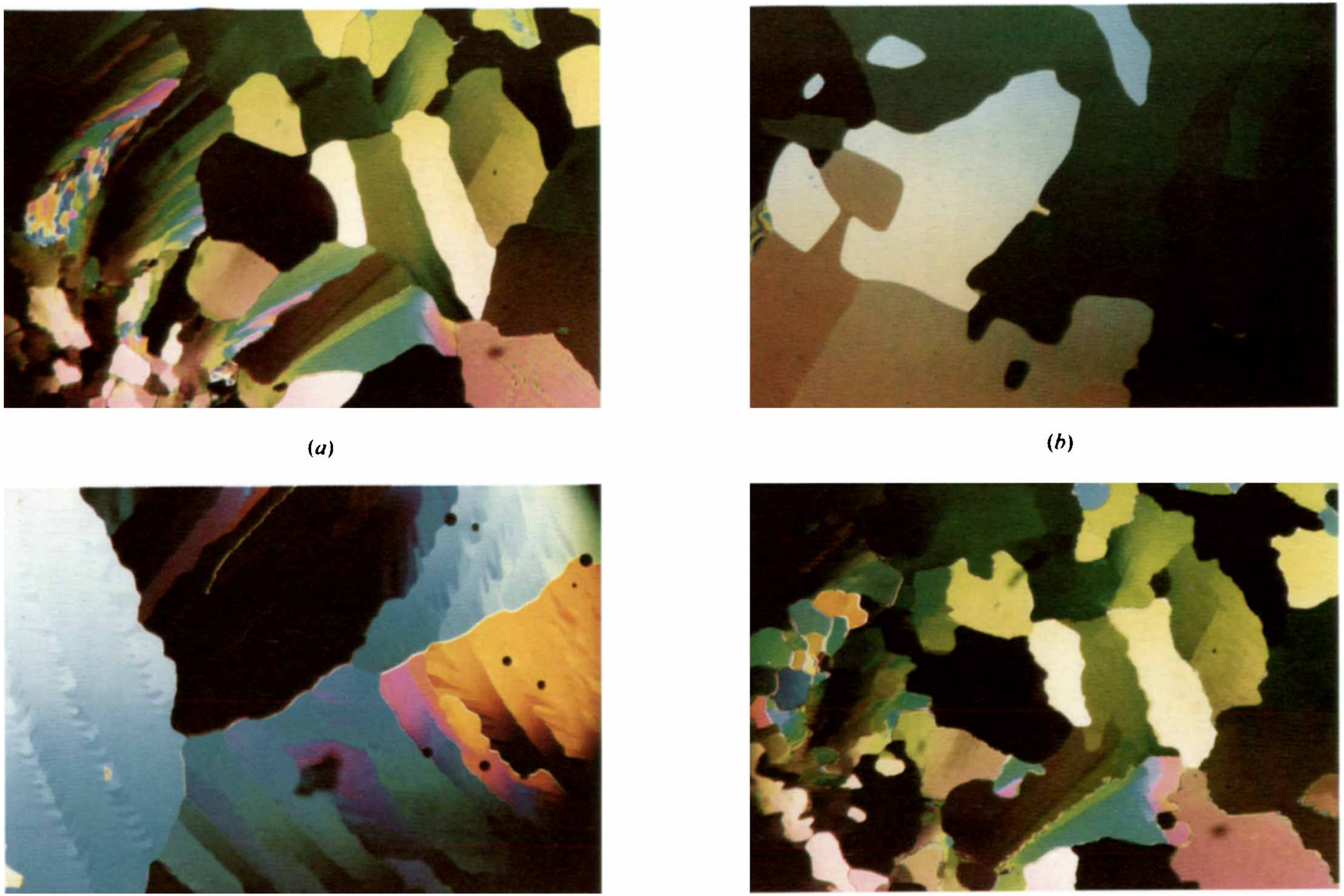
The various phase transitions that interconvert the five smectic phases with nematic phases are subject to substantial supercooling in some cases. With a 2°/min cooling rate, the N–S(I) and N–S(II) transitions are supercooled by 1–2°, the N–S(III) by *ca.* 3°, and the N–S(IV) by *ca.* 7°C. This provides a further indication of the highly-ordered, crystalline nature of these smectic phases that is implied by their X-ray diffraction data. In general, the various S–S transitions are subject to only slight supercooling, by 1–2° at most. Pronounced supercooling occurs in the K–S transitions, the most severe case (> 30°C) being that of the K–S(IV) transition in mixtures rich in CCH-2.

Each of these phases exhibits a variety of mosaic microscopic textures, depending on the composition of the sample and its thermal history. While S(I) and S(IV) can be fairly readily identified by their textures, S(II) and S(III) are extremely difficult to differentiate by this method. Representative photographs comparing the mosaic textures of the S(I)–S(III) phases obtained under various conditions are shown in figure 7. The S(I) phase in CCH-2/CCH-4 mixtures is most readily identified by the texture obtained when it is formed by cooling from the nematic phase (e.g. figure 7 (*a*)). The ridges that appear in some of the monodomains are the result of the N–S(I) transition being fairly broad, and are much more distinct at temperatures closer to the transition. A more uniform mosaic texture is obtained when this phase is formed by heating from S(IV) or S(III) (e.g. figure 7 (*b*)), and the phase transition is accompanied by a marked reorganization of the monodomains in the lower temperature phase. Figure 7 (*c*) shows an example of the S(II) phase textures, generated by cooling from the nematic phase. Other examples of the mosaic microscopic textures of this phase for pure CCH-3 have been reported previously [22]. The mosaic texture of the S(III) phase tends to be characterized by a jagged appearance of the domain boundaries when it is formed by cooling from S(I) or S(II) (figure 7 (*d*)), but more uniform mosaic textures are obtained when the sample is allowed to anneal or when the phase is formed directly from the nematic phase in pure CCH-4.

The S(IV) phase also exhibits a number of textures depending on sample composition and thermal history, and examples of these are shown in figure 8. This phase is, in all cases, extremely rigid and non-deformable. Formation of the S(IV) phase by cooling from the nematic in pure CCH-2 results initially in a sawblade-like texture (figure 8 (*a*)) that transforms slowly into a mosaic one (figure 8 (*b*)) upon annealing at 27–35°C for long periods of time (several days, at least). In the mixed liquid crystals, the S(IV) texture (upon cooling from the higher temperature Sm phases) is characterized by contracted mosaic monodomains (figure 8 (*c*)). An example of the ridged mosaic texture of this phase in pure CCH-3 has been reported elsewhere [22]; figure 8 (*d*) shows another contracted mosaic texture characteristic of this phase.

4. Summary and conclusions

The miscibility studies reported herein provide important new information on the relationships between the highly-ordered smectic phases in CCH-*n* mesogens, supplementing that previously available from X-ray diffraction studies. The $n = 3$, 4, and 5 members of the series all form very similar, bilayer crystal-B (or B-like) phases. The structures of the monotropic S_1 phases of CCH-3 and CCH-5 are identical [3], and possess a slightly lower degree of order than the enantiotropic bilayer crystal-B phase of CCH-4. The enantiotropic smectic phase of the $n = 2$ homolog possesses rhombohedral packing with threefold symmetry [4], and is miscible with the monotropic S_2 phase of CCH-3 and a previously unreported, low-temperature monotropic smectic phase of CCH-4. Mixtures of CCH-2 and CCH-4 exhibit an injected smectic (B-like) phase that is less-ordered than those exhibited by either of the pure mesogens. On the



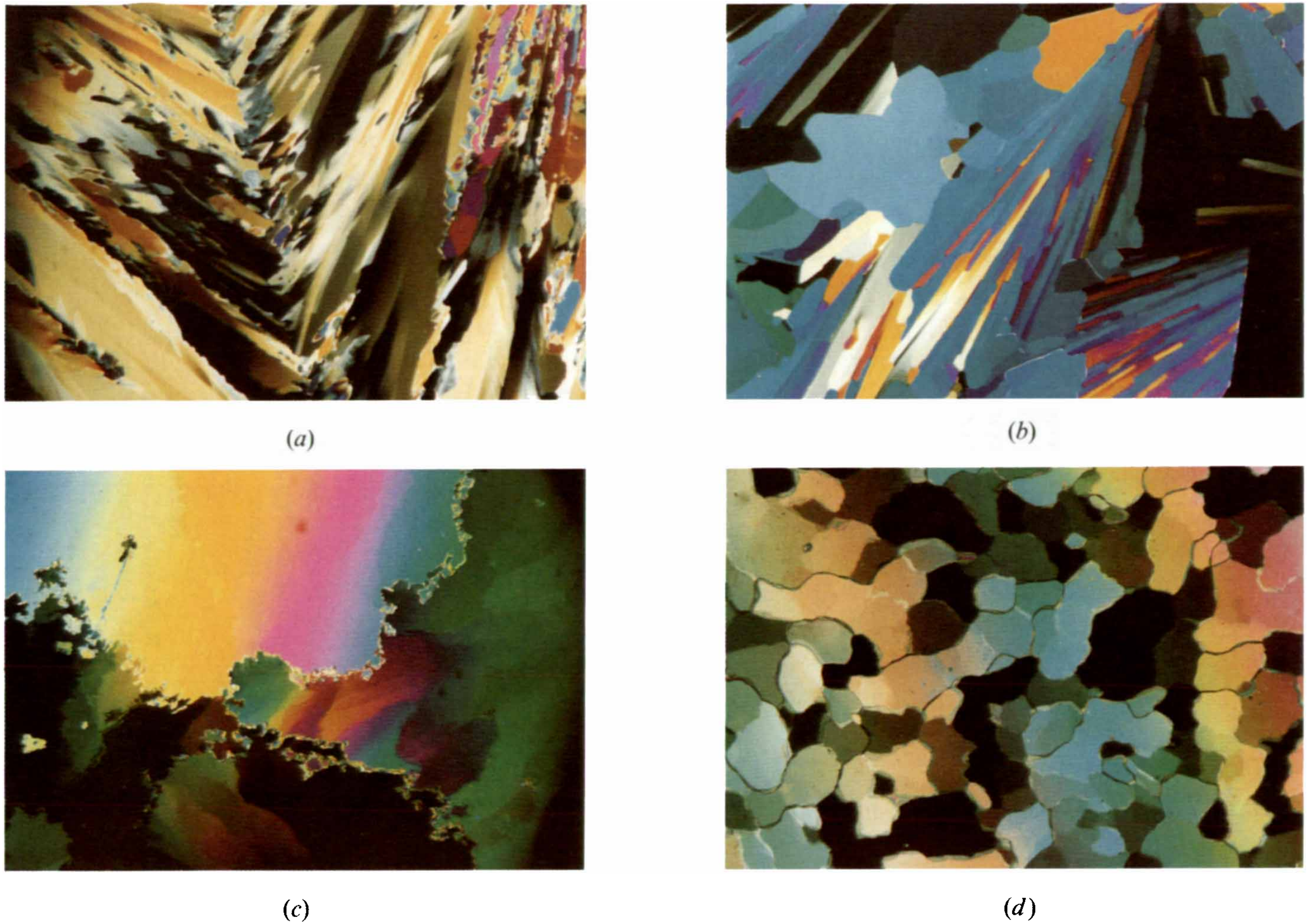
(*a*)

(*b*)

(*c*)

(*d*)

Figure 7. Microscopic textures of the hexagonal S(I)–S(III) phases in pure and mixed CCH-*n* liquid crystals. (*a*) S(I) phase of 37 per cent CCH-2/CCH-4 (35°C), cooled from nematic; (*b*) S(I) phase of 54 per cent CCH-2/CCH-4 (28°C), warmed from S(III); (*c*) S(II) phase of CCH-3 (50°C), cooled from nematic; (*d*) S(III) phase of 37 per cent CCH-2/CCH-4 (29°C), cooled from S(I) (see figure 7(*a*)).



(*a*) (*b*) (*c*) (*d*)

Figure 8. Microscopic textures of the rhombohedral S(IV) phase in CCH-*n* liquid crystals: (*a*) saw-blade texture in pure CCH-2 (39°C), cooled from nematic; (*b*) mosaic texture (23°C), formed by annealing the saw-blade texture in CCH-2; (*c*) contracted mosaic texture in 37 per cent CCH-2/CCH-4 (19°C), cooled from S(III); (*d*) contracted mosaic texture in 45 per cent CCH-3/CCH-4 (22°C), cooled from S(III).

basis of N–S transition enthalpies, we tentatively conclude that this new phase is also of lower-order than the S_I phase of CCH-3.

5. Experimental

The 4′-alkylbicyclohexyl-4-carbonitriles were used as received from E. Merck (Darmstadt).

D.S.C. experiments were carried out on a Setaram DSC111 differential scanning calorimeter, interfaced to a Hewlett-Packard HP85 microcomputer that controls the experiment and provides data storage and hard copy facilities. Samples were prepared by weighing the appropriate amounts of the mesogens into a roundbottom flask, dissolving the mixture in dichloromethane (Caledon HPLC), evaporating the solvent on the rotary evaporator, and finally pumping on the mixture under vacuum (*c.* 10^{-3} torr) for about an hour to ensure complete removal of the solvent. The mixtures were then weighed into aluminum crucibles and crimp-sealed. For each mixture, D.S.C. thermograms were recorded between −20°C and 90°C in heating and cooling cycles, using a 2°/min temperature program in each case. Each run was repeated at least once to ensure reproducibility.

Transition enthalpies were calculated from the D.S.C. thermograms by standard methods using software supplied by the manufacturer, or after manual estimation of D.S.C. peak areas by the cut-and-weigh method. The two procedures were shown to give equivalent results within our quoted limits of error.

Thermal microscopy experiments were carried out in transmission using a Reichert Hot-stage microscope equipped with a calibrated glass thermometer and polarizing filters, or a Vickers petrographic microscope fitted with an RCA CC010 colour video camera (whose signal was fed into a conventional video recorder/colour monitor), polarizing filters, and a home-made brass hot-stage. Hot-stage temperatures were recorded with a Cole-Parmer Type K thermocouple thermometer, and were calibrated with a series of melting point standards.

Still photographs were recorded using a Leitz Laborlux petrographic microscope fitted with a Leitz photoattachment, NPL flat-field lenses, the brass hot-stage and thermocouple thermometer, a 15 W tungsten lamp, Koehrler illumination, a 10 × ocular, 6·3 × objective, and a Wratten 80A blue filter. Photographs were recorded (1·0 × 1·5 mm field) on Kodacolor VR-G CB-135 film.

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