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Smectic polymorphism in a series of three-ring enaminoketone compounds

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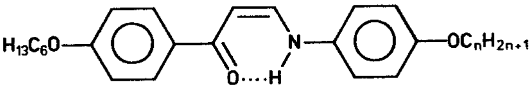
Liquid crystalline properties of 1-(4′-alkoxyphenylamino)-3-(4′-hexyloxyphenyl)-prop-1-en-3-ones, from methoxy to heptadecyloxy, have been examined by optical, DSC, and X-ray methods. The phase diagram for the series exhibits a rich polymorphism of tilted smectic phases, for example, five mesophases were found for the hexyloxy derivative. A characteristic feature of the phase diagram is a gap in the crystal G phase area. For the heptyloxy homologue, a direct crystal H–smectic F phase transition was found; in the case of shorter as well as longer terminal substituents, the phase sequence crystal H–crystal G–smectic F is observed. Calorimetric and X-ray studies revealed the existence of a tricritical point on the crystal G–smectic F transition line.

1. Introduction

Novel β-enaminoketone derivatives revealing liquid crystalline properties have been recently reported [1–3]. For some homologous series of three-ring compounds the phase properties have been studied in detail [2, 3]. In the case of compounds having a short terminal substituent, a rare phase sequence involving unordered, hexatic, and crystal untilted smectics was found. In this work, the phase properties of another series of enaminoketones terminating in a much longer substituent:



are presented. The compounds (denoted for short as HEX*n*) as examined by microscopy, microcalorimetry and X-ray methods, appeared to exhibit tilted smectic behaviour. Here we concentrate on their phase properties, as well as their phase transitions and critical behaviour.

2. Results

2.1. *Synthesis and characterization of HEX compounds*

These compounds were synthesized by reacting hydroxymethylene derivatives of 4-hexyloxyphenylacetophenone with 4-alkoxyanilines and purified by crystallization

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from toluene. Purity of the compounds was checked by DSC. A typical synthetic procedure is described for 1-(4′-methoxyphenylamino)-3-(4′-hexyloxyphenyl-prop-1-en-3-one: The sodium salt of 3-(4′-hexyloxyphenyl)-3-oxo-propanal was obtained by the Claisen formulation reaction by adding 4-hexyloxyacetophenone (15 mmol) and ethyl formate (5 ml) to the sodium powder (0·4 g) dispersed in ethyl ether (25 ml) and stirring the mixture for 12 h. After the ether and the excess of ethyl formate had evaporated, the remaining crude sodium salt (yield *c.* 70 per cent) was dissolved in methanol. To that solution (*c.* 10 mmol) in methanol (20 ml), 10 mmol of anisidine in the same solvent (20 ml) were added, then neutralized with acetic acid and left. After 12 h yellow crystals of the product were filtered off and recrystallized. Yield 3·0 g (87 per cent), mp 134°C, clp 199·5°C, elemental analysis gave calculated: C, 74·74 per cent, H, 7·71 per cent, N, 3·96 per cent, found: C, 74·87 per cent, H, 7·82 per cent, N, 3·90 per cent. IR and NMR spectra are consistent with the molecular structure. ^{1}H MNR ($CDCl_3$): δ 0·75–2·00 (m, 11 H, $(CH_2)_4CH_3$), 3·80 (s, 3 H, OCH_3), 4·00 (t, $J = 6{\cdot}2$ Hz, 2 H, OCH_2), 5·92 (d, $J = 8{\cdot}0$ Hz, 1 H, H^2), 6·75–7·20 (m, 6 H, aromatic), 7·37 (dd, $J = 8{\cdot}0$ Hz, 14·2 Hz, 1 H, H^1), 7·90 (d, $J = 8{\cdot}5$ Hz, 2 H, $H^{2''}$, $H^{6''}$), 12·11 (d, $J = 14{\cdot}2$ Hz, 1 H, NH). A relatively low value of $J_{C^1HC^2H}$ as well as high values of J_{C^1HNH} and δ_{NH} confirm a stabilized by hydrogen bonding, *cis–s–cis* configuration of the enaminoketone moiety in solution [2 (b)]. This configuration is preserved in the crystal, as results from single-crystal X-ray structure analysis show [2 (a)], as well as in meso- and isotropic phases, as results from DSC thermograms also show [2 (b)].

2.2. *Phase diagram and microscopic studies*

The phase diagram of the HEX*n* series is shown in figure 1. Phase identification based on observation of textures and miscibility tests was confirmed by X-ray analysis. Our analysis was confirmed, for some phases, by studies of aligned samples [4]. A tendency toward formation of tilted phases is so strong that no untilted phases were observed at all.

All phase transitions presented in the phase diagram can be observed microscopically. It is of interest that the textures of smectic F and crystal G phases depend on the length of the terminal tails (see figures 2 and 3). For lower homologues, the appearance of a S_F phase from a S_C is accompanied by a freezing of the schlieren texture. From the S_F phase, the crystal G phase appears as evidenced by a mosaic texture formation. For higher homologues, both transitions, although less pronounced, are still well discernible and occur in a narrow temperature range, within 0·2°C. On cooling the crystal G phase, a mosaic texture with zig-zag defects was observed, thus providing evidence for the formation of the crystal H phase [5, 6].

For compound HEX7, a direct transition from the smectic F to crystal H phase was observed, while for both shorter and longer homologues the crystal G phase appears between these phases. The topology of a phase diagram having a crystal G phase gap was confirmed by studies of phase transitions in HEX6–HEX7 and HEX7–HEX8 binary mixtures (see figure 4 (*a*, and *c*)). The identity of the crystal G phase for short and long homologues was deduced from the phase diagram of the HEX6–HEX8 system (see figure 4 (*b*)). Phase diagrams with such a gap in a phase area are rather rare among homologous series of calamitic liquid crystals [7]. Recently, a nematic gap was observed in the smectic A area in the phase diagram of a homologous series of non-symmetrical dimers which exhibit a S_A phase [8]. However, different structures of smectic phases for short and long chain members of

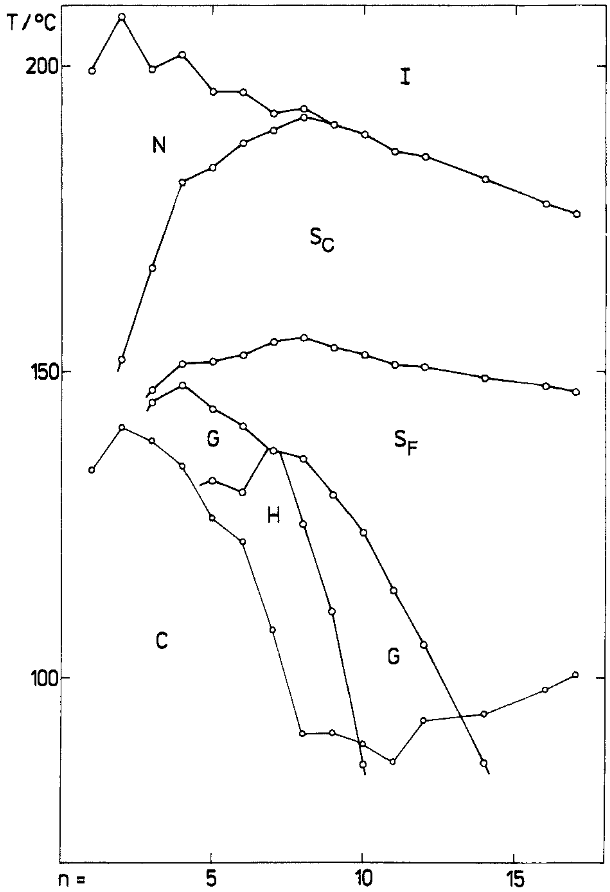


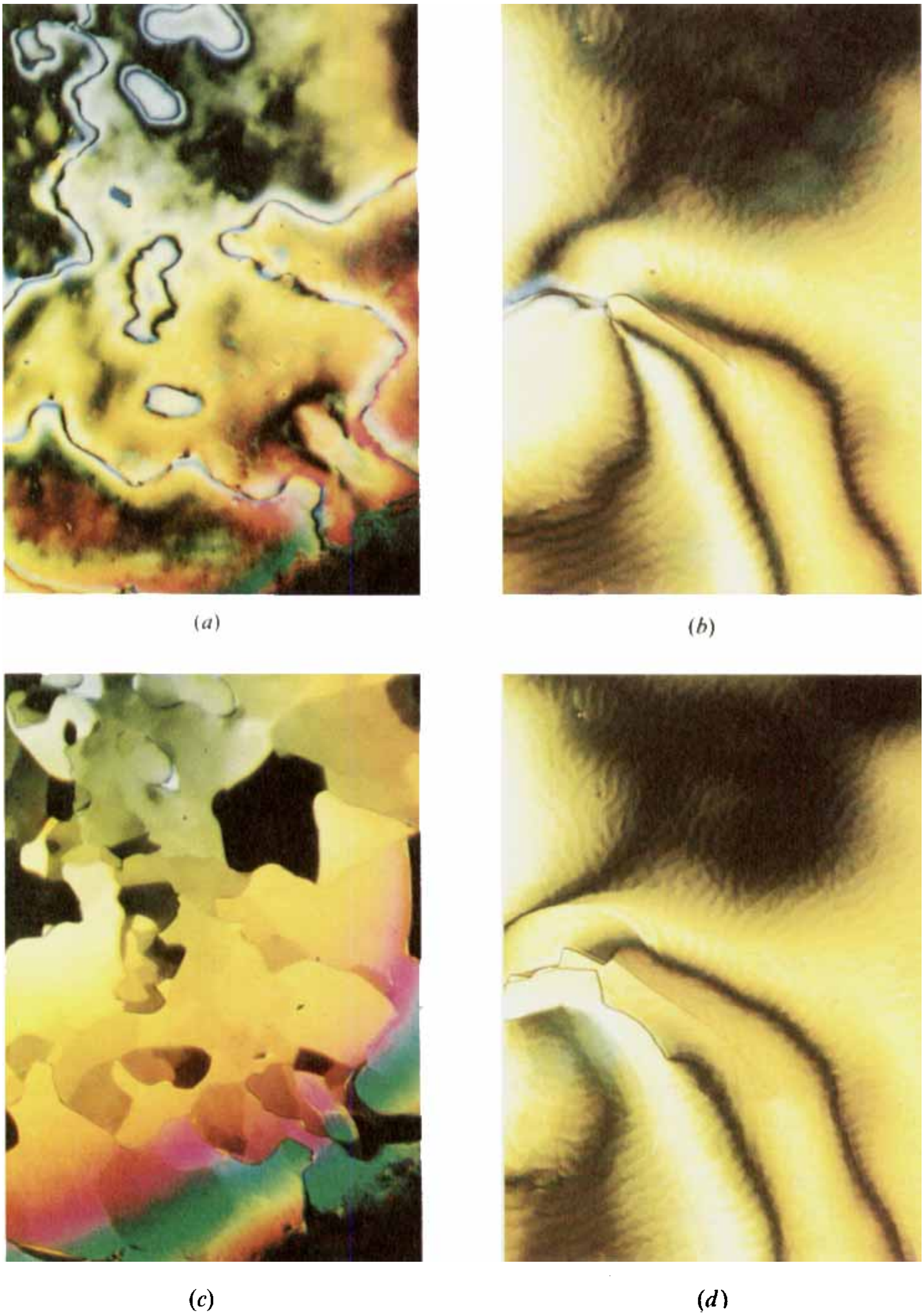
Figure 1. Phase diagram for the homologous HEX*n* series.

the series were reported in that case, whereas in our study full miscibility of the phases is confirmed.

2.3. *Calorimetric studies*

The studies were performed using Perkin–Elmer DSC7 set-up. The enthalpies and temperatures of the phase transitions are summarized in table 1. Thermograms obtained for some compounds revealing the crystal G–S_F–S_C phase sequence are presented in figure 5. As shown, the transition from the fluid phase, S_C to the hexatic one, S_F, is accompanied by strong anomalies of the heat capacity, which cause distinct broadening of the transition peaks. Such anomalies are a characteristic feature of second order transitions, as for example the N–S_A [9, 10].

In contrast, peaks corresponding to the transition from hexatic S_F to crystal G phases are sharp, without precritical specific heat anomalies, thus indicating a first order phase transition. The relevant enthalpy is relatively small, of the order of 0·1 $J\,g^{-1}$, and decreases systematically with increasing molecular length (see figure 6). For compounds HEX12 and HEX14 no relevant peak in the thermograms is present, although for both compounds the phase transition is still observable



(*a*) (*b*)

(*c*) (*d*)

Figure 2. Textures of HEX6 (left) and HEX12 (right) in the smectic F (upper row) and crystal G phases (lower row): (*a*) 150°C, (*b*) 135°C, (*c*) 110°C, (*d*) 105°C.

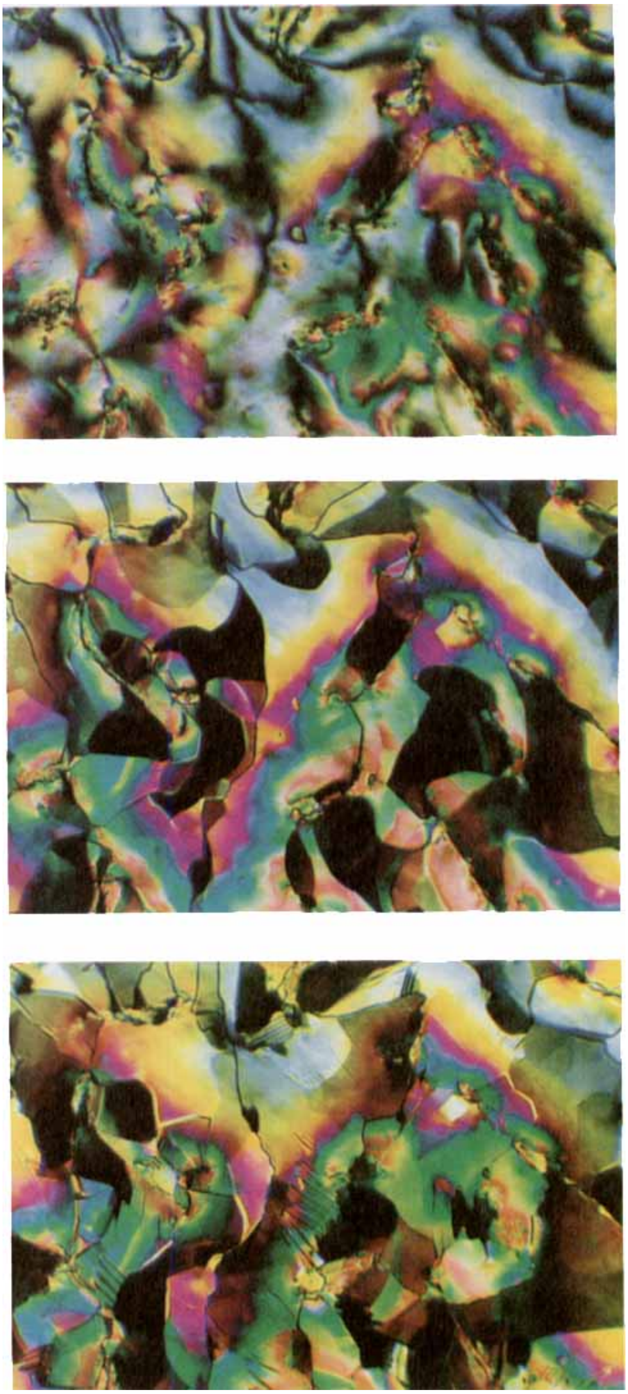


Figure 3. Textures of HEX6. From the upper texture: S_F phase (150°C), crystal G phase (140°C) and crystal H phase (130°C).

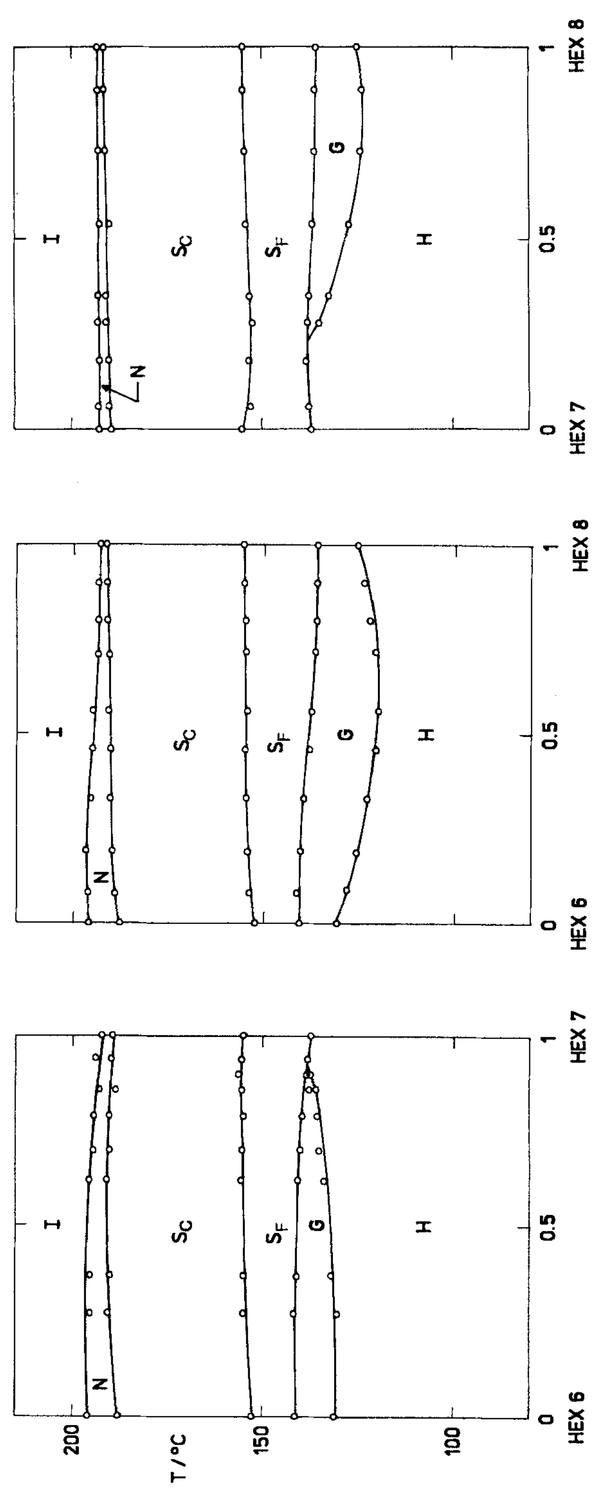


Figure 4. Phase diagrams for some binary systems. Concentrations are in mole fractions.

Table 1. Temperatures (°C) and, in parentheses, enthalpies (kJ mol^{-1}) of the phase transitions for the compounds $H_{13}C_6O$–C_6CO–CH=CH–NH–C_6H_4–OC_nH_{2n+1} (HEX*n* series).

n	C		H		G		S_F		S_C		N		I
1	●	133·8 (33·1)	●	—	●	—	●	—	●	—	●	199·3 (1·35)	●
2	●	140·7 (10·0)	●	—	●	—	●	—	●	151·9 (1·85)	●	208·3 (1·85)	●
3	●	138·6 (9·88)†	●	—	●	145·0 (2·30)†	●	147·0 (0·55)	●	167·0 (2·50)	●	199·4 (1·70)	●
4	●	134·4 (10·3)	●	—	●	147·8 (0·87)	●	151·2 (1·05)	●	181·2 (2·70)	●	201·9 (2·10)	●
5	●	126·0 (9·71)	●	132·2 (0·25)	●	143·9 (0·45)	●	151·6 (1·50)	●	183·4 (3·80)	●	195·9 (2·30)	●
6	●	122·3 (19·7)	●	130·0 (0·13)	●	147·0 (0·28)	●	152·7 (1·95)	●	187·4 (4·15)	●	195·8 (2·65)	●
7	●	107·8 (20·8)	●	137·2 (0·22)	●	—	●	155·0 (2·05)	●	189·1 (5·20)	●	192·3 (2·65)	●
8	●	90·8 (14·1)	●	125·1 (0·06)	●	135·8 (0·15)	●	155·5 (2·45)	●	191·5 (9·85)†	●	193·1	●
9	●	91·1 (28·3)	●	111·0 (0·05)	●	130·1 (0·08)	●	153·9 (2·35)	●	190·3 (10·6)	●	—	●
10	●	89·2 (27·9)	●	89·0	●	123·8 (0·05)	●	152·8 (2·45)	●	188·8 (11·1)	●	—	●
11	●	86·3 (37·7)	●	—	●	114·3 (0·015)	●	151·1 (2·70)	●	186·1 (10·9)	●	—	●
12	●	93·0 (37·7)†	●	—	●	105·6 (0·00)	●	150·9 (2·60)	●	185·3 (11·3)	●	—	●
14	●	94·1 (43·0)†	●	—	●	86·2 (0·00)	●	149·0 (2·75)	●	181·4 (11·1)	●	—	●
16	●	97·9 (56·7)	●	—	●	—	●	147·7 (2·70)	●	177·6 (11·5)	●	—	●
17	●	100·5 (66·0)	●	—	●	—	●	146·7 (3·05)	●	175·9 (12·0)	●	—	●

† Subsequent polymorphic transition peaks not resolved.

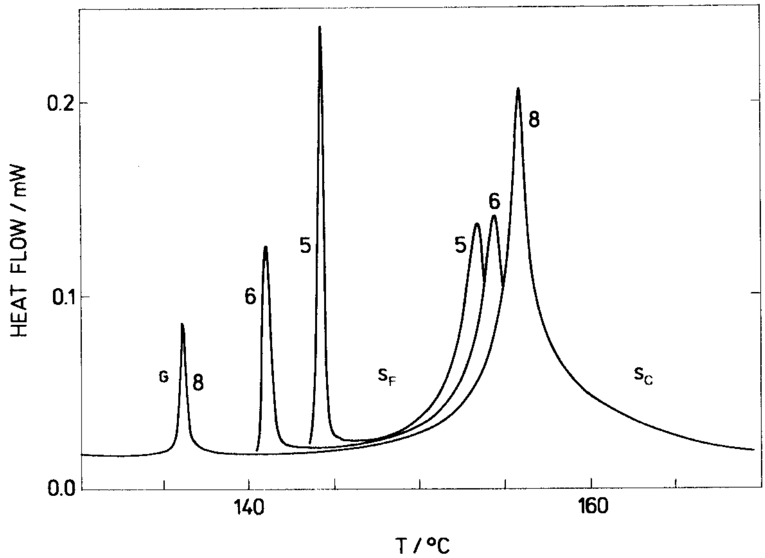


Figure 5. DSC scans (5°C min^{-1}, 1 mg sample) across the crystal G, smectic F and smectic C phases for some HEX*n* homologues.

microscopically. As can be seen from figure 6(*b*), a point at which the transition enthalpy reaches zero is located at $n = 11{\cdot}3$. This is a tricritical point, in which the first order phase transition turns into the second order one for binary mixtures.

It seems that for the series studied, the position of the tricritical point is controlled by a temperature range of the hexatic phase (see figure 6). The broadening of the S_F phase lowers the enthalpy change of the S_F-crystal G phase transition. For

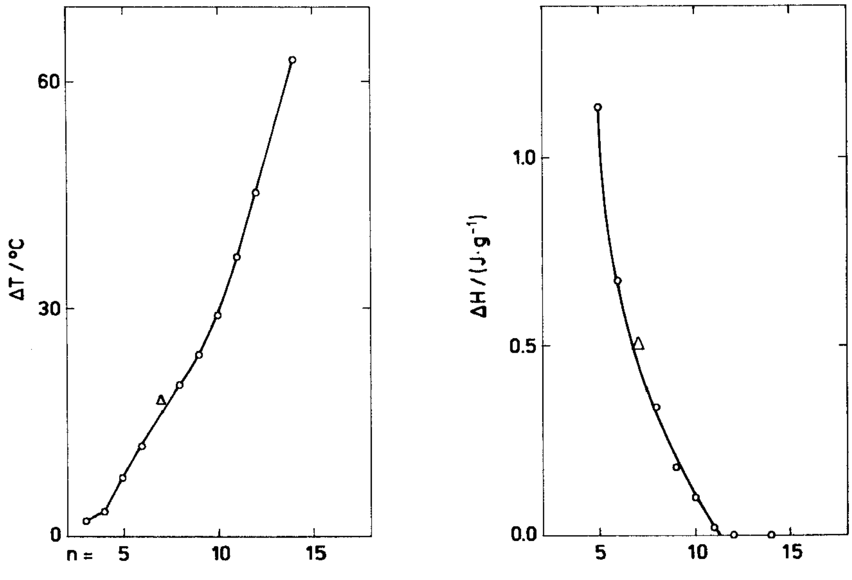


Figure 6. The temperature range of the smectic F phase (left) and enthalpy of the S_F-crystal G phase transitions (right): Data for pure compounds (○) and for equimolar mixtures HEX6–HEX8 (Δ), corresponding to $n = 7$.

a phase broader than 40°C no enthalpy change accompanies this transition. This kind of behaviour, well known for the N-S_A phase transition, was recently found also for the S_B(hex)-crystal B transition [3], the broader the less ordered (hexatic) phase the smaller the transition enthalpy is observed.

2.4. *X-ray studies*

X-ray measurements were performed for powder samples of HEX6 and HEX12. For all the smectic phases of both compounds only first order, (001) low angle reflections, corresponding to interlayer distances, were observed. In the high angle region, the shape of the diffraction lines changes with temperature. For the S_C and S_F phases, a single, diffuse reflection line was observed confirming the absence of long range positional order within the smectic layers. The transition to the three dimensional crystal G phase is accompanied by the appearance of much sharper Bragg reflections [11, 12]. For HEX6, only a single line assigned to the (110) reflection was observed. For the HEX12 several lines were observed with the strongest ones attributed to (110) and (200) reflections. For this compound the interlayer distance, and thus also the tilt angle, does not change noticeably at the S_F-crystal G phase transition (see Table 2). This observation confirms the possibility of a continuous phase transition between the hexatic and crystal smectics.

3. Discussion

Although the studied compounds have an unconventional ring in their mesogenic core, they reveal properties typical for three-ring, rod-like mesogens. In contrast to previously studied enaminoketone derivatives having a pirydil ring [2 (*b*)] instead of a phenyl one, the studied compounds exhibit a strong tendency toward formation of tilted rather than orthogonal smectic phases. An interesting feature of the phase diagram is the existence of a gap in the crystal G phase area for one of the compounds of the homologous series. In binary mixtures, the corresponding gap is rather narrow, only 0·32 mole fraction. This suggests the molecular interactions, which are responsible for mesogenic phase formation, are highly sensitive to the molecular structure. The crystal G phase is destabilized in favour of a more ordered crystal H phase.

As the easy formation of tilted phases for the HEX series results, subsequent phase transitions between unordered, hexatic, and crystalline tilted phases appear for several compounds, thus allowing studies of relevant phase transitions. Theoretically, it has been argued that coupling between bond orientational order and molecular tilt should induce long range hexatic order in the fluid S_C phase [14]. As a consequence, there is no symmetry change between fluid and hexatic phases, thus, a

Table 2. X-ray diffraction data for HEX12. Only data referring to sharp diffraction lines are given. The tilt angle θ is calculated based on a CPK molecular length of 3·92 nm.

T°C	Phase	d nm	D nm	θ°
150	S_C	3·12	—	37
140	S_F	3·17	—	36
110	S_F	3·19	—	35·5
105	S_F	3·19	—	35·5
100	G	3·19	0·444 (110), 0·442 (200) 0·511, 0·456, 0·421, 0·410	35·5

first order transition from S_F to S_C or no transition at all is only possible [15]. There are also some arguments [14] that the transition from hexatic to crystal smectic should be of the first order type. Our experimental results are not fully consistent with these predictions.

We found that the S_C–S_F transition, as studied in compounds belonging to the HEX series, is accompanied by strong pretransitional anomalies in the specific heat. Their presence suggest a second order or very weak first order rather than a typical first order transition. It should be pointed out that in other groups of enaminoketone derivatives [2 (b), 3], for which the phase sequence crystal B–S_B(hex)–S_A between untilted phases exists, the S_B(hex)–S_A transition accompanied by strong heat anomalies was also observed. The plausible explanation for the similarity of the systems is a weak coupling between bond order and molecular tilt in the HEX compounds.

An additional argument for the similarity of tilted and orthogonal systems is the presence of a critical point on the line of the phase transition between hexatic and crystal smectics. Our data for the HEX series indicate the existence of the tricritical point of the S_F–crystal G phase transition line, which is not predicted by theory. The position of that point on the phase transition line seems to be mainly controlled by the temperature range of the hexatic S_F phase. In our case, a normalized critical phase width, $1\text{-}T_{S_FS_G}/T_{S_CS_F}$, is *c.* 0·15. However, for an analogous transition between untilted phases [2 (b), 3], a critical phase width is several times lower.

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