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Orthogonal hexatic smectic phase—rare or common?

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The hexatic smectic B (Hex B) phase is commonly encountered among hydrogen-bonded liquid crystal materials. Among enaminketone and Schiff's base compounds, twenty homologous series (*c.* 10^2 compounds) exhibiting orthogonal mono- or bi-layer hexatic phases were identified by combined microscopy and DSC. Phase transitions from crystal B (CrB) of S_F to Hex B as well as from Hex B to S_F , S_A or S_C phases were observed within the range 50 to 190°C. Temperature ranges of the Hex B phase detectable by DSC varied from 0.2 to 20°C. Within two groups of three-ring enaminketones, the formation of the Hex B phase was found to be controlled by both inductive and mesomeric components of the Hammett constants of the terminal substituents of the molecules.

1. Introduction

It is well known that liquid crystalline phases are built up by orientational nematic and translational smectic ordering. An additional bond orientational ordering (BOO), if present within translationally disordered smectic layers, forms fascinating hexatic phases [1, 2], predicted theoretically in 1978 [3] and found experimentally a few years later [4]. The relevant smectics are excellent model systems for studying 2-D melting phenomena, to test current theories of phase transitions in liquid crystals, to investigate accompanying critical fluctuations, etc. Among hexatic phases, tilted smectics (S_I and S_F) are mostly observed, whereas the orthogonal hexatic smectic B (Hex B) phase has been reported so far for a very limited number of compounds belonging to four homologous series based on two-ring mesogenic cores (see, for example, [2]).

In the present paper we report several homologue series, based on a new type three-ring core with built-in hydrogen bonded quasi-rings [5], which exhibit the Hex B phase. We suggest that the orthogonal Hex B phase should not be considered as an exceptionally rare phase. The 'rarity' of this mesophase is only apparent and seems in this particular case to be related to inadequacy in simple microscopic observations. We have found, however, that combined microscopic and high-sensitivity DSC methods are good enough to study homologous series with the crystal B (CrB–Hex B–smectic A (S_A)) phase sequence and to construct binary phase diagrams. Results for some series are discussed, in relation to molecular structure.

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2. Results

2.1. Identification of the Hex B phase

Because of their complexity, X-ray scattering methods [6] which identify mesophases unequivocally, are hardly used as routine methods to test the phase properties of newly synthesized materials. In this section, the possibility of application of the much simpler and more commonly used methods of optical microscopy and DSC to identify the Hex B phase and to construct relevant phase diagrams is discussed.

2.1.1. Microscopic observations

To recognize the majority of smectic mesophases some simple microscopic methods are good enough [7]. In particular, uniaxial S_A and S_B phases are easily identified due to their non-birefringent homeotropic textures. Observation of focal-conic textures is the simplest method to differentiate between these mesophases, as well as to distinguish transitions from S_A to Hex B and from S_A to CrB phase. The former transition is accompanied by the gradual vanishing of radiating patterns along the lengths of fan-shaped areas [8], whereas the latter is marked by the appearance of transition bars [7]. However, more or less pronounced transition bars may also be observed for the S_A –Hex B phase transition [8], in cases when the Hex B phase becomes similar to the CrB phase. Such mimicry takes place if strong crystalline order fluctuations exist within the hexatic phase, as in systems having a narrow range, *c.* 1°C, hexatic phase between S_A and CrB phases. In a homologous series, such a 'quasi-crystalline' Hex B phase appears in the vicinity of the triple point in the phase diagram (cf. § 2.2.1.) at which

three lines related to the phase transitions CrB–S_A, CrB–Hex B and Hex B–S_A converge. On moving away from the triple point (i.e. for homologues having longer terminal substituents [9]), the temperature range of the hexatic phase is broadened and crystalline-type fluctuations are decreased. As a result, in a homologous series, confusing transition bars which sometimes accompany the S_A–Hex B phase transition always disappear for sufficiently high homologues. Thus, texture changes, which might provide and erroneous interpretation for a single compound, are easily interpreted unequivocally when studied within a homologous series.

In testing *c.* 10² compounds having hexatic B phases we have never observed any remarkable changes of natural textures during transitions between CrB and Hex B phases. For some compounds, however, this phase transition results in a spectacularly sharp melting of CrB mono-crystals or in a sudden change in the mechanical response of samples subjected to an external stress. Careful observation of the mobility of defects or the boundaries of air bubbles may also point to this transition, as well as the transition between hexatic and disordered phases. In conclusion, texture observations have but limited application in studying the Hex B phase in systems with untilted mesophases and are useless for the precise determination of phase transition temperatures. Therefore, for the identification of the Hex B phase from studies of miscibility with reference compounds, some other methods are necessary to construct the relevant binary phase diagrams. For that purpose, the DSC method is preferred for its precision and simplicity.

2.1.2. DSC studies

DSC scans through S_B and S_A phases reveal two characteristic peaks at temperatures limiting the Hex B phase [8,10]. The amplitude and/or shape of both peaks are controlled by the temperature range of the hexatic phase (or, equivalently, by the terminal chain length). The low temperature peak, which corresponds to destroying of the translational order in favour of the hexatic order, is sharp and rather small (of the order of 0.1 J g⁻¹). With broadening of the hexatic phase range and increase its BOO, this peak systematically decreases [8,11] and finally disappears, although the phase transition CrB–Hex B still remains strongly discontinuous [12]. It is the first example of the first order phase transition in liquid crystals with an inherent absence of any latent heat.

The high temperature peak, which corresponds to destroying the BO order during the Hex B–S_A phase transition, is strongly influenced by the crystalline-type fluctuations. As a result, DSC thermograms for a narrow range Hex B phase are practically the same as those observed at the transition between crystalline B and S_A phases. Thermograms reflect the behaviour of the specific

heat typical for this type of phase transition (cf. figure 1 (a) of the present paper and figure 3.11 of [2]). For a very narrow range hexatic phase, the only signature of the presence of this ‘quasi-crystalline’ phase is the low temperature peak of the CrB–Hex B phase transition. However, rather slow scanning rates, *c.* 0.1–0.2 °C min⁻¹, are necessary to separate this peak efficiently.

On broadening the hexatic phase range, DSC thermograms evolve to forms typical for the isolated Hex B–S_A phase transition. Then, signals become diffuse, due

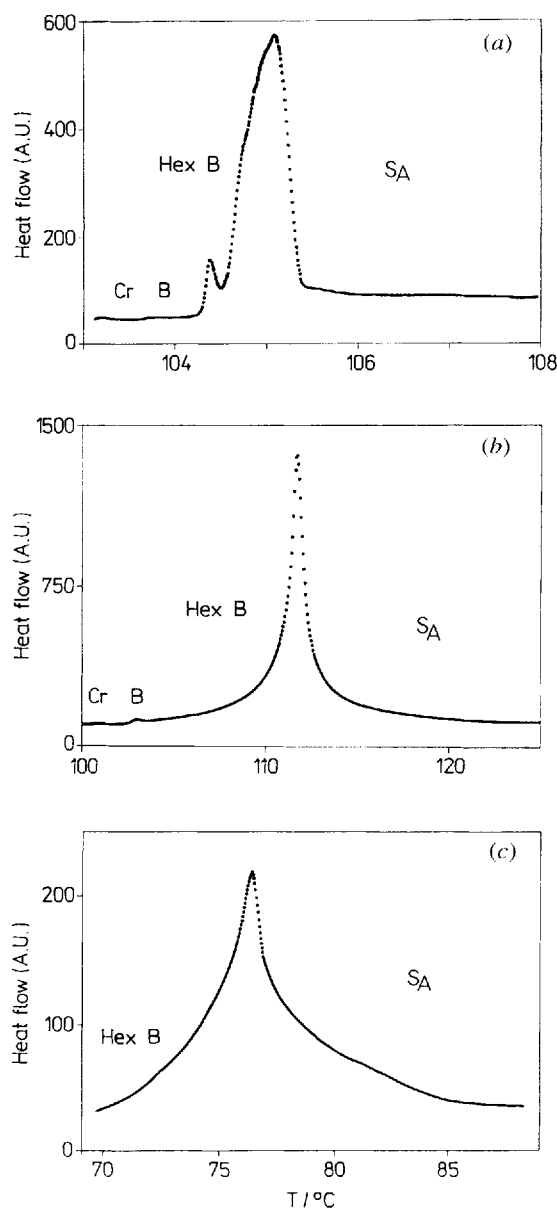


Figure 1. DSC scans through CrB Hex B and S_A phases for different ranges of the hexatic phase: 0.25 °C (a), 5.5 °C (b) and > 20 °C (c). Data for the PHE5 (series 9) taken at 0.20 °C min⁻¹ (a), the PIR5 (series 1) at 5 °C min⁻¹ (b) and the 9THBr (series 17) at 5 °C min⁻¹ (c).

to pretransitional increase in the heat capacity, but no peak rounding is observed. Pretransitional effects, which result mainly from the in-plane density changes [2], appear on both sides of the phase transition (see figure 1 (b)). They are particularly pronounced for series with a broad range S_A phase and, within a series, for its high homologues. As a result, pretransitional anomalies are seen even as far as 10–25°C from the transition temperature, suggesting the proximity of a continuous phase transition. Typical thermograms are roughly symmetrical (see figure 1 (b)), but less symmetrical cusp-type curves are also observed (see figure 1 (c)). Evolution of DSC signals is very typical for the CrB–Hex B– S_A phase sequence described above. Signals of the same type are also observed for analogous phase sequences, for example CrH– S_F – S_C [11], in tilted systems. Thus, the DSC method can be used to recognize the phase sequence from crystal to disordered smectics, via a hexatic phase, regardless of tilt, as well as to determine phase transition parameters (temperatures,

enthalpies). The presence of c_p anomalies on both-sides of a transition on DSC thermograms is a reliable signature of the transition from a hexatic to a fluid smectic phase.

The DSC method is also capable of detecting phase transition between tilted and orthogonal hexatics. In some thienyl derivatives (see § 2.2.2.), we found, for the first time in pure compounds, the tilt-driven transition S_F –Hex B, as well as its inverted version, Hex B– S_F [13]. The former phase transition is continuous, with a small, but quite measurable step in the specific heat, whereas the latter one may also be of the first order type, with a small transition enthalpy. No pretransitional c_p anomalies seem to accompany these phase transitions.

2.2. Hex B materials

Phase evolution from crystalline to disordered smectics, via the orthogonal hexatic phase, has been observed recently among heterocyclic, asymmetrically terminally substituted enaminketones [5]. We attempted to modify

Table 1. Phase transition temperatures (°C) for some members of the pyridyl and phenyl enaminketone series, 1–12.

Series	<i>n</i>	<i>X</i>	<i>Y</i>	Cr	CrB	Hex B	S_A					
1	6	N	C(CH ₃)	•	75.2	•	102.0	•	107.1	•	191.2	•
2	6	N	CH	•	58.5	•	53.5	•	59.3	•	130.3	•
3	6	CH	N	•	92.2	•	87.9	•	95.1	•	106.8	•

Series	<i>n</i>	<i>X</i>	Cr	CrB	Hex B	S_A					
4	6	F	•	90.5	•	101.5	•	112.5	•	174.5	•
5	6	Cl	•	88.4	•	149.5	•	158.5	•	223.9	•
6	6	Br	•	93.0	•	167.2	•	174.6	•	131.3	•
7	6		•	133.6	•	185.2	•	189.6	•	230.7	•
8	6	CF ₃	•	101.6	•	169.1	•	172.6	•	220.5	•

Series	<i>n</i>	<i>X</i>	Cr	CrB	Hex B	S_A					
9	6	H	•	85	•	107.3	•	107.8	•	123.3	•
10	6	F	•	84	•	128.2	•	131.3	•	184.5	•
11	6	Cl	•	83.3	•	157.9	•	159.9	•	217.4	•
12	6	Br	•	104.4	•	178.3	•	173.3	•	223.6	•

the parent molecular structure (series 1, in table 1) by changing aromatic rings in the mesogenic core. We also terminally substituted the molecules with a variety of short, polar groups, as well as synthesizing compounds devoid of such groups. As a result, we succeeded in obtaining several novel materials revealing the Hex B phase. Their chemical constitution is briefly reviewed below.

2.2.1. Compounds with a Cr₁B–Hex B–S_A phase sequence

As long as the linear geometry of mesogenic core is preserved (series 2–12) see table, the phase sequence Cr₁B–Hex B–S_A, observed in the parent series 1, remains unchanged. Phase transition data for all the modified series are presented in table 1 for homologues with a fixed alkoxy

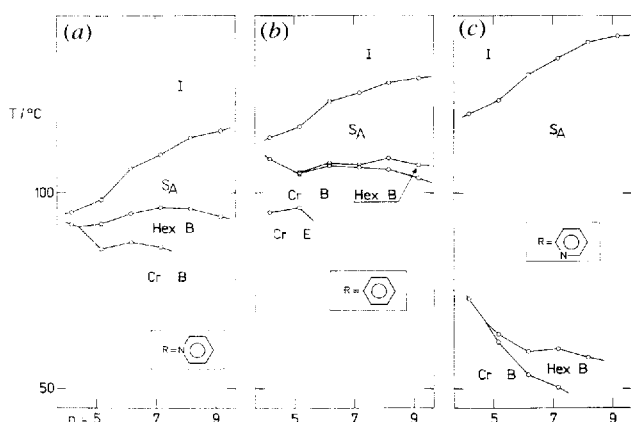


Figure 2. Phase diagrams for $R\text{-COCH=CHNH-C}_6\text{H}_4\text{-OC}_n\text{H}_{2n+1}$ homologous series; series 3 in (a), series 9 in (b) and series 2 in (c). Structures for R are shown in the insets.

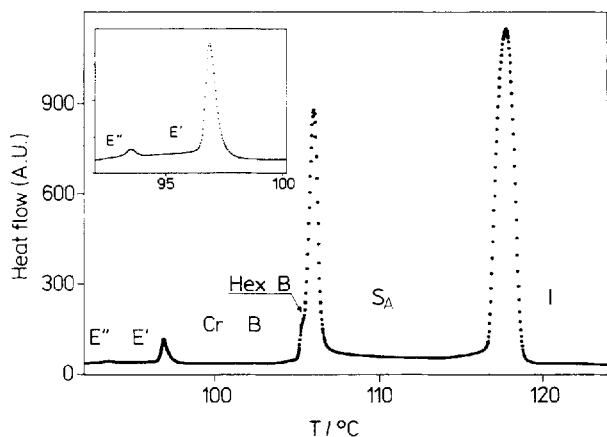


Figure 3. DSC thermograms for PHE5 (series 9). The inset contains detail for the signals for phases transitions CrE''–CrE' and CrE'–CrB. See also figure 1(a). Super-cripts are used to distinguish between the different CrE phases, not to identify them.

chain. Slight core bending, which was obtained by introducing a five-membered ring into the core, causes more complex phase sequences, as observed for the thienyl derivatives (cf. § 2.2.2.). The exception is an unsubstituted ring (thienyl, furyl) which acts by an axially symmetrical prolongation of the phenyl-enaminoketone core. Because of the low phase transition temperatures of furyl compounds (series 13), studies over full range of the Hex B phase may be performed under convenient experimental conditions, below 100°C (cf. data in table 2).

Typical phase diagrams obtained from DSC studies are presented in figure 2 for three homologous series, 2, 3 and 9, to illustrate the role of details of the molecular structure. It is seen that localization of the triple point near $n = 6$ is rather insensitive to the small changes in structure, in contrast to the very sensitive phase transition temperatures. For example, the presence and position of a nitrogen atom in the ring influences markedly the range of both S_A and Hex B phases. In particular, the PHE series, 9, is characterized by a relatively narrow temperature range of the Hex B phase (see figure 2(b)). For this series ΔT increases, but weakly with length of the terminal chain, whereas the Hex B phase is one order of magnitude broader for the MPR series, 2 (see figure 2(c)).

In PHE series, a full sequence of enantiotropic orthogonal phases is observed for the first time for pure homologues $n = 5, 6$. For compound PHE5, the rare polymorphism of the crystal E phase [14] with a first order phase transition between subphases E'' and E' is also of interest. As a consequence of a narrow hexatic phase in this system ($\Delta T = 0.25^\circ\text{C}$), all remaining phase transitions are also first order, as can be seen on DSC thermograms (see figure 3). The thermodynamic data are: CrE'' 93.6°C (0.03 J g⁻¹) CrE' 96.3°C (0.61 J g⁻¹) CrB 105.1°C (0.34 J g⁻¹) Hex B 105.4°C (8.5 J g⁻¹) S_A.

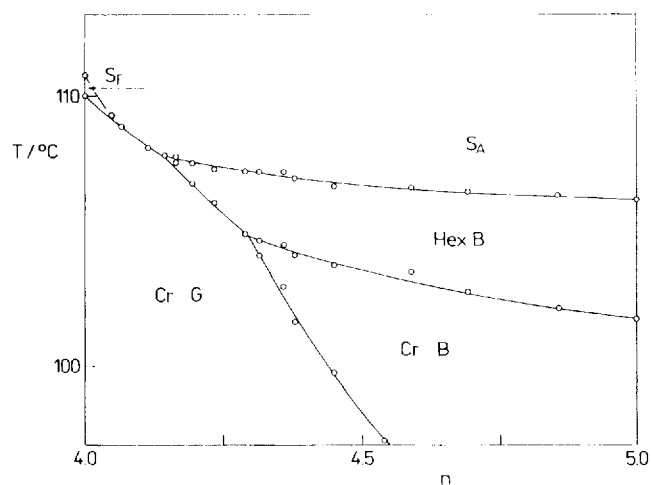
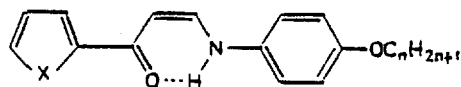
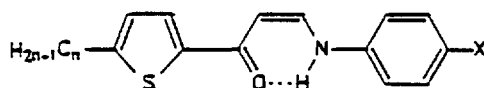


Figure 4. Phase diagram for the binary system PIR4-PIR5 (series 1, homologues $n = 4$ and 5).

Table 2. Phase transition temperatures (°C) for some members of the furyl and thienyl enaminketone series, 13–18.



Series	<i>n</i>	<i>X</i>	Cr	CrB	Hex B	<i>S_A</i>					
13	9	O	•	67.9	•	75.3	•	81.9	•	102.2	•
14	9	S	•	82.0	•	92.6	•	95.1	•	111.6	•



Series	<i>n</i>	<i>X</i>	Cr	<i>S_F</i>	CrB	Hex B	<i>S_A</i>				
15	1	OC ₁₆ H ₃₃	•	88.9		•	92.9‡	•	131.0	•	
16	6	Cl	•	73.4		•	77.0	•	159.4	•	
17	6	Br	•	89.0	•	75.2	•	94.3	•	165.7	•
18	6		•	106.2†	•	96.5	•	111.0	•	162.8	•

† Also CrG–*S_F* phase transition at 93.2°C.

‡ Phase transition to *S_C* phase followed by transition to *S_A* phase at 111.8°C.

2.2.2. Compounds with other phase sequences/structures

Tilted hexatic and tilted crystalline phases were observed, in addition to orthogonal phases, for some compounds belonging to the PIR series **1**. In consequence, new triple points were found, as for example, CrG–Hex B–*S_A* and CrG–CrB–Hex B in binary mixtures (see, figure 4). An interesting *S_F*–Hex B–*S_A* point [2] may also be present in this system, which may result from possible phase transition between tilted and orthogonal hexatics. However, due to the rather narrow temperature range of the *S_F* phase, it was not possible to decide, by the DSC method, if this point really exists.

Tilt-changing phase sequences of hexatic and disordered smectics were observed, without any doubts, for thienyl compounds from the THI series, **15**. For the THI14 and THI16 homologues, the sequence of phases, subsequently appearing on heating, are Hex B–*S_F*–*S_C* and Hex B–*S_C*–*S_A* respectively. The phase sequence Hex B–*S_F* is quite anomalous, because tilted phases, in comparison with orthogonal phases, should be the low temperature phases. For other thienyl compounds, (series **18**), a normal phase sequence *S_F*–Hex B–*S_A* with two continuous phase transitions is found. Detailed results for the phase transitions, as well as of phase diagram studies are presented elsewhere [13].

So far, only a simple, monolayer Hex B phase is known. In order to obtain a bilayer phase, it seems necessary to terminate molecules with substituents which promote a strong association tendency. Dipolar groups, for example, NO₂ and CN, yield in-plane ordered bilayer orthogonal

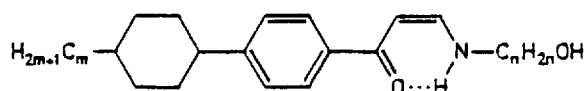
smectics, but rarely [15]. A new idea is to search for the Hex B₂ phase among liquid crystalline compounds involving association by hydrogen bonding groups such as OH, NH₂ or COOH, placed at the end of terminal alkyl substituents.

In fact, we found the enantiotropic bilayer Hex B₂ phase for some hydroxy terminated compounds from series **19**. An orthogonal hexatic phase was tentatively identified by microscopic observations of homeotropic textures and mechanical tests of sample stiffness, and finally confirmed by X-ray scattering studies. The high-temperature phases of these compounds are partial bilayer smectics, *S_{Cd}* and *S_{A,d}*. Thus, the compounds of series **19** are interesting examples of mesogens revealing a coupling between the degree of molecular association, via hydrogen bonds, and the ordering within the smectic layers. Moreover, they seem to be the only mesogens which stabilize their mesophases by both inter- and intra-molecular hydrogen bonds.

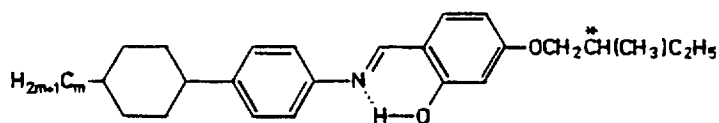
Compounds analogous to **19**, but terminated with NH₂ or COOH groups, instead of an OH group, also form orthogonal liquid crystalline phases. However, their phase transitions are not sharp and during the diffuse transitions, mesophases coexist over wide temperature ranges. Most probably, this points to a participation of terminal groups in opening *cis-s-cis*-enaminketone rings and forming an equilibrium admixture of *trans-s-cis* and *trans-s-trans*-structures.

The appearance of the hexatic B phase in hydrogen bonded compounds is, by no means, limited to enaminketone

Table 3. Phase transition temperatures (°C) for some members of the phenylcyclohexyl enaminketone and salicylideneimine series, 19–20.



Series	<i>m</i>	<i>n</i>	Cr	Hex B ₂	S _{Cd}	S _{Ad}					
19	10	6	•	66.2	•	83.2	•	112.4	•	143.3	•



Series	<i>n</i>	Cr	Hex B	S _A				
20	6	•	83.4	•	117.4	•	189	•

tones. We observed this phase, followed by the S_A phase, in some Schiff's bases. In particular, the Hex B phase was found in the chiral compounds of series 20. In this particular case, no essential asymmetry in length of the terminal substituents is necessary to induce the Hex B phase, in the manner previously reported for 'classical' hexatic compounds [2].

3. Discussion and conclusions

Because of several hexatic series of hydrogen bonded compounds of different molecular structures that have been found the orthogonal Hex B phase should be considered as a regular, not a rare mesophase, especially in systems which exhibit the S_B–S_A phase sequence. Besides the simple monolayer Hex B phase, there has been found a bilayer Hex B₂ phase among associated compounds. The rarity of reports on the orthogonal hexatic phase are, most probably, due to difficulties in identification of this mesophase by microscopic studies. The most sure method to identify the Hex B phase is by X-ray diffraction. X-ray measurements if performed on single domain samples show quantitatively the extent of positional and bond orientational ordering, and thus easily enable one to distinguish the hexatic phase from liquid- or crystal-like phases. Unfortunately, obtaining such samples is in most cases rather complicated [4, 12]. However, we have here argued that a combination of microscopy and high sensitivity DSC might be sufficient enough to identify the Hex B phase among other untilted phases, as well as to construct relevant miscibility phase diagrams with reference substances. The most characteristic signature of the Hex B–S_A phase transitions are pretransitional *c_p* anomalies which are always present sufficiently far

from the triple point. In contrast, the CrB–Hex B transition is accompanied by very small or zero thermal effects.

As yet, no conclusive opinions are to be found in the literature about the molecular structure of hexatic B mesogens; the experimental material gathered so far is rather limited. The ability to form a particular mesophase is obviously a function of many molecular factors determining the geometry and electronic structure of the molecules. Thus, the particular factors governing formation of the Hex B phase are hardly recognizable. However, an analysis of data for several compounds having similar molecular geometries, as well as similar mesogenic cores, might reveal some essential factors. Both a geometrical and an electronic asymmetry of the terminal substituents appear to be responsible factors for three ring enaminketones, 1–18, together with a large transverse dipole moment of the mesogenic core [5]. In contrast to previously reported materials, we observed the hexatic B phase in compounds having both short and long terminal substituents. Examining the series 4–12 and several related non-hexatic compounds, we found a correlation between the appearance of the Hex B phase and the electron-donor/electron-acceptor properties of the terminal groups. Unexpectedly, simple Hammett constants [16] were found insufficient to describe the hexatic properties and both inductive and mesomeric components of the Hammett constants [16(b)] need to be considered. As presented in figure 5, the Hex B phase exists only for polar groups located in a limited area of the σ_1 , σ_M map. The temperature range of the Hex B phase increases, within a homologous series, with increasing length of the alkoxy chain, in agreement with the theoretical generic phase diagram [9] (cf. figure 2). For a given alkoxy group,

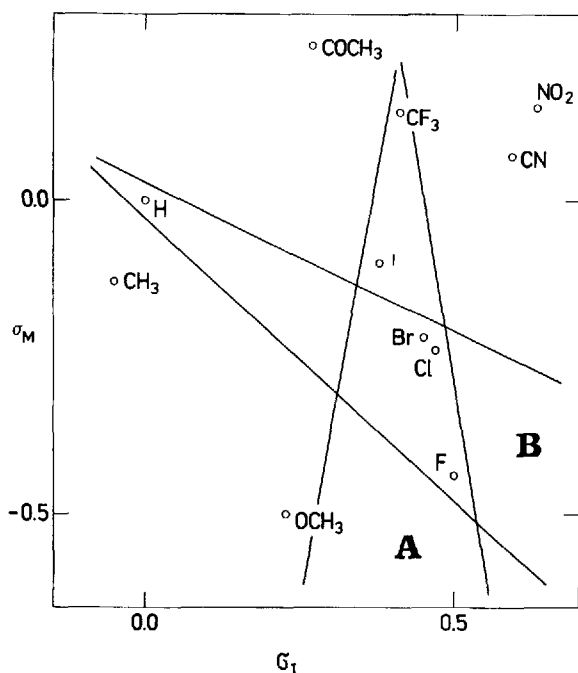


Figure 5. Inductive and mesomeric Hammett constants, σ_I and σ_M , for some terminal molecular substituents X . Existence of the Hex B phase is limited to area A for mesogens $\text{AlkO-C}_6\text{H}_4\text{-COCH}=\text{CHNH-C}_6\text{H}_4\text{-X}$ (series 4–8), and to area B for mesogens $\text{AlkO-C}_6\text{H}_4\text{-NHCH}=\text{CHCO-C}_6\text{H}_4\text{-X}$ (series 9–12).

the increases with increasing mesomeric donor properties of a short polar substituent (lower σ_M values), but also with their inductive electron-accepting properties (higher σ_I values). As a result, fluorine is the best substituent for designing materials with the broadest Hex B phase range.

To verify the current understanding of the nature of hexatic ordering and of the relevant phase transitions [1, 2], there is a need for novel Hex B, compounds. Our enaminketones provide easily synthesizable [5, 11] model materials to examine systems with a crystalline—hexatic—disordered smectic phase sequence in orthogonal, tilted and mixed type systems. Series with a narrow ($0\text{--}2^\circ\text{C}$) or wide ($> 20^\circ\text{C}$) Hex B phase range were found. The temperature range of a neighbouring disordered S_A phase, which may influence the properties of the hexatic phase, was varied in the range 7 to 90°C . The series with the broadest S_A phase (11, 15), which reveals very strongly pronounced anomalies in the specific heat, might be used to examine the relevant critical exponent α .

In conclusion, the hexatic smectic B phase is certainly not rare, because it has been observed in the many hydrogen bonded materials, carefully examined by us. We

will believe that the presence of hydrogen bonded quasi-rings in the mesogenic core does not cause any enhanced tendency for Hex B phase formation. However, based on such structures, it seems to be possible to design and synthesize compounds with required phase sequences and temperatures, in order to study the fundamental physical properties of this theoretically important phase.

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