Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Enaminoketones as new hydrogen bonded liquid crystals

Wieslaw Pyzuk[a]; Ewa Gorecka[a]; Adam Krowczynski[a]; Damian Pociecha[a]; Jadwiga Szydlowska[a]; Jan Przedmojski[ab]; Li Chen[ac]
[a] Laboratory of Dielectrics and Magnetics, University of Warsaw, Warsaw, Poland [b] Technical University of Warsaw, Warsaw, Poland. [c] Kent State University, Kent, Ohio, USA

To cite this Article Pyzuk, Wieslaw , Gorecka, Ewa , Krowczynski, Adam , Pociecha, Damian , Szydlowska, Jadwiga , Przedmojski, Jan and Chen, Li(1996) 'Enaminoketones as new hydrogen bonded liquid crystals', Liquid Crystals, 21: 6, 885 — 891

To link to this Article: DOI: 10.1080/02678299608032906

URL: http://dx.doi.org/10.1080/02678299608032906

LIQUID CRYSTALS, 1996, VOL. 21, NO. 6, 885–891

Enaminoketones as new hydrogen bonded liquid crystals

by WIESLAW PYZUK, EWA GORECKA*, ADAM KROWCZYNSKI,
DAMIAN POCIECHA, JADWIGA SZYDLOWSKA, JAN PRZEDMOJSKI†,
and LI CHEN‡

Laboratory of Dielectrics and Magnetics, University of Warsaw, Al. Zwirki i
Wigury 101, 02-089 Warsaw, Poland

(*Received 13 May 1996; accepted 5 August 1996*)

The relation between molecular structure of enaminoketone derivatives and their mesomorphic properties is discussed. It has been observed that the electron accepting terminal groups (F,Cl,Br,CN) promote formation of orthogonal phases while strongly electron donating groups (OC_nH_{2n+1}) favour tilted phases. Among the synthesised compounds, materials useful for structural studies of two dimensional (2D) melting in orthogonal, as well as the tilted systems, were found. It has been determined that the heat effects in the melting process from crystalline smectic into liquid-like smectic, through the hexatic state, are correlated to the density changes.

1. Introduction

Hydrogen bonds (HB) [1] are formed between hydrogen donors such as –COOH, –OH, –NH and acceptors such as O–C, O–, N–, etc. Usually their energies are sufficient (typical HB energies are from 10 to $100\,J\,mol^{-1}$) to produce thermally stable molecular moieties. In designing thermotropic mesogens, hydrogen bonds have been used to join two or more protomesogenic molecules [2, 3] or to form quasi-rings within the mesogenic core [4, 5]. The resulting calamitic or discotic structures reveal mesomorphic properties if the structure is sufficiently rigid and anisotropic. The main advantage of HB structures is the variability of the molecular patterns which can be obtained by simple synthetic procedures. This enables extensive studies of the relation between molecular structure and mesomorphic properties. Important also are the chelating properties of HB ligands leading to metallomesogens [6].

In the present paper, the liquid crystalline properties of materials which build up the mesogenic core with independent HB rings are briefly reviewed. Attention has been focused on enaminoketone derivatives as ideal materials for the synthesis of liquid crystals due to their high reproducibility of hydrogen bond formation, their remarkable thermal stability and the linear geometry of substituents.

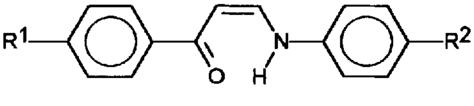
2. Mesophase sequence

In general, formation of a liquid crystal [7] is controlled by repulsive and attractive intermolecular forces. Due to the complex nature of these interactions, the simple molecular factors discriminating the existence of a particular mesophase cannot usually be determined. However, for a given class of molecular species, the smectic polymorphism can be related to the factors modifying the electron distribution within the mesogenic core. The mesogenic centre can be provided with electrons or electrons can be withdrawn from it by pendant, terminal or lateral groups with electron donating (Hammett constant $\sigma<0$) or electron accepting (Hammett constant $\sigma>0$) properties [1, 8], respectively.

In order to correlate smectic polymorphism with the Hammett constants, the temperature–chain length phase diagrams for compounds with the same mesogenic molecular core structure, but with various electron donating terminal substituents were studied.

2.1. *Main series*

The diagrams have been examined for the homologous series of HB enaminoketone compounds (**1**). All compounds have the same phenyl-*cis*-enaminoketone-phenyl mesogenic core



1

terminated by electron-donating or -accepting terminal groups R^1 and alkoxy chains OC_mH_{2m+1} as R^2.
It has been observed that:

---

*Author for correspondence.
Email: gorecka@zoolook.chem.uw.edu.pl.
†Technical University of Warsaw, Warsaw, Poland.
‡Kent State University, Kent, Ohio, USA.

0267–8292/96 $12·00 © 1996 Taylor & Francis Ltd.

(a) For strongly electron donating substituents ($R^1 = OC_nH_{2n+1}$ $\sigma \sim -0{\cdot}3$) a CrG–S_F–S_C sequence of strongly tilted smectics ($\theta_{max} \sim 40°$) has been found (figure 1(*a*)). For the longest homologues $R^2 > OC_{12}H_{25}$ and $R^1 = OCH_3$, a short S_A phase preceding the S_C phase also appears. No orthogonal phases were observed in the series with long alkoxy chains R^1. For these compounds the CrG phase is depressed to promote the hexatic S_F phase and the disordered S_C phase. Moreover for $R^1 = OC_6H_{13}$ [5] and $R^1 = OC_{10}H_{21}$, a splitting of the CrG phase area into two sub-phases with similar properties was observed (inset in figure 1 (*a*)).

(b) For weak electron donating properties of R^1 ($R^1 = CH_3$, $\sigma = -0{\cdot}17$), the phase sequence determined for short homologues is similar to that in (a), but the tilt is distinctly decreased ($\theta_{max} \sim 10°$), figure 1 (*b*). For long homologues, $n > 12$, no tilted phases survive and S_A and CrB phases are observed. In the intermediate homologue, $n = 11$, the tilted hexatic S_F phase and the orthogonal crystal B phase are separated by an unidentified, most probably weakly tilted hexatic phase (figure 1 (*b*)).

(c) For an electronically inactive ($R^1 = H$, $\sigma = 0$) group, as well as for weak or moderate electron acceptors (R^1 = halogen $\sigma = 0{\cdot}06$ to $0{\cdot}23$, $R^1 = OCF_3$ $\sigma = 0{\cdot}28$ or $R^1 = CF_3$ $\sigma = 0{\cdot}54$), the sequence of orthogonal smectic phases is observed [9]. For shorter terminal chains, direct phase transition from CrB to S_A was detected, while for homologues with $n > 5$, the hexatic B phase intervened between the CrB and smectic A phases (figure 1 (*c*)). Moreover, for the compounds with reversed positions of the terminal groups R^1 and R^2, an identical phase sequence was found.

(d) For pronounced electron accepting abilities ($R^1 = CN$ $\sigma = 0{\cdot}66$ or $R^1 = NO_2$ $\sigma = 0{\cdot}78$), both B phases vanish and a phase sequence with a partially bilayered S_{Ad} phase and a re-entrant nematic N_{re} phase was detected [10].

2.2. *Modifications of the mesogenic core*

Alternatively, the smectic polymorphism might also be studied in relation to the electric dipole moment of the molecular structure. The dipole moment of the mesogenic core in **1** arises mainly from the enaminoketone group. Based on Gaussian calculations by the Hartree–Fock method, the dipole moment of the enaminoketone moiety has been estimated to be ~3·5 D and its components, parallel and perpendicular to the molecular long axis, are nearly equal (~2·5 D).

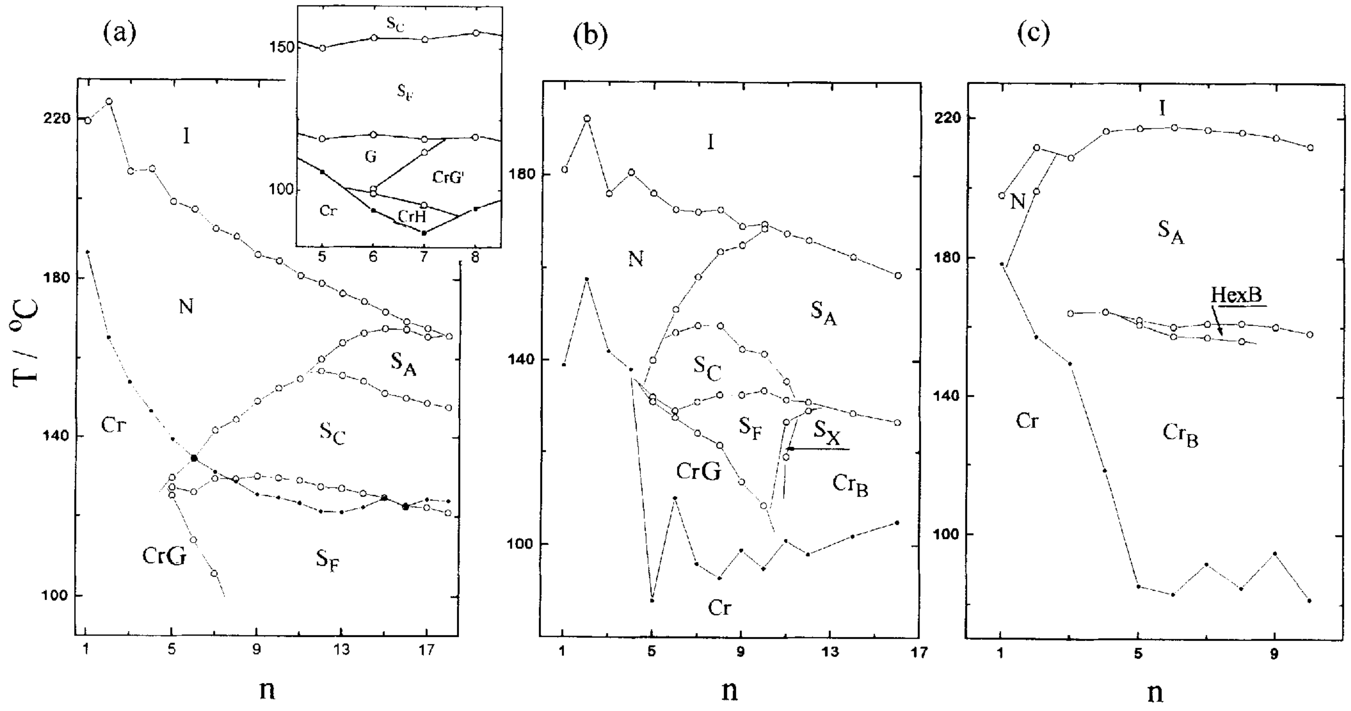
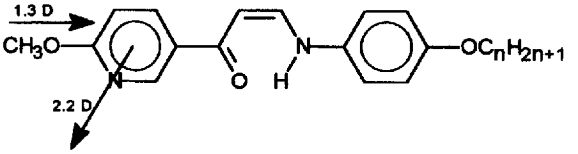


Figure 1. Phase diagrams for the series of compounds **1** terminating in (*a*) a strongly electron donating group $R^1 = OCH_3$ (in the inset is part of the phase diagram for the compounds **1** with $R^1 = OC_{10}H_{21}$); (*b*) a weakly electron donating group $R^1 = CH_3$; (*c*) a weakly electron accepting group $R^1 = Cl$.

Replacing the phenyl moiety in structure **1** by a pyridyl ring—see structure **2**—would affect mainly the longitudinal dipole moment of the core, while the transverse dipole moment could remain nearly unchanged, since the rotation of the hetero-ring with respect to the enaminoketone group is not expected to be strongly hindered.



2

For the compounds **2**, the total longitudinal dipole moment is comparable to that in compound **1** with $R^1 = H$; the difference is ~0·2 D. As a result, both homologous series reveal similar sequences of orthogonal phases (figure 2).

Summarising, our studies allow us to establish the following conclusion: molecular factors decreasing electron density at the mesogenic core favour untilted smectic phases (S_A, HexB), of low organisation.

Having recognised the molecular structures responsible for a given phase sequence, one can modify the molecular structure in order to obtain desired phases in convenient temperature ranges. Based on the above results, materials designed specially for studies of hexatic phases were synthesised. Several homologous series exhibiting the liquid hexatic-crystalline smectic phase sequence in orthogonal as well as tilted type systems have been obtained.

3. Phase transition in orthogonal systems

Common to liquid crystalline phases is an inherent long range axial ordering. The additional ordering which breaks rotational invariance and generates new mesophases is bond orientational order (BOO) [11]. Long-range BOO, described by non-zero values of the order parameter $\Phi = \langle \phi_0 \exp(6i\phi(r)) \rangle$, exists in three hexatic phases with in-plane, triangular, translational symmetry. In the HexB phase, the molecules are orthogonal to the smectic planes, whilst in smectic I and smectic F phases, they are tilted in the direction of the hexagon bond or the hexagon bond angle, respectively [7, 12].

Although extensively studied theoretically, and recently also experimentally, the development of long-range BOO is still one of the most intriguing features of phase transitions in LC physics [13]. The phase transition at which the BOO is built up is described by a complex order parameter and should belong to the 3D-*XY* universality class characterised by the critical exponents $\alpha = -0{\cdot}007$ and $\beta = 0{\cdot}35$ [13, 14]. Since nearly all experiments provide α close to the mean field value 0·5 [13], the influence of a near-by tricritical point has been postulated. This point might be generated in the vicinity of the triple point (where the liquid hexatic-crystalline

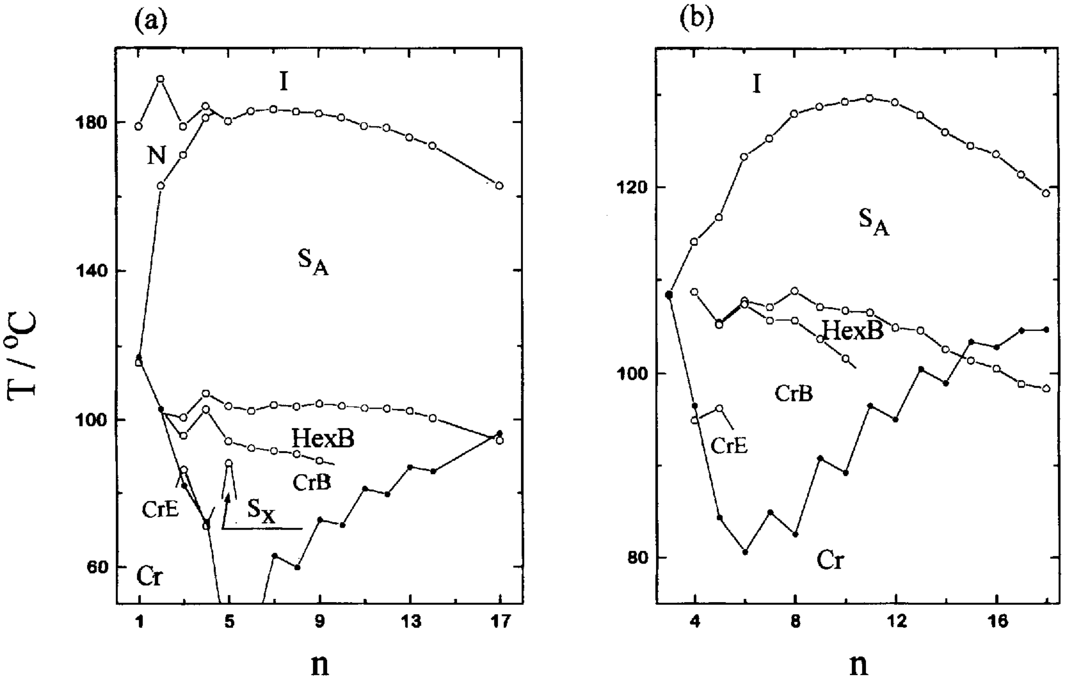


Figure 2. The phase diagrams for (*a*) the series of compounds **2** in which the phenyl ring was replaced by the 3*N*-pyridyl ring terminated with $R^1 = OCH_3$ (S_X is most probably a CrE phase); (*b*) the series of compounds **1** with $R^1 = H$.

phases co-exist) by BOO coupling to the other order parameters. Fluctuations of herringbone ordering [15], in-plane crystal density [16] and smectic layer undulations [17] have been suggested as responsible factors.

For our studies among enaminoketone derivatives, hexatic materials with a sequence of orthogonal phases and a broad temperature range of the fluid S_A and crystalline B (CrB) phases have been chosen in order to avoid the influence of tilt, layer fluctuations and herringbone order.

Previous X-ray measurements performed with these systems have shown that the HexB-S_A phase transition is second order and that the BOO evolves continuously with a critical exponent β $\sim$0·2 [18]. Present studies indicate that the continuous development of BOO is accompanied by a gradual increase of the in-plane transitional correlation length ξ_{II} from $\sim$20 Å in liquid phase to $\sim$100 Å in the hexatic phase (figure 3). On the contrary, the CrB–HexB phase transition was found to be strongly discontinuous and the positional correlation length jumps from $\sim$200 Å in the HexB to at least 5000 Å in the CrB phase [19]. There is also the jump of the BOO order parameter at CrB–HexB, as evidenced by the abrupt, significant change in the χ-scan peak width (figure 4).

Furthermore, the temperature dependence of the in-plane intermolecular distance D and the interlayer spacing d (figure 5) and the specific heat Cp (figure 6) distinctly differ at the liquid–hexatic and the hexatic-crystalline smectic phase transitions. The fluid–hexatic phase transition is accompanied by pretransitional anomalies in D and strong anomalies of Cp in both the S_A and HexB phases and significant changes of d in the S_A phase occur when approaching the phase transition temperature. On the other hand, at the CrB–HexB phase transition, changes in neither D nor d are observable (figure 5) and the transition enthalpy is small and quickly decreases along the transition line with increasing temperature range of the hexatic phase (inset figure 5). In most homologous series studied, the transition enthalpy becomes undetectable ($\Delta H < 0{\cdot}005\,\mathrm{J\,g^{-1}}$) for a HexB phase broader than 10 K. It should be noticed that the heat effects are fairly well correlated to the crystal density $-d\rho/dT$ (figure 6) evolution which has been calculated from the in-plane molecular distance and the layer spacing, $\rho(D,d) = 3^{1/2}M/2N_AD^2d$ where M is the molar mass of the substance and N_A is the Avogadro number. Thus, it might be suggested that the thermal effects at CrB–HexB–S_A phase transitions arise mainly from the intermolecular distance changes, whereas destroying long range in-plane positional or BO order is only weakly correlated to the amplitude of specific heat anomalies.

4. Phase transitions in tilted systems

Besides the homologous series exhibiting the sequence of orthogonal S_A–HexB–CrB phases, homologous series with tilted counterparts S_C–S_F–CrG were also studied. Although precise X-ray and calorimetric measurements are necessary to get quantitative results, some general conclusion could be drawn. Both tilted and orthogonal systems are similar in their thermal properties.

(a) Strong heat capacity anomalies are always detected at the hexatic-fluid smectic phase transition.

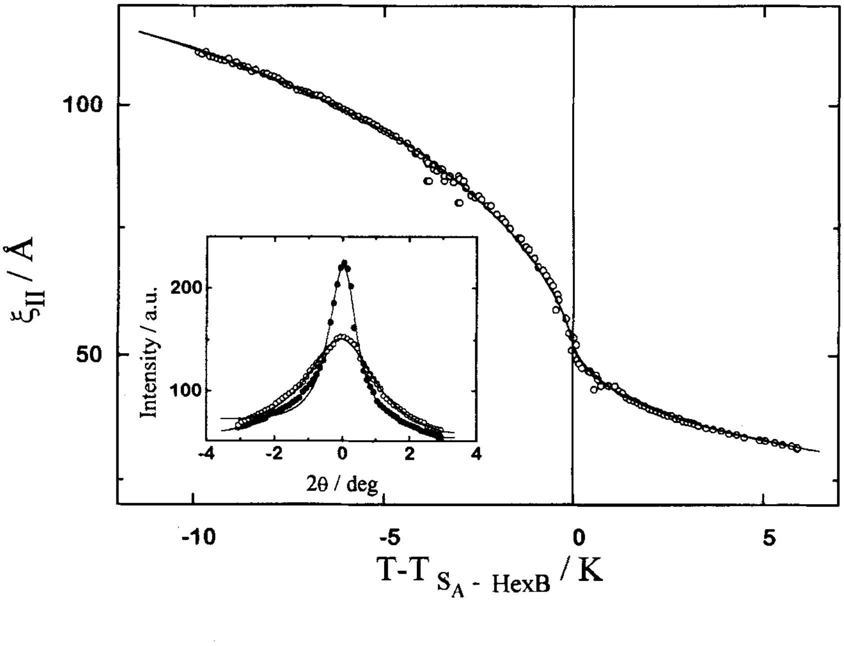


Figure 3. Temperature dependence of the in-plane translational correlation length ξ_{II} at the HexB–S_A phase transition (for compound 1 with $R^1 = OC_6H_{13}$ and $R^2 = F$). In the inset are 2θ scans in the S_A phase at $T = T_{S_A\text{-HexB}} + 5\,K$ (open circles) and in the HexB phase at $T = T_{S_A\text{-HexB}} - 5\,K$ (filled circles). The width of the peak in a 2θ scan is inversely proportional to the range of the in-plane translational correlation length ξ_{II}.

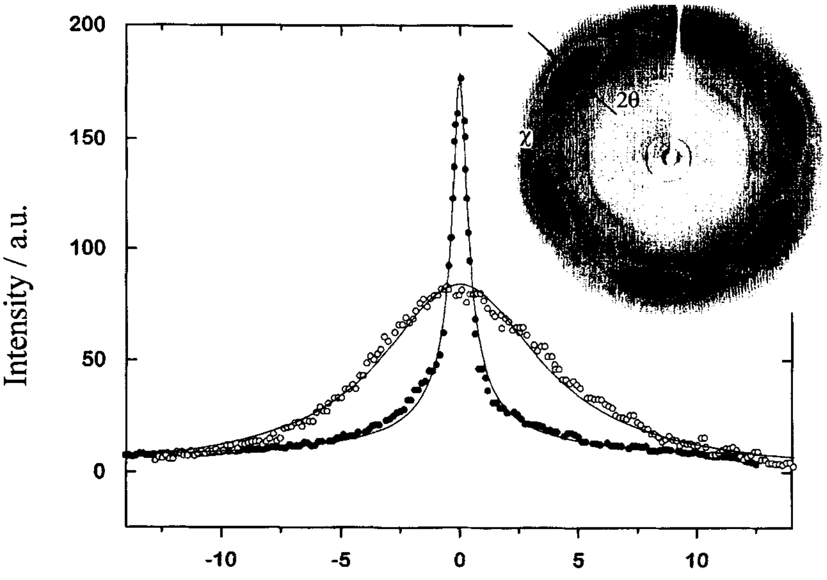


Figure 4. χ-scan in the HexB phase (open circles) at $T = T_{CrB\text{-}HexB} + 0{\cdot}1$ K and the CrB phase (filled circles) at $T = T_{CrB\text{-}HexB} - 0{\cdot}1$ K (for compound 1 with $R^1 = OC_6H_{13}$ and $R^2 = F$). The width of the peak in the χ-scan is inversely proportional to the range of bond orientational order. In the inset is the X-ray diffraction pattern from the in-plane structure with the 2θ and χ scans indicated.

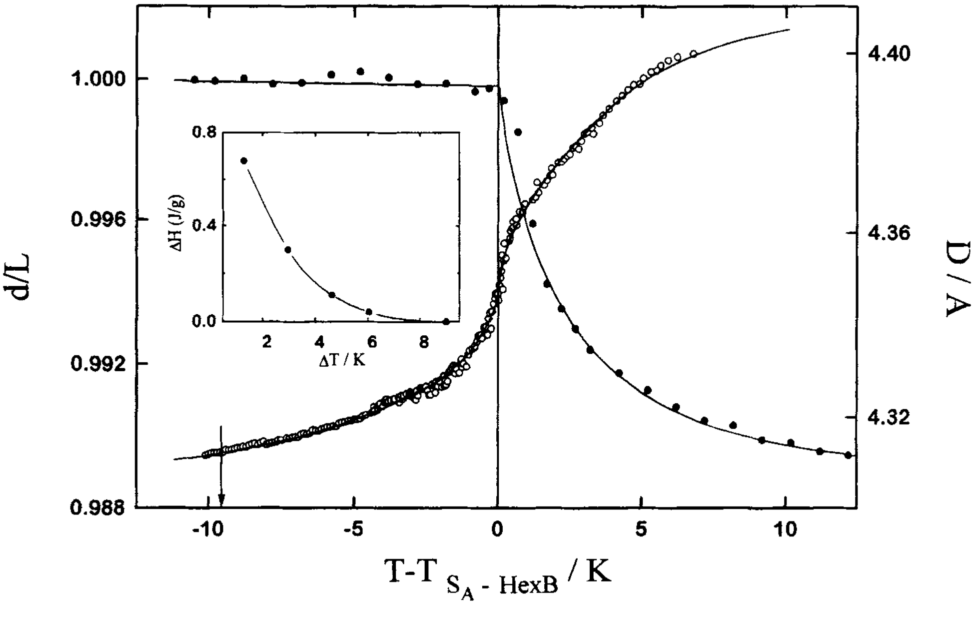


Figure 5. Temperature dependence of the in-plane molecular distance D and the ratio of layer thickness d to molecular length L (for compound **1** with $R^1 = OC_6H_{13}$ and $R^2 = F$). The arrow indicates the phase transition between the HexB and CrB phases; lines are a guide for the eye. In the inset, the CrB–HexB phase transition enthalpy is plotted as a function of the temperature range of the HexB phase (for the series of compounds 1 with $R^1 = F$ and $R^2 = OC_nH_{2n+1}$).

(b) The enthalpy of the hexatic–crystalline phase transition strongly decreases with increasing temperature range of the hexatic phase and vanishes at an apparent critical point for hexatic phases broader than 40 K. One main difference between tilted and orthogonal systems is the sensitivity of the phase transition temperatures to molecular chain length. In all the tilted systems, the hexatic phase was found to be significantly wider than in the orthogonal counterparts.

5. Conclusions

The HB compounds studied were found to be attractive from the standpoint of LC physics. Their main advantage is the extraordinary number of molecular structures which can be easily obtained. Studies of phase sequence in relation to molecular properties have proved that factors providing the mesogenic core with electrons enhance the molecules' ability to form orthogonal mesophases. It has also been shown that among homologous series exhibiting orthogonal phases, the HexB phase

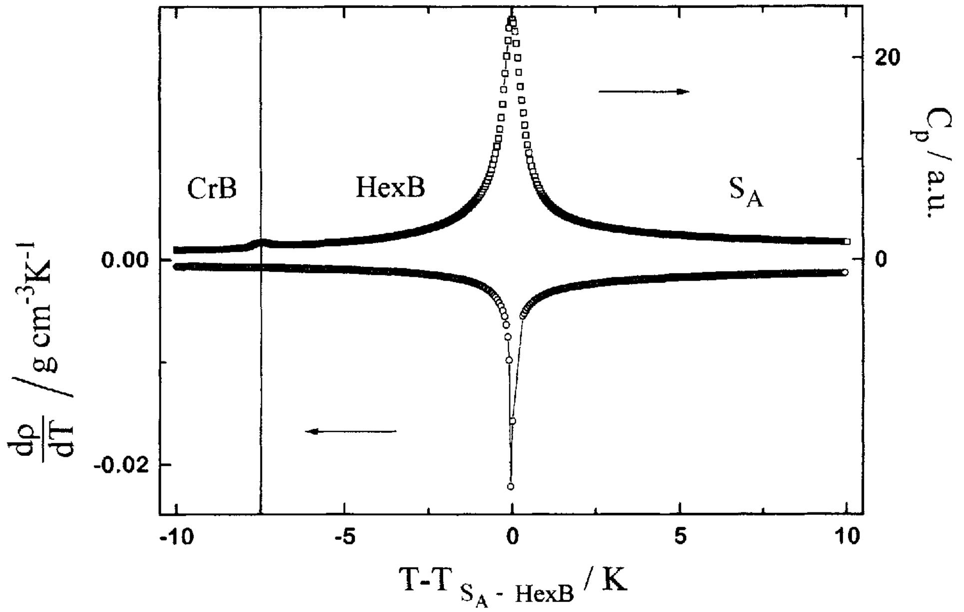


Figure 6. Heat capacity anomalies Cp (squares) and density changes $d\rho/dT$ (circles) for compound **1** with $R^1 = OC_6H_{13}$ and $R^2 = F$ in relation to the CrB–HexB–S_A phase transition. The density changes were calculated from the smoothed data for the in-plane molecular distance and the layer thickness.

appears commonly for homologues with $n>5$ and its width increases with increasing length of the terminal chain. The thermal effects at liquid–hexatic and hexatic–crystal smectic phase transitions are correlated to the density changes. In both orthogonal and tilted systems, the phase transition to the fluid smectic phase is accompanied by a pronounced transition enthalpy and strong in-plane as well as inter-plane molecular distance changes. On the other hand, at the hexatic–crystalline phase transition, the enthalpy is small or undetectable, as are the changes of layer spacing and in-plane molecular distance.

6. Experimental

The enaminoketone compounds were synthesised according to the procedure described in [5]. The phase transitions were detected by optical observations (Zeiss Jenapol-U microscope equipped with Mettler FP82HT hot stage) and differential scanning calorimetry (Perkin Elmer DSC-7). The X-ray diffraction patterns and the quantitative data related to the in-plane molecular order were obtained using a Siemens X-1000 system equipped with a two-dimensional position sensitive area detector and heating stage. The pyrolytic graphite monochromator provided the resolution in azimuthal angle (χ) 1·5° and in momentum transfer parallel to the layers Q_{II} 0·05 Å^{-1} (FWHM). The in-plane molecular distance D and the range of the in-plane translational order ξ_{II} were obtained from the 2θ peak position and its width, respectively, by fitting the peak shape to the Lorentzian function with a non-linear background. The temperature of the sample in X-ray measurements was controlled with an accuracy better than 0·05 K. The studies of precise layer thickness d were performed with a DRON system for homeotropically aligned samples in the reflection mode; this allowed d to be obtained with an accuracy ±0·02 Å. The director tilt was calculated by comparing layer thickness in tilted and orthogonal phases.

This work is a contribution to the KBN 2P 303-02407 project. The synthesis of materials was supported by a UW BST-523/29/96 grant. Part of the cost of the X-ray measurements was met by NSF-ALCOM-STC grant no 89-20147.

References

[1] Staab, H. A., 1962, *Introduction to Theoretical Organic Chemistry* (Weinheim: Verlag Chemie).
[2] (*a*) Kato, T., and Frechet, J. M. T., 1989, *J. Am. chem. Soc.*, **111**, 8533; (*b*) 1989, *Macromolecules*, **22**, 3816.
[3] Paleos, C. M., and Tsiouruas, D., 1995, *Angew. Chem.*, **107**, 1839.
[4] Pyzuk, W., Gorecka, E., and Krowczynski, A., 1991, *Liq. Cryst.*, **10**, 593.
[5] Gorecka, E., Pyzuk, W., Krowczynski, A., and Przedmojski, J., 1993, *Liq. Cryst.*, **14**, 1837.
[6] Pyzuk, W., Gorecka, E., Krowczynski, A., and Przedmojski, J., 1993, *Liq. Cryst.*, **14**, 773.
[7] Chandrasekhar, S., 1992, *Liquid Crystals* (Cambridge: Cambridge University Press).
[8] Takeda, H., Sakurai, Y., Miyake, H., Doi, T., Kusabayashi, S., and Takagi, T., 1990, *J. Chem. Soc. Faraday Trans.*, **86**, 3429.
[9] Krowczynski, A., Szydlowska, J., Gorecka, E., and Pyzuk, W., 1994, *SPIE*, **2375**, 182.

[10] Krowczynski, A., Pyzuk, W., Gorecka, E., and Szydlowska, J., 1994, *Mol. Cryst. liq. Cryst.* **249,** 27.

[11] Birgenau, R. J., and Litster, J. D., 1978, *J de Phys. Lett.* **39,** L-339.

[12] De Gennes, P., and Prost, J., 1993, *The Physics of Liquid Crystals* (Oxford Scientific Publications).

[13] Huang, C. C., 1992, *Bond Orientational Order in Condensed Matter Systems* edited by K. J. Strandburg (New York: Springer-Verlag).

[14] (*a*) Brock, J. D., Birgeneau, R. J., Litster, J. D., and Aharony, A., 1989, *Contemp. Phys.*, **30,** 321; (*b*) Brock, J. D., Noh, D. Y., McClain, B. R., Litster, J. D., Birgeneau, R. J., Aharony, A., Horn, P. M., and Liag, J. C., 1989, *Z. Phys.B-Condensed,* **74,** 197; (*c*) Brock, J., 1992, *Bond Oriented Order in Condensed Matter Systems,* edited by K. J. Strandburg (New York: Springer Verlag).

[15] Bruisma, R., and Aeppli, G., 1982, *Phys. Rev. Lett.*, **48,** 1625.

[16] Aharony, A., Birgenau, R. J., Brock, J. D., and Lister, J. D., 1986, *Phys. Rev. Lett.*, **57,** 1012.

[17] Selinger, J. D., 1988, *J. Phys. France*, **49,** 1387.

[18] Gorecka, E., Chen, Li, Lavrentovich, O., and Pyzuk, W., 1994, *Europhys. Lett.*, **27,** 507.

[19] Gorecka, E., Chen, Li, Pyzuk, W., Krowczynski, A., and Kumar, S., 1994, *Phys. Rev. E*, **50,** 2863.