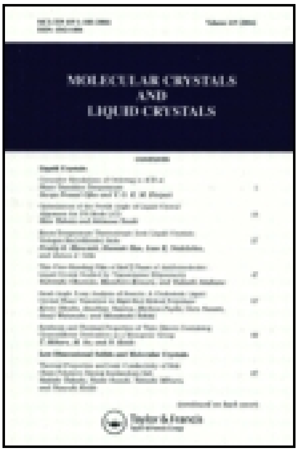

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# Tilted and Orthogonal Smectics in Thienyl and Furyl Substituted Enaminoketones

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# Tilted and Orthogonal Smectics in Thienyl and Furyl Substituted Enaminoketones

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Influence of molecular shape on appearance of a sequence of liquid crystalline phases was examined for substituted and non-substituted tienyl and furyl enaminoketones. Increasing of molecular bend promote tilted mesophases.

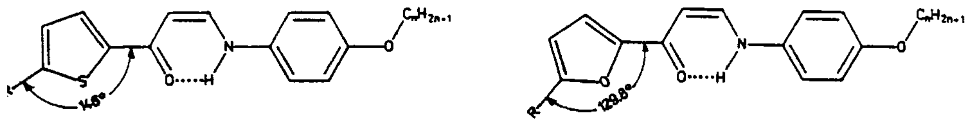
## INTRODUCTION

To establish a relation between a molecular structure and mesophase formation is an attractive tusk from basic interest and in view of possible applications. In most cases it is relatively easy to tell whether molecules are mesogenic but the particular mesophase sequence and other physical properties are difficult to predict since they are influenced by subtle details of the molecular structure. In this communication we described the effect of the molecular shape on tilted and orthogonal smectic phase formation. For our studies enaminoketone derivatives were chosen for their simple synthesis. A bend of the moleule was introduced due to the 2,5 substituted thienyl or furyl rings inserted in the terminal position of the mesogenic core. Based on x-ray molecular structure investigations it is known that the angle between two moieties attached to the pentagonal ring is 146° and 129.8° for the thienyl and furul ring[1] (Scheme).

## EXPERIMENTAL

The identification of mesophase was based on microscopic observations of the textures[2] with a Nikon polarizing microscope equipped with a Metler hot stage. Calorimetric measurements were performed using a DSC7 Perkin - Elmer set-up.

The enaminoketone derivatives were synthesized according to the procedure similar as described earlier[3]. The NMR spectra confirmed the assumed molecular structures.



R = H, $CH_3$, $C_4H_9$, $C_6H_{13}$

R = H, $CH_3$

SCHEME

## RESULTS AND DISCUSSION

The phase transition temperatures and phase transition enthalpies changes are collected in TABLE I. The phase diagrams of investigated homologous series are shown in Figure 1

### Thienyl derivatives - THO series

The compounds of the homologous series THO (R = H ) exhibit only orthogonal mesophases: smectic A, hexatic B, crystal B and E (Figure 1a) . The presented phase diagram shows the typical topology for the compounds revealing $S_A$ - $Hex_B$ - $Cry_B$ phase sequence[4]. As in the previously studied series the transition lines converged in the triple point $S_A$-$Hex_B$-$Cry_B$ located for the material with normalized width of the $S_A$ phase $r_{AB}$ = $T_{IA}$ / $T_{AB}$ - 1 between 0.16 (n =8) and 0.18 (n =9). This confirms that the suggested earlier[4] $r_{AB}$ = 0.17 is critical for the appearance of the hexatic phase. However contrary to the previously studied series the temperature range of the $Hex_B$ phase is only weakly affected by increasing the terminal chain length. As for the microscopic observation the $Cry_B$ - $Hex_B$ transition is detectable only when heating a virgin monocrystal, which spills at the temperatures relevant to the $Cry_B$ - $Hex_B$ transition. This effect is due to the destruction of three dimensional structure of the $Cry_B$ phase. The $S_A$ - $Hex_B$ phase transition is accompanied by the appearance of transition bars on a fan texture in all THO compounds. This effect characteristic for the $S_A$ - $Cry_B$ phase transition has already been observed for the $S_A$ - $Hex_B$ phase transition[4] in the compounds with very narrow hexatic B phase less than 1.5 K, close to the $S_A$-$Hex_B$-$Cry_B$ triple point. In the series THO the transition bars are however observed for the compounds with significantly broader hexatic phase (~4 K).

**TABLE I** Temperatures (° C) and, in parentheses entalpies (J/g) of the phase transitions for the compounds of the thienyl series:

$H\text{-}C_4H_2S\text{-}COC_2H_2NH\text{-}C_6H_4\text{-}OC_nH_{2n+1}$

| n | Cry | | $\mathrm{Cry}_E$ | | $\mathrm{Cry}_B$ | | $S_B$ | | $S_A$ | | Iso |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 6 | • | 104.8 (91.7) | • | 90.3 (0.01) | • | 93.5 (7.5) | - | - | • | 101.3 (18.2) | • |
| 8 | • | 96.3 (6.6) | | - | • | .4 (7.1) | - | - | • | 110.5 (18.7) | • |
| 9 | • | 82.1 (67.6) | | - | • | 91.2 (0.05) | • | 94.7 (6.6) | • | 111.6 (18.5) | • |
| 10 | • | 81.0 (61.6) | | - | • | 91.6 (0.05) | • | 94.1 (6.1) | • | 113.9 (18.7) | • |
| 14 | • | 95.2 (84.6) | | - | • | 89.1 (0.001) | • | 93.0 (5.2) | • | 115.3 (18.3) | • |

$C_4H_9\text{-}C_4H_2S\text{-}COC_2H_2NH\text{-}C_6H_4\text{-}OC_nH_{2n+1}$

| n | Cry | | $S_F$ | | $S_C$ | | Iso |
|---|---|---|---|---|---|---|---|
| 11 | • | | • | 107.0 (4.6) | • | 136.3 (20.4) | • |
| 12 | • | | • | 107.1 (5.1) | • | 136.1 (20.0) | • |
| 13 | • | 56.9 (50.3) | • | 105.9 (5.5) | • | 134.3 (20.1) | • |
| 14 | • | 58.3 (56.6) | • | 105.3 (5.9) | • | 133.1 (20.0) | • |
| 15 | • | 67.1 (58.7) | • | 104.6 (7.0) | • | 131.8 (20.2) | • |
| 17 | • | 75.8 (35.1) | • | 103.6 (2.3) | • | 128.9 (18.5) | • |
| 18 | • | 76.1 (64.2) | • | 102.5 (5.2) | • | 126.9 (17.8) | • |

$C_6H_{13}\text{-}C_4H_2S\text{-}COC_2H_2NH\text{-}C_6H_4\text{-}OC_nH_{2n+1}$

| n | Cry | | $\mathrm{Cry}_G$ | | $S_F$ | | $S_C$ | | N | | Iso |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | • | 79.3 (79.5) | - | | - | - | - | - | • | 109.5 (1.6) | • |
| 2 | • | 86.5 (70.7) | • | 64.7 (2.5) | • | 67.1 (0.7) | • | 85.7 (2.8) | • | 130.4 (2.4) | • |
| 3 | • | 74.5 (29.1) | • | 72.3 (1.6) | • | 77.3 (0.9) | • | 99.8 (5.9) | • | 118.9 (2.8) | • |
| 4 | • | 76.8 (29.0) | • | 85.7 (.63) | • | 96.5 (2.3) | • | 126.0 (7.2) | • | 133.3 (4.2) | • |
| 5 | • | 51.0 (35.9) | • | 87.6 (.42) | • | 102.2 (5.7) | • | 131.8 (18.4) | - | - | • |
| 6 | • | 57.3 (59.0) | • | 91.2 (.30) | • | 107.7 (5.1) | • | 139.1 (21.3) | - | - | • |
| 8 | • | 55.2 (66.1) | • | 97.3 (.16) | • | 114.4 (8.8) | • | 143.0 (22.9) | - | - | • |
| 10 | • | 54.7 (68.4) | • | 95.5 (.05) | • | 114.3 (9.2) | • | 142.6 (22.8) | - | - | • |
| 12 | • | 50.8 (43.3) | • | 90.8 (.03) | • | 113.5 (8.5) | • | 140.1 (22.7) | - | - | • |
| 13 | • | 59.0 (50.4) | • | • | • | 111.7 (7.0) | • | 137.6 (22.5) | - | - | • |
| 14 | • | 60.2 (34.1) | • | [a] | • | 113.2 (7.5) | • | 137.2 (22.3) | - | - | • |

[a] phase transition not detectable by DSC and texture studies

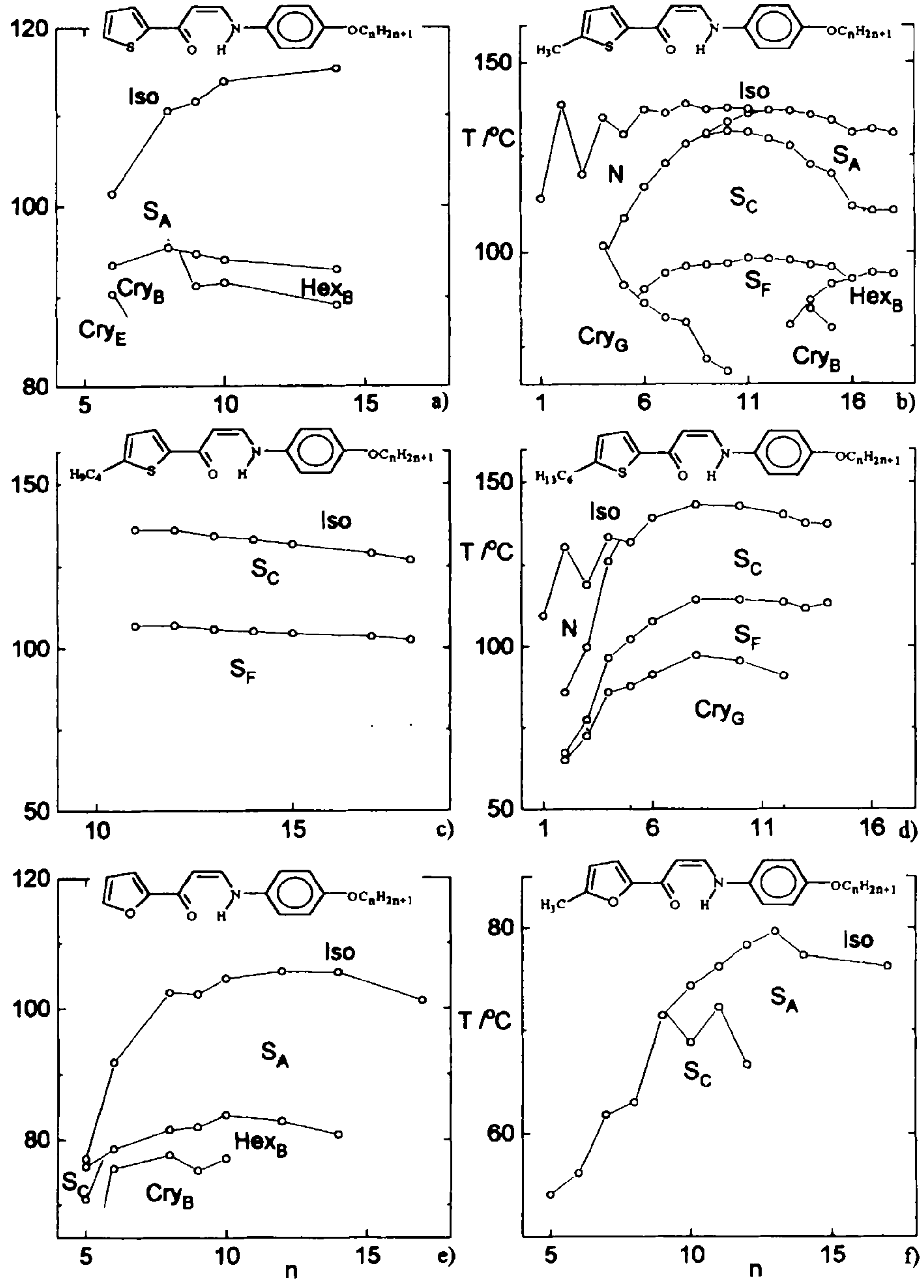


FIGURE 1 Phase diagrams (black dots - melting points)

Additionally wishbone defects[2] appear on the fan texture in the $S_A$ phase when the samples heated from $Hex_B$ phase.

The heat effects accompanying the creation of the long range bond orientational order and the long range positional order are substantially different[5]. The significant heat capacity anomalies with nearly constant amplitude along the transiton line were found for the $S_A$- $Hex_B$ phase transition. Much smaller effects were detected at theCry$_B$ - $Hex_B$ phase transition and they quickly decrease to vanish when moving away from the $S_A$-$Hex_B$-$Cry_B$ triple point.

### THI series

The phase diagram of the homologues series THI with substituents R = $H_3C$ (Figure 1b) was fully described[6]. The series exhibit complex polymorphism of orthogonal and tilted mesophases.

### TH4 and TH6 series.

The compounds of the homologous series TH4 and TH6 with R = $H_9C_4$, $H_{13}C_6$ substituent, respectively reveal mostly enantiotropic nematic and smectic phases. They exhibit only tilted smectics: liquid-like $S_C$ and hexatic $S_F$ in both series as well as the crystalline $Cry_G$ in TH6 series (Figure 1c, d). The phase transition between the liquid-like and hexatic smectics is accompanied by characteristic DSC signal with substantial heat capacity anomalies with almost constant amplitude for all homologues of the series. The enthalpy changes corresponding to the phase transition between the hexatic $S_F$ and crystal $Cry_G$ phases decrease monotonically with elongation of the molecules. For the compounds with n = 13 and 14 the transition enthalpy become undetectable ($\Delta H < 0.01$ J/g). Simultaneously, for these compounds the $S_F$ - $S_G$ phase transition becomes less pronounced in the microscopic studies whereas it was easily detectable for shorter homologues where schlieren texture of smectic F phase changes into mosaic shlieren texture of the smectic G phase.

### Furyl derivatives - FU0 series

The homologues of the series FU0 containing in the mesogenic core non-substituted furyl ring (R = H) reveals basically orthogonal phases $S_A$, $Hex_B$, $Cry_B$. The topology of the phase diagram (Figure 1e) is similar to that detected for the compounds with the non-substituted thienyl ring TH0 , however for shortest terminal chains (e.g. n = 5) narrow tilted $S_C$ phase intrudes between the $S_A$ and $Hex_B$ phases. As in the TH0 series rearranging the phase structure to the long range bond orientational order at the $S_A$ - $Hex_B$ phase transition is accompanied by substantial heat effects, whereas along the $Hex_B$ - $Cry_B$ phase transition line the transition enthalpy changes are rather small and decrease to vanish for homologues $n \geq 11$. At the $S_C$ - $Hex_B$ phase transition on broken fan texture transversal lines resembling the transition bars are visible.

### FUI series

The compounds of the series FUI with $R = CH_3$ exhibit the liquid like smectics $S_A$ and $S_C$ only. The more organized liquid crystalline phases do not appear. This series has substantially lower clearing points than the other presented. The $S_C$ - $S_A$ phase transition is of the second order what was confirmed by continuous tilt changes.

## CONCLUSION

The compounds with the pentagonal thienyl and furyl rings in the three ring mesogenic core were studied. It has been found that the non-substituted heterocycles promote othogonal phases. Elongation of substituents attached to the pentagonal ring makes the overall shape of the molecule more bent. This molecular modification promotes tiled mesophases. It has been found that for the appearance of the orthogonal hexatic phase the preceding $S_A$ phase should have normalized width $r_{AB} = \sim 0.17$. In both tilted and orthogonal systems building the long range in-plane bond structure is accompanied by strong heat capacity anomalies whereas building the long range positional order is accompanied only by small enthalpy changes. In both systems the hexatic - crystalline transition enthalpy decreases steeply with increasing terminal chain length. Also texture changes become less pronounced with increasing homologue number n.

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## References

1. A.I Kitajgorodskj, P.M. Zorkij, W.K Belskij, "Stroenie organičeskogo weščestwa", Izdatelstwo Nauka 1980, 533.
2. G.W.Gray and J.W.G.Goodby, "Smectic Liquid Crystals - Textures and Structures", Leonard Hill, Glasgow and London, 1984.
3. E.Górecka, W.Pyżuk, A.Krówczyński, and J.Przedmojski, *Liq.Cryst.*, **14**, 1837 (1993).
4. W.Pyżuk, A.Krówczyński and E.Górecka, *Mol.Cryst.Liq.Cryst.*,**75**, 237, (1993), W. Pyzuk, E. Górecka, J. Szydłowska, A. Krówczyński, D. Pociecha and J. Przedmojski, *Phys. Rev. E*, **52** (1995).
5. G.Iannacchione, E. Gorecka, W. Pyzuk, S. Kumar and D. Finotello, *Phys.Rev.E*, **51**, 3346, (1995).
6. W.Pyżuk, J.Szydłowska, E.Górecka, A.Krówczyński, D.Pociecha and J.Przedmojski, *Mol.Cryst.Liq.Cryst.*, **260**, 449, (1995).