Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Novel Series of Enaminoketone Liquid Crystals Having Hexatic Smectic B Phase

Wiesław Pyżuk [a], Adam Krówczynsk [a] & Ewa Górecka [a]
[a] Laboratory of Dielectrics and Magnetics, Department of Chemistry, University of Warsaw, 02-089 Warsaw, Al., żwirki-Wigury, 101, Poland
Version of record first published: 24 Sep 2006.

To cite this article: Wiesław Pyżuk , Adam Krówczynsk & Ewa Górecka (1993): Novel Series of Enaminoketone Liquid Crystals Having Hexatic Smectic B Phase, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 237:1, 75-84

To link to this article: http://dx.doi.org/10.1080/10587259308030125

Mol. Cryst. Liq. Cryst., 1993, Vol. 237, pp. 75–84
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Novel Series of Enaminoketone Liquid Crystals Having Hexatic Smectic B Phase

WIESŁAW PYŻUK, ADAM KRÓWCZYNSKI and EWA GÓRECKA

Laboratory of Dielectrics and Magnetics, Department of Chemistry, University of Warsaw, 02-089 Warsaw, Al. Żwirki-Wigury 101, Poland

(Received March 11, 1992; in final form November 5, 1992)

Several homologous series of liquid crystals having an aminoketone mesogenic core (*Liq. Cryst.*, **10**, 593 (1991)), have been synthesized to derive some new wide-temperature untilted smectics. Compounds belonging to three of six novel series have the hexatic smectic B phase between smectic A and enantiotropic crystal smectic B phases. Eleven of them exhibit first order phase transition between smectic B phases, whereas for other compounds this phase transition is not detectable neither by DSC nor texture studies. Molecular modifications leading to further untitled hexatic compounds are suggested.

Keywords: liquid crystals, phase transitions, smectic B hexatic phase

I. INTRODUCTION

The hexatic untilted phase, SmB(hex), is distinguished by the presence of a peculiar ordering, intermediate between the unordered smectic A and the crystalline smectic B.[1] This phase is intensively studied now, experimentally and theoretically, in thin films as well as in the bulk.[2–6] However, the bulky hexatic SmB phase had been known only for four series of two-ring liquid—crystalline compounds[7–9] and for a single three-ring compound.[10] In practice, studies of phase transitions and properties were limited to the series of the mnOBC compounds. Such circumstances lead to essential difficulties in generalization of experimental results and their comparison to theoretical predictions.

The smectic B(hex) phase has been found recently among new enaminoketone liquid crystals. These compounds have a mesogenic core stabilized by an intramolecular hydrogen bond of the *cis-s-cis* aminopropen-1-one-3 quasi-ring.[11] In the present work we are reporting the initial results of our attempts to find some further series of three-ring enaminoketones exhibiting hexatic B phase. Phase diagrams for five novel homologous series are presented. For three of them hexatic phase has been found between enantiotropic crystal smectic B and fluid smectic A phases. This fact enables studies of both phase transitions, i.e. SmB(cry)-SmB(hex) and SmB(hex)-SmA in a particular compound.

II. EXPERIMENTAL

New compounds have been synthesized analogically to our previous synthesis of the enaminoketone liquid crystals[11-12] (see also[13]). The only difference now, is the choice of other methylketones as starting materials. Phase transitions were determined from differential scanning calorimetry (DSC-7, Perkin-Elmer) and microscopic (Jenapol-U, Zeiss) studies.

The DSC traces are typical.[8] Here characteristic are the peaks of the SmB-SmA transitions, being either sharp or diffused over a remarkable temperature range, depending on the absence or presence of pretransitional anomalies in the specific heat. Sharp peaks are connected with the transition involving the crystalline SmB

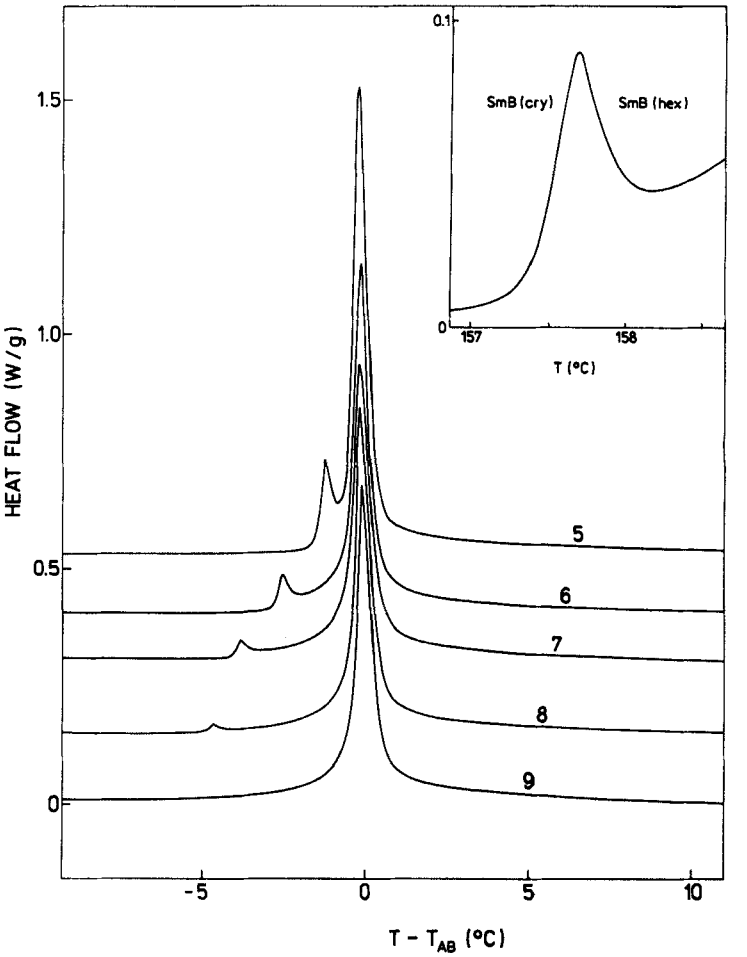

FIGURE 1 DSC scans (5°C/min, 1 mg samples) through the smectic phases for homologues $n = 5$ to 9 of the series (IV). Note diffuse peaks of the transition between SmB and SmA phases and small peaks of the transition between SmB(cry) and SmB(hex) phases. An increase of the hexatic range is followed by decreasing transition enthalpy. In the inset, the low—temperature peak for the homologue $n = 6$ is presented in a large scale.

phase. The shape of the peaks which correspond to transition to hexatic phase can be different and depends, most probably, on the transition order. For the examined series these peaks are usually diffused (Figure 1). Beside these well pronounced peaks, additional small, well reproducible peaks of the first-order SmB(cry)-SmB(hex) phase transition are observed on thermograms of some compounds (Figure 1).

As regards microscopic observations, typical transition bars were observed during the SmA-SmB(cry) phase transition. No bars accompanying the SmA-SmB(hex) transition, with the exception of a very narrow hexatic phase, and no relevant wishbone effect[7] were observed. Corresponding photomicrographs are presented on Figure 2. Usually this transition is continuous and accompanied only by a gradual smoothing of a fan texture. Therefore, the phase transition temperature cannot be determined. No remarkable texture changes accompany the SmB(cry)-SmB(hex) phase transition. The best method to detect this transition microscopically is the observation of virgin monocrystals while heated. At the temperature of melting to the crystal B phase, their birefringence vanishes, but the crystalline form usually still persists. This is due to a three dimensional molecular arrangement, which becomes destroyed during the transition to the hexatic phase. In result, at the transition temperature the smectic crystals rapidly spill for some compounds.

Final identification of mesogenic phases was based on miscibility tests and phase diagrams of binary systems with reference compounds, preferably with other enaminoketone liquid crystals, as compounds having similar chemical structure. A typical phase diagram is shown and discussed in Sect. 4. To confirm the identification of the hexatic phase, in some cases X-ray studies were used.

III. RESULTS AND DISCUSSION

In order to design wide-temperature untilted smectics we have modified the chemical structure of some hexatic compounds, 1-(4′-alkoxyphenylamino)—3-[5″-(2″-methylpirydil)]-propen-1-one-3-s[11],

$$H_3C—C_6H_3N—COCH{=}CHNH—C_6H_4—OC_nH_{2n+1} \quad \text{(series (I))}$$

In the first step of the modification procedure we introduced into the molecules a phenyl ring instead of a pirydine one, thus cancelling the dipole moment of the aromatic part. In the resulting compounds:

$$H_3C—C_6H_4—COCH{=}CHNH—C_6H_4—OC_nH_{2n+1} \quad \text{(series (II))}$$

the total molecular dipole moment remains non-zero due to the presence of the strongly polar enaminoketone group.[11] The phase diagrams (Figure 3) show that this seemingly small change of the peripherial dipole moment has a drastical influence on the phase sequence, leading to the occurrence of tilted smectic phases in the modified series (II). Untilted smectic B phase, appearing below smectic A or tilted phases, is present for long-tail members of the series. However, this is the crystalline rather than hexatic phase.

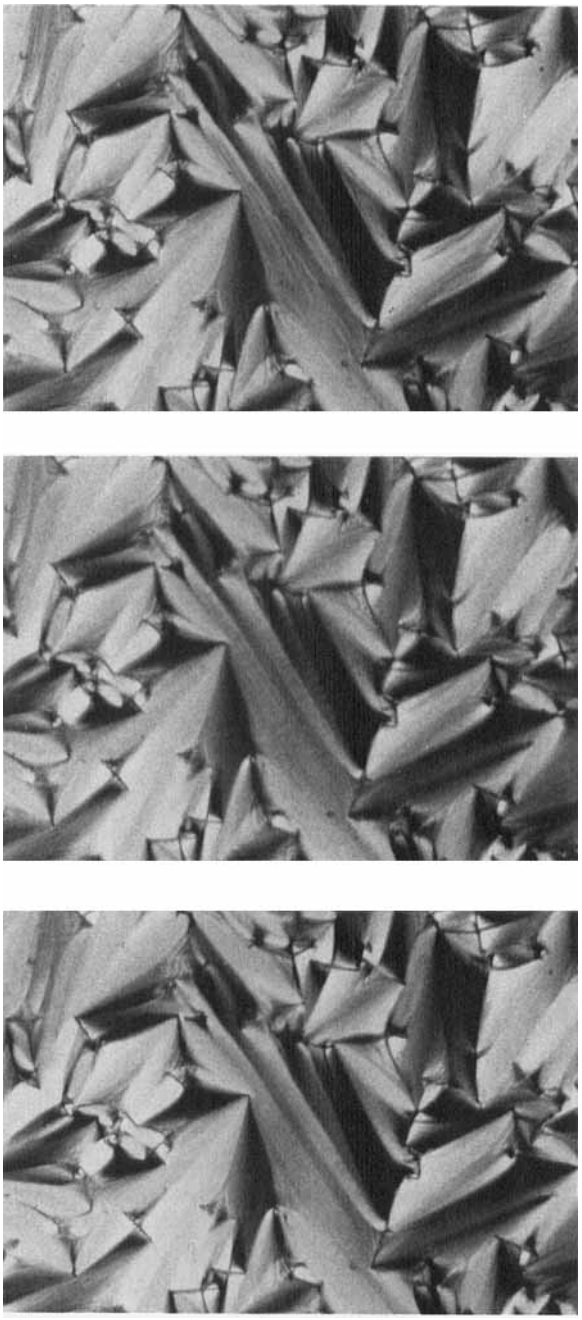

FIGURE 2 Textures of the homologue $n = 6$ of the series (V). From the upper: SmA phase (175°C), transition SmA-SmB(hex) (173.3°C) and SmB(hex) phase (172°C). Note faint transition bars. The texture of the crystal SmB phase is not shown as it is essentially the same as that for the hexatic phase. See Color Plate X.

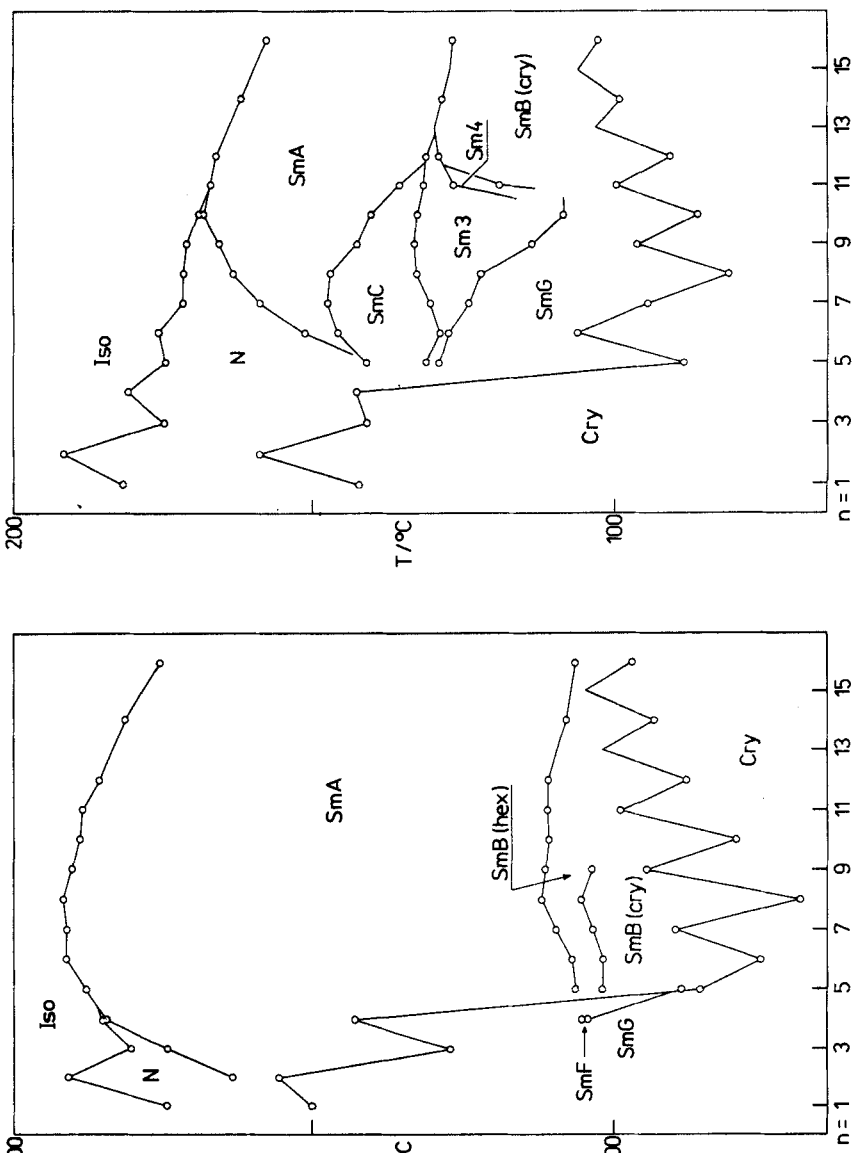

FIGURE 3 Phase diagrams for series (I)–(II) of methyl terminated enaminoketone liquid crystals. Series (I)[11] on left, series (II) on right, for their chemical formulae see text. Sm3 and Sm4 are tilted phases, the former is tentatively identified as SmF.

The above described negative result suggests that the presence of a small dipole moment, say 1 to 2 D, in the aromatic part of aminoketone molecules is necessary for the phase sequence SmA-SmB(hex)-SmB(cry). Therefore, as a second molecular modification we substitute the terminal methyl group in the series (II) by a halogen atom, thus introducing a longitudinal dipole moment and keeping the molecular shape unchanged. Phase diagrams of the resulting series:

$$F—C_6H_4—COCH{=}CHNH—C_6H_4—OC_nH_{2n+1} \quad \text{(series (III))}$$

$$Cl—C_6H_4—COCH{=}CHNH—C_6H_4—OC_nH_{2n+1} \quad \text{(series (IV))}$$

$$Br—C_6H_4—COCH{=}CHNH—C_6H_4—OC_nH_{2n+1} \quad \text{(series (V))}$$

$$I—C_6H_4—COCH{=}CHNH—C_6H_4—OC_nH_{2n+1} \quad \text{(series (VI))}$$

are presented in Figure 4. It is seen that the expected hexatic phase is, in fact, present for compounds belonging to the series (III)–(V). The phase temperature range decreases with increasing radius of the terminal halogen (F, Cl, Br) and within a series, it increases with increasing length of the terminal alkoxy chain (see also Table I). The maximum width of the hexatic phase detectable in DSC experiments, is 6.1, 4.5 and 3.2 K for F, Cl and Br substituent, respectively. A correlation between the range of hexatic SmB and of preceeding SmA phases is evident from Figure 4. As it is clear from results for I substituent, three-ring enaminoketone compounds do not form the hexatic phase if an normalized width of the smectic A phase, $r_{AB} = 1 - T_{IA}/T_{AB}$, drops below a critical value of $r_{AB} = 0.17$.

All phase diagrams of the series (III)–(V) reveal the SmA-SmB(hex)-SmB(cry) phase sequence and have a topology theoretically predicted for binary systems[6] with the A-B(hex)-B(cry) triple point and the tricritical point on the SmA-SmB(hex) transition line. As it was found recently,[11] the line of the first-order phase transition between both smectics B terminates with a critical point, in our case just above $n = 8$. The existence of this point has not been previously anticipated. An extension of the first-order transition line on phase diagrams cannot be given for longer homologues because an eventual continuous transition is not detectable neither from texture observations nor DSC studies.

To discuss the molecular factors responsible for the stabilization of the hexatic phase, an analysis of more extensive experimental data is necessary. For this reason in progress are syntheses of further compounds, for which existence of the SmB(hex) phase is expected. Several new series could be easily derived by simple modifications of parent structures. For example, a revolving of the enaminoketone quasi-ring or a change of alkoxyl to alkyl group might be taken into account. To check the first possibility we have synthesized some compounds of the formula:

$$X—C_6H_4—NHCH{=}CHCO—C_6H_4—OC_nH_{2n+1},$$

where X is a halogen. All obtained compounds ($n = 5,6$) reveal the hexatic smectic B phase, much wider than the corresponding compounds of series (III)–(VI), (e.g.,

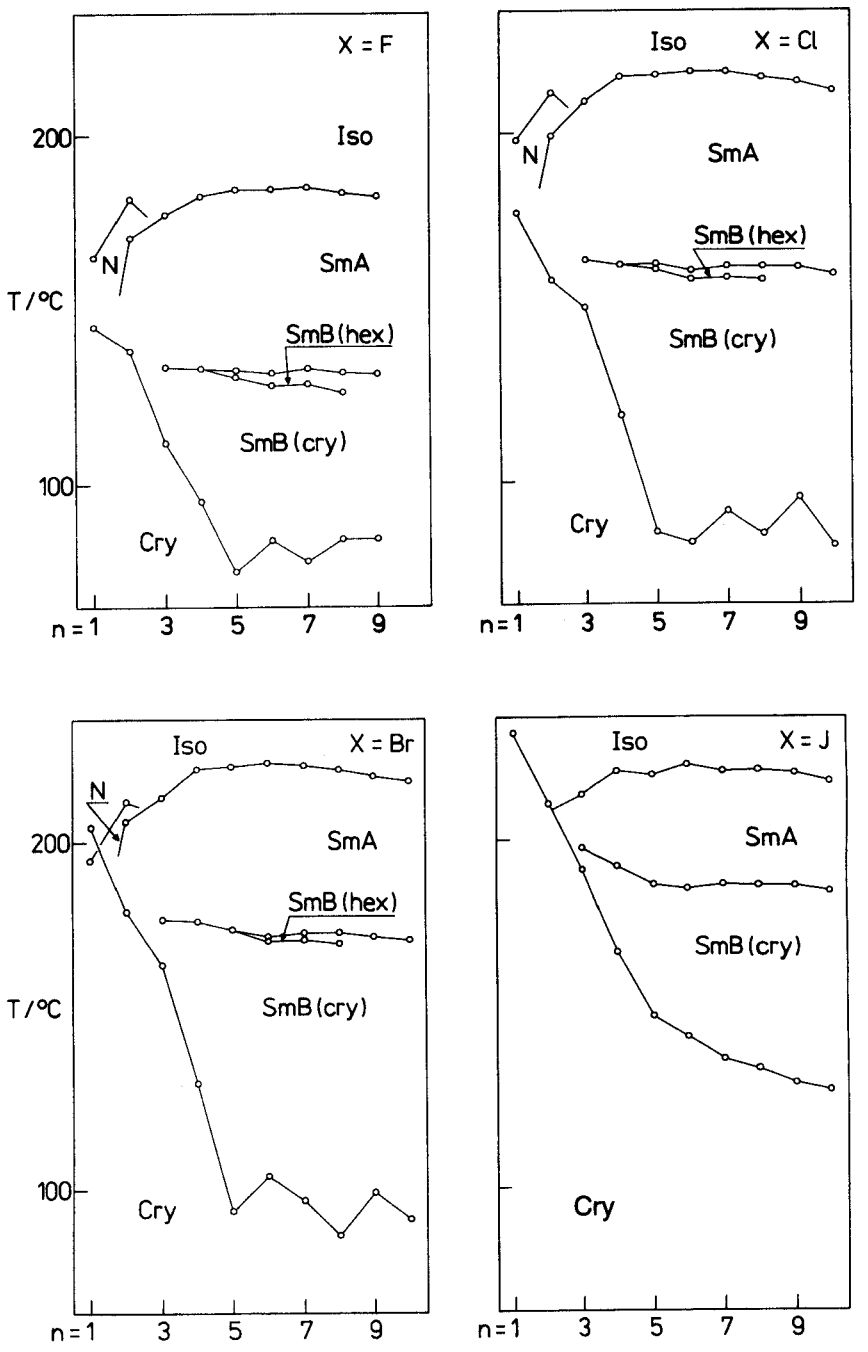

FIGURE 4 Phase diagrams for series (III)–(VI) of halogen terminated enaminoketone compounds. For their chemical formulae see the text. Note the presence of a critical point on the phase transition line between smectic B phases.

TABLE I

Temperatures (°C) of phase transition between smectic phases and, in parentheses, enthalpies (J/g) of the first-order transition between smectic B phases or between crystal B and fluid A smectics vs. alkoxy carbon number (n) for the series (III)–(V) of 1-(4′-alkoxyphenylamino)3-(4″-halogen-phenyl)-propen-1-one-3-s:

n	B(cry)	B(hex)	A	B(cry)	B(hex)	A	B(cry)	B(hex)	A
	Fluor series			Chlor series			Brom series		
3	133.2 *(9.1)*	—		164.1 *(11.9)*	—		178.8 *(12.1)*	—	
4	132.6 *(7.4)*	—		164.4 *(9.7)*	—		177.4 *(9.7)*	—	
5	130.9 *(0.68)*	132.2		161.0 *(0.47)*	162.2		174.2*)	174.7	
6	128.2 *(0.29)*	131.1		157.6 *(0.26)*	159.9		171.9 *(0.22)*	173.3	
7	127.7 *(0.11)*	132.3		157.3 *(0.11)*	160.9		171.9 *(0.10)*	174.3	
8	125.7 *(0.04)*	131.8		156.6 *(0.04)*	161.1		170.9 *(0.03)*	174.1	
9	**)	131.2		**)	160.8		**)	173.7	

*) Extrapolated data, unresolved DSC peak gives total enthalpy of 8.4 J/g.

**) Phase transition not detectable by DSC and texture studies.

the phase transitions for the compound [X = F, n = 6] are: Cry 90.5°C (50.8 J/g) SmB(cry) 101.5°C (0.05 J/g) SmB(hex) 112.5°C (3.8 J/g) SmA 174.5°C (15.9 J/g) Iso, thus, the range of the hexatic range is 11°C).

That the eventual modifications should keep molecular shape unchanged it is shown by the results of our third molecular modification. To bend the molecule without any essential changing its molecular dipole moment, a tiophene ring has been substituted for pirydine ring in compounds of the series (I). The phase diagram of the resulting derivatives of 2-methyl-5-acetyltiophene:

$$H_3C—C_4H_2S—COCH{=}CHNH—C_6H_4—OC_nH_{2n+1} \quad \text{(series (VII))}$$

as being much involved and not completed yet, is not presented here. For this series we found, however, that the crystalline smectic B phase appears below the smectic C phase and the hexatic B smectic phase does not exist at all.

In conclusion, the untilted hexatic smectic phase can be easily found among three-ring enaminoketone liquid crystals having a wide SmA phase. It can preferably be obtained by simple modifications of non-hexatic parent structure of 1-(4′-alkoxyphenylamino)-3-(4″-tolyl)-propen-1-one-3-s (series (II)). Preferred are those modifications of the tolyl group which lead to a non-vanishing small longitudinal dipole moment. (Alternatively, the Hammett's constants, σ, of the terminal substituents should be in the range 0.0 to 0.3). In this way a lot of new hexatic compounds having the SmB(cry)-SmB(hex)-SmA phase transitions between enantiotropic phases becomes available. It makes the studies of this unique phase sequence much easier. It should also be noted that the involved phase transitions can be either first or second-order, depending on the choice of compounds. Relevant results of the DSC studies will be described separately.

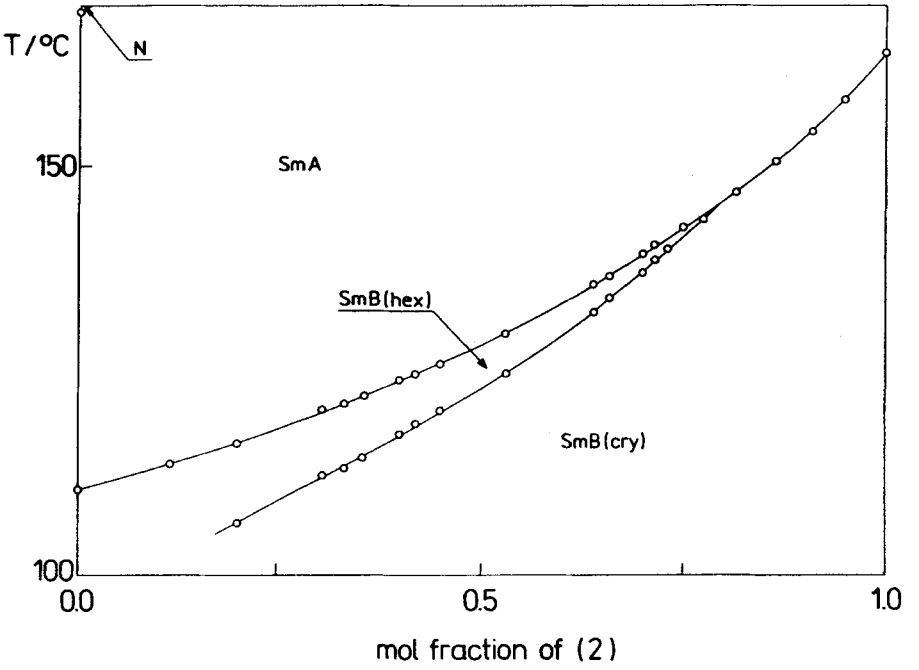

FIGURE 5 Binary phase diagram for the system of the homologues $n = 11$, series (I), (component 1), and $n = 3$, series (IV), (component 2). The hexatic B phase is observed between the triple point and the critical one. Location of the latter is determined from analysis of the transition enthalpies. Note the connection of the present phase diagram with phase diagrams of homologous series (I) and (IV) (Figures 3 and 4).

Since as much as 4×10^4 thermotropic LCs are known today, the very limited number of hexatic B materials reported in the literature is somewhat surprising. Most probably, the hexatic phase exists in many already examined materials, but its presence has been overlooked during older studies limited to microscopic methods only. Also in the course of careful DSC studies, if the method is applied to single compounds only and not to homologous series, this phase is easy to be missed. As an example, a typical binary phase diagram constructed by the DSC method is presented on Figure 5. Pure components, although belonging to the hexatic series, (I) and (IV), either do not show DSC peaks of the SmB(cry)-SmB(hex) transition (component 1) or are not hexatic at all (component 2). In such case the hexatic phase is observed only in a limited concentration range, between the triple and critical points.

Acknowledgment

The KBN grant 201019101 is greatly acknowledged. Thanks are due to A. Niedźwiedzka for studies of binary phase diagrams and for her help in phase identification as well as to T. Krupkowski for the discussion.

References

1. R. Pindak, D. E. Moncton, S. C. Davey and J. P. Goodby, *Phys. Rev. Letters*, **46**, 1135 (1981).
2. R. Geer, T. Stoebe, C. C. Huang, R. Pindak, G. Srajer, J. W. Goodby, M. Cheng, J. T. Ho and S. W. Hui, *Phys. Rev. Letters*, **66**, 1322 (1991).
3. T. Pitchford, G. Nounesis, S. Dumrongrattana, J. M. Viner, C. C. Huang and J. W. Goodby, *Phys. Rev. A*, **32**, 1938 (1985).
4. R. Mahmood, M. Levis, R. Biggers, D. Johnson and M. E. Neubert, *Phys. Rev. A*, **33**, 519, (1986).
5. A. Aharony, R. J. Birgenau, J. D. Brock and J. D. Litster, *Phys. Rev. Letters*, **57**, 1012 (1986).
6. G. Nounesis, R. Greer, H. Z. Liu, C. C. Huang and J. W. Goodby, *Phys. Rev. A*, **40**, 5468 (1989).
7. J. W. Goodby, *Mol. Cryst. Liq. Cryst.*, **72**, 95 (1981); J. W. Goodby and R. Pindak, *Mol. Cryst. Liq. Cryst.*, **75**, 233 (1981).
8. G. Poeti, E. Fanelli and D. Gouillon, *Mol. Cryst. Liq. Cryst.*, **82**, 107 (1982).
9. G. W. Gray and J. W. Goodby, "Smectic Liquid Crystals. Textures and Structures," Leonard Hill, Glasgow, 1984.
10. Nguyen Huu Tinh, H. Gasparoux, C. Destrade, *Mol. Cryst. Liq. Cryst.*, **123**, 277 (1985).
11. W. Pyżuk, A. Krówczyński and E. Górecka, *Liq. Cryst.*, **10**, 593 (1991).
12. W. Pyżuk, E. Górecka and A. Krówczyński, *Liq. Cryst.*, **11**, 797 (1992).
13. Y. G. Galyametdinov, G. I. Ivanova and I. B. Ovchinnikhov, *Zh. Obsch. Khim.*, **61**, 234 (1991).