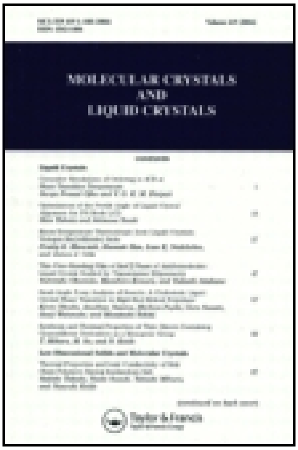

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Enaminoketone mesogens having polar terminal groups

Adam Krówczyński [a], Wieslaw Pyżuk [a], Ewa Górecka [a] & Jadwiga Szydlowska [a]

[a] Laboratory of Dielectrics and Magnetics, Department of Chemistry, University of Warsaw, Warsaw, AI. Zwirti i, Wigury 101, 02-089, Poland

Version of record first published: 24 Sep 2006.

To cite this article: Adam Krówczyński , Wieslaw Pyżuk , Ewa Górecka & Jadwiga Szydlowska (1994): Enaminoketone mesogens having polar terminal groups, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 249:1, 27-32

To link to this article: http://dx.doi.org/10.1080/10587259408038652

Mol. Cryst. Liq. Cryst. 1994, Vol. 249, pp. 27–32
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Enaminoketone mesogens having polar terminal groups

ADAM KRÓWCZYŃSKI, WIESŁAW PYŻUK, EWA GÓRECKA
and JADWIGA SZYDŁOWSKA

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

Homologous series of 4"-nitro- and 4"-cyano- derivatives of 1-(4'-alkoxyphenylamino)-3-phenyl-1-propen-3-ones and a structurally similar series of 1-(4'-alkoxyphenylamino)-3-(4"-pyridyl-N-oxide)-1-propen-3-ones were synthesized and studied by DSC and optical methods. The compounds behave typically for strongly polar mesogens: the smectic A_d phase exists above a critical chain length and the reentrant nematic phase is observed in the vicinity of the critical double point. For pyridyl N-oxides, a second-order SmA_d - SmC_d phase transition line is observed.

1. INTRODUCTION

Due to dipolar as well as charge transfer interactions, strongly polar rod-like molecules may form a variety of mesophases. Among smectics, monolayer/bilayer or partly bilayer systems are usually realized and reentrant phenomena[1] are often observed for the latter. It is well known that the reentrance is connected with strong molecular asymmetry enabling formation of "soft" molecular dimers and competition between different types of ordering corresponding to mono- and bilayer structures. Sufficient electrical asymmetry is provided by terminal cyano and nitro groups and numerous relevant reentrant mesogens exist.[2-4] However, several strongly polar rings, such as pyridyl N-oxides, sydnones, thian-1-oxides, etc., have not been tested as moieties useful in designing of reentrant systems.

In this work two homologous series, 1 and 2, of new compounds terminated with standard polar groups are described and compared to structurally similar series **3**. As the enaminoketone group exhibits a pronounced tendency towards forming a stable hydrogen-bonded quasi-ring of *cis-s-cis* conformation,[5] the compounds are, in fact, three-ring calamitic mesogens:

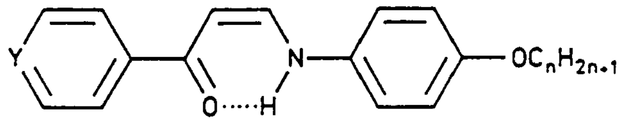

FIGURE 1 General formulae for the compounds of the series **1** (Y = O_2N-C), **2** (Y = NC-C) and **3** (Y = O^--N^+).

For their convenient molecular structure, the presence of reentrant nematic phase in these systems is highly probable. Actually, we have observed this phase not only for cyano derivatives, but also, for the first time, for pyridyl N-oxides.

2. RESULTS

Phase diagrams of the series **1-3** are presented in Fig.2 and thermal effect accompanying phase transitions are collected in Table I. It is seen there that both temperature stability of the SmA phase and its transition heat to the N and Iso phases decrease drastically with decreasing terminal alkoxy chain length. It results from a narrowing of the SmA phase area in the vicinity of the double critical point. Its presence is confirmed by observation of the reentrant nematic phases for some rapidly supercooled compounds, **2**(n=6) and **3**(n=4). Probably, the same critical point exists for other series of pyridyl N-oxides, for which similar types of phase diagrams were reported.[6] Obviously, the only possible type of the SmA phase in the system is the SmA$_d$ phase.

A detail examination of the SmA$_d$ - N phase transition was difficult because supercooled compounds as well as some mixtures easily recrystallize when heated. However, for two homologous series it was possible to determine the critical chain length from binary phase diagrams (Fig.3). For the cyano and pyridyl-N-oxide series it amounts to n = 5.34 and 3.87, respectively, for the nitro series the critical point lies below n= 2.8. The presence of the smectic A$_d$ phase below n = 4 is rather exceptional.[2,3] Location of critical points for lower n reflects, most probably, rather compact structure of the mesogenic core.

The SmA$_d$ is the only smectic phase observed for the series **1**, **2**. For the series **3**, this phase is limited, at low temperatures, by the SmC phase. Transition between both these phases is of the second order as the jump in the specific heat, without pretransitional anomalies is seen on the DSC thermograms. As similar

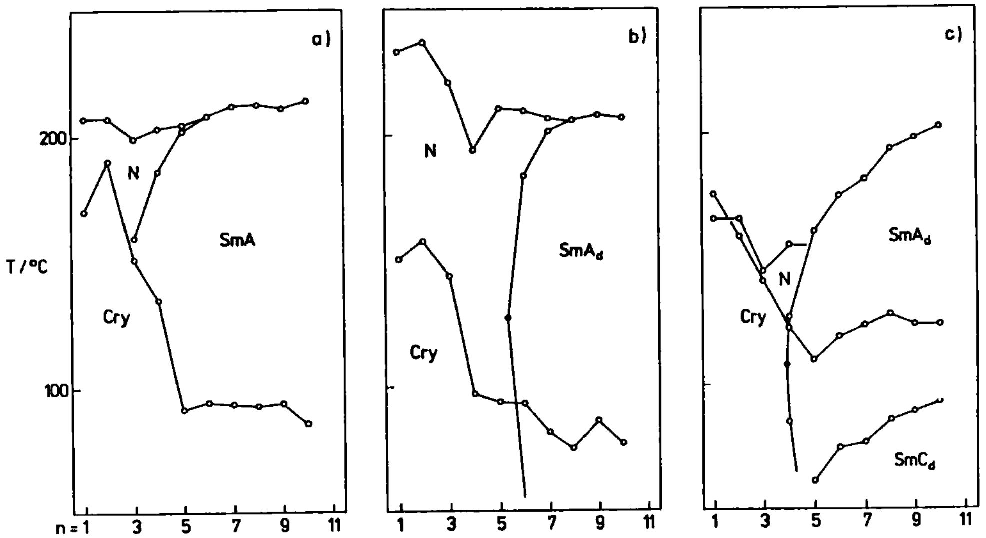

FIGURE 2 Phase diagrams for the homologous series 1 (a), 2 (b) and 3 (c). Consult Fig.1 for chemical structures. Full dots denote location of the critical points in reentrant systems.

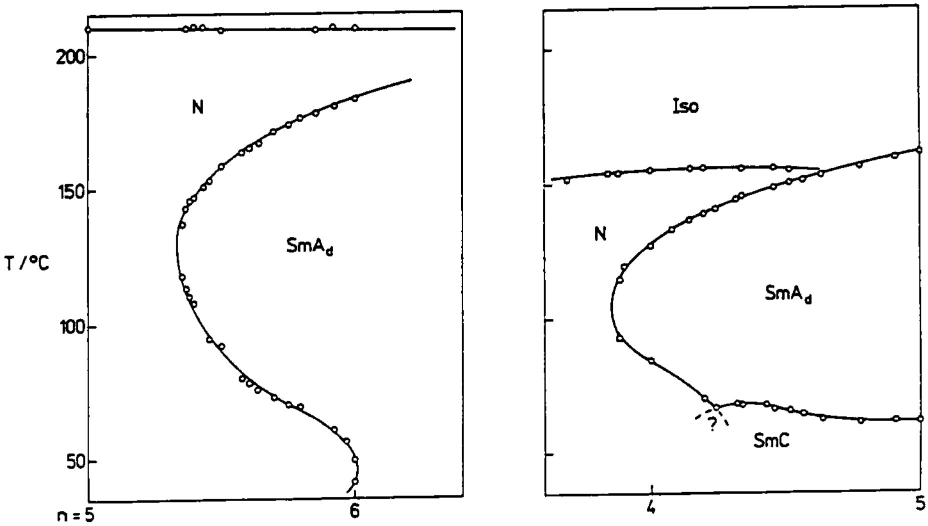

FIGURE 3 Phase diagrams for binary mixtures of neighbouring homologues; n is the mean carbon chain length of the terminal group. Left: series 2; right: series 3.

thermograms correspond to the SmA$_d$-SmC$_d$ phase transition,[4] the smectic C phase is most likely the partly bilayer one. For the presence of this phase, a N$_{re}$AC triple point should exist in binary mixtures but this point was not accessible in our experiments because of crystallization. The specific heat jump varies

TABLE I Temperatures (in °C) and, in parentheses, enthalpies (in J/g) or specific heat jumps (J/(K·g)) for the SmC_d-SmA_d transition of the compounds of the series 1 to 3.

The series 1 ($O_2N\text{-}C_6H_4\text{-}CO(CH)_2NH\text{-}C_6H_4\text{-}OC_nH_{2n+1}$):

n	Cry	SmA_d	N	Iso
1	170.3 (98.4)	–	206 (1.4)	
2	190.4 (104.5)	–	208 (2.2)	
3	150.9 (79.8)	159.3 (0.5)	198.7 (1.75)	
4	134.8 (91.2)	186.1 (2.05)	202.8 (2.15)	
5	91.3 (59.8)	201.9 (7.0)	204.4 (1.5)	
6	93.8 (53.1)	207.7 (10.8)	–	
7	93.6 (82.5)	211.3 (12.8)	–	
8	93.0 (91.6)	212.5 (14.1)	–	
9	93.4 (81.9)	211.1 (12.9)	–	
10	85.7 (82.0)	213.9 (16.4)	–	
16	96.7 (96.8)	198.7 (16.8)	–	

The series 2 ($NC\text{-}C_6H_4\text{-}CO(CH)_2NH\text{-}C_6H_4\text{-}OC_nH_{2n+1}$):

n	Cry	SmA_d	N	Iso
1	150.4 (90.5)	–	232.9 (4.8)	
2	157.6 (89.5)	–	236.8 (4.35)	
3	144.0 (76.8)	–	220.9 (2.8)	
4	97.6 (54.9)	–	193.9 (2.45)	
5	93.3 (57.5)	–	210.6 (2.15)	
6	92.9 (60.0)[a]	183.5 (0.3)	209.4 (3.20)	
7	81.4 (78.4)	201.5 (1.8)	206.4 (2.95)	
8	75 (72.9)	205.9 (9.9)	–	
9	86 (69.6)	208.2 (12.3)	–	
10	77.0 (89.1)	206.7 (12.8)	–	
12	77.6 (75.6)	207	–	
16	89.3 (104.7)	198.1 (16.0)	–	

The series 3 ($O^-N^+C_5H_4\text{-}CO(CH)_2NH\text{-}C_6H_4\text{-}OC_nH_{2n+1}$):

n	Cry	SmC_d	SmA_d	N	Iso
1	176.1 (108)	–	–	161 (1.2)	
2	159.3 (99.0)	–	–	166.2 (1.2)	
3	139.6 (77.4)	–	–	146	
4	122.7 (82)[b]	–	176 (0.02)	155.4 (1.25)	
5	110 (54.2)	–	160.7 (4.6)	–	
6	119.3 (66.2)	74.3 (0.15)	174.9 (7.05)	–	
7	123.3 (68.7)	76.5 (0.23)	182 (9.9)	–	
8	128.1 (75.6)	85.7 (0.25)	193.6 (11.2)	–	
9	124.2 (70.4)	89.3 (0.28)	198.2 (12.7)	–	
10	124.1 (70.7)	93.2 (0.30)	202.5 (12.9)	–	
16	124.0 (77.6)	107.1 (0.16)	200.3 (11.2)	–	

[a] also $SmA\text{-}N_{re}$ and $N_{re}\text{-}SmA_d$ phase transitions at 41 and 49 °C, respectively.

[b] also $N_{re}\text{-}SmA_d$ phase transitions at 85 °C.

nonmonotonously along the SmA_d-SmC_d phase transition line and a rapid decrease in the c_p jump with the decreasing chain length suggests, in analogy to ref.[4], that the transition line might terminate with a critical end point.

3. DISCUSSION AND CONCLUSIONS

The phase diagrams for three studied series having almost the same dipole moments (dipole moments for nitrobenzene, benzonitrile and pyridine N-oxide are 4.1 ± 0.1 Debye units) and differing rather slightly in molecular shape, are similar. The nematic phase exists for the shortest homologues and partly bilayer smectic A phase - for the longer ones. In contrast, less polar halogen analogues of the series **1** and **2** form wide, untilted monolayer smectic phases.[7] Methyl derivatives reveal similar phase sequence but for longer homologues only. Shorter chains promote, however, tilted monolayer smectics.[7] Rather complex polymorphism of tilted phases solely is observed for alkoxy derivatives.[8] Therefore, a type of realized phase diagram depends on a dipole moment of the terminal group. More precisely, appearance of particular phases, which is connected with a distribution of the electron density within molecules, can be correlated with the Hammett's constant of variable molecular fragments. Similar correlation was reported for some conventional three-ring compounds terminated with one fixed alkoxy substituent and a second variable polar one.[9]

In spite of similarity of the phase diagrams of the series **1-3**, a remarkable difference in range of their nematic phases is evident. Isotropization temperatures as well as corresponding thermal effects increase in the order of Y:

$$O^{-}N^{+} < O_2N\text{-}C < NC\text{-}C$$

and their difference amounts even to ca. 80 °C between extreme series. This phenomenon may reflect differences in non-polar, e.g. charge-transfer type, interactions between molecules.

In conclusion, it is possible to discuss the phase sequence of new enaminoketone compounds in terms of relation between molecular structure and formation of particular mesophases. For three-ring aromatic mesogens terminated with terminal and alkoxy groups, the phase sequence depends on the Hammett's constants of the former. Pyridyl-N-oxide moiety was found as a novel molecular fragment enabling occurrence of reentrant phases in LC systems.

4. EXPERIMENTAL

All compounds were synthesized from appropriate methyl ketones, which were converted into propenals and treated with N-alkylamines to give final products.[5] The latter were purified by crystallization from hexane and their purity was controlled by the DSC method. Pyridine N-oxides crystals are red-orange (lower homologues) or yellow (higher ones), for n = 4 both these colours can be seen in a mixture of polymorphic forms, which crystallizes from hydrocarbon solvents.

Ortho- and conoscopic observations were made using Jenapol-U, Zeiss, polarizing microscope with HT82 Mettler hot stage. Thermograms were taken using DSC-7 Perkin-Metler set-up at a scan 5 °C/min or less if necessary.

Acknowledgements

This work is a part of the KBN 2010191 research project. Financial support for the synthetic part from the Ministry of National Education (grant UW BST-412-29) is also greatly acknowledged.

References

1. P.E. Cladis, *Mol. Cryst. Liq. Cryst.*, **185**, 85 (1988).
2. N.H. Tinh, *J. Chim. Phys.*, **80**, 83 (1988).
3. D. Demus, H. Zaschke, *"Flüssige Kristalle in Tabellen II"*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig (1984).
4. W. Pyżuk, E. Górecka, J. Mieczkowski, J. Przedmojski, *J. Phys. II France*, **2**, 1465 (1992).
5. W. Pyżuk, A. Krówczyński, E. Górecka, *Liq. Cryst.*, **10**, 593 (1991).
6. D.J. Byron, D. Lacey, R.C. Wilson, *Mol. Cryst. Liq. Cryst.*, **75**, 225 (1981); **76**, 253 (1981).
7. W. Pyżuk, A. Krówczyński, E. Górecka, *Mol. Cryst. Liq. Cryst*, (1993) in press.
8. E. Górecka, W. Pyżuk, A. Krówczyński, J. Przedmojski, *Liq. Cryst.* (1993) - in press; E. Górecka, A. Krówczyński, W. Pyżuk, J. Przedmojski, 14th ILCC, Pisa, **A-P90**, (1992).
9. H. Takeda, Y. Sakurai, S. Takenaka, H. Miyake, T. Doi, S. Kusbayashi, T. Takagi, *J. Chem. Soc. Faraday Trans.*, **86**, 3429 (1990).