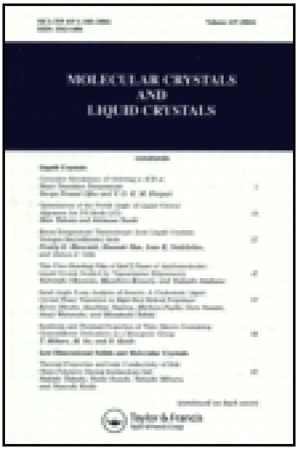


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

New Liquid Crystalline Material Exhibiting a Reentrant Nematic Phase

Shunsuke Takenaka [a] , Hideyuki Nakai [a] & Shigekazu Kusabayashi [a]

[a] Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka, 565, Japan

Version of record first published: 20 Apr 2011.

To cite this article: Shunsuke Takenaka , Hideyuki Nakai & Shigekazu Kusabayashi (1983): New Liquid Crystalline Material Exhibiting a Reentrant Nematic Phase, Molecular Crystals and Liquid Crystals, 100:3-4, 299-305

To link to this article: http://dx.doi.org/10.1080/00268948308075359

Mol. Cryst. Liq. Cryst., 1983, Vol. 100, pp. 299–305
0026-8941/83/1004-0299/$18.50/0

New Liquid Crystalline Material Exhibiting a Reentrant Nematic Phase

SHUNSUKE TAKENAKA, HIDEYUKI NAKAI, and
SHIGEKAZU KUSABAYASHI

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka, 565, Japan

(*Received January 26, 1983; in final form April 20, 1983*)

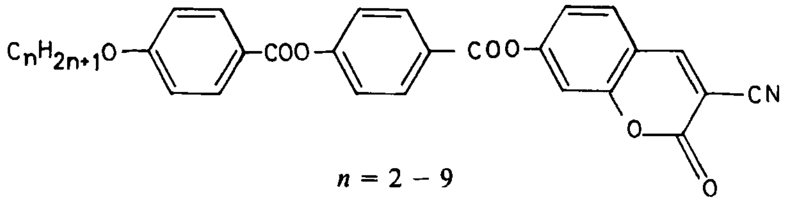
The thermal properties of a homologous series of 3-cyano-7-(4′-(4″-alkoxybenzoyloxy)benzoyloxy) coumarins have been examined. All homologues (the ethoxy to nonyloxy homologues) form high stability of the nematic phase. The heptyloxy homologue shows a reentrant behavior of the type, C–N–S_A–N–I.

INTRODUCTION

Since discovery of a phase transition of the type N–S_A–N–I under a high pressure,[1,2] it has been known that some mesogenic compounds give rise to somewhat interesting polymesomorphic behaviors, i.e., reentrant behaviors of the types such as C–N–S_A–N–I,[3-5] C–S_A–N–S_A–N–I,[6,7] and C–N–S_C–S_A–N–I.[8]

Usually, the compounds exhibiting these behaviors have plural aromatic rings, a polar terminal group such as a cyano, and a long alkyl chain, preferably alkoxy as a terminal group at the other side. Suitable linkages forming conjugation along the entire molecule are also necessary for the enhancement of the polarizability.[9,10]

We have prepared new homologous series of mesogens, 3-cyano-7-(4′-(4″-alkoxybenzoyloxy)benzoyloxy) coumarins. The composition of the molecules is quite analogous to the reentrant mesogens.



$n = 2 - 9$

We will report the preparation and the thermal properties of the homologous series.

EXPERIMENTALS

Method

Transition temperatures were determined using a Nikon Model POH polarizing microscope fitted with a Mettler FP 52 heating stage and FP 5 control unit. Transition enthalpies were measured with a Daini-Seikosha SSC 560 differential scanning calorimeter. Indium (99.9%) was used as a calibration standard with a heating rate of 5 °C/min.

Preparation

3-Cyano-7-hydroxycoumarin[11]-To a solution of 2,4-dihydroxybenzaldehyde (5 g, 0.036 mole) and malononitrile (2.4 g, 0.036 mole) in absolute ethanol (30 ml) was added piperidine (2 drops) with stirring, heat being evolved. A pale yellow solid separated from the orange-red solution. The reaction mixture was poured onto water (ca. 250 ml) with stirring, and then concentrated hydrochloric acid (100 ml) was added. The resulting solution was heated for 30 minutes at 60 °C with stirring. After cooling, the solid precipitated was collected by filtration and recrystallized from ethanol, yielding 3-cyano-7-hydroxycoumarin as orange needles (2.8 g, 42%), mp. > 270 °C.

3-Cyano-7-(4′-(4″-nonyloxybenzoyloxy)benzoyloxy)coumarin-A solution of 4-(4′-nonyloxybenzoyloxy)benzoyl chloride (1.57 g, 0.0039 mole) which was obtained by the method of Young *et al.*[12] and 3-cyano-7-hydroxycoumarin (0.73 g, 0.0039 mole) in a mixed solvent of pyridine (20 ml) and benzene (80 ml) was refluxed for 6 hrs. After cooling, the reaction mixture was poured onto ice-cold dilute hydrochloric acid, and the product was extracted with chloroform. The chloroform layer was washed with water and dried over sodium sulfate. After removing the solvent, the residue was purified by column chromatography on silica gel using chloroform as an elution solvent, and then recrystallized from benzene, giving 3-cyano-7-(4′-(4″-nonyloxybenzoyloxy)benzoyloxy)-coumarin as white needles (0.8

g, 37%). The identity of the ester was checked by an infrared absorption spectroscopy; $\nu_{CN} = 2230$, $\nu_{COO} = 1730\ cm^{-1}$. The purity of the ester was checked by elementary analysis, as shown below.

Other homologues were prepared similarly.

ELEMENTARY ANALYSIS DATA

		Calculated (%)			Found (%)		
n		C	H	N	C	H	N
2	$C_{26}H_{17}NO_7$	68.57	3.76	3.08	68.56	3.64	2.99
3	$C_{27}H_{19}NO_7$	69.08	4.08	2.98	69.33	4.17	3.07
4	$C_{28}H_{21}NO_7$	69.56	4.38	2.90	69.57	4.19	2.85
5	$C_{29}H_{23}NO_7$	70.01	4.66	2.82	70.02	4.61	3.05
6	$C_{30}H_{25}NO_7$	70.44	4.93	2.74	70.65	4.97	2.65
7	$C_{31}H_{27}NO_7$	70.84	5.18	2.67	70.74	5.08	2.51
8	$C_{32}H_{29}NO_7$	71.22	5.42	2.60	71.29	5.39	2.42
9	$C_{33}H_{31}NO_7$	71.60	5.64	2.53	71.47	5.61	2.78

4-Pentylphenyl 4′-(4″-octylbenzoyloxy)benzoate was prepared by the method of J. C. Dubois *et al.*[13] The transition temperatures were C-80.3-S_A-117.2-N-163.1-I (°C). 4′-(4″-Octyloxybenzoyloxy)-benzylideneamino-4-benzonitrile was prepared by the method of D. Demus *et al.*[9] The transition temperatures were C-106.4-N-142.1-S_A-201.3-N-257.5-I (°C).

RESULTS AND DISCUSSION

The transition temperatures for the homologous series are summarized in Table I.

TABLE I

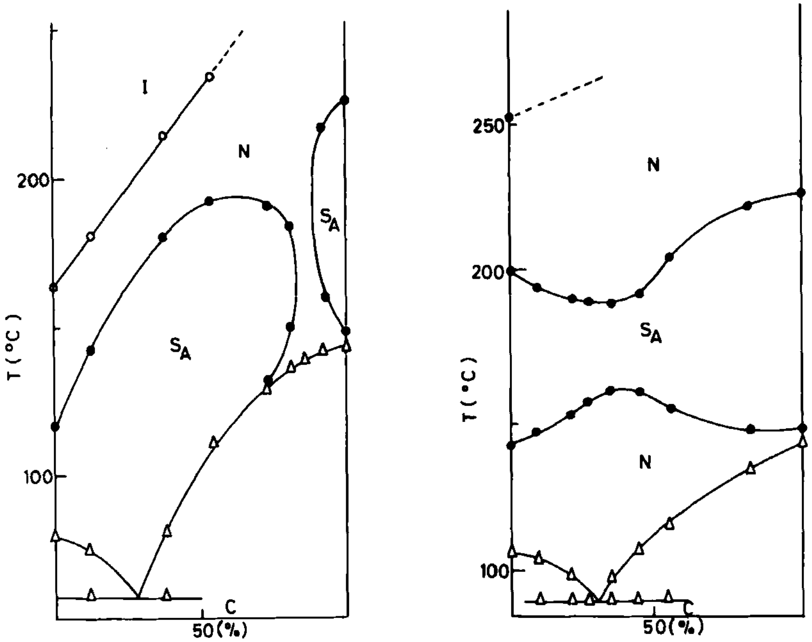
Transition temperatures (°C)

Carbon number	C		N		S_A		N		I
2	·	210.8	—		—		·	300	·
3	·	209.8	—		—		·	300	·
4	·	189.8	—		—		·	300	·
5	·	162.8	—		—		·	300	·
6	·	154.1	—		—		·	300	·
7	·	145.9	·	147.6	·	227.4	·	295	·
8	·	146.6	—		·	247.1	·	300	·
9	·	150.3	—		·	255.1	·	300	·

The nematic–isotropic transition temperatures are the virtual values. All values were taken on heating.

The homologous series form high stability of the nematic phase where the molecules tend to align homeotropically when placed between two glass plates. The nematic–isotropic transition temperatures are assumed to be more than 300 °C, though these tend to decompose above 250 °C. For example, the virtual transition temperature for the heptyloxy homologue was estimated to be 295 °C from extrapolation of the binary phase diagram for the system of the homologue and 4-pentylphenyl 4′-(4″-octylbenzoyloxy)-benzoate, as shown in Figure 1a.

The smectic phase commences from the heptyloxy homologue. To identify the smectic phase, the binary phase diagrams were examined. In Figure 1a the smectic phase for the heptyloxy homologue is not miscible with the smectic A phase for 4-pentylphenyl 4′-(4″-octylbenzoyloxy)benzoate. However, the smectic A phase for 4-(4″-octyloxybenzoyloxy)benzylideneamino-4-benzonitrile is miscible with the smectic phase for the heptyloxy homologue as well as the nematic



(a) (b)

FIGURE 1 Isobaric phase diagrams of (a) the heptyloxy homologue (on right) and 4-pentylphenyl 4′-(4″-octylbenzoyloxy)-benzoate (on left), and (b) 4′-(4″-octyloxybenzoyloxy)-benzylideneamino-4-benzonitrile (on left).

phases. These facts indicate that the smectic phase for the heptyloxy homologue is assigned to a smectic A modification. As mentioned by several authors, there have been known two types of molecular organization for the smectic A phase i.e., the monolayer and bilayer.[14] Probably the smectic phase for the former has the monolayer organization, and the latter the bilayer, since the latter has a cyano group as a polar terminal group.[15,16] It has been known that the smectic A phase with the monolayer alignment is usually miscible with the bilayer one, but sometimes immiscible.[17,18] Presumably these are the cases. In addition to the usual nematic and smectic A phases, the heptyloxy homologue enantiotropically forms a nematic phase just

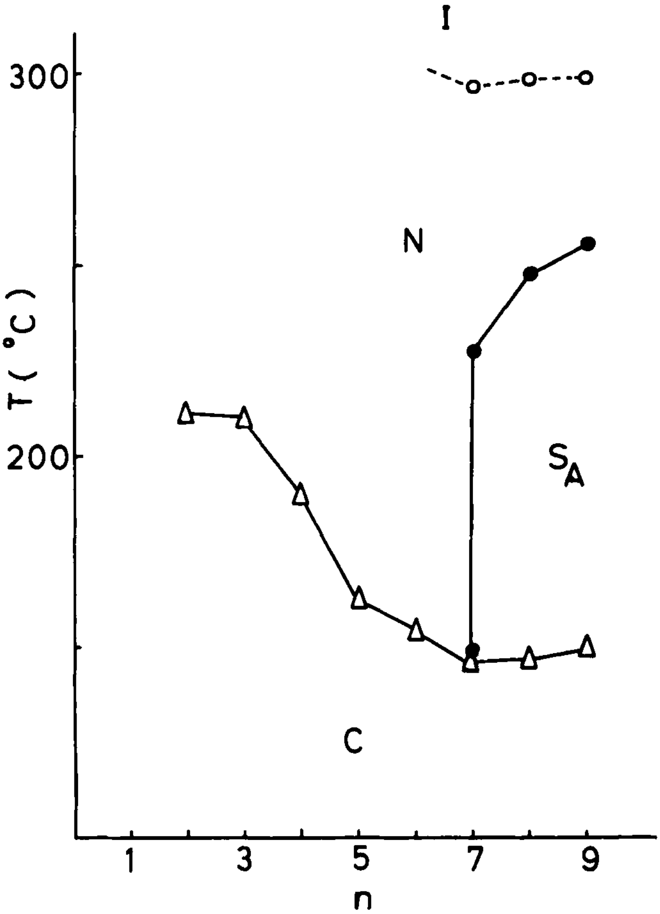


FIGURE 2 Plot of transition temperatures against *n*.

below the smectic A, giving rise to a reentrant behavior. This is confirmed by an examination of the binary phase diagram shown in Figure 1b. The nematic–smectic A and smectic A–nematic transitions were impossible to detect by the DSC thermogram, the transition enthalpies being quite small, presumably less than 50 J mole^{-1}. Although the octyloxy and nonyloxy homologues form high stability of the nematic and smectic A phases, these do not show the reentrant behavior. The plot of the transition temperatures against the carbon numbers in the alkoxy chain is shown in Figure 2.

Structural point of view, the coumarin core seems to unfavor the enhancement of the mesophase stability compared with a phenyl or a naphthyl group, for coumarin has a large molecular breadth. However, the carbonyl group forming an angle of 60° with respect to the longer molecular axis would strengthen the lateral interactions due to the dipole-dipole interaction, enhancing the stability of the smectic A phase. In fact, some homologous series having coumarin as well as the present series have been known to exhibit high stability of smectic phases.[19] On the other hand, the terminal alkoxy and cyano groups enhance the mutual conjugation along the entire molecule, increasing the polarizability anisotropy, a general requisite for stability of mesophase. The formation of the bilayer alignment of molecules in the smectic A phase due to the strong interactions of the terminal cyano group is responsible for the appearance of the reentrant behavior.

References

1. P. E. Cladis, R. K. Bogardus and D. Aadsen, *Phys. Rev.*, **A-18**, 2292 (1978).
2. P. E. Cladis, *Phys. Rev. Lett.*, **35**, 48 (1975).
3. J. C. Dubois, N. H. Tinh, A. Zann and J. Billard, *Nou. J. Chim.*, **2**, 647 (1978).
4. D. Demus, G. Pelzl, A. Wiegeleben and W. Weissflog, *Mol. Cryst. Liq. Cryst.*, **56**, 289 (1980).
5. M. Subramanya Raj Urs and B. K. Sadashiva, *Mol. Cryst. Liq. Cryst.*, **72**, 227 (1982).
6. N. H. Tinh, A. Zann, J. C. Dubois and J. Billard, *Mol. Cryst. Liq. Cryst.*, **56**, 323 (1980).
7. N. H. Tinh and H. Gasparoux, *Mol. Cryst. Liq. Cryst.*, **49**, 287 (1979).
8. W. Weissflog, G. Pelzl, A. Wiegeleben and D. Demus, *Mol. Cryst. Liq. Cryst.*, **56**, 295 (1980).
9. W. Weissflog, G. Pelzl and D. Demus, *Mol. Cryst. Liq. Cryst.*, **76**, 261 (1981).
10. N. H. Tinh, M. Joussot-Dubien and C. Destrade, *Mol. Cryst. Liq. Cryst.*, **56**, 257 (1980).
11. W. Baker and C. S. Howers, *J. Chem. Soc.*, **119** (1953).
12. W. R. Young, I. Haller and D. C. Green, *J. Org. Chem.*, **37**, 3707 (1972).
13. J. C. Dubois, A. Zann and A. Beguin, *Mol. Cryst. Liq. Cryst.*, **42**, 139 (1977).
14. G. R. Luckhurst and G. W. Gray, 'The Molecular Physics of Liquid Crystals', Page 285, Academic Press, New York (1979).

15. D. Guillon, P. E. Cladis and J. Stamatoff, *Phys. Rev. Lett.*, **41**, 1598 (1978).
16. A. J. Leadbetter, J. C. Frost, J. P. Gaugham, G. W. Gray, and A. Mosley, *J. de Phys.*, **40**, 375 (1979).
17. G. Sigaud, F. Haudowin, M. F. Achard and H. Gasparoux, *J. de Phys.*, **40**, C3-356 (1979).
18. B. Engelen, G. Heppke, R. Hopf and F. Schneider, *Mol. Cryst. Liq. Cryst*, **49**, 193 (1979).
19. K. N. Trivedi and N. N. Thaker, *Mol. Cryst. Liq. Cryst.*, **78**, 263 (1981).