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The Thermal Properties of Liquid Crystalline Materials Incorporating Piperazine Skeleton

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Synopsis. The thermal and electric properties of the homologous series of liquid crystalline materials incorporating a piperazine skeleton have been examined. Some piperazine compounds having a cyano group as the terminal function give rise to a wide-range nematic phase. On the other hand, the homologous series of α,α'-bis(4-alkyl-1-piperadinylimino)-*p*-xylenes and 1,4-bis(4-alkylbenzylideneamino)piperazines show strong smectic properties.

Liquid crystalline materials incorporating a saturated cyclic system such as cyclohexane,[1] and 1,3-dioxane[2] are currently of interest for applications involving optical devices. Piperazine is a saturated six-membered ring incorporating two nitrogen atoms at the 1 and 4 positions. Some piperazine compounds are known to exhibit mesomorphic properties.[3,4] In this paper, we describe the thermal properties of a new homologous series of liquid cyrstalline materials incorporating piperazine.

Experimental

The preparation of *N*-alkylpiperazine compounds has been described in a previous paper.[5]

Results and Discussion

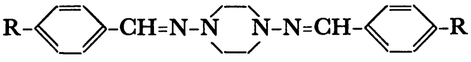
The transition temperatures and latent heats of series **1**, **2**, **3**, and **4** are summarized in Tables 1, 2, 3, and 4, respectively.

One of the characteristics of the piperazine core is that a tautomerization around the nitrogen atoms at the 1 and 4 positions gives rise to cis and trans isomers in which the former would be very unfavorable for mesophase stability. However, we can assume that the cis isomer should be energetically very unstable because of a relatively strong repulsive interaction between both substituents at the 1 and 4 positions.

As a whole, the piperazine compounds show apparent smectic properties compared with the corresponding phenyl and cyclohexyl compounds, as shown in Table 5. Series **1** reveals the nematic and smectic phases, though the thermal stability of the nematic phase is lower than that of compound **5**. Series **2** reveals only highly stable smectic phases, while the phenyl and cyclohexyl compounds **6** and **7** show a nematic phase. A similar trend is observed in series **3**, and also **4**, having alkyl groups at the terminals. Furthermore, these compounds tend to reveal relatively tight smectic phases such as the smectic B modification. For series **1** and **2**, the smectic-isotropic transition temperatures tend to decrease while increasing the carbon number in the alkyl or the alkoxyl chains (similar to usual nonpolar mesogens). The nonpolar interaction around the piperazine and phenyl cores along the lateral direction of the molecules would facilitate a layer arrangement of the molecules, increasing the smectic properties.

When the terminal function is replaced by a cyano group, series **3** and **4** tend to exhibit highly stable nematic phase. The effective order for the nematic stability is benzene>cyclohexane>piperazine, though the difference is quite small. In general, mesogens having a cyano group at a terminal function tend to show strong nematic properties, *e.g.*, **8** and **9**. Opposite to the general trend, the butyl homolog of series **3** and thereafter show a smectic B phase and the hexyl homolog also shows a smectic A phase, while these

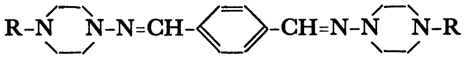
Table 2. The transition temperatures for series **2**(T/°C)



R	C		S^a)		S_B		I
n-C_3H_7	.	150.9	.	236.4	.	239.9	.
n-C_4H_9	.	104.0	.	211.6	.	256.1	.
n-C_5H_{11}	.	100.1	.	204.6	.	241.6	.
n-C_6H_{13}	.	87.1	.	193.6	.	237.1	.
n-C_7H_{15}	.	92.4	.	185.8	.	231.2	.
n-C_8H_{17}	.	79.9	.	170.5	.	219.6	.

a) The smectic phase has not been characterized.

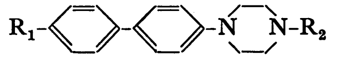
Table 1. The transition temperatures (T/°C) and latent heats for series **1**



R	C		S_1^a)		S_B		N		I	ΔH_{N-I} (kJ/mol)
CH_3	.	159.5	—		—		.	211.3	.	
n-C_3H_7	.	188.6	—		—		.	206.1	.	1.3
n-C_4H_9	.	171.3	.		(.	167.3)	.	195.6	.	1.8
n-C_5H_{11}	.	50.5	.	151.1	.	174.1	.	197.6	.	2.3
n-C_6H_{13}	.	114.2	.	173.0	.	182.8	.	186.1	.	3.4

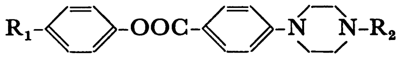
The value in parenthes indicates a monotropic transition.
a) The smectic phase has not been characterized.

Table 3. The transition temperatures (T/°C) and latent heats for series **3**



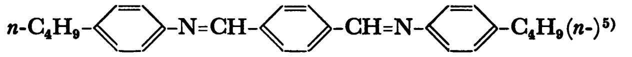
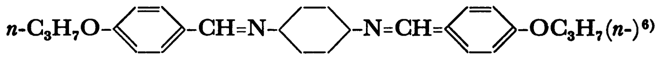
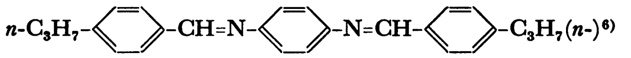
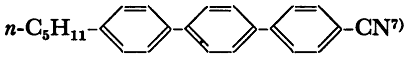
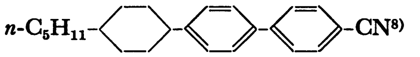
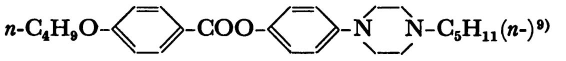
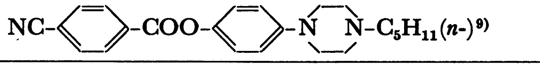
R_1	R_2	C		S_B		S_A		N		I	ΔH_{N-I}
n-C_2H_5	-C_2H_5(n-)	.	174.3	.	193.8	—		—		.	
	C_4H_9(n-)	.	187.2	.	202.1	—		—		.	
n-C_6H_{13}	C_4H_9(n-)	.	157.3	.	199.6	—		—		.	
CN	C_4H_9(n-)	.	145.1	.	159.9	—		.	214.1	.	0.8
	C_5H_{11}(n-)	.	114.7	.	160.7	—		.	210.6	.	0.6
	C_6H_{13}(n-)	.	116.6	.	160.5	.	183.1	.	203.1	.	1.0

Table 4. The transition temperatures (T/°C) and latent heats for series **4**



R_1	R_2	C		S_A		N		I	ΔH_{N-I} (kJ/mol)
n-C_3H_7	C_3H_7(n-)	.	96.3	.	118.8	.	157.8	.	0.9
	C_5H_{11}(n-)	.	104.7	.	162.5	.	175.3	.	2.0
n-C_4H_9O	C_4H_9(n-)	.	100.0	.	165.0	.	194.3	.	3.7
CN	C_3H_7(n-)	.	124.6	—		.	202.4	.	0.7
	C_4H_9(n-)	.	110.3	—		.	202.4	.	0.8
	C_5H_{11}(n-)	.	92.9	—		.	204.3	.	0.5
	C_6H_{13}(n-)	.	84.5	—		.	184.8	.	0.6
	C_7H_{15}(n-)	.	85.7	—		.	180.6	.	0.5

Table 5.

5		C-59.8-S-143-S_C-171-S_A-198-N-260-I
6		C-210-N-220-I
7		C-125-N-247-I
8		C-130-N-239-I
9		C-95-N-219-I
10		C-98-N-198-I
11		C-96-S_B-119-S_A-129-N-221-I

homologs have a cyano group at the terminal function. In series **4**, the butoxy homolog shows a smectic A phase in addition to a nematic one, while compound **10** shows only a nematic phase. On the other hand, the cyano compounds in series **4** show only a nematic phase, while compound **11** shows smectic A and B phases in addition to a nematic one. The opposite trend indicates that an electric circumstance around the piperazine cores is very important in determining the mesomorphic properties of these compounds.

References

1) R. Eidenschink, D. Erdmann, J. Krause, and L. Pohl, *Angew. Chem.*, **89**, 105 (1977), and **90**, 133 (1978).

2) D. Demus and H. Zaschke, *Mol. Cryst. Liq. Cryst.*, **63**, 129 (1981).

3) K. Kinashi, S. Takenaka, and S. Kusabayashi, *Mol. Cryst. Liq. Cryst.*, **67**, 49 (1981).

4) H. Schubert, W. Schulze, H.-J. Deutscher, V. Uhlig, and R. Kuppe, *J. Phys.*, **C1-36**, C1-379 (1975).

5) M. E. Neubert and L. J. Maurer, *Mol. Cryst. Liq. Cryst.*, 43, 313 (1977).

6) D. Demus, H. Demus, and H. Zaschke, "Flüssige Kristalle in Tabellen" VEB Deutscher Verlag für Grundstoff Industries, Leipzig (1974).

7) G. W. Gray, K. J. Harrison, and S. A. Nash, *J. Chem. Soc., Chem. Commun.*, **1974**, 431.

8) B. Granwehr and R. Anehm, *Chem. Abstr.*, **92** (15), 128592n (1980).

9) H.-J. Deutscher, H.-M. Vorbrodt, and H. Zaschke, *Z. Chem.*, **21**, 9 (1981).