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

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Version of record first published: 14 Oct 2011.

To cite this article: Keiichi Kinashi , Shunsuke Takenaka & Shigekazu Kusabayashi (1981): Syntheses and Mesomorphic Properties of New Liquid Crystalline Materials Involving Piperazine Skeleton, Molecular Crystals and Liquid Crystals, 67:1, 49-58

To link to this article: http://dx.doi.org/10.1080/00268948108070874

Mol. Cryst. Liq. Cryst., 1981, Vol. 67, pp. 49–58
0026–8941/81/6704–0049$06.50/0

Syntheses and Mesomorphic Properties of New Liquid Crystalline Materials Involving Piperazine Skeleton

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(*Received July 30, 1980*)

Some mesogenic materials involving a piperazine skeleton were prepared and the thermal properties were examined by DSC and microscopic analyses. Although the piperazines have a thermal flexibility similar to cyclohexyl ring, a lateral interaction due to lone pair electrons of nitrogens largely enhances the thermal stability of the mesophase. The piperazine compounds tend to preserve a smectic arrangement.

Generally, mesogenic compounds are made up of hard core and flexible terminal groups. The hard core portion, usually, is such aromatic rings as phenyl, naphthyl, and heteroaromatic groups.[1] Recently, saturated cyclic rings such as cyclohexyl and 2,2,2-bicyclooctyl groups have been used for the core group.[2–5] Nematogens involving cyclohexyl group have a comparatively low melting point, and are frequently used for electronic devices. In this connection, we are interested in piperazine which involves two nitrogen atoms in a saturated six membered ring. Although the piperazine skeleton will possess a thermal flexibility similar to cyclohexyl ring, it is expected to increase the polarity and polarisability due to mutual conjugation between the lone pair electrons of nitrogens and the substituent groups at the nitrogens.

This paper describes the preparations and the thermal properties of some mesogenic compounds involving piperazine.

Paper presented at the 8th International Liquid Crystal Conference, Kyoto, June 30–July 4, 1980.

EXPERIMENTAL

Homologous series of N-(4-alkoxyphenyl)-N′-n-alkylpiperazine (I), N-n-alkyl-N′-(4-substituted benzylidenamino)piperazine (II), 1,4-bis-N-(N′-n-alkylpiperazino)benzene (III), and N-(4-(4′-n-alkylphenyl)phenyl)-N′-n-alkylpiperazine (IV), were synthesised by well known synthetic routes.[6–8] I, III, and IV were purified by column chromatography on alumina, followed by recrystallization from ethanol, and II was purified by recrystallization from ethanol. The elementary analyses were in good agreement with the calculated values.

Microscopic and DSC analyses

The identification of the mesophase and measurement of the transition temperatures were carried out by a Nikon POH polarizing microscope equipped with a Mettler FP–52 heating stage. The differential scanning calorimetry (DSC) was performed utilizing a Daini–Seikosha SSC–560S apparatus.

Nuclear Magnetic Resonance Studies

The nuclear magnetic resonance (NMR) spectra were taken with a JASCO J–10 automatic spectrometer.

RESULTS

NMR studies of piperazine compounds

The NMR spectra of N-tolyl-N′-n-butylpiperazine in 6D-DMSO at 25 and 136°C are shown in Figure 1.

The spectrum at 25°C shows signals at 6.60–7.16 (4H, complicated A_2B_2 type, aromatic protons), 2.62 and 3.30 (8H, multiplet, methylene protons at the piperazine skeleton), 2.25 and 2.29 (3H, two singlets, methyl protons at the aryl position), and 0.91 and 0.93 ppm (3H, two triplets, methyl protons at the butyl group). The intensity ratio for the signals of methyl protons at aryl or butyl groups is affected by temperature, and becomes almost unity at 136°C. This fact indicates that this compound in solution has two conformers which are distinguishable within a NMR time scale. The energy difference between two conformers was evaluated as 0.31 Kcal/mole from the Arrhenius type plots for the intensity ratio of the methyl signals at 2.29 and 2.25 ppm. Similar complicating spectral feature was observed in the N-(4-fluorophenyl)-N′-n-hexylpiperazine.

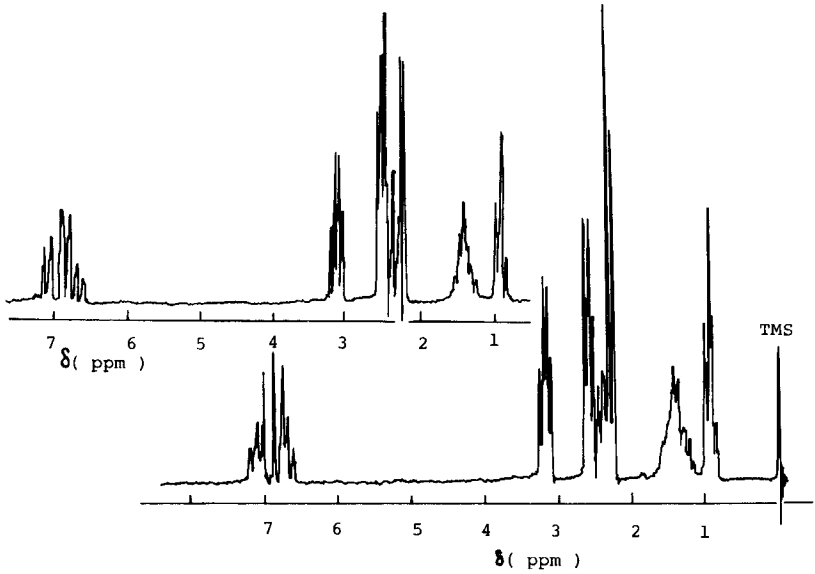


FIGURE 1 NMR spectra of N-tolyl-N′-n-butylpiperazine in 6D-DMSO; lower: at 25°C; upper: at 135°C.

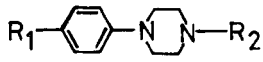
On the other hand, the NMR spectrum of N-anisyl-N′-n-butylpiperazine shows signals at 6.85 (4H, broad singlet, aromatic protons), 3.75 (3H, singlet, methoxy protons), 3.10 and 2.60 (8H, multiplet, methylene protons at the piperazine skeleton), and 0.91 ppm (3H, triplet, methyl protons at the butyl group), indicating that this compound is present as single conformer within a NMR time scale. Similarly, III and IV derivatives exhibit the simple spectral feature.

Thermal properties of piperazine compounds

In a series of I, the substituent, R_1, at the aryl position largely affects the thermal stability of a mesophase and the transition temperature. For example, 4-fluoro (R_2 = n-C_7H_{15}) and 4-chloro (R_2 = n-C_6H_{13}) derivatives of I exhibit no mesophase, where the melting points are 38.3 and 64.5°C, respectively. Although 4-methyl (R_2 = n-C_4H_9) and 4-n-butyl (R_2 = n-C_6H_{13}) derivatives of I have comparatively low melting points (2.5 and −2.3°C, respectively), these also exhibit no mesophase. As the R_1 is replaced by alkoxy group, however, many compounds exhibit smectic and nematic phases, as shown in Table I.

TABLE I

Transition temperatures for the N-(4-alkoxyphenyl)-N′-n-alkylpiperazines, (I)



Compounds											
R_1	R_2	K		Smectic 1		Smectic 2		Nematic		Isotropic	
OCH_3	C_3H_7	.	51.9	-	(27.9)	-	(33.6)	-			.
	C_4H_9	.	38.7	-	(26.2)	-	(36.7)	-			.
	C_5H_{11}	.	38.0	-	(23.5)	-	(31.2)	-			.
	C_6H_{13}	.	31.6	-	(14.0)	-	(28.7)	-			.
	C_7H_{15}	.	36.1	-	(23.8)	-	(27.7)	-	(33.6)		.
	C_8H_{17}	.	45.1	-		-		-	(34.9)		.
	C_9H_{19}	.	48.3	-		-		-	(38.5)		.
	$C_{10}H_{21}$	.	56.5	-		-		-			.
OC_2H_5	C_2H_5	.	84.9	-		-		-			.
	C_4H_9	.	49.3	-		.	67.1	-			.
OC_4H_9	C_4H_9	.	7.4	.	76.0	.	96.2	-			.
	C_5H_{11}	.	11.3	.	53.4	-		-			.
	C_6H_{13}	.	20.8	.	54.5	.	83.4	-			.
OC_6H_{13}	C_4H_9	.	18.2	.	43.4	.	74.1	-			.

( ), monotropic transition(cooling data); K, Crystal

The smectic 2 phase (S_2) exhibiting a fan-shaped texture, is assigned to the smectic A phase from the miscibility relation. Schiff-base compounds, II, also exhibit mesophases, as shown in Table II.

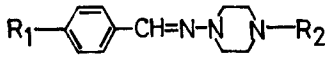
When the substituent, R_1, is replaced by a cyanide group, the smectic phase becomes unstable and nematic phase is observed monotropically.

Table III shows the thermal properties of 1,4-bis-N-(N′-n-alkylpiperazino) benzene, (III).

These derivatives show three kinds of smectic phases, i.e., S_1, S_2, and S_3. The S_3 phase exhibits a typical lancet texture, similar to the S_B phase of 1,4-bis-(4-n-alkylphenyl)piperazine derivatives.[9] The S_2 and S_1 phases exhibit a strongly double refracting lancet texture.

TABLE II

Transition temperatures for the N-n-alkyl-N′-(4-substituted benzylidenamino)piperazines, (II)

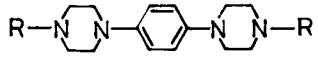


Compounds										
R_1	R_2	K		Smectic		Nematic		Isotropic		
OCH_3	C_6H_{13}	.	51.4	.	59.8	-		.		
OC_2H_5	CH_3	.	99.4	-		-		.		
	C_5H_{11}	.	70.6	.	72.9	.	79.8	.		
	C_6H_{13}	.	55.1	.	81.4	-		.		
OC_4H_9	CH_3	.	81.0	-		-		.		
	C_5H_{11}	.	64.0	.	89.6	-		.		
CN	C_5H_{11}	.	95.4	-		-	(39.2)	.		
	C_6H_{13}	.	54.2	-		-	(35.4)	.		

(), monotropic transition; K, Crystal

TABLE III

Transition temperatures for the 1,4-bis-N-(N′-n-alkylpiperazino)benzenes, (III)



Compounds R	K		Smectic 1		Smectic 2		Smectic 3		Isotropic	
CH_3	.	177.5	-		-		-			.
C_2H_5	.	166.3	-		-		-			.
C_3H_7	.	163.3	-		-		.	171.5		.
C_4H_9	.	36.3	.	106.9	.	113.4	.	179.5		.
C_5H_{11}	.	50.0	-		-		.	155.9		.
C_6H_{13}	.	30.0	.	76.7	.	107.9	.	182.8		.
C_7H_{15}	.	27.7	.	82.0	.	100.4	.	175.5		.
C_8H_{17}	.	58.1	.	64.5	.	93.4	.	178.3		.
C_9H_{19}	.	52.6	.	75.3	.	87.3	.	174.1		.

K, Crystal

In order to determine the smectic phases, the miscibility relation between 1,4-bis-N-(N′-n-butylpiperazino)benzene and 1,4-bis-(4-n-butylphenyl)piperazine[9] was examined, as shown in Figure 2.

This diagram indicates that the S_3 and S_1 phases correspond to the S_B and S_E phases, respectively. As is evident from the figure, both compounds form a 1:1 molecular complex in both solid and mesophase states. One smectic phase of 1,4-bis-N-(N′-n-amylpiperazino)benzene is assigned to the S_E phase by the similar manner. Then, the data in Table III are arranged, as shown in Figure 3.

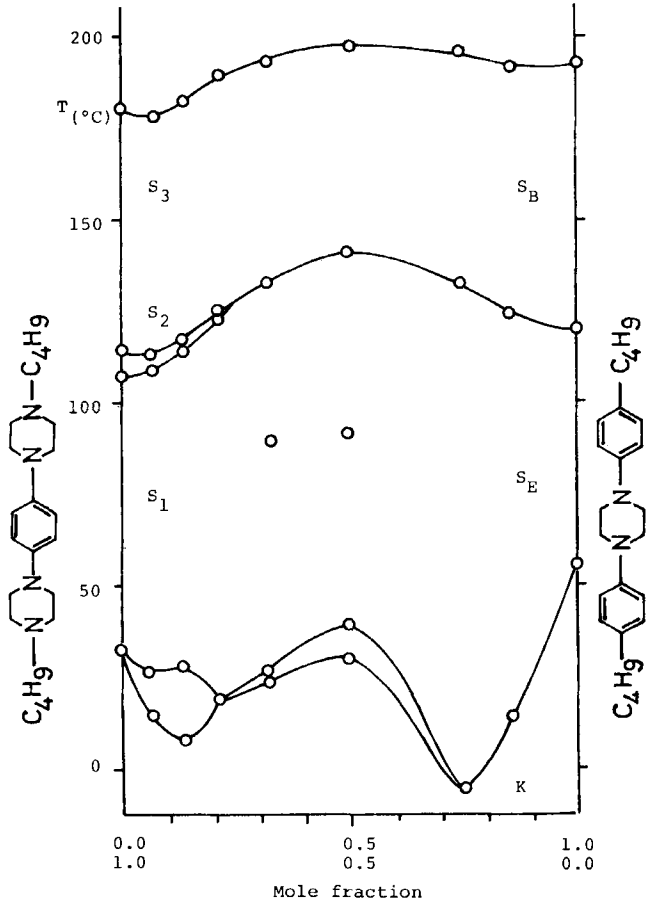


FIGURE 2 Diagram of isobaric state for the mixture of 1,4-bis-N-(N′-n-butylpiperazino) benzene (on left) with 1,4-bis-(4-n-butylphenyl)piperazine (on right).

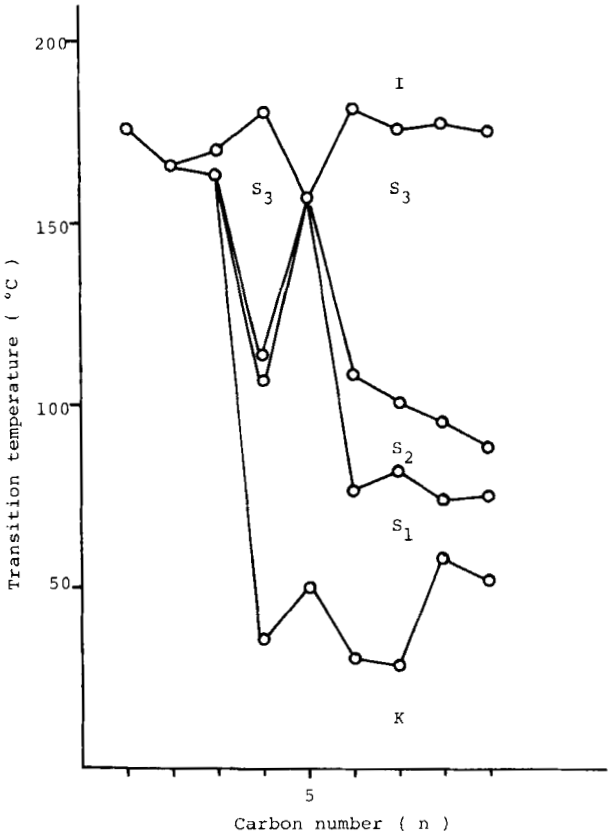
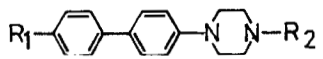


FIGURE 3 Transition temperatures of 1,4-bis-N-(N′-n-alkylpiperazino)benzene, III; K, crystal; S_i, smectic; I, isotropic.

TABLE IV

Transition temperatures for the N-(4-(4′-alkylphenyl)phenyl)-N′-n-alkyl-piperazines, (IV)



Compounds		K	Smectic	Isotropic
R_1	R_2			
C_2H_5	C_2H_5	. 174.3 .	193.8 .	
	C_4H_9	. 187.2 .	202.1 .	
C_6H_{13}	C_4H_9	. 157.3 .	199.6 .	

K, Crystal

As far as we know, the phase change, S_B–S–S_E, is very rare, though the S_2 phase is undetermined.

The transition temperatures for N-(4-(4′-n-alkylphenyl)phenyl)-N′-n-alkylpiperazine, (IV), are summarized in Table IV.

DISCUSSION

Two most preferable conformations of N-substituted piperazine, A_1 and B_1, have been postulated by Aroney *et al.*,[10] as shown in Figure 4.

That is, the conformer (A_1) is an equatorial, equatorial disubstituted chair form, and (B_1) axial, equatorial di-substituted boat form. They suggested that the B_1 form was predominant and a contribution of the other forms, A_2, B_2, and B_3 was small. The lateral equilibrium in the figure should be too fast to distinguish each signal for respective isomers by the ordinal NMR spectroscopy. On the other hand, the vertical equilibrium should be comparatively slow, and each signal for respective isomers is detectable by the normal NMR technique. In fact, the NMR spectra for N-tolyl-N′-n-butylpiperazine indicate the presence of two kinds of conformers in 6D–DMSO solution. This fact is in good agreement with the suggestion that N,N′-ditolylpiperazine in solution is present as mixtures of the A_1 and B_1 form.[10] Therefore, the energy difference obtained from the NMR data, 0.31 Kcal/mole, is attributable to the average energy difference between the conformer A_i and B_i. The reason why the alkylphenylpiperazine compounds do not show any mesomorphic property may be concerned with the conformational variation. When R_1 is alkoxy groups in I, however, the NMR spectra do not exhibit such complicating feature, indicating that these derivatives in solution are present as either one of conformer A_i or B_i. Aroney *et al.* concluded that the conformer, B_1, was more favourable than the A_1 in solution.[10] Considering the fact that many alkoxy compounds in Table I and II exhibit nematic and smectic phases, we are rather perplexed, because the conformer, B_1, has considerable angular shape and seems to be very unfavourable for the mesophase stability. On the other hand, the conformer, A_1, has a linear structure and is suitable for the mesophase stability. Therefore, we assume that in alkoxyphenylpiperazine compounds of I and II the conformer, A_1, is predominant in such neat solution as mesophase state, and the linear structure stabilizes the mesophase.

By the similar reason, III and IV in solution are present as mixtures of the A_i, where the conformer, A_1, is assumed to be predominant.

The lone pair electrons of nitrogens in the conformer, A_1, thrust out to the plane of piperazine ring and are expected to enhance the lateral interaction between adjacent molecules. Certainly, the thermal stability for the smectic

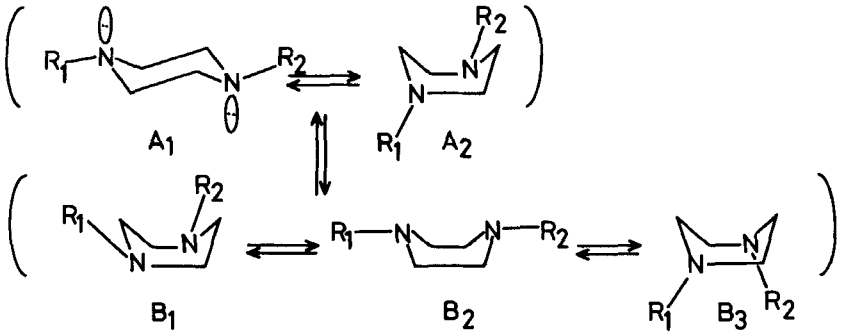


FIGURE 4 Conformational equilibria of N,N′-disubstituted piperazine; R_1, R_2 = n-alkyl and/or aryl groups.

phases of I and II appears to be notable. In a series of I and II, the smectic-isotropic transition temperatures decrease by the order of piperazine ≈ benzene[11,12] > cyclohexane.[13]

An interesting fact in Table II is that a cyanide group at the aryl position rapidly decreases the thermal stability of the smectic phase, and the cyano derivatives exhibit a nematic phase. This may be due to the fact that the cyanide group decreases the electron density of the nitrogens, resulting in a decrease of the lateral interaction and increases of an anisotropic polarizability. The characteristic is also recognized in the tricyclic systems of III and IV derivatives. In the series of the tricyclic systems, the effectiveness in enhancing smectic-isotropic transition temperatures is terphenyl[11] > N-biphenylpiperazine (IV) > N,N′-diphenylpiperazine[13] > 1,4-bis-N-piperazinobenzene (III) > 1,4-diphenylcyclohexane.[11] Two factors may be of importance here. First, the flexibility of the core portion seems to decrease the mesophase stability by the order of phenyl > cyclohexane ≈ piperazine. Secondly, the electronic effect mentioned above decreases it by the order of phenyl ≈ piperazine ≫ cyclohexane. In addition, a dipole moment operating along the long molecular axis produced by mutual conjugation between the lone pair electrons of nitrogens and the aryl groups at the nitrogens, may act an important role for the mesophase stability.

Conclusively, although N,N′-disubstituted piperazines are present as mixtures of few conformers, they have intrinsic mesomorphic properties due to strong lateral interaction of the lone pair electrons of nitrogens.

References

1. G. R. Luckhurst and G. W. Gray, *The Molecular Physics of Liquid Crystals*, Academic Press, London, 1979.
2. E. Eidenschink, D. Erdmann, J. Krause, and L. Pohl, *Angew. Chem.*, **89**, 103 (1977).

3. H. J. Deutscher, F. Kuschel, H. Schubert, and D. Demus, Deutsche Demokratische Republik, Patent, D.O.S.Nr 24 29 093 (1975).
4. H. Schubert, R. Dehne, and V. Uhlig, *Z. Chem.*, **12**, 219 (1972).
5. M. J. S. Dewar and R. M. Riddle, *J. Am. Chem. Soc.*, **97**, 6658 (1975); M. J. S. Dewar and A. C. Griffin, *ibid.*, **97**, 6662 (1975).
6. V. Prelog and G. J. Driza, *Collection Czechoslov. Chem. Comm.*, **5**, 497 (1975).
7. A. F. McKay and H. H. Brownell, *J. Org. Chem.*, **15**, 648 (1950).
8. E. Aconroy (American Cyanamide Co.), U.S. patent 2663706.
9. D. Demus and L. Richter, *Texture of Liquid Crystals*, Verlag Chemie, Weinheim (1978).
10. M. Aroney and R. J. W. Le Féure, *J. Chem. Soc.*, (*London*) 2161 (1960).
11. D. Demus, H. Demus, and H. Zaschke, *Flüssig Kristalle in Tabellen*, VEB Deutscher Verlag für Grundstoff Industries, Leipzig (1974).
12. G. W. Smith, Z. G. Gardlund, and R. J. Curtis, *Mol. Cryst. Liq. Cryst.*, **19**, 327 (1973).
13. L. Pohl, R. Eidenschink, K. Krause, and D. Erdmann, *Phys. Lett.* **A60**, 421 (1977).
14. H. Schubert, W. Schulze, H.-J. Deutscher, U. Uhlig, and R. Kuppe, *J. Phys.*, **36**, C1–376 (1975).