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# Mesomorphic Properties of N-n-Alkyl-N'-(4-(2-Carbethoxyethenylphenyl)]-Piperazines

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# Mesomorphic Properties of N-*n*-Alkyl-N′-[4-(2-Carbethoxy-ethenylphenyl)]-Piperazines

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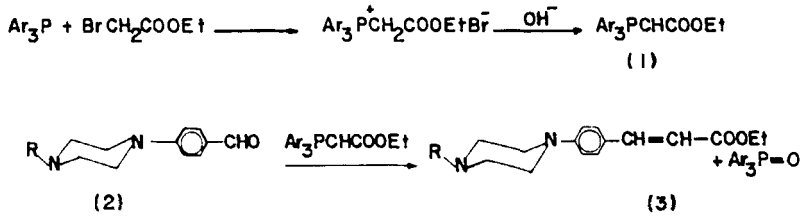
We have synthesized and studied the physical properties by calorimetric, optical and X-ray methods, the N-*n*-alkyl-N′-[4-(2-carbethoxyethenylphenyl)]-piperazines. These compounds have two smectic phases and no nematic phase; the high temperature smectic phase is identified as probably being a smectic B and the lower temperature phase as a probable smectic E. The transition heats are anamolous as the smectic–isotropic transition has a higher transition heat than the "crystal"–smectic transition heat.

## INTRODUCTION

Interest in stable and broad temperature range liquid crystals has grown in recent years as a result of their increased applications. Recently we reported the mesogenic properties of N-*n*-alkyl-N′-[4-(2-cyanoethenylphenyl)]-piperazines[1] and continuing the investigation of piperazine derivatives we now present studies of the N-*n*-alkyl-N′-[4-(2-carbethoxyethenylphenyl)]-piperazines (Scheme 1, 1–3) since the presence of an ester group in a compound that shows mesomorphic phases generally increases the mesomorphic range.[2,3]

**SCHEME I**




## RESULTS AND DISCUSSION

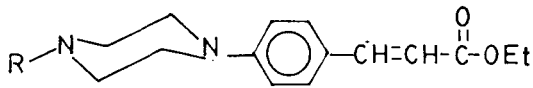
The transition temperatures and transition heats of the N-*n*-alkyl-N′-[4-(2-carbethoxyethenylphenyl)]-piperazines (3) are shown in Table I. The compounds exhibit only smectic phases over a wide temperature range. The high clearing points are probably due to the fact that the nitrogen atom of the piperazine ring participates in a conjugated system increasing the stability of the mesophases and the conjugation between the carbonylic function and the nitrogen increases the lateral dipole moment and thus favors lateral attractions which stabilize the smectic phase. A plot of the transition temperatures versus the number of carbon atoms in the alkyl chain is shown in Figure 1.

The transition temperatures and transition heats were determined using a Perkin-Elmer DSC-2 calibrated with Indium. The transition temperatures, except for the melting points, were confirmed using a Leitz Ortholux-Pol microscope with a Mettler FP-52 hot stage. The melting points could not be determined with the microscope because the first smectic phase is so highly structured that the change in texture at the melting point is not perceptible. Even the smectic 1–smectic 2 (hereafter S1 and S2) transition is not perceptible on the first heating, for the same reason, but it is clearly observable after the compound is heated close to the S2–I transition temperature.

The DSC data for the S2–I transition are extremely interesting as the transition heats for this transition are always larger than those of the lowest temperature transition which we denote as a crystalline–smectic 1 transition ("melting" point) in Table I. As pointed out by a reviewer, these transition heats are too small for a normal melting process and may indicate that the lowest temperature transition is really a transition from a quasi-crystalline phase to a quasi-crystalline smectic 1 phase (i.e. smectic E) or some type of complex melting process. In the case of C4, C5 and C6 the "melting" point peak is always close to the S1–S2 transition temperature but sharp and much

TABLE I

Transition temperatures and enthalpies for the N-*n*-alkyl-N′-[4-(2-carbethoxyethenylphenyl)]-piperazines (3).




| Compounds R | temp. in °C K | Smectic 1 | Smectic 2 | I | The phase transition enthalpies, Kcal/mol K | Smectic 1 | Smectic 2 | I |
|---|---|---|---|---|---|---|---|---|
| *n*-$C_4H_9$ | 96.3[a] | 104.0 | 153.9 | | 1.26 | 0.51 | 3.01 | |
| *n*-$C_5H_{11}$ | 88.8[a] | (88.5) | 149.1 | | 2.42 | 0.41 | 2.95 | |
| *n*-$C_6H_{13}$ | 74.2[a] | 81.0 | 146.2 | | 1.57 | 0.31 | 2.41 | |
| *n*-$C_7H_{15}$ | 61.0[a] | 74.0 | 142.5 | | 1.86 | 0.40 | 2.80 | |
| *n*-$C_8H_{17}$ | 62.0[a] | 75.0 | 143.0 | | 2.08 | 0.40 | 3.10 | |
| *n*-$C_9H_{19}$ | 60.0[a] | 73.0 | 141.4 | | 2.85 | 0.55 | 3.40 | |

K = crystalline, I = isotropic

( ), monotropic transition

[a]It is possible that this transition does not correspond to a transition from a true three-dimensional ordered crystal to a "crystalline" smectic phase.

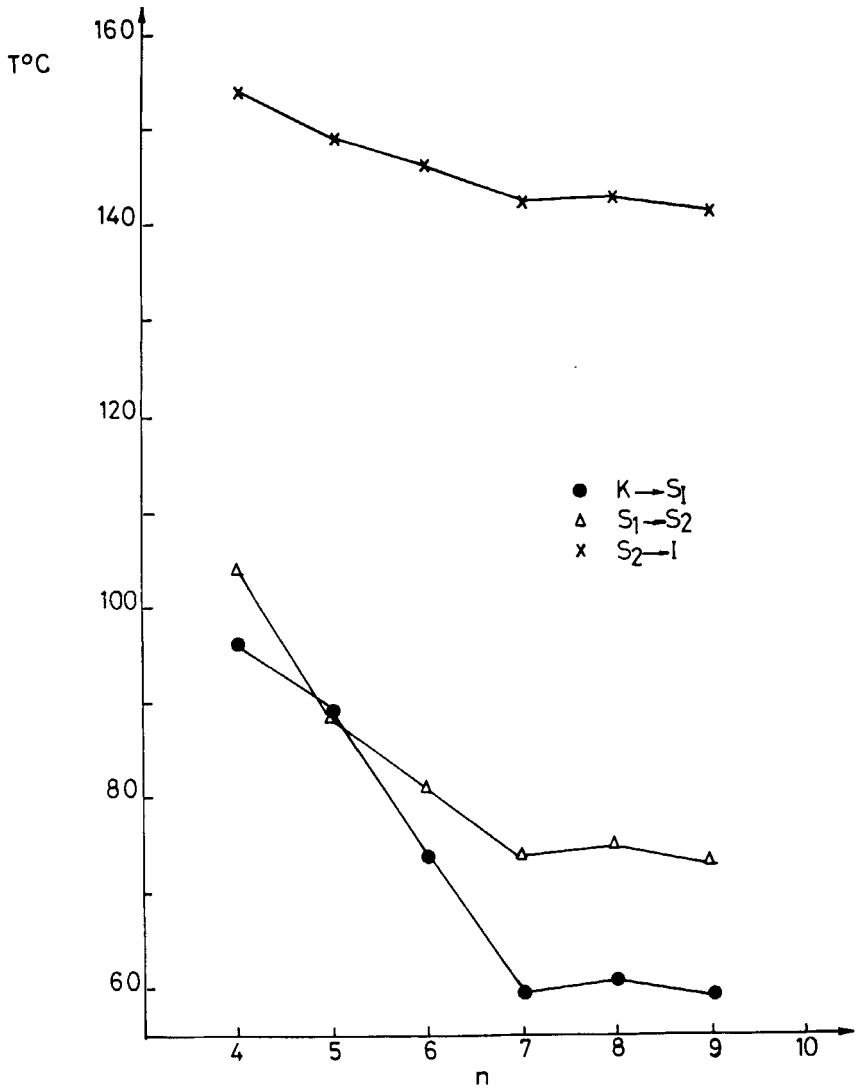



FIGURE 1 Plot of transition temperatures against the number of carbon atoms ($n$) in the alkyl chain (R) of the N-$n$-alkyl-N′-[4-(2-carbethoxyethenylphenyl)]-piperazines (3).

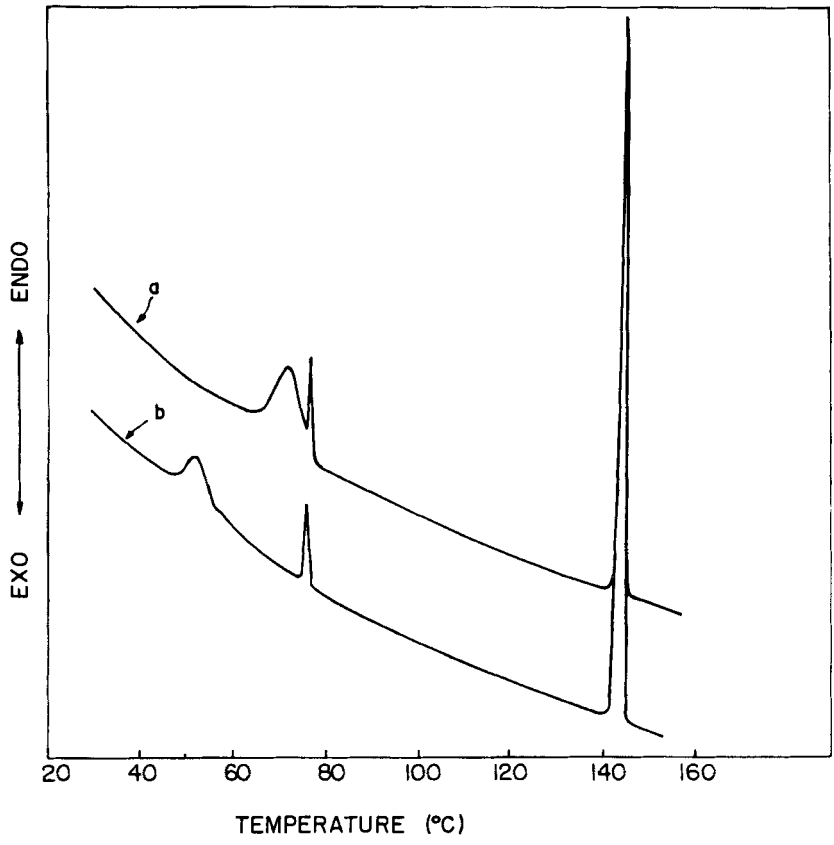



FIGURE 2 DSC-2 thermograms of compound C8: mass = 2.4 mg; scanning rate—5 degrees/minute; sensitivity—5 millicalories/s. (a) Thermogram of virgin sample and (b) the same sample rerun after being at room temperature for five hours.

larger than the S1–S2 peak. On cooling to room temperature and immediately reheating, the sample gives an identical thermogram. For compounds C7, C8 and C9, on first heating the "melting" peak is broad and terminates in a sharp peak that corresponds to the S1–S2 transition. After cooling to room temperature and immediately repeating the thermogram the broad "melting" peak is absent but the S1–S2 and S2–I peaks are the same as in the initial thermogram. If the once heated sample is left at room temperature for approximately five hours the "melting" peak reappears but sharper and separated from the S1–S2 peak. Figure 2 illustrates this behaviour showing a thermogram of a virgin C8 sample and a second thermo-

gram of the same sample after being at room temperature for five hours.

The calorimetric data would ordinarily lead to the conclusion that these compounds are not mesomorphic but the optical and X-ray observations we will discuss below lead to the conclusion that these compounds really have two smectic phases as we have affirmed in the discussion of the calorimetric data.

In the polarizing microscope at the S2–I transition the smectic phase first separates in needle-like forms that coalesce to a needle or plate or mosaic-like texture with some spherulites. The S2–S1 transition is not easy to observe because the optical texture changes very little. Careful observation shows that on cooling the S2–S1 transition is marked by the appearance of linear striations in the plates and circular striations in the spherulites and on reheating the striations disappear. In the S2 phase it is possible to shear the cover slip but the viscosity of S1 is too high to move the cover slip. On shearing the cover slip in S2 it is possible to obtain a homeotropic texture and on entering the S1 phase, at times, the texture remains uniform and with a very weak birefringence. It would be highly improbable that on entering a true crystalline phase the texture would remain so uniform.

Conoscopic observations were made with a Leitz 350 heated stage on the homeotropic S2 and uniformly oriented S1. The S2 phase is uniaxial positive and the S1 phase is biaxial positive with the acute bisectrix parallel to the microscope axis. Thus in both phases the long axis of the molecule must be perpendicular to the smectic layers. This would lead to a conclusion that probably S2 corresponds to smectic B and S1 to smectic E.

X-ray diffraction patterns were recorded for compounds C8 and C5 on a flat plate camera using 1 mm Lindemann capillaries in a temperature controlled oven. A virgin sample of C8 at room temperature gave 3 sharp rings that using Bragg's law correspond to distances of 26.8 ± 2.0 Å, 4.5 ± 0.1 Å and 3.9 ± 0.1 Å. In the S2 phase there were two sharp rings at 26.6 ± 2.0 Å and 4.5 ± 0.1 Å, independent of temperature within experimental error. On cooling to room temperature there exist three sharp rings corresponding to 26.5 ± 2.0 Å, 4.6 ± 0.1 Å and 3.9 ± 0.1 Å which are the same distances the unheated sample gave. Therefore we conclude that C8 is essentially a smectic phase at room temperature which coincides with the calorimetric and optical data. The C5 compound in the S2 phase at a temperature of 120°C gave two sharp rings corresponding to distances 23.1 ± 2.0 Å and 4.6 ± 0.1 Å. In the S1 phase at a

temperature of 80°C there were 3 sharp rings corresponding to 20.9 ± 2.0 Å, 4.6 ± 0.1 Å and 4.0 ± 0.1 Å. At room temperature C5 gives a typical crystalline pattern with many reflections. Therefore X-ray data for C5 are also in agreement with the calorimetric and optical data.

We conclude from the data presented that the S2 phase should probably be called smectic B and the S1 phase smectic E.[4,5]

## EXPERIMENTAL

The structures of the compounds were confirmed by analysis of their IR (Perkin-Elmer 237 B and 577), $^1$H-NMR (Varian T-60 A) and $^{13}$C-NMR (Varian CFT-20) spectra. Combustion analysis was also carried out (Table II).

The homologous series of N-*n*-alkyl-N′-[4-(2-carbethoxyethenyl-phenyl)]-piperazines (3) was synthesized by condensation between the aldehydes (2) and the ylide (1) (see Scheme 1) using the same method described in the preparation of the N-*n*-alkyl-N′-[4-(2-cyanoethenylphenyl)]-piperazines.[1] The esters (3) were purified by chromatography over silica gel using ethyl acetate as eluent, followed by crystallization from petroleum ether 40–60°C.

### N-*n*-Butyl-N′-[4-(2-carbethoxyethenylphenyl)]-piperazine (3a).

IR (KBr): 1700 (C=O) and 1605 cm$^{-1}$ (C=C). $^1$H-NMR: 0.9 (*t*, 3, $CH_3$); 1.10–1.68 (*m*, 7, $CH_2$ and $\underline{CH_3}$—$CH_2$—O); 2.33 (*t*, 2, $CH_2N$); 2.51 and 3.25 (2*m*, 8, $CH_2N$); 4.19 (*q*, 2, O—$\underline{CH_2}$—$CH_3$); 6.22 and 7.62 (2*d*, —$\underline{CH}$=CH—COOEt, $J_{H-H}$ trans 16 Hz), 6.82 and 7.40 (2*d*, 4, J = 8 Hz, arom.).

### N-*n*-Pentyl-N′-[4-(2-carbethoxyethenylphenyl)]-piperazine (3b).

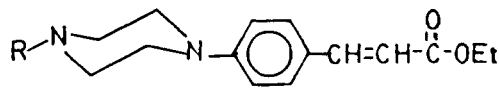
IR (KBr): 1695 (C=O) and 1602 cm$^{-1}$ (C=C). $^1$H-NMR: 0.90 (*t*, 3, $CH_3$); 1.08–1.62 (*m*, 9, $CH_2$ and $\underline{CH_3}$—$CH_2$—O); 2.37 (*t*, 2, $CH_2N$); 2.53 and 3.27 (2*m*, 8, $CH_2N$); 4.21 (*q*, 2, O—$\underline{CH_2}$—$CH_3$); 6.22 and 7.58 (2*d*, —$\underline{CH}$=CH—COOEt, $J_{H-H}$ trans 16 Hz); 6.78 and 7.37 (2*d*, 4, J = 8 Hz, atom.).

### N-*n*-Hexyl-N′-[4-(2-carbethoxyethenylphenyl)]-piperazine (3c).

IR(KBr): 1700 (C=O) and 1602 cm$^{-1}$ (C=C). $^1$H-NMR: 0.87 (*t*, 3, $CH_3$); 1.08–1.68 (*m*, 11, $CH_2$ and $\underline{CH_3}$—$CH_2$—O); 2.38 (*t*, 2, $CH_2N$);

TABLE II

Elemental analysis of N-*n*-alkyl-N′-[4-(2-carbethoxyethenylphenyl)]-piperazines (3)




| Compounds | R | Empirical formula (mol. weight) | C | | H | | N | |
|---|---|---|---|---|---|---|---|---|
| | | | Calc. | Found | Calc. | Found | Calc. | Found |
| 3a | *n*-$C_4H_9$ | $C_{19}H_{28}N_2O_2$ | 72.15 | 72.19 | 8.92 | 8.80 | 8.86 | 8.23 |
| 3b | *n*-$C_5H_{11}$ | $C_{20}H_{30}N_2O_2$ | 72.70 | 72.56 | 9.09 | 8.55 | 8.48 | 8.02 |
| 3c | *n*-$C_6H_{13}$ | $C_{21}H_{32}N_2O_2$ | 72.15 | 72.36 | 8.86 | 8.89 | 7.73 | 7.41 |
| 3d | *n*-$C_7H_{15}$ | $C_{22}H_{34}N_2O_2$ | 73.74 | 73.57 | 9.49 | 9.82 | 7.82 | 7.75 |
| 3e | *n*-$C_8H_{17}$ | $C_{23}H_{36}N_2O_2$ | 74.61 | 74.82 | 9.84 | 9.77 | 7.25 | 7.24 |
| 3f | *n*-$C_9H_{19}$ | $C_{24}H_{38}N_2O_2$ | 74.19 | 73.98 | 9.68 | 9.93 | 7.53 | 7.56 |

2.51 and 3.25 (2*m*, 8, $CH_2N$); 4.19 (*q*, 2, O—$CH_2$—$CH_3$); 6.22 and 7.60; (2*d*, —CH=CH—COOEt, $J_{H-H}$ trans = 16 Hz); 6.81 and 7.38 (2*d*, 4, J = 9 Hz, arom.). $^{13}$C-NMR ($CDCl_3$): 167.14 (1, C=O); 152.88, 129.74, 125.38, 115,10 ($C_1$, $C_3$, $C_4$, $C_2$, arom.); 144.52 and 114.24 (CH=CH—COOEt); 53.28 and 48.12 (N—$CH_2$—$CH_2$—N′); 60.02 (1, $CH_2$—$CH_3$); 58.77 (1, $C_1$); 32.20 (1, $C_5$); 27.50 (2, $C_2$ and $C_3$); 23.10 (1, $C_5$); 14.52 (1, $C_6$); 14.34 (1, O—$CH_2$—$CH_3$).

**N-*n*-Heptyl-N′-[4-(2-carbethoxyethenylphenyl)]-piperazine (3d).**

IR (KBr): 1701 (C=O) and 1608 $cm^{-1}$ (C=C). $^1$H-NMR ($CDCl_3$): 0.92 (*t*, 3, $CH_3$); 1.06–1.85 (*m*, 13, $CH_2$ and $CH_3$—$CH_2$—O); 2.25 (*t*, 2, $CH_2N$); 2.57 and 3.30 (2*m*, 8, $CH_2N$); 4.27 (*q*, 2, O—$CH_2$—$CH_3$); 6.30 and 7.80 (2*d*, —CH=CH—COOEt, $J_{H-H}$ trans 16 Hz); 6.88 and 7.47 (2*d*, 4, J = 9 Hz, arom.). $^{13}$C-NMR ($CDCl_3$): 167.45 (1, C=O); 152.46, 129.40, 124.86, 114.73 ($C_1$, $C_3$, $C_4$, $C_2$, arom.); 144.52 and 114.24 (CH=CH—COOEt); 52.98 and 47.86 (N—$CH_2$—$CH_2$—N′); 60.04 (1, $CH_2$—$CH_3$); 58.71 (1, $C_1$); 31.75 (1, $C_5$); 29.18 (1, $C_4$); 27.47 (1, $C_3$); 26.85 (1, $C_2$); 22.58 (1, $C_6$); 14.39 (1, $C_7$); 14.03 (1, $CH_2$—$CH_3$).

**N-*n*-Octyl-N′-[4-(2-carbethoxyethenylphenyl)]-piperazine (3e).**

IR (KBr): 1703 (C=O) and 1608 $cm^{-1}$ (C=C). $^1$H-NMR $(CD_3)_2CO$: 0.85 (*t*, 3, $CH_3$); 1.05–1.68 (*m*, 17, $CH_2$ and $CH_3$—$CH_2$—O); 2.37 (*t*, 2, $CH_2N$); 2.48 and 3.18 (2*m*, 8, $CH_2N$); 4.25 (*q*, 2, O—$CH_2$—$CH_3$); 6.17 and 7.50 (2*d*, —CH=CH—COOEt, $J_{H-H}$-trans 16 Hz), 6.80 and 7.37 (2*d*, 4, J = 8 Hz, arom.). $^{13}$C-NMR ($CDCl_3/C_6D_6$): 167.23 (1, C=O); 152.38, 129.34, 124.84, 114.68 ($C_1$, $C_3$, $C_4$, $C_2$, arom.); 144.46 and 114.13 (—CH=CH—COOEt); 52.87 and 47.72 (N—$CH_2$—$CH_2$—N′); 59.83 (1, $OCH_2$—); 58.55 (1, $C_1$); 31.78 (1, $C_6$); 29.44 (1, $C_5$); 29.17 (1, $C_4$); 27.48 (1, $C_3$); 26.81 (1, $C_2$); 22.60 (1, $C_7$); 14.20 (1, $C_8$); 13.93 (1, O—$CH_2$—$CH_3$).

**N-*n*-Nonyl-N′-[4-(2-carbethoxyethenylphenyl)]-piperazine (3f).**

IR (KBr): 1701 (C=O) and 1605 $cm^{-1}$ (C=C). $^1$H-NMR ($C_6D_6$): 0.88 (*t*, 3, $CH_3$); 1.02–1.68 (*m*, 15, $CH_2$ and O—$CH_2$—$CH_3$): 2.17 (*t*, 2, $CH_2N$); 2.43 and 3.17 (2*m*, 8, $CH_2N$); 4.18 (*q*, 2, O—$CH_2$—$CH_3$); 6.30 and 7.72 (2*d*, —CH=CH—COOEt, $J_{H-H}$ trans 16 Hz); 6.75 and 7.38 (2*d*, 4, J = 9 Hz, arom.). $^{13}$C-NMR $(CD_3)_2CO$: 167.78 (1, C=O); 153.88, 130.54, 125.43, 115.55 ($C_1$, $C_3$, $C_4$, $C_2$, arom.); 145.43 and 114.81 (—CH=CH—COOEt); 54.02 and 48.75

(N—$CH_2\underline{CH_2}$—N′); 60.49 (1, O—$CH_2$—); 59.37 (1, $C_1$); 32.79 (1, $C_7$); 30.47 (1, $C_5$); 30.22 (2, $C_4$ and $C_6$); 28.39 (1, $C_3$); 27.89 (1, $C_2$); 23.51 (1, $C_8$); 14.95 (1, $C_9$); 14.59 (1, O—$CH_2$—$\underline{CH_3}$).

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