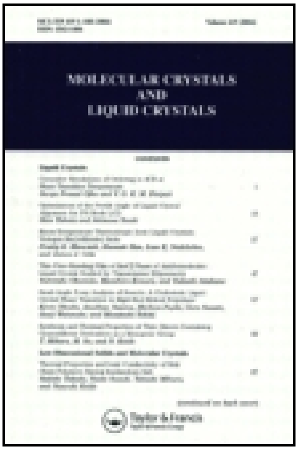

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Synthesis and Mesogenic Properties of N-n-alkyl-N′-(4-n-Pentyloxyphenyl)-Piperazines

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Synthesis and Mesogenic Properties of N-*n*-alkyl-N′-(4-*n*-Pentyloxyphenyl)-Piperazines

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The N-*n*-alkyl-N′-(4-*n*-pentyloxyphenyl)-piperazines (4) exhibit ordered smectic phases at temperatures below 100°C. For 3, 4, 5 and 6 carbons in the alkyl chain, two smectic phases are present and for 7, 8 and 9 carbons only one smectic phase is present. The ΔH values for 4, 5, 6 and 7 carbons are anomalous. From optical and X-ray data, the smectic phases are identified as probably smectic E and B phases.

INTRODUCTION

Previously, we reported the synthesis and mesomorphic properties of the N-*n*-alkyl-N′-[4-(2-cyanoethenylphenyl)]-piperazines[1] (compounds I), N-*n*-alkyl-N′-[4-(2-carbethoxyethenylphenyl)]-piperazines[2] (compounds II) and the N′-(4-Acylphenyl)-N-alkylpiperazines[3] (compounds III). The structural formulas for compounds I, II and III are shown in Figure 1. Compounds I exhibited relatively wide temperature range nematic phases in the lower homologs together with a smectic A phase. The higher homologs had only a smectic A interdigated bilayer phase. The melting points were generally on the order of 60°C. Compounds II and III exhibited only smectic phases. The smectic phases were orthogonal and identified as probable smectic E and B phases (we say probable because miscibility studies were not performed). Calorimetric data for compounds II were abnormal in that the enthalpy change for the smectic-isotropic transition was always larger than for any other temperature transition. The calorimetric data for compounds III were normal and the melting points were on the order of 60°C.

Since the melting points of compounds III, in particular, were relatively low we decided to synthesize some alkoxyphenyl derivatives of piperazine. The original intention was to try to induce smectic C phases in the piperazine derivatives since

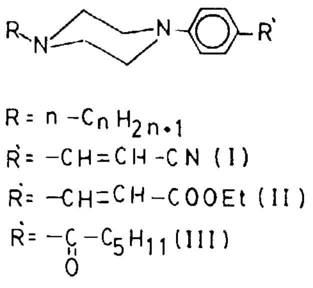
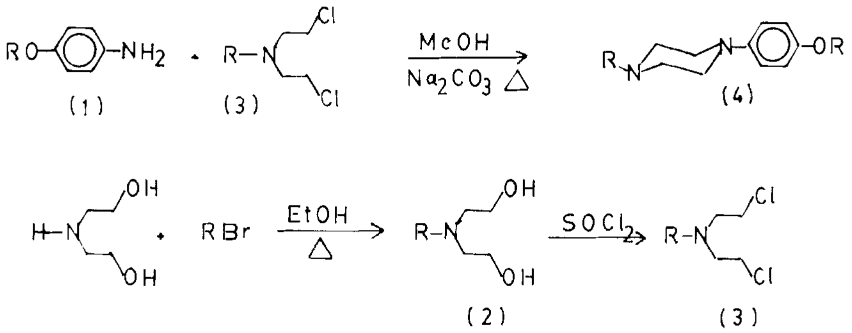


FIGURE 1

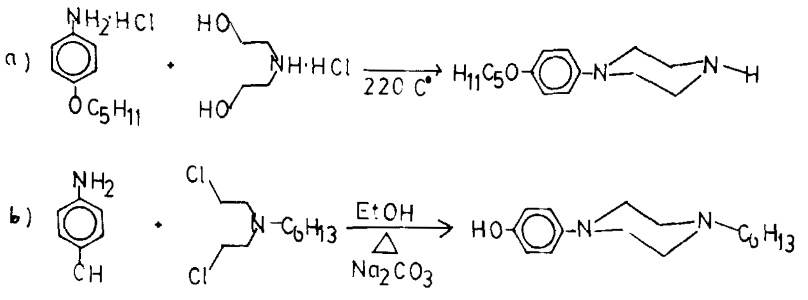
smectic C phases many times appear when there are two lateral dipoles produced by alkoxy chains.[4] In our case, there would be only one lateral dipole but we thought it is worthwhile to see what changes would be produced in the mesomorphic properties. Our interest in obtaining smectic C phases is related to the production of ferroelectric liquid crystals. If it were possible to obtain low temperature smectic C phases in the title compounds then our next step would be to introduce an assymmetric carbon atom in the molecule to obtain ferroelectric behavior.

SYNTHESIS

The N-*n*-alkyl-N'-(4-*n*-pentyloxyphenyl)-piperazines (4) were synthesized according to the procedure shown in Scheme I. The first attempt to obtain the above compounds was by Scheme II, procedures (a) and (b). In procedure (a) we could not find an appropriate solvent to extract the products and in procedure (b) we could not find appropriate solvents to purify the crude product.



SCHEME 1



SCHEME II

RESULTS AND DISCUSSION

The N-*n*-alkyl-N'-(4-*n*-pentyloxyphenyl)-piperazines show only ordered smectic phases. Figure 2 shows a plot of the phase transition temperatures as a function of the number of carbon atoms (*n*) in the alkyl chain and Figure 3 is a plot of transition heats as a function of (*n*). Table I gives the temperatures and transition heats for the series. The transition heats and temperatures were determined using a Perkin-Elmer DSC-2 Calibrated with Indium. The transition temperatures, except the melting points, were confirmed using a Leitz Ortholux-Pol microscope with a Mettler FP-52 hot stage.

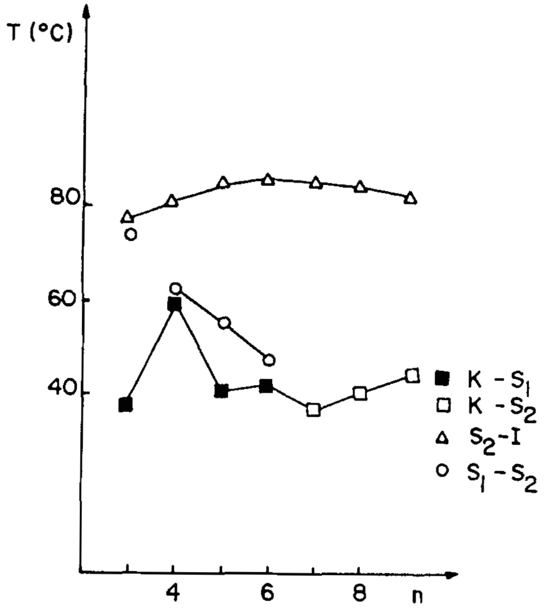


FIGURE 2 Plot of transition temperature versus the number of carbon atoms (*n*) in the alkyl chain (*R*) of the N-*n*-alkyl-N'-(4-*n*-pentyloxyphenyl)-piperazines (4).

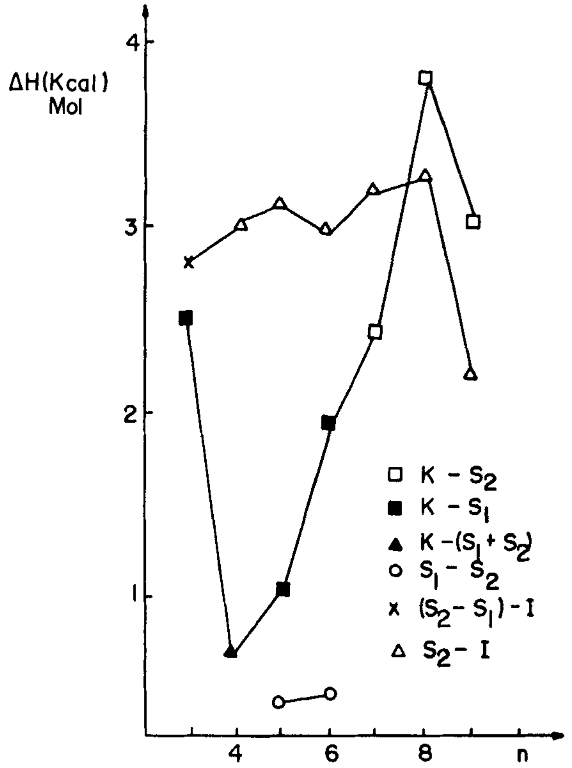


FIGURE 3 Plot of transition enthalpies versus the number of carbon atoms (n) in the alkyl chain (R) of the N-n-alkyl-N'-(4-pentyloxyphenyl)-piperazines (4).

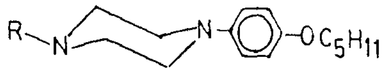
For n = 3, 4, 5, 6 there are two smectic phases S2 and S1 (S2—the higher temperature phase) and for n = 7, 8, 9 the S1 phase disappears. The trend of the transition temperatures for the transition to the isotropic phase is normal; however, the trend of the S1–S2 transition is abnormal in that it decreases very strongly with increasing (n). The transition heats for n = 4, 5, 6, 7 are not "normal" as the S2–I transition heat is larger than that of any lower temperature transition; in fact larger that the sum of the transition heats for all observable lower temperature transitions. This type of behavior was also observed in compounds II.

DSC cooling scans show that the I–S2 transition supercooled very little whereas the S2–S1, S1–K and S2–K transitions supercool considerably. For example, in a cooling scan of n = 6, the S2–S1 transition supercooled about 3°C and the S1–K transition about 10°C. Supercooling of transitions between two ordered smectic phases is common and the supercooling observed for the transition to the "Crystalline" phase K can be considered normal for transitions between crystalline and liquid crystalline Phases. Once heated samples, after being left at room temperature and rerun on the DSC, show essentially identical thermograms as did the virgin samples.

The textures of the phases were observed using the polarizing microscope. The S2–I transition is marked by the appearance of needle or block-like forms that

TABLE I

Transition temperatures and enthalpies for the N-*n*-alkyl-N'-(4-*n*-pentyloxyphenyl)-piperazines (4)



Compounds	*R*	The Phase Transition Temperature in °C	 Enthalpy (ΔH) in Kcal/mol
4a	n—C_3H_7	K 36.5 S_1 74.0 S_2 76.5 I	K 2.81 $(S_1 + S_2)^a$ 2.51 I
4b	n—C_4H_9	K 59.5 S_1 61.5 S_2 81.2 I	K 0.70 $(S_1 + S_2)^b$ 3.08 I
4c	n—C_5H_{11}	K 39.5 S_1 54.0 S_2 84.8 I	K 1.04 S_1 0.47 S_2 3.11 I
4d	n—C_6H_{13}	K 40.5 S_1 46.5 S_2 85.5 I	K 1.93 S_1 0.49 S_2 2.99 I
4e	n—C_7H_{15}	K 35.4 S_2 84.8 I	K 2.46 S_2 3.15 I
4f	n—C_8H_{17}	K 39.5 S_2 84.0 I	K 3.82 S_2 3.26 I
4g	n—C_9H_{19}	K 42.5 S_2 82.5 I	K 3.02 S_2 2.21 I

K = Crystalline, S = smectic, N = nematic, I = isotropic

[a] and [b] impossible to separate peaks on DSC, ΔH is sum of two transitions

coalesce to a mosaic texture with some lancets. It was always possible to observe some mosaic blocks with the homeotropic texture. For $n = 3, 4, 5, 6$ at the S2–S1 transition, the texture within the mosaic blocks becomes more broken and in particular some of the blocks that were formerly homeotropic became weakly birefringent; these blocks showed extinction at 90° intervals on rotation of the microscope stage. In S2 it was possible to shear the converslip but not in S1.

Convergent light observations were made with a Leitz 350 heated stage on the homeotropic blocks of S2 and these same blocks after the transition to S1. The S2 phase is uniaxial positive and S1 phase is biaxial positive with the acute bisectrix parallel to the microscope axis. This implies that both S2 and S1 are orthogonal phases.

X-ray diffraction patterns were recorded for $n = 5$ and 7 on a flat plate camera using 0.7 mm Lindemann capillaries in a temperature controlled oven. For $n = 5$ at room temperature, there four sharp rings that, using Bragg's law, correspond to distances of 22.1 ± 2.0 Å, 4.5 ± 0.1 Å, 4.1 ± 0.1 Å and 3.9 ± 0.1 Å. In the S1 phase at 45°C there were three sharp rings corresponding to 22.1 ± 2.0 Å, 4.3 ± 0.1 Å and 4.0 ± 0.1 Å. In S2 at 65°C there were only two sharp rings corresponding to 22.2 ± 2.0 Å and 4.2 ± 0.1 Å. For compound $n = 7$, there were four sharp rings at room temperature corresponding to distances of 25.4 ± 2.0 Å, 4.5 ± 0.1 Å, 4.1 ± 0.1 Å and 3.9 ± 0.1 Å; in the S2 phase at 46°C there were two sharp rings at 25.4 ± 2.0 Å and 4.2 ± 0.1 Å.

The X-ray results are ambiguous for the K phase which we have called "Crystalline." Three high angle rings are really insufficient proof that the phase is crystalline. Therefore phase K could be a very disordered crystal, a new type of smectic phase or perhaps even a mixture of the two. The $n = 5$ compound was recently studied by Klamke[5] *et al.*, using more sophisticated X-ray techniques and they claim that between 25°C and 39°C there is a third smectic phase with three high angle reflections as we have observed. They also claim that this smectic phase has not been previously observed in any other compound. They give 25°C as the true melting Point. However to obtain the crystalline phase, they say it is necessary to recrystallize the compound from acetone at a temperature of −10°C.

The molecular length was measured for the most extended conformation of the molecule using molecular models (Dreiding Stereomodels, Buchi, West Germany). For $n = 5$, the molecular length was 23.2 Å and for $n = 7$, it was 25.5 Å. Comparison of the molecular length from the models and the distance from the small angle X-ray peak confirms that both S1 and S2 are orthogonal phases.

We conclude from the optical and X-ray data that S2 should be classified as a probable smectic B (uniaxial, orthogonal, one high angle X-ray peak) and S1 as a probable smectic E phase (biaxial, orthogonal, two high angle X-ray peaks).[6]

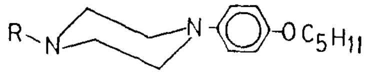
Experimental Part

The structures of the compounds were confirmed by elemental analysis (Table II) and analysis of their IR spectra (Perkin-Elmer 237 B and 577), ^{1}H-NMR (Varian T-60 A, TMS as internal reference), and ^{13}C-NMR (Varian CFT-20).

*4-*n*-Pentyloxyaniline (1)* was prepared using the method described by Keller

TABLE II

Elemental analysis of N-*n*-alkyl-N'-(4-*n*-pentyloxyphenyl)-piperazine (4)



Compounds	*R*	Empirical Fórmula (mol. weight)	C		H		N	
			Calc.	Found	Calc.	Found	Calc.	Found
4a	*n*—C_3H_7	$C_{18}H_{30}N_2O$	74.48	74.38	10.34	10.31	9.65	9.92
4b	*n*—C_4H_9	$C_{19}H_{32}N_2O$	75.00	74.96	10.53	11.44	9.21	9.94
4c	*n*—C_5H_{11}	$C_{20}H_{34}N_2O$	75.47	75.24	10.59	10.63	8.81	8.56
4d	*n*—C_6H_{13}	$C_{21}H_{36}N_2O$	75.90	75.51	10.84	11.23	8.43	8.65
4e	*n*—C_7H_{15}	$C_{22}H_{38}N_2O$	76.30	76.78	10.98	11.13	8.09	8.03
4f	*n*—C_8H_{17}	$C_{23}H_{40}N_2O$	76.66	77.10	11.11	11.37	7.77	8.08
4g	*n*—C_9H_{19}	$C_{24}H_{42}N_2O$	77.00	77.20	11.23	11.14	7.49	7.61

and Liebert.[8] *p*-Aminophenol was first converted to its N-acetyl derivative by reaction with acetic anhydride,[7] then alkylated using *n*-pentyl bromide in EtOH/KOH solution[8] and the resulting amides hydrolyzed with 20N KOH in methanol.[8] The crude product was purified by vacuum distillation (b.p. 103°C/0.09 mm Hg) in a yield of 87% (based on the 4-aminophenol).

Preparation of N-*n*-alkyl-β-β′-dichlorodiethylamines (3)

Diethanolamine was alkylated using the method described by Wilson and Tishler,[9] and the diols (2) purified by vacuum distillation yields and boiling points are given in Table III. These were converted to (3) with thionyl chloride in chloroform[9] and used without further purification.

Preparation of N-*n*-alkyl-N′-(4-*n*-pentyloxyphenyl)-piperazine (4).

A mixture of 0.07 mole of N-*n*-alkyl-β,β′-dichlorodiethylamine hydrochloride[10] (3), 0.07 mole of *p*-*n*-alkyloxyphenylaniline (1) in CH_3OH was stirred and refluxed for 6 hours. After cooling, 0.035 mole of sodium carbonate was added and the solution refluxed again for 2–4 hours. The methanolic solution was evaporated and the residue recrystallized from dioxane 4 times to give the salt in a yield of 45%. The products were dissolved in 10% NaOH to liberate the base, extracted with CH_2Cl_2, washed with water, dried, filtered and the filtrate evaporated. These solids could not be recrystallized. However, analytical data showed these materials were pure and confirmed their structures.

N-*n*-propyl-N′-(4-pentyloxyphenyl)-piperazine (4a)

IR(KBr): 1510 (C=C); 1245 (C—O) and 820 (C—H) cm^{-1}.
^1H-NMR(C_6D_6): 0.92 (*t*, 6, CH_3); 1.12–2.02 (*m*, 8, CH_2); 2.25 (*t*, 2, CH_2N); 2.43 and 3.03 (2*m*, 8, CH_2N); 3.75 (*t*, 2, O—CH_2); 6.80 (*s*, 4, arom.).
^{13}C-NMR (C_6D_6): 153.76, 146.45, 118.33, 115.40 (C_4, C_1, C_3, C_2, arom.); $\underline{53.78}$ and 50.95 (N—CH_2—$\underline{CH_2}$—N′); 68.33 (1, O—C_1); 60.72 (1, N—C_1); 29.58 (1, O—C_2); 28.68 (1, O—C_3); 22.84 (1, O—C_4); 20.55 (1, N—C_2); 14.31 (1, O—C_5); 12.17 (1, N—C_3).

TABLE III

Boiling temperatures and yields for the N-*n*-alkyldiethanol amines (2)

n	Yield %	Boiling Point	°C
3	78.5	110	0.4 mm Hg
4	71.5	102	0.02 ″
5	80.0	104	0.02 ″
6	80.0	106	0.03 ″
7	88.0	120	0.09 ″
8	78.0	144	0.35 ″
9	77.0	160	0.40 ″

N-*n*-Butyl-N′-(4-pentyloxyphenyl)-piperazine (4b)

IR(KBr): 1505 (C=C); 1245 (C—O) and 820 cm^{-1}.
^{1}H-NMR(C_6D_6): 0.90 (*t*, 6, CH_3); 1.08–2.02 (*m*, 10, CH_2); 2.28 (*t*, 2, CH_2N); 2.45 and 3.03 (2*m*, 8, CH_2N); 3.77 (*t*, 2, OCH_2); 6.92 (*s*, 4, arom.).
^{13}C-NMR (C_6D_6): 153.77, 146.45, 118.33, 115.40 (C_4, C_1, C_3, C_2, arom.); $\underline{53.87}$ and 50.95 (N—CH_2—$\underline{CH_2}$—N′); 68.32 (1, O—C_1); 58.56 (1, N—C_1); 29.57 (2, N—C_2 and O—C_2); 28.67 (1, O—C_3); 22.83 (1, O—C_4); 20.96 (1, N—C_3); 14.31 (2, N—C_4 and O—C_5).

N-*n*-Pentyl-N′-(4-pentyloxyphenyl)-piperazine (4c)

IR(KBr): 1510 (C=C); 1250 (C—O) and 820 (C—H) cm^{-1}.
^{1}H-NMR(C_6D_6): 0.92 (*t*, 6, CH_3); 1.08–2.05 (*m*, 12, CH_2); 2.28 (*t*, 2, CH_2N); 2.45 and 3.07 (2*m*, 8, CH_2N); 3.77 (*t*, 2, OCH_2); 6.92 (*s*, 4, arom.).
^{13}C-NMR (C_6D_6): 153.68, 146.43, 118.31, 115.31 (C_4, C_1, C_3, C_2, arom.); $\underline{53.78}$ and 50.93 (N—CH_2—$\underline{CH_2}$—N′); 68.22 (1, O—C_1); 58.84 (1, N—C_1); 30.03 (1, N—C_3); 29.54 (1, O—C_2); 28.58 (1, O—C_3); 27.10 (1, N—C_2); 22.83 (2, O—C_4 and N—C_4); 14.23 (2, O—C_5 and N—C_5).

N-*n*-Hexyl-N′-(4-pentyloxyphenyl)-piperazine (4d)

IR(KBr): 1510 (C=C); 1245 (C—O) and 820 (C—H) cm^{-1}.
^{1}H-NMR(C_6D_6): 0.92 (*t*, 6, CH_3); 1.10–2.03 (*m*, 14, CH_2); 2.28 (*t*, 2, CH_2N); 2.45 and 3.05 (2*m*, 8, CH_2N); 3.72 (*t*, 2, OCH_2); 6.87 (*s*, 4, arom.).
^{13}C-NMR (C_6D_6): 153.86, 146.53, 118.50, 115.47 (C_4, C_1, C_3, C_2, arom.); $\underline{53.86}$ and 51.03 (N—CH_2—$\underline{CH_2}$—N′); 68.31 (1, O—C_1); 58.93 (1, N—C_1); 32.26 (1, N—C_4); 29.54 (1, O—C_2); 28.65 (2, N—C_3 and O—C_3); 27.50 (1, N—C_2); 23.08 (1, N—C_5); 22.81 (1, O—C_4); 14.29 (2, N—C_6 and O—C_5).

N-*n*-Heptyl-N′-(4-pentyloxyphenyl)-piperazine (4e)

IR(KBr): 1510 (C=C); 1245 (C—O) and 820 (C—H) cm^{-1}.
^{1}H-NMR(C_6D_6): 0.92 (*t*, 6, CH_3); 1.12–1.97 (*m*, 16, CH_2); 2.30 (*t*, 2, CH_2N); 2.47 and 3.07 (2*m*, 8, CH_2N); 3.77 (*t*, 2, O—CH_2); 6.90 (*s*, 4, arom.).
^{13}C-NMR (C_6D_6): 153.68, 146.37, 118.25, 115.31 (C_4, C_1, C_3, C_2, arom.); $\underline{53.79}$ and 50.94 (N—CH_2—$\underline{CH_2}$—N′); 68.23 (1, O—C_1); 58.86 (1, N—C_1); 32.28 (1, N—C_5); 29.58 (2, O—C_2 and N—C_4); 28.59 (1, O—C_3); 27.81 (1, N—C_3); 27.42 (1, N—C_2); 23.01 (1, N—C_6); 22.82 (1, O—C_4); 14.24 (2, O—C_5 and N—C_7).

N-*n*-Octyl-N′-(4-pentyloxyphenyl)-piperazine (4f)

IR(KBr): 1510 (C=C); 1245 (C—O) and 820 (C—H) cm^{-1}.
^{1}H-NMR(C_6D_6): 0.92 (*t*, 6, CH_3); 1.08–2.02 (*m*, 18, CH_2); 2.30 (*t*, 2, CH_2N); 2.47 and 3.05 (2*m*, 8, CH_2N); 3.75 (*t*, 2, OCH_2); 6.92 (*s*, 4, arom.).
^{13}C-NMR (C_6D_6): 153.86, 146.54, 118.42, 115.48 (C_4, C_1, C_3, C_2, arom.); $\underline{53.88}$ and 51.04 (N—CH_2—$\underline{CH_2}$—N′); 68.32 (1, O—C_1); 58.95 (1, N—C_1); 32.29 (1,

N—C_6); 30.03 (1, N—C_5); 29.76 (1, N—C_4); 29.57 (1, O—C_2); 28.67 (1, O—C_3); 27.90 (1, N—C_3); 27.51 (1, N—C_2); 23.09 (1, N—C_7); 22.82 (1, O—C_4); 14.30 (2, O—C_5 and N—C_8).

N-*n*-Nonyl-N′-(4-pentyloxyphenyl)-piperazine (4g)

IR(KBr): 1510 (C=C); 1250 (C—O) and 825 (C—H) cm^{-1}.
^{1}H-NMR(C_6D_6): 0.92 (*t*, 6, CH_3); 1.07–1.97 (*m*, 20, CH_2); 2.28 (*t*, 2, CH_2N); 2.45 and 3.02 (2*m*, 8, CH_2N); 3.72 (*t*, 2, OCH_2); 6.80 (*s*, 4, arom.).
^{13}C-NMR (C_6D_6): 153.71, 146.38, 118.33, 115.33 (C_4, C_1, C_3, C_2, arom.); $\underline{53.79}$ and 50.95 (N—CH_2—$\underline{CH_2}$—N′); 68.24 (1, O—C_1); 58.87 (1, N—C_1); 32.23 (1, N—C_7); 30.05 (2, C_5 and N—C_6); 29.67 (1, O—C_2); 29.49 (1, N—C_4); 28.59 (1, O—C_3); 27.89 (1, N—C_3); 27.43 (1, N—C_2); 23.02 (2, O—C_4 and N—C_8); 14.22 (2, O—C_3 and N—C_9).

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