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J. Bartulín [a] , C. Zúñiga [a] , A. Ramírez [a] & C. Aguilera [a]
[a] Departmento de Quimica, Facultad de Ciencias, Universidad de Concepción, Casilla 3-C, Concepciön, Chile
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J. BARTULÍN, C. ZÚÑIGA, A. RAMÍREZ and C. AGUILERA

Departamento de Química, Facultad de Ciencias, Universidad de Concepción, Casilla 3-C, Concepción, Chile

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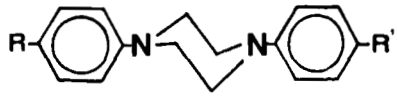
New thermotropic unsymmetrically substituted N,N′-diarylpiperazine derivatives are synthesized and characterized. Phase behaviour comparison of these new unsymmetricals and the symmetrical already reported in the literature indicate greater mesophase stability for the formers. The liquid crystalline behaviour of these piperazine derivatives, in particular, their transition temperatures and the mesophasic width, could be explained on the basis of their structural features. These mesophases are studied by differential scanning calorimetry (DSC) and polarized light microscopy.

INTRODUCTION

The synthesis and investigation of the physical properties of new liquid crystalline compounds are important for studying the relationship between structure of the molecules and characteristics of the mesomorphic state.

H. Shubert et al.[1] studied the homologous series of N,N′-diarylpiperazines symmetrically substituted with alkyl or alkoxy terminal



R : $C_nH_{2\,n+1}$, $OCOC_nH_{2\,n+1}$

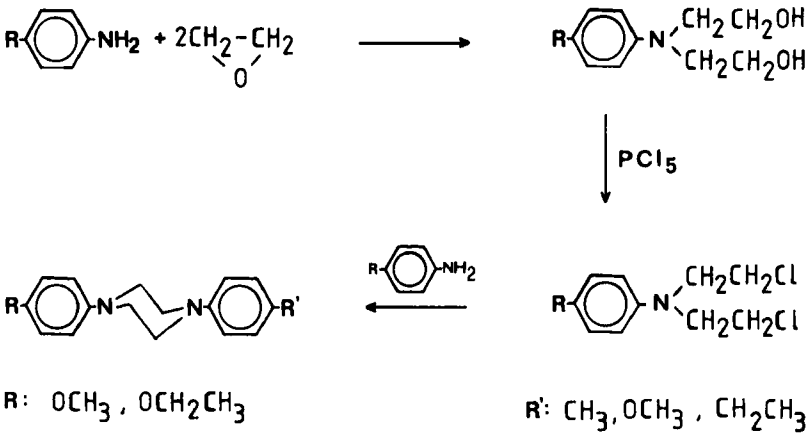
R' : $OC_nH_{2\,n+1}$

n : 1,2

groups. It is of interest to determine the effect, in particular of short terminal groups, on mesomorphic behaviour of unsymmetricals N,N′-substituted-diaryl-piperazine derivatives.

RESULTS AND DISCUSSION

The simplest known method of obtaining unsymmetrically substituted N,N′-diarylpiperazines is represented by the following reactions sequence 2,3).



The first step of the sequence was carried out in an autoclave at 90°C for 16 hr. Good yields were obtained for p-anilines containing electron donating groups, in comparison to those obtained for less basic amine such as p-haloaniline. p-Acetylaniline did not reacted. Varied yield (40–70%) were obtained for the alkyl and alkoxy derivatives of N,N′-diarylpiperazine.

The transition temperatures of the first series of derivatives are compiled in Table I. These compounds were studied using the polarizing light microscope and the DSC.

All of these compounds show enantiotropic liquid crystalline behaviour, except the compound 2. These compounds possess only a narrow temperature range in which enantiotropic mesophase exists. High transition temperatures observed, as expected, caused by the short terminal alkyl and alkoxy groups.[4] The symmetricals N,N′-(p-methyl, p-ethyl, p-methoxy of p-ethoxy)-diarylpiperazines do not exhibit mesomorphic properties and they have higher melting point that the unsymmetrical ones.[5]

TABLE I

Phase transition of liquid crystalline N,N'-diarylpiperazine derivatives

Compound	R	R'	Phase transition[a] temperature in °C	ΔHi[b] kcal mol^{-1}	ΔSi[b] calmol^{-1}K^{-1}
1	OCH_3	CH_3	K 172 N 173 I	-	-
2	OCH_3	C_2H_5	K 172 (N 157) I	0.26	0.60
3	OC_2H_5	CH_3	K 170 N 186 I	0.35	0.75
4	OC_2H_5	C_2H_5	K 166 S 182 I	6.64	14.59
5	OC_2H_5	OCH_3	K 209 N 212 I	0.40	0.82

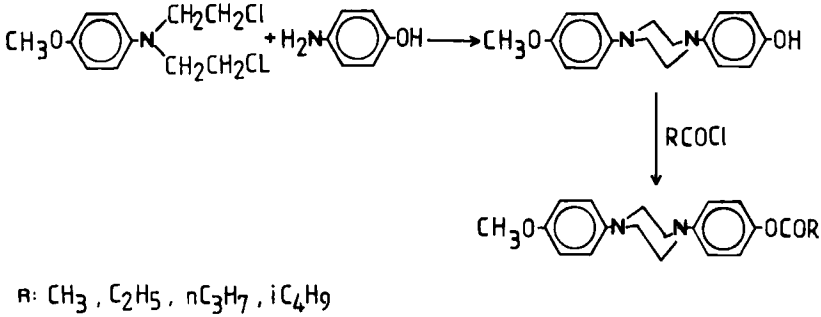
a) K: crystalline, N: nematic, I: isotropic

( ): monotropic nematic

b) -, means property could not be measured accurately.

The compounds 3 and 4 differ only in one methylene unit. This difference did not affect mesomorphic range and both of them present the same range of 16°C. We found that compound 4's melting point enthalpy and entropy (1,68 Kcal/mole and 3,82 cal/mole °K respectively), being lower than those of its mesophase-isotropic liquid transition point (see Table I). This phenomenon has been observed generally for smectic phases by various authors.[6,7] The compound 5 possessing two polar groups have higher melting temperature and only one mesomorphic range of 3°C.

One way of obtaining the type of compounds having low transition temperature and high mesomorphic range is through incorporation of an ester group in the mesogen. This new series of compounds was separately synthesized according to the following scheme.



R: CH_3, C_2H_5, nC_3H_7, iC_4H_9

Table 2 shows the transition temperatures of these phases.

All of the synthesized compounds (6–9) exhibit enantiotropism, follows properties typical of a homologous series. There exists a lowering of melting point with elongation of the side chain. Lower melting points are observed for the compounds having lateral branched alkyl group. Smectic phases are common with long lateral chains, but are rare with short chains. The mesogenic range of these compounds oscillate between 31° and 62°C, depending on the terminal groups.

EXPERIMENTAL

Synthesis of unsymmetrically substituted N,N-diarylpiperazine derivatives.

The intermediary compounds such as Bis-N-(β-hydroxyethylene)-anilines, Bis-N-(β-chlorethylene)-p-alkyl or p-alkoxyanilines, were prepared as described by Ross.[2]

TABLE II

Phase transition of liquid crystalline N,N'-diarylpiperazine derivatives

Compound	R	R'	Phase transition temperature in °C	ΔHi[b] kcal mol^{-1}	ΔSi[b] cal mol^{-1} K^{-1}
6	OCH_3	CH_3COO	K 164 N 207 I	0.34	0.71
7	OCH_3	C_2H_5COO	K 148 S 155 N 193 I	0.35	0.76
8	OCH_3	nC_3H_7COO	K 144 N 206[c] I	-	-
9	OCH_3	iC_4H_9COO	K 139 N 170 I	-	-

c) : determined on Hot Stage Mettler FP800.

N,N'-arylpiperazine

A mixture of 0.1 mol p-alkoxy(or p-alkylphenylene) bis-(β-chlorethylene) amine and 0.3 mol of p-alkyl (or -alkoxy) aniline in 150 ml acetone/H_2O (3:1) was stirred and left overnight at room temperature. The mixture was heated at reflux for 2 hr and then filtrated. In the case when no precipitate was obtained, the reaction mixture was steam distilled to remove the excess of amine. The residue was vigorously shaken with concentrated ammonia, filtered and recrystallized from ethanol-water or dioxane. Yield 40–70%.

N-(4-Methoxyphenylene)-N'-(4-methylphenylene)-piperazine(1) Recrystallization in dioxane/ethanol (3).

IR(KBr) 1610(C=C), 1250(C—O and 825 cm^{-1} (CH). ^{1}HNMR ($CDCl_3$) δ 2.30 (s,3,CH_3), 3.27 (s,3,CH_2), 3.78 (s,3,CH_3O), 6.97 (s,4,alkoxy Ar) and 6.92 and 7.18 (2d,4, J = 10Hz, alkyl Ar); ^{13}C-NMR($CDCl_3$) 154.19; *129.76*; 114.64 (C_1',C_4',C_3',C_2',Ar) 149.30, 145.70, 118.45, 116.69 (C_4,C_1,C_3,C_2,Ar); 50.09; *50.97* (N—CH_2—CH_2N'); 55.64 (1,OCH_3); 20.41 (1,CH_3).

N-(4-Methoxyphenylene)-N'-(ethylphenylene)-piperazine (2).

Recrystallization from ethanol/water. IR(KBr) 1620(C=C), 1125(C—O) and 830 cm^{-1} (C—H). ^{1}HNMR ($CDCl_3$) 1.20 (t,3,CH_3), 2.62 (q,2,CH_2), 3.28 (s,8,CH_2) 3.78 (s,3,CH_3O), 6.97 (s,4,alkoxy Ar), 7.2 and 6.97 (2d,4,J = 8Hz, alkyl Ar). ^{13}C-NMR ($CDCl_3$) 153.90, 136.01, 128.51, 114.56 (C_1',C_4',C_3',C_2', Ar), 149.10, 145.90, 118.45; 116.60 (C_4,C_1,C_3,C_2,Ar), 50.00, *50.97* (N—CH_2—CH_2—N'), 55.64 (1,OCH_3), 27.93 (1,CH_2), 15.71 (1,CH_3).

N-(4-Ethoxyphenylene)-N'-(4-methylphenylene)-piperazine (3):

Recrystallization in ethanol/benzene IR (KBr) 1605 (C=C), 1225 (C—O) and 815 cm^{-1} (C—H). ^{1}H-NMR ($CDCl_3/C_6D_6$) 1.47 (t,3,CH_3), 2.25 (s,3,CH_3), 3.15 (s,8,CH_2), 3.89 (q,2,CH_2), 6.77–7.20 (m,8,Ar).

N-(4-Ethoxyphenylene)-N'-(4'-ethylphenylene-piperazine (4).

Recrystallization in ethanol/benzene, IR (KBr) 1620 (C=C), 1220 (C—O) and 820 cm^{-1} (C—H). ^{1}H-NMR ($CDCl_3$) 1.22 (t,3,CH_3'), 1.30 (t,3,CH_3); 2.55 (q,2,CH_2), 3.18 (s,8,CH_2), 3.92 (q,2,CH_2O); 6.83–7.30 (m,8,Ar). ^{13}C-NMR ($CDCl_3$) 153.50, 136.02, 128.50, 115.40 (C_1',C_4',C_3',C_2',Ar); 149.40, 145.68, 118.46, 116.68 (C_4,C_1,C_3,C_2,Ar), 50.00, 50.97, (N CH_2CH_2N'), 63.86 (1,CH_2O), 27.94 (1,CH_2); 15.71 (1,CH_3—CH_2O), 14.94 (1,CH_3).

N-(4-Ethoxyphenylene)-N'-(4'-methoxyphenylene)piperazine (5)

Recrystallization in dioxane. IR (KBr) 1531 (C=C), 1250 (C—O) and 833 cm^{-1} (C—H). ^{1}H-NMR ($CDCl_3$) 1.38 (t,3,CH_3), 3.23 (s,8,CH_2), 3.77 (s,3,OCH_3), 4.0 (q,2,CH_2), 6.98 and 7.35 (s,8,Ar). ^{13}C-NMR ($CDCl_3$) 145.79 (2,C_4,C'4) 118.46 (2,C_1,C_1') 115.34 (2,C_3,C_3'), 114.63 (2,C_2,C_2'); 50.99 (2,N—CH_2—CH_2—N'); 63.87 (1,CH_2O); 55.65 (1,OCH_3), 14.94 (1,CH_3).

SYNTHESES OF N-(4-METHOXYPHENYLENE)-N'-(4'-ACYLOXYPHENYLENE)-PIPERAZINE DERIVATIVES:

N-(4-Methoxyphenylene)-N'-(4'-hydroxyphenylene)-piperazine.

A mixture of 0.1 mole of p-methoxyphenyl-bis-(β-chloroethylene) amine, 0.1 mole of p-hydroxyaniline and 0.2 mole of $NaHCO_3$ in 200 ml of acetone-water (1:1) was refluxed for 2 h, solvents were removed under vacuum and to the residue was added ethanol and refluxed for 6 h. The insoluble NaCl was removed by filtration. The solvent was evaporated and the product recrystallized from isopropanol.
IR(KBr) 3300 (OH), 1506 (C=C). ^{1}H-NMR (CD_3COOD): 3.67 (s,8,CH_2), 3.80 (s,3,OCH_3), 6.83–7.55 (2m,8,Ar). ^{13}C-NMR (CD_3COOD); 157.88, 141.67, 121.27, 115.88 (C_4,C_1,C_3,C_2,Ar), 156.43, 138.63, 122.14, 117.27 (C_1',C_4',C_3',C_2',Ar), 55.93 (1,OCH_3), *51.93*, 53.77 (N—*CH_2*—CH_2—N').

N-(4-Methoxyphenylene)-N'-4'-acetyloxyphenylene)-piperazine (6).

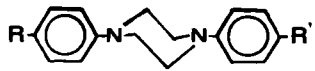
Recrystallization from Petroleum ether (100–140°C). IR (KBr) 1750 (C=O), 1610 (C=C), 1210 (C—O) and 830 cm^{-1} (C—H). ^{1}H-NMR ($CDCl_3$) 2.25 (s,3,CH_3CO), 3.23 (s,8,CH_2), 3.75 (s,3,OCH_3), 6.88 and 6.95 (2s,8,Ar). ^{13}C-NMR ($CDCl_3$), 149.29, 145.59, 118.54, 114.63 (C_4C_1,C_3,C_2,Ar), 154.26, 144.02, 121.95, 117.16 (C_1',C_4',C_3',C_2',Ar), 49.88, *50.94* (NCH_2*CH_2* and N'), 55.57 (1,OCH_3), 21.06 (1,*CH_3*CO).

N-(4-Methoxyphenylene)-N'-(4'-n-propanoyloxyphenylene)-piperazine (7).

IR (KBr) 1742 (C=O) and 1510 cm^{-1} (C=C). ^{1}H-NMR (CD_3COOD); 1.20 (t,3,CH_3), 2.48 (q,2,*CH_2*-CH_3), 3.15(s,8,CH_2), 3.65 (s,3,OCH_3) 6.67–7.17 (2s,8,Ar).

TABLE III

Elemental analysis of N,N'-diarylpiperazine derivatives (1–9)



N°	R	R'	Empirical Formula (mol·weight)	C		H		N	
				Calc.	Found	Calc.	Found	Calc.	Found
1	CH_3O	CH_3 [3)]	$C_{18}H_{22}N_2O$	76.60	76.45	7.80	8.21	9.93	-
2	CH_3O	C_2H_5	$C_{19}H_{24}N_2O$	77.03	76.16	8.11	8.40	9.45	9.15
3	C_2H_5O	CH_3	$C_{19}H_{24}N_2O$	77.02	77.28	8.11	8.43	9.46	8.70
4	C_2H_5O	C_2H_5	$C_{20}H_{26}N_2O$	77.41	77.46	8.39	8.90	9.03	8.56
5	C_2H_5O	OCH_3	$C_{19}H_{24}N_2O_2$	73.03	73.53	7.69	8.07	8.97	8.84
6	CH_3O	O_2CCH_3	$C_{19}H_{22}N_2O_3$	69.95	69.51	6.75	6.84	8.59	8.46
7	CH_3O	$O_2CC_2H_5$	$C_{20}H_{24}N_2O_3$	70.59	71.04	7.06	7.01	8.24	9.04
8	CH_3O	$O_2CC_3H_7$	$C_{21}H_{26}N_2O_3$	71.19	71.49	7.34	7.07	7.91	8.40
9	CH_3O	$iO_2CC_4H_9$	$C_{22}H_{28}N_2O_3$	71.74	71.64	7.60	7.36	7.61	7.94

N-(4-Methoxyphenylene)-N'-(4'-n Butanoyloxyphenylene)-piperazine (8).

IR (KBr) 1751 (C=O) and 1510 cm^{-1} (C=C). ^{1}H-NMR ($CDCl_3$), 1.00 (t,3,CH_3), 1.75 (m,2,CH_2); 2.50 (t,2,OCH_2); 3.20 (s,8,CH_2), 3.72 (s,3,OCH_3), 6.88, 6.95 (2s,8,Ar). ^{13}C-NMR ($CDCl_3$) 171.81 (1,C=O); 149.15; 145.73, 118.38; 114.68 (C_4,C_1,C_3,C_2,Ar); 154.23, 144.18, 121.79, 116.93 (C_1',C_4',$C_3'C_2'$,Ar); 55.51 (1,OCH_3); *49.84*; 50.72 (NCH_2CH_2 and N'); 36.17, 18.38, 13.41 (C_2,C_3,C_4 alkyl chain).

N-(4-Methoxyphenylene)-N'-(4'-isovaleroyloxyphenylene)-piperazine (9).

IR(KBr) 1754 (C=O) and 1511 cm^{-1} (C=C). ^{13}C-NMR ($CDCl_3$) 171.23 (1,C=O); 149.16, 145.74, 118.34, 114.69 (C_4,C_1,C_3,C_2,Ar); 154.23, 144.18, 121.80, 116.93 (C_1',C_4',C_3',C_2',Ar) 55.50 (1,OCH_3), 49.84, 50.71 (N—*CH_2*—CH_2—N'), 43.30 (1,CH_2); 25.71 (1,CH); 22.21 (2,CH_3). ^{1}H-NMR ($CDCl_3$. 1.05 (d,6,2CH_3); 2.30 (d,2,CH_2CO); 3.13 (s,8,CH_2), 3.73 (s,3,OCH_3); 6.82–6.90 (2s,8,Ar).

Spectral analyses were obtained through following instruments: IR-Perkin-Elmer 237 and 577; NMR (H^1-Varian T-60A, ^{13}C-Varian CFT-20), TMS as internal reference.

The transition temperatures were measured on a Perkin Elmer DSC-2. For the polarizing microscopy a Leitz Ortholux Pol-BKII was used.

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