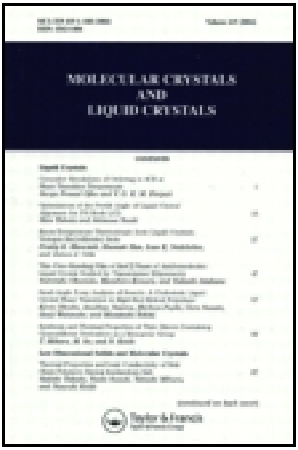

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Mesogenic Esters of the 4-(Alkylpiperidino) Benzoic Acids†

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A number of alkyl and 4-substituted phenyl 4-(4-alkylpiperidino) benzoates have beer prepared and their properties examined.

INTRODUCTION

During the last few years several heteroalicyclic units, especially the 1,3-dioxan unit, have been widely used for the synthesis of liquid crystal materials, along with well-known alicyclic units (cyclohexane, bicyclo(2.2.2)octane). Nevertheless, only a few data are known[1-3] about the influence of the 4-alkylpiperidino-unit on the properties of liquid crystal materials.

EXPERIMENTAL

A number of alkyl and 4-substituted phenyl 4-(4-alkypiperidino) benzoates have been synthesized in this work. The synthesis was performed according to the following scheme:

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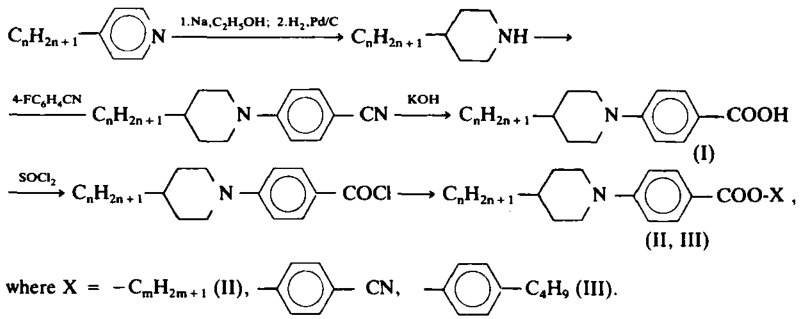


4-Alkylpyridines were obtained by alkylation of 4-picoline.[4] The catalytic hydrogenation of the 4-alkylpyridines proceeded very poorly, and therefore these compounds were first reduced by the action of metallic sodium in boiling ethanol. The mixture of 4-alkylpiperidine and 4-alkyl-1,2,5,6-tetrahydropyridine obtained was then hydrogenated in the presence of the palladium catalyst. The 4-(4-alkylpiperidino)benzonitriles were obtained by heating 4-fluorobenzonitrile with the 4-alkylpiperidines[2,3] without any solvent at 180°C; they were then hydrolyzed by heating with potassium hydroxide in ethyleneglycol solution to give the 4-(4-alkylpiperidino)benzoic acids (I).

RESULTS AND DISCUSSION

The acids (I), beginning with the n-heptyl homologue, exhibit nematic properties, while the higher members are smectic (see Table I).

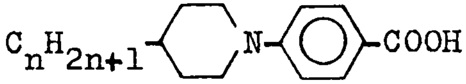
The acids (I) were converted into the acid chlorides in the usual manner, with thionyl chloride. The chlorides (without any purification) were esterified by the action of the sodium alcoxides in an excess of the alcohol, or by the action of the substituted phenols in pyridine solution. The phase transition temperatures of the esters (II) and (III) are presented in the Table II and III.

The alkyl 4-(4-alkylpiperidino)benzoates (II) exhibit enantiotropic smectric A mesophase over a rather wide temperature range in contrast to the alkyl 4-alkylbiphenyl-4′-carboxylates or alkyl 4-(4-alkylcyclohexyl)benzoates, which are non-mesomorphic. Probably, introduction of a nitrogen atom increases the dipole-dipole interactions between neighbouring molecules; this may favour the anti-parallel orientation of the molecules[2] and increase the thermal stability of the mesophase.

The esters (II) function as polar components of mixtures: the thermostability of the smectic mesophase increases when they are mixed

TABLE I

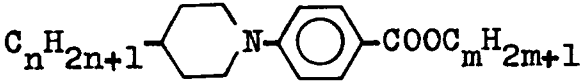
The phase transition temperatures and elemental analysis data for 4-(4-alkylpiperidino)benzoic acids (I)



Compound	n	The phase transition temp., in °C			Found, %			Empirical formula	Calculated, %		
		C-S	S-N/I	N-I	C	H	N		C	H	N
Ia	0	220	—	—	70.3	7.3	7.0	$C_{12}H_{15}NO_2$	70.22	7.37	6.82
Ib	1	240	—	—	71.2	7.7	6.5	$C_{13}H_{17}NO_2$	71.21	7.81	6.39
Ic	2	240	—	—	72.0	8.4	5.9	$C_{14}H_{19}NO_2$	72.07	8.21	6.00
Id	3	240	—	—	73.0	8.5	5.6	$C_{15}H_{21}NO_2$	72.84	8.58	5.66
Ie	4	258	—	—	73.6	8.9	5.4	$C_{16}H_{23}NO_2$	73.53	8.87	5.36
If	5	205	—	—	74.0	9.3	5.1	$C_{17}H_{25}NO_2$	74.14	9.15	5.09
Ig	6	210	—	—	74.9	9.4	4.9	$C_{18}H_{27}NO_2$	74.70	9.40	4.84
Ih	7	206	—	245	75.4	9.7	4.5	$C_{19}H_{29}NO_2$	75.21	9.63	4.62
Ii	8	199	225	240	75.7	9.8	4.4	$C_{20}H_{31}NO_2$	75.67	9.84	4.41
Ij	9	205	222	—	76.0	10.1	4.4	$C_{21}H_{33}NO_2$	76.09	10.03	4.23
Ik	10	197	224	—	76.6	10.3	4.1	$C_{22}H_{35}NO_2$	76.48	10.21	4.05

TABLE II

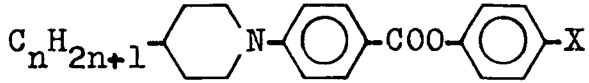
The phase transition temperatures, enthalpies and elemental analysis data for alkyl 4-(4-alkylpiperidino)benzoates (II)



Compound	n	m	The phase transition temp., in °C		The phase transition enthalpies, kcal/mol		Found, %			Empirical formula	Calculated, %		
			C- S_A	S_A-I	C- S_A	S_A- I	C	H	N		C	H	N
IIa	5	1	86.5	90.5	3.0	1.6	74.6	9.4	4.9	$C_{18}H_{27}NO_2$	74.70	9.40	4.84
IIb	5	3	37.8	68.0	2.3	1.5	75.6	9.8	4.5	$C_{20}H_{31}NO_2$	75.67	9.84	4.41
IIc	5	4	42.0	57.8	3.5	1.7	76.2	10.0	4.3	$C_{21}H_{33}NO_2$	76.09	10.03	4.23
IId	5	5	45.5	59.0	3.2	1.6	76.4	10.1	4.2	$C_{22}H_{35}NO_2$	76.48	10.21	4.05

TABLE III

The phase transition temperatures and elemental analysis data for aryl-4-(4-n-alkylpiperidino)benzoates (III)



Compd.	n	X	The phase transition temp., in °C			Found, %			Empirical formula	Calculated, %		
			C - S_A	S_A - N/I	N - I	C	H	N		C	H	N
IIIa	0	CN	154	-	(110)	74.6	6.0	9.0	$C_{19}H_{18}N_2O_2$	74.49	5.92	9.14
IIIb	1	CN	125	-	158	75.1	6.3	8.8	$C_{20}H_{20}N_2O_2$	74.98	6.29	8.74
IIIc	2	CN	125	-	188	75.4	6.6	8.4	$C_{21}H_{22}N_2O_2$	75.42	6.63	8.38
IIId	3	CN	130	-	206	75.9	6.9	8.1	$C_{22}H_{24}N_2O_2$	75.83	6.94	8.04
IIIe	4	CN	94	-	198	76.3	7.3	7.7	$C_{23}H_{26}N_2O_2$	76.21	7.23	7.73
IIIf	5	CN	115.5	-	202	767	7.5	7.5	$C_{24}H_{28}N_2O_2$	76.56	7.50	7.44
IIIg	6	CN	90	-	187	76.9	7.8	7.2	$C_{25}H_{30}N_2O_2$	76.89	7.74	7.17
IIIh	7	CN	105	145	180	77.1	8.0	6.9	$C_{26}H_{32}N_2O_2$	77.19	7.97	6.92
IIIi	8	CN	116	161	181	77.5	8.2	6.6	$C_{27}H_{34}N_2O_2$	77.48	8.18	6.69
IIIj	9	CN	95	173	180	77.9	8.3	6.5	$C_{28}H_{36}N_2O_2$	77.74	8.39	6.48
IIIk	10	CN	82	179	-	78.0	8.6	6.3	$C_{29}H_{38}N_2O_2$	77.99	8.58	6.27
IIIl	1	C_4H_9	109	-	113	78.5	8.3	4.0	$C_{23}H_{29}NO_2$	78.59	8.32	3.99
IIIm	4	C_4H_9	106	155	157	79.4	9.0	3.6	$C_{26}H_{35}NO_2$	79.35	8.96	3.56
IIIn	5	C_4H_9	105	168	-	79.5	9.2	3.6	$C_{27}H_{37}NO_2$	79.56	9.15	3.44
IIIo	6	C_4H_9	109	164	-	79.9	9.3	3.4	$C_{28}H_{39}NO_2$	79.76	9.32	3.32
IIIp	7	C_4H_9	104	165	-	80.1	9.4	3.2	$C_{29}H_{41}NO_2$	79.95	9.49	3.22
IIIq	8	C_4H_9	104	165	-	80.2	9.7	3.1	$C_{30}H_{43}NO_2$	80.13	9.63	3.11

with mesogens of low polarity. In mixtures with the 4-cyanophenyl derivatives, the esters (II) exhibit both smectic and nematic mesophases. In the latter case, the thermal stability of the nematic phase is much lower than the value obtained by a linear extrapolation. For example, the mixture (1:1 by weight) of butyl 4-(4-pentylpiperidino)benzoate (IIc) with 4-hexyloxyphenyl 4-butylbenzoate (nematic from 29–49°C) is smectic A only ($T_{\mathrm{Sm-I}} = 45$°C), whereas the mixture of this ester with 4-(4-pentylbicyclo(2.2.2)octylbenzonitrile (nematic from 65–102°C) is nematic (C 26°C N 39°C I).

The 4-cyanophenyl 4-(4-alkylpiperidino)benzoates (III) exhibit high values of the positive dielectric anisotropy. The dielectric permittivities of the ester (IIIf) were measured for a 10% solution (C 45°C SmA 50°C N 107°C I) in 4-butyloxyphenyl 4-hexylbicyclo(2.2.2)octylcarboxylate (nematic from 49–95°C). The extrapolation procedure gave the values $\epsilon_{\parallel} = 41.0$, $\epsilon_{\perp} = 8.8$ and $\Delta\epsilon = 32.2$ at $T = 0.85\ T_{\mathrm{N-I}}$. The dielectric anisotropy of the pure compound (IIIe) undergoes a sign inversion at a frequency of 1.5 MHz at 110°C. The dielectric permittivity values at this temperature are the following (frequency in MHz, $\epsilon_{\parallel}$, $\epsilon_{\perp}$): 0.4, 17.6, 7.2; 0.6, 13.0, 7.2; 0.8, 10.5, 7.2; 1.0, 8.8, 7.1; 2.0, 6.1, 7.1; 3.0, 5.2, 7.1.

The polar esters(III a-k) form an induced smectic A mesophase when mixed with nematogens of low polarity, and only the nematic phase when mixed with polar nematogens. For example, when 4-cyanophenyl 4-(4-butylpiperidino)benzoate (IIIe) is mixed (1:1 by weight) with the above mentioned 4-hexyloxyphenyl 4-butylbenzoate, with 4-cyano-4′-pentyloxybiphenyl, and with 4-(4-pentylbicyclo(2.2.2) octylbenzonitrile, the phase transition temperatures of the mixtures obtained are respectively Sm 80°C N 118°C I, C 40°C N 127°C I, and C 37°C N 138°C I.

All the 4-butylphenyl 4-(4-alkylpiperidino)benzoates with alkyl higher than 4-n-pentyl-derivatives (III n-q)-exhibit the smectic A phase only. It is interesting that the phase transition temperatures are practically the same for a number of the higher homologues.

The acids (I), as well as the esters (II and III) are colourless crystalline compounds, which do not change their thermal parameters or decompose noticeably upon storing. In direct sunlight or upon UV-irradiation they become dark and lose their mesomorphic properties, though at a significantly slower rate than the initial 4-(4-alkylpiperidino)benzonitriles.

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