A Study of the Effect of a Lateral Methoxy Group on the Transition Temperature of the Liquid Crystalline Phases of the 4-(4-n-Heptyloxybenzoyloxy)-benzylidene-4-n-alkoxyaniline Series

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Transition temperatures of the liquid crystalline phases for the two homologous series 4-(4-n-heptyloxybenzoyloxy)benzylidene-4-n-alkoxyanilines and 4-(4-n-heptyloxybenzoyloxy)-3-methoxybenzylidene-4-n-alkoxyanilines were measured. A comparison of results between the two series shows that the lateral group lowers the temperature of the nematic–isotropic transition and eliminates a smectic phase.

Because of the various applications of liquid crystals, systematic studies of homologous series which correlate molecular structure with mesomorphic properties are of considerable interest.[1,2] (A review of recent work in this area is presented in ref. 3.) Of special interest are the effects of lateral substitution on mesogens which exist over a wide temperature range. Previous studies[4,5] have shown that the addition of a lateral group does not destroy the mesophases if the ratio of width to length of the molecule is smaller than a certain critical value; when this condition is satisfied, the lateral substitution of a chloro or a methyl group has been shown significantly to reduce the crystal–mesophase transition temperature.

In this work the first ten members of the 4-(4-n-heptyloxybenzoyloxy)benzylidene-4-n-alkoxyanilines (**1a**) were prepared and compared with series (**1b**) with a methoxy group substituted in the 3-position of the middle aromatic group.

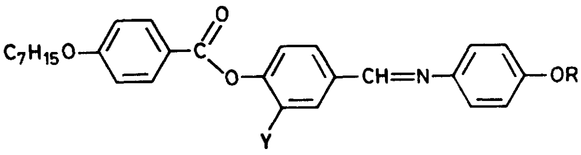
The transition temperatures for series (**1a**) can be seen in Table 1, and Figure 1 shows the temperature dependence of series (**1a**) as a function of the number of carbon atoms (n) in the alkoxy chain. A very wide nematic range is seen to exist for the first members of the series. The usual even–odd alternations of temperature of the nematic–isotropic (N–I) transition are observed, and a nematic phase is present in all compounds of the series, a smectic mesophase (S_C) appears for all compounds with $n \geq 2$ and a second monotropic smectic (S_B) mesophase appears for $n \geq 3$. As n increases the nematic range is reduced. The m.p. and the onset of the monotropic S_B phase show little dependence on n. Similar results have been described for the homologous series 1,4-phenylene bis(alkoxybenzoates)[6] but the phenylene benzoates are not easily supercooled and crystallize close to the m.p. and therefore a smectic B phase is not observed. Gray[7] had discussed the effects of molecular structure changes on the nematic phase and smectic polymorphism.

The behaviour of series (**1b**) is shown in Figure 2 and Table 2. The N–I transition temperature, like that of series (**1a**), is an alternating curve that decreases with n. This series has no smectic phase and the interval of temperature over which the nematic phase exists is essentially the same for all n. It would appear that the presence of the lateral methoxy group increases with the width of the molecule sufficiently to diminish the van der Waals attraction responsible for the parallel alignment in the nematic phase, thus decreasing the temperature interval of the existence of this phase and also causing a complete disappearance of the smectic phases. As stated above, the presence of a lateral group often considerably lowers the m.p. but this is not the case for these two series. We believe this might be because the crystal-structure packing in series (**1b**) is very similar to the nematic packing but an X-ray study would be necessary to prove this point. The S_C and S_B phases were identified and their textures observed by using polarizing optical microscopy.[8]

Table 1. Transition temperature (°C) for 4-(4-n-heptyloxybenzoyloxy)-benzylidene-4-n-alkoxyaniline (**1a**)

n	K		S_B		S_C		N		I
1	.	100.4			.		.	247.7	.
2	.	101.5			.	(73.8)	.	250.0	.
3	.	114.3	.	(85.2)	.	(108.0)	.	235.0	.
4	.	90.4	.	(87.1)	.	128.4	.	234.6	.
5	.	89.4	.	(79.1)	.	141.5	.	221.5	.
6	.	92.0	.	(80.9)	.	150.0	.	221.7	.
7	.	101.4	.	(84.7)	.	157.0	.	215.5	.
8	.	89.7	.	(82.3)	.	162.6	.	213.4	.
9	.	92.9	.	(80.4)	.	168.8	.	208.7	.
10	.	90.4	.	(77.2)	.	167.4	.	205.3	.

Monotropic transitions in parentheses.



(1)

	Y	R
(1a)	H	C_nH_{2n+1}
(1b)	OCH_3	C_nH_{2n+1}

n = 1,2,3,......10

Experimental

Measurements of transition temperatures and microscopic observations of textures of the mesophases were made using a Leitz–Ortholux polarizing microscope in conjunction with a Mettler FP-52 hot-stage, i.r. spectra were recorded for KBr discs with a Perkin-Elmer model 283 spectrometer, and ^1H n.m.r. spectra were measured for $CDCl_3$ solutions with tetramethylsilane as the internal standard with a Varian T60 spectrometer.

The *4-n-heptyloxybenzoic acids* and *4-n-alkoxybenzoyl chlorides* were prepared as described by Neubert *et al.*[9]

The 4-(*4-n-heptyloxybenzoyloxy*)*benzaldehydes* and 4-(*4-n-heptyloxybenzoyloxy*)-*3-methoxybenzaldehydes* were prepared by the methods of ref. 10.

The 4-(*4-n-heptyloxybenzoyloxy*)*benzylidene-4-n-alkoxyanilines* and 4-(*4-n-heptyloxybenzoyloxy*)-*3-methoxybenzylidene-4-alkoxyanilines* were prepared from 4-hydroxy- or 3-methoxy-benzaldehydes by adding a slight molar excess of the

Table 2. Transition temperatures (°C) for 4-(4-n-heptyloxybenzoyloxy)-3-methoxybenzylidene-4-alkoxyanilines (**1b**)

n	K		N		I
1	.	107.5	.	154.9	.
2	.	108.8	.	165.6	.
3	.	104.7	.	151.5	.
4	.	103.0	.	153.5	.
5	.	109.3	.	142.5	.
6	.	106.6	.	142.9	.
7	.	91.9	.	135.8	.
8	.	89.5	.	134.0	.
9	.	80.7	.	130.1	.
10	.	86.1	.	128.9	.

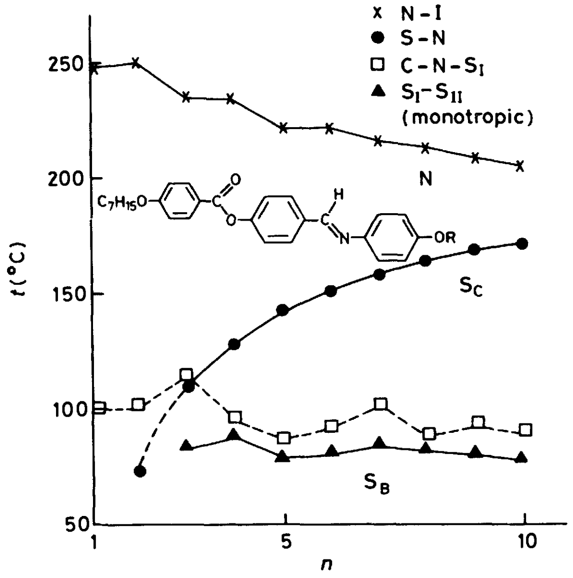


Figure 1. Plot of transition temperatures against the number of carbon atoms (*n*) in the alkoxy chain (RO) of the 4-(4-n-heptyloxybenzoyloxy)-benzylidene-4-n-alkoxyanilines (**1a**)

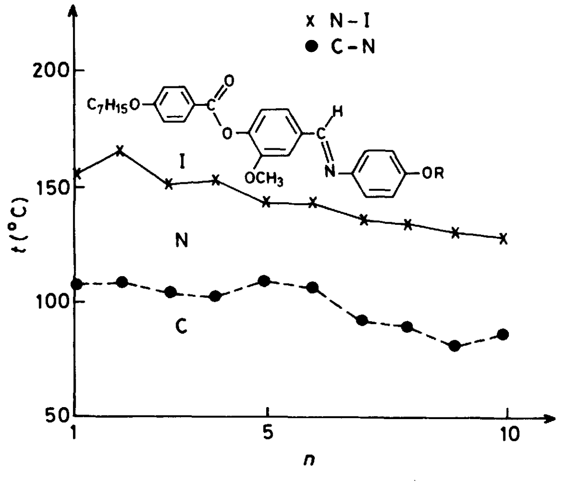


Figure 2. Plot of transition temperatures against the number of carbon atoms (*n*) in the alkoxy chain (RO) of the 4-(4-n-heptyloxybenzoyloxy)-3-methoxybenzylidene-4-n-alkoxyanilines (**1b**)

Table 3. Yields and elemental analyses of series (**1a**)

Molecular formula	Crude yield (%)	Found (%) (Required) C	H	N
n = 1	92	75.4	7.0	2.9
$C_{28}H_{31}NO_4$		(75.5)	(6.9)	(3.1)
n = 2	90	75.7	7.1	2.9
$C_{29}H_{33}NO_4$		(75.8)	(7.2)	(3.0)
n = 3	93	76.2	7.5	3.0
$C_{30}H_{35}NO_4$		(76.1)	(7.4)	(2.9)
n = 4	89	76.2	7.5	2.9
$C_{31}H_{37}NO_4$		(76.3)	(7.6)	(2.8)
n = 5	91	76.7	7.8	2.8
$C_{32}H_{39}NO_4$		(76.7)	(7.7)	(2.7)
n = 6	85	76.8	8.0	2.6
$C_{33}H_{41}NO_4$		(76.9)	(7.9)	(2.7)
n = 7	88	76.2	8.2	2.5
$C_{34}H_{43}NO_4$		(77.1)	(8.1)	(2.6)
n = 8	84	77.3	8.4	2.5
$C_{35}H_{45}NO_4$		(77.3)	(8.3)	(2.5)
n = 9	83	77.4	8.3	2.4
$C_{36}H_{47}NO_4$		(77.5)	(8.4)	(2.5)
n = 10	86	77.3	8.5	2.4
$C_{37}H_{49}NO_4$		(77.7)	(8.5)	(2.4)

Table 4. Yields and elemental analyses of series (**1b**)

Molecular formula	Crude yield (%)	Found (%) (Required) C	H	N
n = 1	89	73.4	6.8	2.8
$C_{29}H_{33}NO_5$		(73.2)	(6.9)	(2.9)
n = 2	90	73.8	7.3	2.8
$C_{30}H_{35}NO_5$		(73.6)	(7.1)	(2.8)
n = 3	87	73.7	7.1	2.6
$C_{31}H_{37}NO_5$		(73.9)	(7.3)	(2.7)
n = 4	93	74.2	7.6	2.8
$C_{32}H_{39}NO_5$		(74.3)	(7.5)	(2.7)
n = 5	93	74.3	7.6	2.6
$C_{33}H_{41}NO_5$		(74.6)	(7.7)	(2.6)
n = 6	88	74.7	7.6	2.4
$C_{34}H_{43}NO_5$		(74.8)	(7.9)	(2.5)
n = 7	85	75.0	8.2	2.5
$C_{35}H_{45}NO_5$		(75.1)	(8.0)	(2.5)
n = 8	87	75.3	8.1	2.3
$C_{36}H_{47}NO_5$		(75.4)	(8.2)	(2.4)
n = 9	91	75.8	8.4	2.4
$C_{37}H_{49}NO_5$		(75.6)	(8.3)	(2.3)
n = 10	84	75.4	8.6	2.4
$C_{38}H_{51}NO_5$		(75.8)	(8.5)	(2.3)

appropriate *p*-alkoxyaniline[11] and purified by several recrystallizations from ethanol or a mixture of ethanol and benzene. Yields and elemental analyses are shown in Tables 3 and 4.

Data for 4-(4-*n-heptyloxybenzoyloxy*)*benzylidene*-4-*n-pentylaniline* which are typical of the homogous series (**1a**) as a whole as follows (Found: C, 76.7; H, 7.8; N, 2.8. $C_{32}H_{39}NO_4$ requires C, 76.7; H, 7.9; H, 2.7%); $\nu_{max.}$(KBr) 2 962—2 872 (CH_2), 2 926—2 850 (CH_2), 1 730vs (CO), 1 605—1 590 (C=C), 1 470—1 390 (CH_3), 1 465 (CH_2), 1 280 (CO_2), 1 245—1 030 (COC), 850—830 (C=C), and 730 rock (CH) cm^{-1}; δ_H (60 MHz; solvent $CDCl_3$; standard Me_4Si) 0.90 (6 H, 2 t, 2 CH_3), 1.20—1.94 [16 H, br m, $(CH_2)_8$], 3.86—4.13 (4 H, 2 t, 2 OCH_2), 6.79—8.19 (12 H, m, ArH), and 8.42 (1 H, s, CH=N).

As a typical example of series (**1b**), data for 4-(4-*n-heptyloxybenzoyloxy*)-3-*methoxybenzylidene*-4-*methoxyaniline* are (Found: C, 73.4; H, 6.8; N, 2.8. $C_{29}H_{33}NO_5$ requires C, 73.2; H, 6.9; N, 2.9%); $\nu_{max.}$(KBr) 2 960—2 870 (CH_3), 2 926—2 850 (CH_2), 1 730vs (CO), 1 605—1 585 (C=C), 1 740—1 320 (CH_3), 1 460 (CH_2), 1 290 (CO_2Ar), 1 250—1 020 (COC), 890—810 (C=C), and 730 rock (CH_2) cm^{-1}; δ_H (60 MHz; solvent $CDCl_3$; standard Me_4Si) 0.90 (3 H, t, CH_3), 1.16—1.89 [10 H, br m,

$(CH_2)_5]$, 3.86 (3 H, s, OCH_3), 3.92 (3 H, s, OCH_3), 4.06 (2 H, t, OCH_2), 6.75—8.19 (11 H, m, ArH), and 8.43 (1 H, s, CH=N).

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