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The synthesis and liquid crystalline behaviour of 2-(4-*n*-alkoxyphenyl)-5-methylpyridines

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We have synthesized a new series of polyphenylene compounds with a pyridine ring, 2-(4-*n*-alkoxyphenyl)-5-methylpyridines ($CH_3C_5H_3NC_6H_4OC_iH_{2i+1}$) (**1a-*i***; the carbon number, *i*, of the alkoxy group is 1–9), and studied their phase transitions and mesogenicity using DSC and polarizing microscopy. In the homologous series of **1a-*i***, no mesomorphic phase appeared for $i = 1$–5 and only a monotropic nematic phase was observed for $i = 6$–9. The mesomorphic potential is relatively weaker for the **1a-*i*** than for the **2a-*i*** and **3a-*i*** homologues, which are pyridine-containing three- and four-ring similar systems. This lowering of the mesogenicity may be due to the lack of a phenyl ring between the pyridine ring and the methyl group in the **1a-*i*** homologues.

1. Introduction

Polyphenylene compounds containing nitrogen heterocycles have been fully studied by many groups because they are useful for liquid crystal displays [1–17]. The mesomorphism of pyridine-containing two- and three-ring systems has been an important part of these studies because they are important as liquid crystal forming materials and additives for liquid crystal displays [4, 5, 10, 15–17].

In previous papers [18, 19], we have reported the synthesis of three- and four-ring systems consisting of 2-(4-*n*-alkoxyphenyl)-5-(4-methylphenyl)pyridines, $CH_3C_6H_4C_5H_3NC_6H_4OC_iH_{2i+1}$) (**2a-*i***, $i = 1$–10) and 2-(4′-*n*-alkoxybiphenyl-4-yl)-5-(4-methylphenyl)pyridines ($CH_3C_6H_4C_5H_3NC_6H_4C_6H_4OC_iH_{2i+1}$) (**3a-*i***, $i = 1$–10) (figure 1). Their phase transitions and mesomorphism were studied using differential scanning calorimetry (DSC) and polarizing optical microscopy. The **2a-*i*** compounds showed only a nematic phase when $i \leqslant 3$, but gave the liquid crystalline (LC) polymorphism, $\mathrm{Cr} \rightleftarrows \mathrm{CrH} \leftarrow \mathrm{CrG} \leftrightarrows \mathrm{SmF} \leftrightarrows \mathrm{SmC} \leftrightarrows \mathrm{SmA} \leftrightarrows \mathrm{N} \leftrightarrows \mathrm{I}$, when $i \geqslant 4$. The **3a-*i*** compounds showed nematic phases for $i = 1$ and 2, but underwent characteristic polymesomorphic sequences when $i \geqslant 3$; $\mathrm{Cr} \leftrightarrows \mathrm{CrH} \leftrightarrows \mathrm{SmF} \leftrightarrows \mathrm{SmC} \leftrightarrows \mathrm{SmA} \leftrightarrows \mathrm{N} \leftrightarrows \mathrm{I}$ with $n = 3$ and 4, and $\mathrm{Cr} \leftrightarrows \mathrm{CrH} \leftrightarrows \mathrm{SmF} \leftrightarrows \mathrm{SmA} \leftrightarrows \mathrm{N} \leftrightarrows \mathrm{I}$ with $i = 5$–10. We noted that the LC polymorphism appeared in the homologues in which alkoxy chains are longer than $i = 3$ in the series **2a-*i*** and $i = 4$ in the series **3a-*i***; in other words, both series require a minimum terminal alkoxy length for the generation of the LC polymorphism. In this context, we were interested in finding whether the polymorphism can also be observed in shorter polyphenylene analogues and how the phase transitions appear.

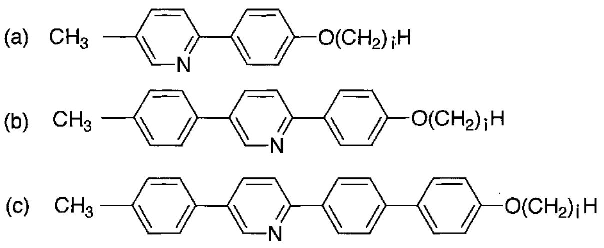

Figure 1. Chemical formulae of (*a*) the 2-(4-*n*-alkoxyphenyl)-5-methylpyridines (**1a-*i***, $i = 1$–9); (*b*) 2-(4-*n*-alkoxyphenyl)-5-(4-methylphenyl)pyridines (**2a-*i***, $i = 1$–10) and (*c*) 2-(4′-*n*-alkoxybiphenyl-4-yl)-5-(4-methylphenyl)pyridines (**3a-*i***, $i = 1$–10).

In this study, a new series of polyphenylene compounds containing a pyridine ring, the 2-(4-*n*-alkoxyphenyl)-5-methylpyridines ($CH_3C_5H_3NC_6H_4OC_iH_{2i+1}$)

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(**1a-*i***; the carbon number, *i*, of the alkoxy group is 1–9) have been synthesized and their phase transitions and mesomorphisms studied using DSC and polarizing microscopy. The phase transition behaviour of **1a-*i*** is compared with that of the series of similar three- and four-ring systems **2a-*i*** and **3a-*i***. The molecular formulae for series **1a-*i***, **2a-*i*** and **3a-*i*** are shown in figure 1.

2. Experimental

2.1. *Synthesis*

Compounds **1a-*i*** were synthesized using the versatile palladium complex assisted aryl–aryl coupling reaction [20]. Representative syntheses of compounds **1a-1** and **1a-6** are described below.

2.1.1. *2-(4-Methoxyphenyl)-5-methylpyridine (1a-1)*

A mixture of 4-methoxyphenylboronic acid (16.0 g, 0.106 mol), aqueous NaOH (6.40 g, 0.16 mol in 100 ml of water), 2-chloro-5-methylpyridine (13.6 g, 0.106 mol) and tetrakis(triphenylphosphine)palladium (1.50 g, 1.30 mmol) in ethylene glycol dimethyl ether (400 ml) was heated at 80°C for 7 h. After adding water (200 ml), the organic layer was shaken with ethyl acetate (200 ml) and the extract dried. The crude product was purified by column chromatography (SiO_2, 1:2 ethyl acetate: hexane) followed by recrystallization from ethanol to give colourless crystals, 9.59 g (45.0% yield) of **1a-1**, m.p. 328 K. ^1H NMR: δ 8.5 (s, 1H), 8.0 (q, 6.8 Hz, 2H), 7.5 (m, 2H), 7.0 (q, 6.8 Hz, 2H), 3.9 (s, 3H), 2.4 (s, 3H). IR: 2963, 2860, 1608, 1582, 1513, 1477, 1250, 1026, 816 cm^{-1}. Found: C, 78.31, H, 6.50, N, 6.89; calc. for $C_{13}H_{13}NO$: C, 78.36, H, 6.58, N, 7.03%.

2.1.2. *2-(4-Hexyloxyphenyl)-5-methylpyridine (1a-6)*

The higher homologues were prepared as follows. 2-(4-Methoxyphenyl)-5-methylpyridine (8.24 g, 41.4 mmol) and hydrobromic acid (3.36 g, 0.414 mol) in acetic acid (35 ml) were heated at 120–130°C under reflux for 24 h. The reaction mixture was poured into water (50 ml) and aqueous sodium hydroxide was added until the pH of the solution was 11–12. The resulting mixture was extracted with ether (100 ml) and the extracts discarded. The aqueous phase was neutralized with MHCl and left to stand overnight. The precipitate of crude materials was then recrystallized from benzene, affording 3.30 g (43.0% yield) of 2-(4-hydroxyphenyl)-5-methylpyridine (HPMP). The purity of the sample was confirmed by TLC (SiO_2, ethyl acetate) and ^1H NMR. Finally, **1a-6** was synthesized by heating a solution of HPMP (0.41 g, 2.2 mmol), 1-bromohexane (0.42 g, 2.4 mmol) and potassium carbonate (0.46 g, 3.3 mmol) in methyl ethyl ketone (15 ml) at 80°C for 7 h. After work-up of the reaction mixture and subsequent purification by column chromatography (SiO_2, 1:2 ethyl acetate : hexane), the product was recrystallized from ethanol to afford 0.42 g (71% yield) of **1a-6**, m.p. 335 K. ^1H NMR: δ 8.5 (s, 1H), 7.9 (q, 8.8 Hz, 2H), 7.5 (m, 2H), 7.0 (q, 4.4 Hz, 2H), 4.0 (t, 6.8 Hz, 3H), 1.3–1.8 (m, 7.2 Hz, 3H), 0.9 (t, 7.2 Hz, 3H). IR: 2948, 2867, 1609, 1582, 1517, 1472, 1253, 1021, 816 cm^{-1}. Found: C, 80.24, H, 8.53, N, 5.09; calc. for $C_{18}H_{23}NO$: C, 80.25, H, 8.61, N, 5.20%.

The other homologues of series **1a-*i*** were synthesized and their purities confirmed by methods similar to those above.

2.2. *Analytical techniques and instruments*

Phase transition temperatures were measured using a differential scanning calorimeter (Seiko Instruments DSC 210 and SSC 5500 system) at heating/cooling rates of 5 K min^{-1} between room temperature and above the melting point. The apparatus was calibrated using indium (T_m 429.6 K, ΔH 28.5 J g^{-1}) and tin (T_m 505.1 K, ΔH 59.5 J g^{-1}). Texture observations were made with crossed polarizers using an optical polarizing microscope (Nikon Optiphot-pol XTP-11) equipped with a Mettler FP 82 hot stage used at a heating/cooling rate of 5 K min^{-1} between room temperature and above the melting or clearing point. ^1H NMR (solvent $CDCl_3$) spectra were recorded on a JEOL JNM-A400 spectrometer using TMS as the internal standard. IR spectra were measured for KBr discs using a Perkin-Elmer FTIR 1640.

3. Results and discussion

The DSC thermograms of **1a-1** and **1a-6** are shown in figure 2 for the first cooling and second heating processes. In **1a-1**, only one exothermic peak was observed at 301 K for the first cooling process. Polarizing optical

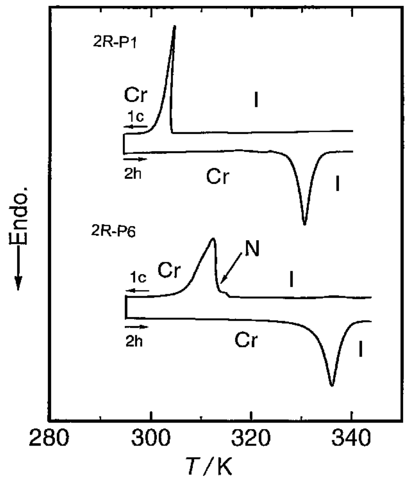

Figure 2. DSC thermograms of **1a-1** (top) and **1a-6** (bottom), representative of compounds **1a-*i*** (*i* = 1–9).

microscopy showed a change from black isotropic liquid to a texture of a crystal with birefringence; no mesomorphic phase was observed during the cooling process. Therefore, the exothermic peak at 301 K corresponds to an isotropic liquid–crystal phase transition. In the second heating process of **1a-1**, only one endothermic peak was observed at 328 K, at which temperature the field of view in the microscope became black with crossed polarizers; this corresponds to the melting of the crystal to the isotropic liquid. No mesomorphic phase was observed during the heating process. The second cooling and third heating processes reproduced the previous thermal hysteresis.

In the first DSC cooling process for **1a-6**, two exothermic peaks were observed at 318 and 314 K. The peak at 317 K is very small ($\Delta S = 1$ J K^{-1} mol^{-1}), showing that the order in the intermediate phase is very close to that in the isotropic liquid. On polarizing microscopy using crossed polarizers, cooling from the isotropic liquid gave a schlieren texture with defects having two or four dark brushes, showing the existence of a nematic phase [21]. Upon further cooling, a large exothermic peak was observed at 314 K in the DSC thermogram. At this temperature the sample changed from nematic to a crystal phase as seen by polarizing microscopy. On the second heating process of **1a-6**, only one endothermic peak corresponding to melting was observed at 335 K. No mesomorphic phase was observed during the heating process by polarizing microscopy. The phase transition temperatures and entropies obtained from the DSC measurements for the homologous series **1a-*i*** ($i = 1$–9) are shown in table 1. The nematic–isotropic phase transition entropies are about 1–2 J K^{-1} mol^{-1}, showing that the order in the nematic phase is very low and very close to that in an isotropic liquid.

In figure 3, the phase transition temperatures are plotted against the end alkoxy carbon number, *i*, for the homologous series **1a-*i***. In this figure, full black circles show the melting transition in the second heating process. The open circles show the freezing points and the open triangles are the I–N phase transition temperature. For carbon number smaller than 5 in the series **1a-*i***, no mesomorphic phase was observed. For carbon numbers 6–9, only a single monotropic nematic phase was observed, and the monotropic liquid crystal temperature region before crystallization occurred was as narrow as about 3 K. This shows that the nematic phase is thermodynamically metastable in **1a-*i***. Odd–even effects of the melting point were clear for end alkoxy carbon numbers of 1–5, but unclear for $i = 6$–9.

Table 1. Phase transition temperatures (T/K) and, in parentheses, transition enthalpies (ΔH/kJ mol^{-1}) followed by entropies (ΔS/J K^{-1} mol^{-1}) of compounds **1a-*i*** in the second heating process. Square brackets show the monotropic phase.

1a-*i*	Cr		N		I
1	•	328/(20, 62)		—	•
2	•	364/(21, 59)		—	•
3	•	349/(24, 70)		—	•
4	•	363/(33, 91)		—	•
5	•	338/(26, 78)		—	•
6	•	335/(27, 81)	•	[318/(0.3, 1)]	•
7	•	332/(31, 96)	•	[324/(0.3, 1)]	•
8	•	332/(31, 94)	•	[325/(0.7, 2)]	•
9	•	338/(41, 120)	•	[326/(0.7, 2)]	•

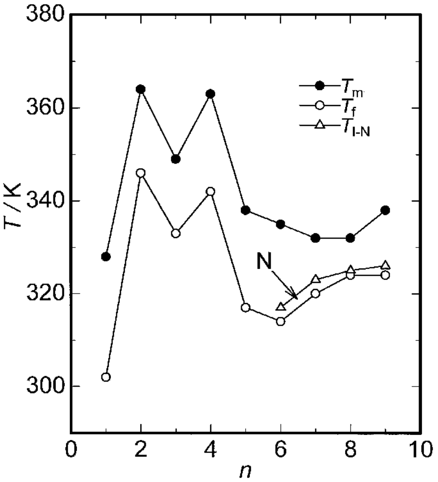

Figure 3. Carbon number dependence of phase transition temperatures in **1a-*i*** ($i = 1$–9). T_m: melting point; T_f: freezing point.

In similar pyridines containing three- and four-ring systems, **2a-*i*** and **3a-*i*** (see figure 1 and table 2 in which the phase transition temperatures of **2a-*i*** and **3a-*i*** are listed), the clearing points are higher than about 480 and 600 K, respectively, and for some of the compounds in the **3a-*i*** series $T_{N\text{-}I}$ could not be determined due to thermal decomposition. In comparison, for the **1a-*i*** system, the melting points are about 350 K and lower than those of the **2a-*i*** and **3a-*i*** compounds. The liquid crystalline phases in **2a-*i*** and **3a-*i*** have higher thermal stabilities than those in **1a-*i*** and also mesomorpic polymorphism was observed for $i \geqslant 4$ in the three- and $i \geqslant 3$ in the four-ring systems. On the other hand, in the pyridine-containing two-ring systems, **1a-*i***, only a monotropic nematic phase was observed for the larger carbon numbers, $i = 6$–9, over a small temperature range (2–3 K), and no mesomorphic polymorphism was observed between the carbon numbers 1 and 9. Therefore, the mesomorphic phases in **1a-*i*** are less stable than those in the corresponding three- and four-ring systems. This suggests that the phenyl ring between the methyl group

Table 2. Phase transition temperatures (T/K) of compounds **2a-*i*** ($i = 1$–10) and **3a-*i*** ($i = 1$–10) in the second heating process.

2a-*i*	Cr		CrH		CrG		SmF		SmC		SmA		N		I	**3a-*i***	Cr		CrH		SmF		SmC		SmA		N		I
1	•	458	—		—		—		—		—		•	513	•	**1**	•	537	—		—		—		—		•	d[a]	
2	•	456	—		—		—		—		—		•	521	•	**2**	•	541	—		—		—		—		•	d[a]	
3	•	444	—		—		—		—		—		•	503	•	**3**	•	522	•	530	•	549	•	553	•	555	•	d[a]	
4	•	425	—		•	429	•	431	•	433	•	434	•	503	•	**4**	•	487	•	522	•	548	•	558	•	574	•	668	•
5	•	(380)[b]	•	406	•	421	•	431	•	441	•	443	•	493	•	**5**	•	445	•	518	•	548	—		•	589	•	654	•
6	•	(373)	•	398	•	403	•	427	•	441	•	447	•	491	•	**6**	•	435	•	514	•	546	—		•	590	•	642	•
7	•	(361)	•	392	•	413	•	430	•	437	•	455	•	484	•	**7**	•	424	•	512	•	545	—		•	597	•	633	•
8	•	(362)	•	389	•	415	•	427	•	434	•	457	•	480	•	**8**	•	415	•	510	•	543	—		•	599	•	623	•
9	•	(363)	•	386	•	408	•	426	•	435	•	460	•	475	•	**9**	•	400	•	506	•	540	—		•	598	•	612	•
10	•	(366)	•	384	•	406	•	424	•	429	•	461	•	472	•	**10**	•	395	•	506	•	539	—		•	600	•	609	•

[a] Thermal decomposition.
[b] Parenthesis show the monotrophic phases.

and the pyridine ring in the three- and four-ring systems contributes decisively to the thermodynamic stability of the enantiotropic mesomorphic phase as well as to the smectic polymorphism in the three- and four-ring systems, probably by weakening the influence of the pyridine ring nitrogen, with its lone pair of electrons which exerts a relatively strong interaction between the molecules, at the methyl end. Another reason for the lower mesogenicity in series **1a-*i*** is of course their lower molecular weights and shorter rigid cores resulting in low N–I temperatures, below the melting points.

In conclusion, in the newly prepared two rings series containing a pyridine ring, the 2-(4-*n*-alkoxyphenyl)-5-methylpyridines ($i = 1$–9), no mesomorphic phase was observed for $i = 1$–6 and only a monotropic nematic phase was found between the alkoxy lengths $i = 6$–9. Clearly, the two-ring system has a much lower mesomorphic thermal stability than the three-ring (**2a-*i***) and four-ring (**3a-*i***) homologues. This is ascribed partly to the lack of the phenyl ring between the pyridine ring and the end methyl groups in **1a-*i*** and its effect in weakening the polar effect of the pyridine ring over the whole molecule.

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