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Effect of the pentafluorophenyloxy group on liquid crystalline behaviour

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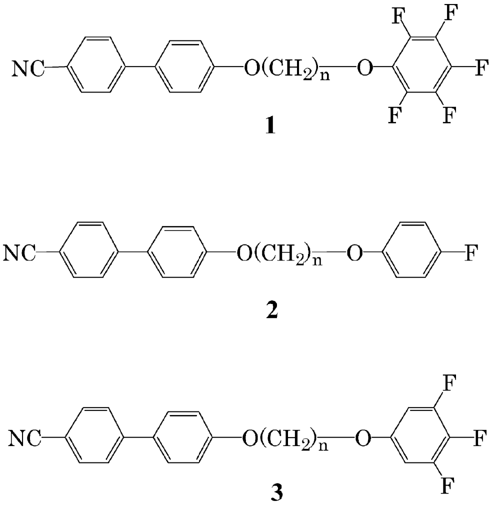
A new series of liquid crystalline compounds, the α-(4-cyanobiphenyl-4′-yloxy)-ω-(pentafluorophenyloxy)alkanes, were synthesized. The nematic–isotropic transition temperatures of the compounds showed a remarkable odd–even effect on increasing the length of the alkyl chain. In order to establish the effect of the pentafluorophenyloxy group, the α-(4-cyanobiphenyl-4′-yloxy)-ω-(4-fluorophenyloxy)alkanes and the α-(4-cyanobiphenyl-4′-yloxy)-ω-(3,4,5-trifluorophenyloxy)alkanes were also prepared. The comparison of the properties of these three series revealed interesting effects of the pentafluorophenyloxy group on the liquid crystalline properties.

1. Introduction

Perfluoroalkyl chains play an important role in determining the liquid crystalline behaviour of perfluoroalkyl-substituted compounds, e.g. in block copolymers containing liquid crystalline segments [1], because the perfluorinated moiety shows a strong tendency to segregate from the non-fluorinated core. However, Guittard and Geribaldi have shown that the introduction of perfluoroalkyl chains into a liquid crystalline molecule does not necessarily lead to an improvement in thermotropic liquid crystallinity [2]. Fluorinated aromatic groups [3] are of interest in the development of liquid crystalline materials for technological applications such as the active matrix device [4]; the influence of perfluorinated aromatic groups on liquid crystal behaviour has been reported in [5–8].

The pentafluorophenyl group is of interest in various fields, e.g. complex formation [9], organic synthesis [10], for the arene/perfluoroarene interaction [11] and in electronic devices [12]. The arene/perfluoroarene interaction leads to the formation of a variety of supramolecular assemblies [13]. Although the perfluoroarenes are generally immiscible with conventional liquid crystalline materials [5], the supramolecular assembly mediated by the perfluoroarene/arene interaction has an interesting influence on liquid crystal phase behaviour [6, 7]. In addition, liquid crystal formation involving pentafluorophenyl derivatives *via* halogen bonding has been reported [8]. We have studied the attachment of the pentafluorophenyloxy group to the well known liquid crystalline molecule, 4-cyano-4′-alkoxybiphenyl, as a terminal bulky moiety. Thus a new series of liquid crystalline compounds containing the pentafluorophenyloxy group, α-(4-cyanobiphenyl-4′-yloxy)-ω-(pentafluorophenyloxy)alkanes **(1)**, have been synthesized (figure 1).



a) n = 12, **b)** n = 11, **c)** n = 10, **d)** n = 9, **e)** n = 8,

f) n = 7, **g)** n = 6, **h)** n = 5, **i)** n = 4

Figure 1.

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2. Experimental

2.1. *Characterization*

Differential scanning calorimetry (DSC) measurements were carried out with a Shimadzu DSC-60 instrument. Microscopy observations were performed under a Nikon Eclipse E600 POL equipped with a hot stage (Tokai Hit ThermoPlate). Elemental analyses were performed in the Analytical Center of Kyoto University. ^{1}H NMR spectra (400 MHz) were obtained with a Jeol GSX 400 spectrometer. The chemical shifts (δ-values) were measured in parts per million (ppm) down-field from tetramethylsilane as an internal reference.

2.2. *Synthesis*

Treatment of 4-cyano-4′-hydroxybiphenyl and α,ω-dibromoalkane in the presence of K_2CO_3 gave α-bromo-ω-(4-cyanobiphenyl-4′-yloxy)alkane [14]. A mixture of α-bromo-ω-(4-cyanobiphenyl-4′-yloxy)alkane (1.0 mmol) and pentafluorophenol (1.2 mmol) in *N*,*N*-dimethylformamide (40 ml) in the presence of K_2CO_3 (1.0 mmol) was stirred for 24 h at room temperature. The reaction mixture was evaporated to give a residue, which was then chromatographed over silica gel. Elution with a mixture of hexane and chloroform gave compound **1** in 15–22% yields.

Under similar conditions the reaction of α-bromo-ω-(4-cyanobiphenyl-4′-yloxy)alkane (1.0 mmol) with 4-fluorophenol or 3,4,5-trifluorophenol (1.2 mmol) in *N*,*N*-dimethylformamide (40 ml) in the presence of K_2CO_3 (1.0 mmol) gave compounds **2** or **3** in 40–68% yields.

2.2.1. 1-(4-Cyanobiphenyl-4′-yloxy)-12-(pentafluorophenyloxy)dodecane (1a). ^{1}H NMR ($CDCl_3$) δ 7.69 (d, 2H, J=8.8 Hz), 7.64 (d, 2H, J=8.8 Hz), 7.53 (d, 2H, J=8.8 Hz), 6.99 (d, 2H, J=8.8 Hz), 4.14 (t, 2H, J=6.4 Hz), 4.01 (t, 2H, J=6.4 Hz), 1.81 (t, 2H, J=6.4 Hz), 1.76 (t, 2H, J=6.4 Hz), 1.5–1.2 (m, 16H). HRFABMS *m*/*z*: calcd for $C_{31}H_{32}NO_2F_5$ (M^+) 545.2353; found 545.2354. Elemental analysis: calcd for $C_{31}H_{32}F_5NO_2$, C 68.25, H 5.91, N 2.57%; found, C 68.40, H 5.82, N 2.56%.

2.2.2. 1-(4-Cyanobiphenyl-4′-yloxy)-6-(pentafluorophenyloxy)hexane (1g). ^{1}H NMR ($CDCl_3$) δ 7.68 (d, 2H, J=8.8 Hz), 7.63 (d, 2H, J=8.8 Hz), 7.52 (d, 2H, J=8.8 Hz), 6.98 (d, 2H, J=8.8 Hz), 4.17 (t, 2H, J=6.4 Hz), 4.02 (t, 2H, J=6.4 Hz), 1.83 (m, 4H), 1.57 (broad s, 4H). HRFABMS *m*/*z*: calcd for $C_{25}H_{20}NO_2F_5$ (M^+) 461.1414; found 461.1414.

2.2.3. 1-(4-Cyanobiphenyl-4′-yloxy)-12-(4-fluorophenyloxy)dodecane (2a). ^{1}H NMR ($CDCl_3$) δ 7.66 (d, 2H, J=8.8 Hz), 7.62 (d, 2H, J=8.8 Hz), 7.51 (d, 2H, J=8.8 Hz), 6.98 (d, 2H, J=8.8 Hz), 6.93 (d, 2H, J=8.8 Hz), 6.81 (m, 2H), 3.99 (t, 2H, J=6.4 Hz), 3.89 (t, 2H, J=6.4 Hz), 1.77 (m, 4H), 1.5–1.2 (m, 16H). Elemental analysis: calcd for $C_{31}H_{36}FNO_2$, 78.61, H 7.66, N 2.96; found, C 78.40, H 7.63, N 2.98%.

2.2.4. 1-(4-Cyanobiphenyl-4′-yloxy)-12-(3,4,5-trifluorophenyloxy)dodecane (3a). ^{1}H NMR ($CDCl_3$) δ 7.67 (d, 2H, J=8.8 Hz), 7.64 (d, 2H, J=8.8 Hz), 7.52 (d, 2H, J=8.8 Hz), 6.99 (d, 2H, J=8.8 Hz), 6.49 (m, 2H), 4.01 (t, 2H, J=6.4 Hz), 3.86 (t, 2H, J=6.4 Hz), 1.78 (m, 4H), 1.5–1.2 (m, 16H). Elemental analysis: calcd for $C_{31}H_{34}F_3NO_2$, C 73.06, H 6.72, N 2.75; found, C 73.21, H 6.69, N 2.75%.

3. Results and discussion

The thermal behaviour of **1** was analysed using differential scanning calorimetry (DSC) and the polarizing microscope. **1a**–**i** exhibited liquid crystallinity, although in **1b**, **1c**, **1f**, and **1h**, liquid crystalline behaviour was seen only on cooling. In this homologous series, **1a** and **1g** (n=12 and 6, respectively) had significantly broader mesomorphic ranges, than the other compounds (figure 2). A focal-conic fan texture and a schlieren texture were observed for **1a** at 50°C and at 59°C, respectively, suggesting that **1a** had smectic A (SmA) and nematic (N) phases. By contrast, only a schlieren texture was observed for **1g**. The liquid crystalline properties of **1a**–**i** are summarized in table 1. It is interesting to note that the phenyloxy analogue of **1g** is a monotropic nematogen having a higher nematic–isotropic transition temperature [15].

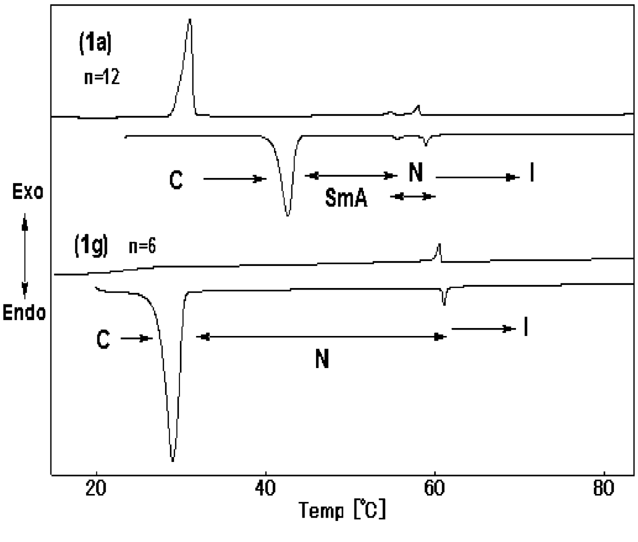

Figure 2. DSC thermograms for **1a** and **1g**, obtained on heating and cooling at 3°C min^{-1}. After a few hours, **1g** crystallized at room temperature. Cr=crystal, SmA=smectic A, N=nematic, I=isotropic liquid.

Table 1. Phase transition temperatures and the thermodynamic data for compounds **1**, **2**, and **3**. T_{Mp}=melting point (°C); T_{SmN}=SmA–N transition temperature (°C); T_{NI}=N–I (isotropic liquid) transition temperature (°C). ΔH=enthalpy change (kJ mol^{-1}). ( ) indicates a monotropic transition.

Compound	*n*	$T_{\mathrm{Mp}}/\Delta H$	$T_{\mathrm{SmN}}/\Delta H$	$T_{\mathrm{NI}}/\Delta H$
1a	12	43/26.0	56/0.4	59/1.1
1b	11	58/41.0	(43/0.4)	(47/0.5)
1c	10	70/42.0	(50/0.3)	(58/1.1)
1d	9	38/26.2		40/1.1
1e	8	50/26.1		60/0.8
1f	7	46/26.0		(25/0.4)
1g	6	30/24.9		61/0.7
1h	5	44/25.1		(17*)
1i	4	61/20.5		65/0.5
2a	12	98/47.0		(77/2.7)
2e	8	104/37.6		(89/1.9)
2g	6	93/31.0		99/1.6
2i	4	102/28.4		111/1.5
3a	12	79/32.9	(40/0.4)	(61/1.1)
3g	6	72/27.4		(63/0.6)
3i	4	92/27.0		(65/0.4)

^{a}Phase transition temperature determined only by polarizing microscopy.

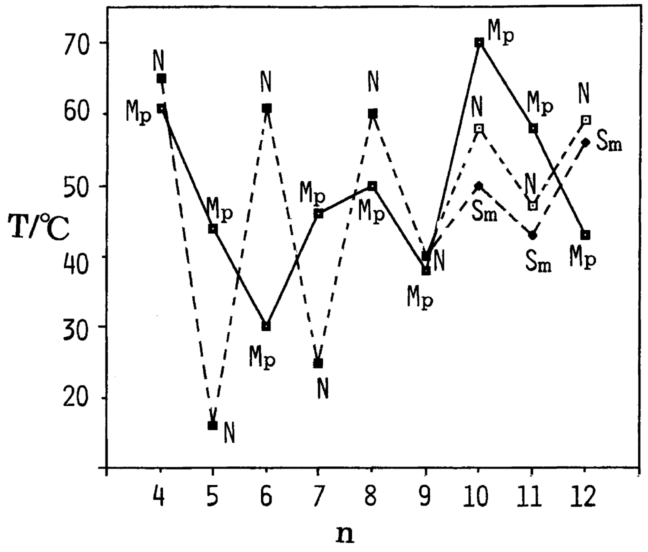

Figure 3. The relationship between the carbon numbers (*n*) of the alkyl chains in **1** and the phase transition temperatures. ———=the relationship of the melting points (Mp); ------=the relationship of the liquid crystal transition temperatures; N=nematic–isotropic transition temperature on heating, or isotropic–nematic transition temperature on cooling, when the compound had no LC properties on heating; Sm=smectic–nematic transition on heating or nematic–smectic transition on cooling.

Gray and Harrison have reported the remarkable odd–even effect exhibited by the nematic–isotropic transition temperatures for several liquid crystalline compounds substituted with a terminal phenyl moiety, such as the ω-phenylalkyl 4-*p*-cyanobenzylideneaminocinnamates [16]. In this connection, the relationship between the number of carbon atoms (*n*) in the alkyl chain for **1a**–**i** and the phase transition temperatures (liquid crystal transition temperatures and melting points) is shown in figure 3. As can be seen, **1a**–**i** also showed a pronounced odd–even effect in their clearing temperatures. The results are similar to the odd–even effects seen for liquid crystal dimers [17]. Thus, the weak odd–even effect shown by the clearing temperatures of the 4-cyano-4′-alkoxybiphenyls was greatly increased by the introduction of the pentafluorophenyloxy group; this is consistent with the data of Gray and Harrison [16]. Furthermore the introduction of the pentafluorophenyloxy group resulted in a lowering of the melting points.

The introduction of the 4-fluorophenyloxy and 3,4,5-trifluorophenyloxy groups, instead of the pentafluorophenyloxy group, into the 4-cyano-4′-alkoxybiphenyls may also lead to similar liquid crystalline behaviour. In order to investigate this possibility, the α-(4-cyanobiphenyl-4′-yloxy)-ω-(4-fluorophenyloxy)alkanes **(2)** and α-(4-cyanobiphenyl-4′-yloxy)-ω-(3,4,5-trifluorophenyloxy) alkanes **(3)** were prepared. Compounds **2** and **3** also exhibited liquid crystalline behaviour, but neither the 4-fluorophenyloxy nor the 3,4,5-trifluorophenyloxy group had such a pronounced effect on the mesomorphic ranges, when compared with the pentafluorophenyloxy group. For example, it can be seen in table 1 that all the 3,4,5-trifluorophenyloxy-substituted compounds that were prepared showed only monotropic liquid crystalline behaviour. By comparison, the pentafluorophenyloxy group (see, for example, **1a** and **1g**), contributed to an improvement in the thermotropic liquid crystalline properties, because of the reduced melting points and the odd–even effect of the clearing temperatures (figure 3). The specific liquid crystalline behaviour of **1** may be attributed to the segregation of the pentafluorophenyloxy and 4-cyanobiphenyl-4′-yloxy groups.

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