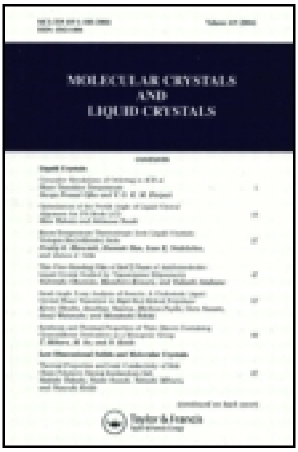

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The Synthesis and Liquid Crystal Properties of certain 4′-Alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl-trans-4-alkylcyclohexane-1-carboxylates

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The Synthesis and Liquid Crystal Properties of certain 4′-Alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl-*trans*-4-alkylcyclohexane-1-carboxylates

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The synthesis and liquid crystal properties of eighteen members of the homologous series of 4′-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl-*trans*-4-alkylcyclohexane-1-carboxylates are reported. The compounds are low melting nematogens possessing a moderately wide N-I range and have refractive indices comparable with that of fused silica. Because of these properties the compounds may have a potential use as additives to mixtures for the TN mode or in applications where nematogens with a uniquely low refractive index are required.

INTRODUCTION

During the last decade, lateral fluoro-substitution of mesogenic compounds have been throughly investigated with the aim of extending and modifying the properties of known liquid crystal systems.[1–4] Initial work, e.g. by Balkwill *et al.*,[1] has been supported by subsequent studies[2–4] and has established that the introduction of a lateral fluoro-substituent into a biphenyl core may modify the properties of a mesogen in one or more of the following ways:

i cause a reduction in the melting point;
ii lead to a reduction of smectic thermal stability or the complete elimination of smectic phases;
iii give rise to tilted smectic phases, eg S_C, S_I.

A fluoro-substituent has a relatively small size and high electronegativity. When located *ortho*- to the inter-ring bond of the biphenyl nucleus, a fluoro-substituent causes a relatively small increase in the degree of twist about this bond resulting in a torsional angle of approximately 51° compared with the torsional angle in biphenyl itself which is approximately 32°.[5] An additional feature is that *ortho*-fluoro-substitution normally does not disrupt the intermolecular forces and the linearity of the molecule sufficiently to prevent mesophase formation, although recent studies of the

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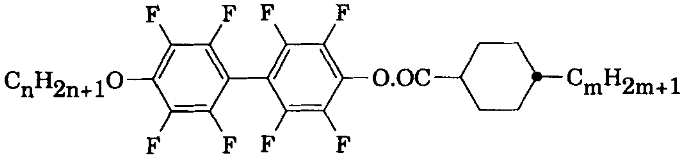
influence of lateral fluorination on the mesomorphic properties of systems containing both biphenyl and terphenyl cores have shown a dependency on the number and disposition of the fluoro-substituents.[6,7]

The effect of very extensive lateral fluoro-substitution on the behaviour of mesogens has not been studied and this paper reports an extension of the investigation of lateral fluoro-substitution to symmetrical poly-substitution within a biphenyl core. We decided to commence this study with an investigation of *fully fluorinated* biphenyl compounds although, intuitively at the outset, we were not confident of obtaining mesomorphic materials derived from a 4,4′-disubstituted biphenyl carrying eight lateral fluoro-substituents in the central core. However, decafluorobiphenyl, although expensive, is commercially available, and the 4- and 4′-fluoro-substituents of this compound may be replaced by nucleophiles. It is therefore a convenient starting material for the preparation of a novel series of symmetrically fluorinated esters (**1**) derived from 4-alkoxy-4′-hydroxy-2,2′,3,3′5,5′6,6′-octafluorobiphenyls (**2**), the synthesis and liquid crystal properties of certain members of which we report here. The esters (**1**), which contain a *trans*-4-alkylcyclohexane-1-carboxylic acid as the acid moiety, were chosen to achieve a balance between the dipolarity of the ester function and the low polarisability of the cyclohexane ring, and with the expectation of achieving a compromise between low melting points and reasonably high T_{N-I} values if the resulting esters were mesomorphic. Other related compounds which also contain the octafluorobiphenyl core unit are covered by patent applications[8,9] and are not reported here.

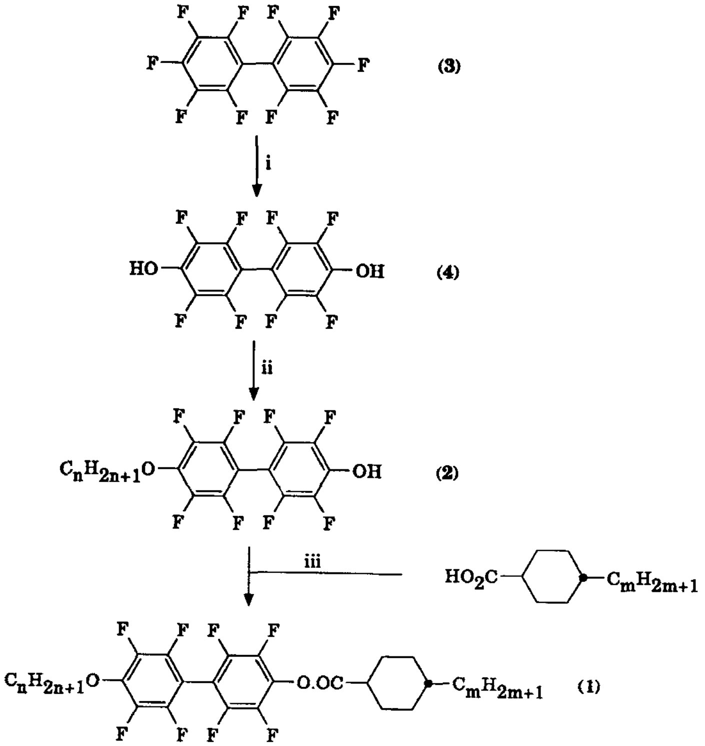


(1)

SYNTHESIS

The synthetic route for the preparation of the esters (**1**) derived from appropriate 4-alkoxy-4′-hydroxy-2,2′,3,3′,5,5′6,6′-octafluorobiphenyls (**2**) and *trans*-4-alkylcyclohexane-1-carboxylic acids is shown in Scheme 1.

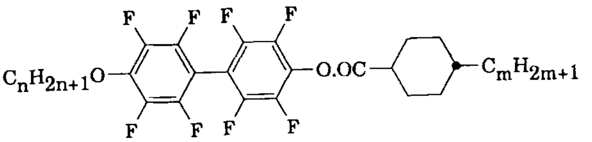
Decafluorobiphenyl (**3**) readily undergoes nucleophilic substitution at the 4- and 4′-positions. When heated under reflux in *tert*-butanol in the presence of potassium hydroxide the fluoro-substituents at the active positions are replaced by the hydroxyl moiety affording 4,4′-dihydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl (**4**). The anomalously low yield (50%) may be attributed to the formation of the *tert*-butoxide anion which itself competes as a nucleophile resulting in the formation of mono-and di-*tert*-butoxy compounds as undesirable side-products.[10] On treatment of compound (**4**) with the appropriate 1-bromoalkane the required 4-alkoxy-4′-hydroxy-2,2′,3,3′,5,5′6,6′-octafluorobiphenyls (**2**) are formed. These, on esterification with a *trans*-4-alkylcyclohexane-1-carboxylic acid by the DCC method,[11] afforded the required 4′-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl-*trans*-4-alkylcyclohexane-1-carboxylates (**I**).



i. *tert*-butanol, KOH, reflux.
ii. 1-bromoalkane, KOH, reflux.
iii. DCC, 4-(N-pyrrolidino)pyridine, CH_2Cl_2, room temperature.

SCHEME 1

TABLE I
Liquid crystal transition temperatures for 4′-*n*-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl-*trans*-4-alkylcyclohexane-1-carboxylates (1).



(1)

Transition temperature/°C

	$m=3$		$m=5$		$m=7$	
n	C—N	N—I	C—N	N—I	C—N	N—I
5	58	105	43	112	58	102
6	56	101	40	109	57	102
7	46	95	41	100	55	97
8	54	94	54	99	57	95
9	52	87	53	93	55	92
10	50	84	53	91	59	91

RESULTS AND DISCUSSION

For each homologous series (alkyl: $m = 3,5,7$) of esters (**1**) six members (alkoxy: $n = 5,6,7,8,9,10$) were prepared. Remarkably, in view of the presence of such a large number of polar fluoro-substituents, these esters have quite low melting points and relatively high T_{N-I} values. None of the homologues studied gives rise to smectic phases. The liquid crystal transition temperatures of the compounds are listed in Table I and shown graphically for each homologous series in Figures 1, 2, and 3 plotted against n, the number of carbon atoms in the alkoxy group.

Systematic studies[12] have established that extensive lateral poly-substitution generally has a very detrimental effect on the liquid crystal thermal stability of biphenyl mesogens. Indeed, 2,2′,6,6′-tetrachlorination of an azomethine derived from 4,4′-diaminobiphenyl causes such a massive decrease (of more than 250°C) in nematic thermal stability that liquid crystal properties are completely extinguised.[13] It is clear

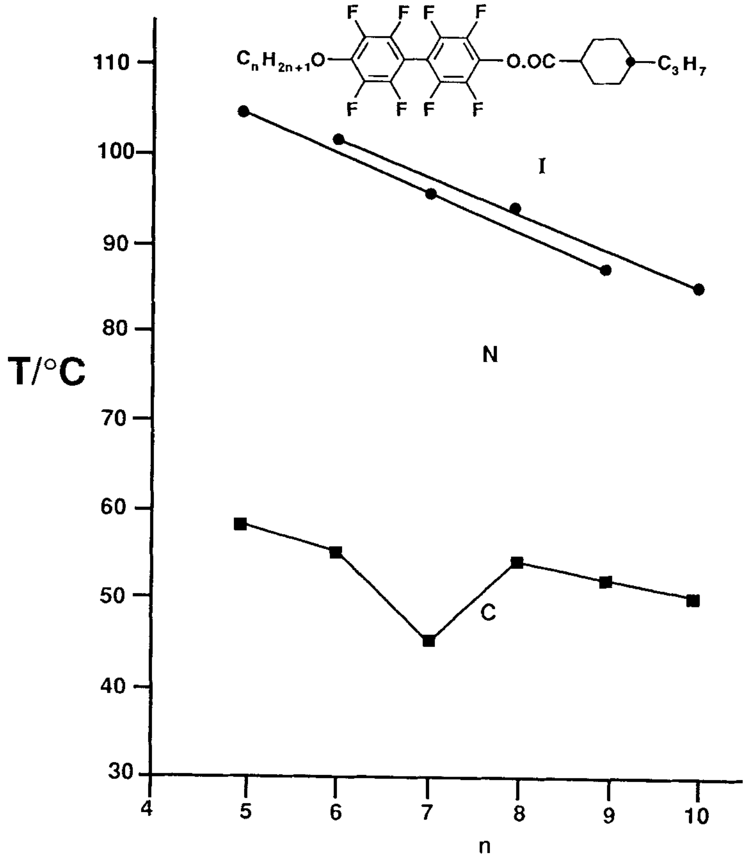


FIGURE 1 4′-*n*-Alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl-*trans*-4-*n*-propylcyclohexane-1-carboxylates: transition temperatures against *n*, the number of carbon atoms in the alkyl group.
■——■ crystal to nematic transition; ●——● nematic to isotropic transition

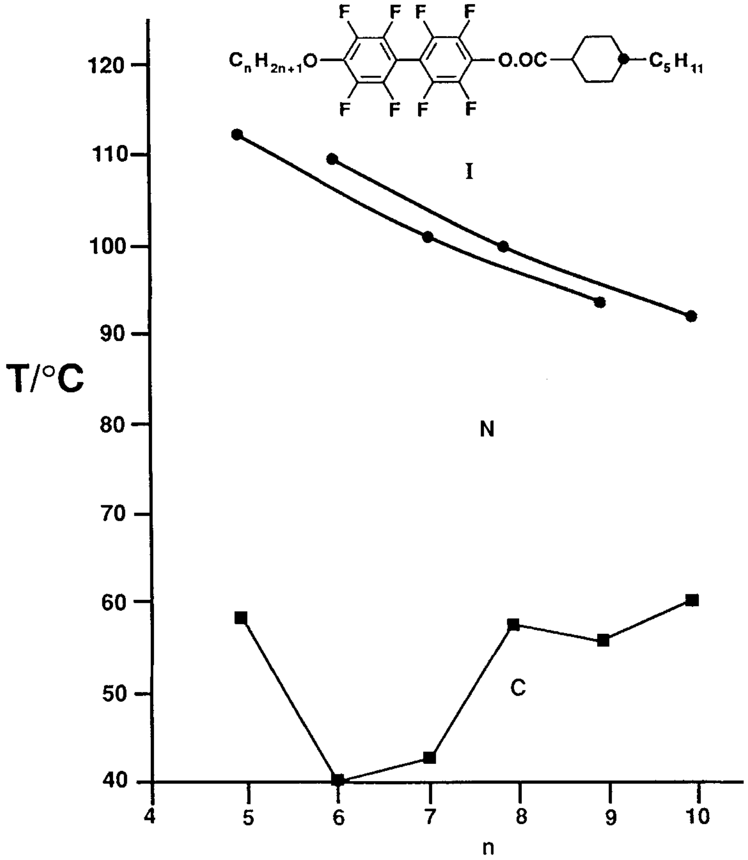


FIGURE 2 4′-*n*-Alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl-*trans*-4-*n*-pentylcyclohexane-1-carboxylates: transition temperatures against *n*, the number of carbon atoms in the alkyl group. ■——■ crystal to nematic transition; ●——● nematic to isotropic transition

from the present work that the smaller *ortho*-fluoro-substituents are more readily tolerated and contrary to initial expectation, complete lateral fluorination of the biphenyl core does not preclude mesomorphic behaviour. The four additional fluoro-substituents in the 3-, 3′-, 5-, and 5′-positions contribute to the dipolarity of the compounds and fill space between molecules maintaining the octafluorobiphenyl core as an essentially cylindrical shape similar to that of biphenyl itself.

The esters (**1**) are low melting nematogens and possess a moderately wide nematic (N-I) range of approximately 40°C. Although the number of compounds is limited, nevertheless, for each series ($m = 3, 5, 7$), when the points for the N-I transition temperatures are plotted against n, the number of carbon atoms in the *alkoxy* group, the usual trend is clearly evident (Figures 1–3). The points, which decrease with increasing values of *n*, show the expected odd-*n*–even-*n* alternation with those for the even-*n* homologues, uppermost. In Figure 4 the points for the N-I transition temperatures of the esters (**1**) are plotted in an alternative manner: for a particular alkoxy group (*n* fixed)

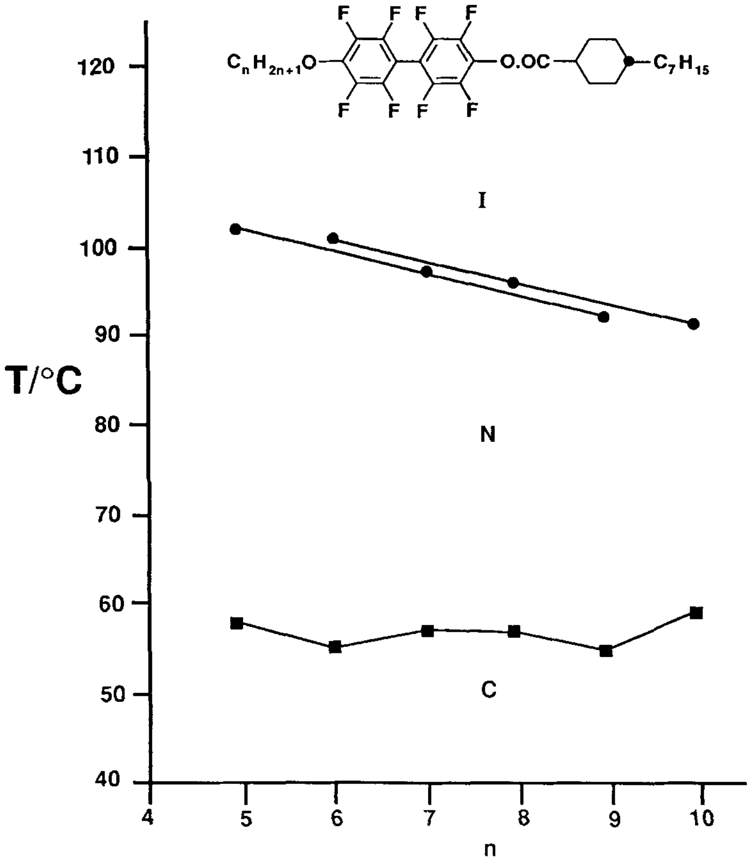


FIGURE 3 4′-*n*-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl-*trans*-4-*n*-heptylcyclohexane-1-carboxylates: transition temperatures against *n*, the number of carbon atoms in the alkyl group. ■——■ crystal to nematic transition; ●——● nematic to isotropic transition

the T_{N-I} values are plotted against m, the number of carbon atoms in the *alkyl* group ($m = 3, 5, 7$). Figure 4 confirms that the N-I transition temperatures decrease with an increase in the alkoxy chain length, and shows that in each case the maximum T_{N-I} value occurs for the $m = 5$ homologue.

Vauchier *et al.*[14] have reported esters derived from 4-alkoxy-2,2′-difluoro-4′-hydroxybiphenyl (**5**) which possess an N-I range of approximately 100 °C. In comparison with this value, there is substantial reduction in the N-I range for the esters derived from (**2**) but the reduction is not as large as might have been expected for an increase in the number of fluoro-substituents from two to eight. The reduction in the N-I range presumably has its origin in an increase in the average interplanar angle of the biphenyl system due to the presence of four *ortho*-substituents, reinforced by the buttressing effect of the remaining four lateral fluoro-substituents. However, the consequent increase in molecular breadth and thickness resulting in increased separation of the molecular axes and destabilisation of the nematic mesophase appears to be offset to

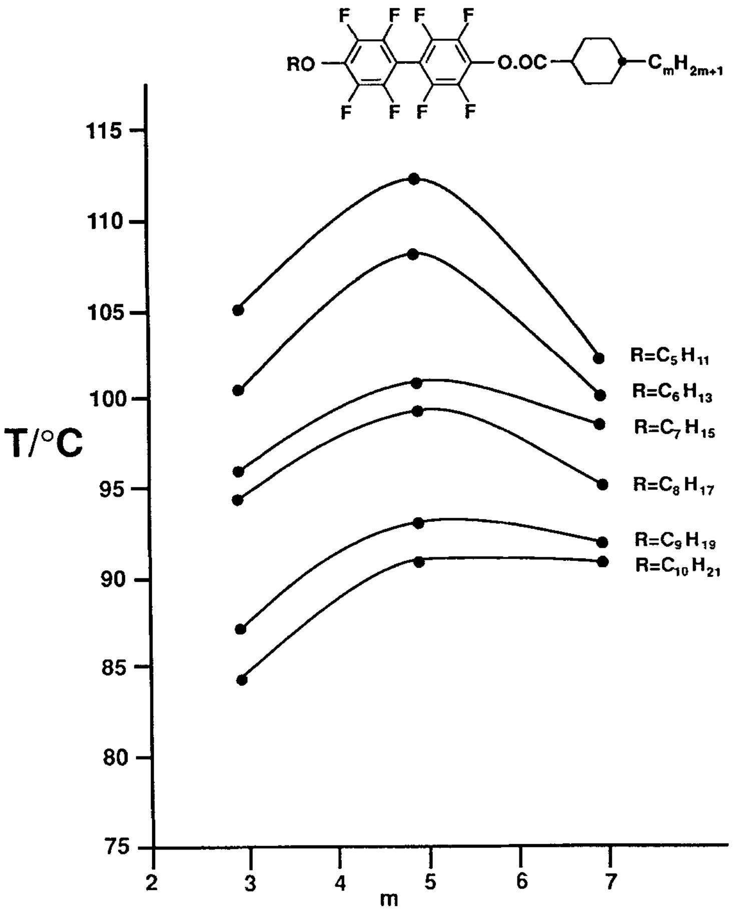
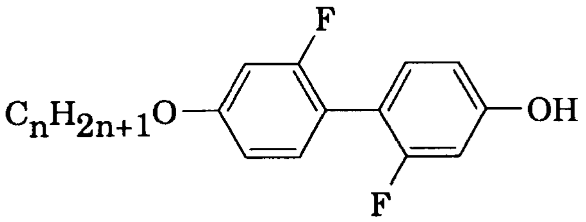


FIGURE 4 4′-*n*-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl-*trans*-4-*n*-alkylcyclohexane-1-carboxylates: transition temperatures against *n*, the number of carbon atoms in the alkyl group.
●——● nematic to isotropic transition

some extent by the space-filling nature and cylindrical shape of the octafluorobiphenyl core.

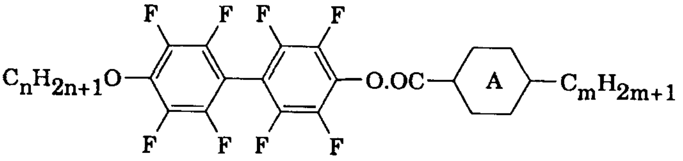


(5)

The effect of replacing the cyclohexyl ring of the esters (**1**) by a phenyl or bicyclo [2.2.2] octyl ring has also been investigated and the results are summarised for the

TABLE II

Liquid crystal transition temperatures for analogous esters derived from 4- alkoxy-4′-hydroxy-2,2′,3,3′,5,5′,6,6′,-octafluorobiphenyl.



			Transition temperature/°C		
Ring A	*n*	*m*	C—N	N—I	*N* range
Bicyclo[2.2.2]octane	5	3	85	152	67
trans-cyclohexane	5	5	43	112	69
benzene	5	5	63	(60)	3

esters lised in Table II. The phenyl ring lowers the nematic thermal stability (T_{N-I}) so that a monotropic nematic phase with a drastically reduced N-I range of only 3 °C results. In contrast, the bicyclo[2.2.2]octyl ring increases T_{N-I} but has very little effect on the nematic range in comparison with the cyclohexyl analogue. The values for the transition temperature reported in Table II reveal the following group order of promotion of mesomorphic behaviour in analogous esters derived from 4-pentyl-4′-hydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl.

Bicyclo[2.2.2]octyl > Cyclohexyl > Phenyl

This order, which in this instance refers only to the nematic phase and is based on a very limited number of compounds, has been observed previously in a much wider range of other mesomorphic compounds.[15]

We are indebted to Dr I C Sage for carrying out physical measurements enabling us to report the data given below. These show the esters (**1**) derived from the 4-alkoxy-4′-hydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyls and *trans*-4-alkylcyclohexane-1-carboxylic acids give rise to low melting mixtures that form nematic phases over a wide temperature range encompassing the room temperature region and beyond. These mixtures have a low dielectric anisotropy, $\Delta\varepsilon$, due to the absence of a strong dipole acting either parallel with or at right angles to the long molecular axis. The low value of the refractive indices, n_0 and n_e, and the value of the birefringence, Δn, presumably result from the very high fluorine content of the esters and the non-polar nature of the cyclohexyl moiety. Overall, these properties indicate the potential use of such mixtures particularly their suitablity for incorporation into electro-optic (e.g. TN mode) devices and applications in which nematogens with a very low refractive index are required. The following data refer to the pentoxy homologues, ie (**1**): $n = 5$; $m = 3,5,7$.

Mixture of propyl (30%); pentyl (40%); heptyl (30%) esters: $T_{N-I} = 102\,°C$ (slow crystallisation at room temperature); dielectric anisotropy, $\Delta\varepsilon = -0.5$; refractive indices (20 °C, 589 nm), $n_e = 1.5723$, $n_0 = 1.4499$, $\Delta n = 0.1224$. Mixture of propyl (33.3%); pentyl (33.3%); heptyl (33.4%) esters: $T_{N-I} = 83$ °C (slow crystallisation at room temperature); dielectric anisotropy, $\Delta\varepsilon = +0.05$; refractive index (20 °C, 589 nm), $n_0 = 1.4515$.

Further work on mesogens containing a polyfluoro-substituted biphenyl core is in progress.

EXPERIMENTAL

Structural confirmation of the structures of the intermediates and the products was obtained by ^{1}H NMR spectroscopy (Hitachi Perkin-Elmer R24-b 60 MHz spectrometer) and infrared spectroscopy (Perkin-Elmer 157 grating spectrophotometer). Mass spectra were determined with an A. E. I. MS 902S spectrometer equipped with a Mass Spectrometry Services 200 console and an INCOS 2300 data system. Thermal optical microscopy was carried out with a Vickers M75 polarising microscope in conjuction with a Mettler FP52 hot stage and FP5 control unit. Thermal analysis was carried out with a Perkin-Elmer DSC 7 differential scanning calorimeter equipped with a data station. Decafluorobiphenyl (**3**) was obtained from Aldrich Chemicals Ltd.

PREPARATION OF MATERIALS

4,4′-Dihydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl (**4**)

Decafluorobiphenyl (20 g, 0.06 mol), potassium hydroxide (30 g, 0.52 mol) and *tert*-butanol (250 cm^3) were heated under reflux. After 5h, the reaction mixture was poured into water (300 cm^3), transferred to a separating funnel and the aqueous layer extracted with ether to remove unchanged decafluorobiphenyl. The phenol was then released by acidification (4M HCl) and extracted into ether. The extract was dried ($MgSO_4$), and the solvent removed, whereafter the residue was purified by crystallisation from toluene affording the 4,4′-dihydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl, 10 g (50%), m.p. 210–211 °C (lit.[16] 198.5-199.5°C), as white needles.

4-Alkoxy-4′-hydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyls (**2**)

4,4′-Dihydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl (5 g, 0.015 mol), and the appropriate 1-bromoalkane (0.015 mol) were gently heated under reflux, with stirring for 4 h. and during the first hour, potassium hydroxide (2.8 g, 0.05 mol) in water (10 cm^3) was added, dropwise, to the mixture. After the requisite time, the reaction mixture was cooled, acidified (4M HCl), and extracted with ether (2 × 50 cm^3). The extracts were combined, dried ($MgSO_4$), and the solvent removed under reduced pressure. The residual oil was purified by flash chromatography on silica gel eluting with 2:1 light petroleum (b.p. 60–80°C) : ethyl acetate, followed by vacuum distillation (Kugelrohr) to give the desired 4-alkoxy-4′-hydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl (35–40%) as a clear oil which solidified on standing, b.p.s (0.04–0.08 mmHg): pentoxy, 160°; octyloxy, 169°; nonyloxy, 195°; decyloxy, 200 °C. The following spectroscopic data for the pentoxy compound are representative of the homologous series:

δ_H ($CDCl_3$) 1.1 (3H,*t*,CH_3), 1.3 (6H,*m*,$(CH_2)_3$), 4.5 (2H,*t*,OCH_2), 5.2 (1H,*s*,OH); V_{max} (film) 3300vbr (O—H str.), 2950*s*, 2900*s* (C—H str.), 1660*w*, 1530*s*, 1500*s*, 1480*s* (C=C str., C—C str.), 1100*s* (C—O str.), 725*s* (C—F str.) cm^{-1}.

*4′Alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl-*trans*-4-alkylcyclohexyl carboxylates* (**1**) Dicyclohexylcarbodiimide (1.1 mol), the appropriate 4-alkoxy-4′-hydroxy-2,2′,-3,3′,5,5′,6,6′-octafluorobiphenyl (1 mol), and *trans*-4-alkylcyclohexylcarboxylic acid (1.1 mol) were added to dry dichloromethane (20 cm^3). A small amount of 4-(*N*-pyrrolidino)pyridine (0.001 mol) was added to catalyse the reaction and the mixture was then stirred overnight. After checking the course of the reaction by tlc, the white precipitate (dicyclohexyl urea) was filtered off and the filtrate evaporated to dryness affording the crude ester. This was purified by column chromatography on silica gel eluting with chloroform, followed by repeated recrystallisation from ethanol to give the pure ester (in excess of 90%), as a white crystalline solid. The esters derived from 4-hydroxy-4′-pentoxy-2,2′,3,3′,5,5′,6,6′-octafluoro-biphenyl and both 4-propylbicyclo-[2.2.2]octane-1-carboxylic acid 4-pentyl benzoic acid were prepared in a similar manner.

The liquid crystal transition temperatures of the resulting esters are listed in Tables I and II. The following data for 4′-decyloxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl-*trans*-4-pentylcyclohexyl-1-carboxylate are typical of the series: Found: C, 62.65; H, 6.5%; *m/z* 650 (2%), 470, 330 181 (100). $C_{34}H_{42}F_8O_3$ requires C, 62.8; H, 6.5%; *M*, 650; V_{max} (KBr) 2950*s*, 2900*s* (C—H str.), 1780*s* (C=O str.), 1500*s*, 1480*s* (C=C str., C—C str.), 1100*s* (C—O str.), 725*s* (C—F str.) cm^{-1}; δ_H ($CDCl_3$) 0.9 (6H,t,2xCH_3), 1.3–1.8 (24H, complex multiplet, alkyl + cyclohexyl H), 4.3 (2H,t,OCH_2).

DSC thermograms, recorded at 10 °C min^{-1} for both heating and cooling cycles, were very similar for each member of the series. The following data for 4′-decyloxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl-*trans*-4-pentylcyclohexyl-1-carboxylate are typical: C—N T_{onset} 53.1 °C, ΔH 28 kJ mol^{-1}; N-I T_{onset} 90.6 °C, ΔH 1.3 kJ mol^{-1}.

Acknowledgements

We wish to thank Merck (UK) Ltd for providing the necessary chemicals for this work to be undertaken, Dr I C Sage for carrying out physical measurements at Merck (UK) Ltd on some of the compounds prepared, and Dr G Haran of the Boots Co plc for mass spectral determinations. ASM acknowledges with thanks many helpful discussions with Dr A R Tajbakhsh during his tenure of a post-doctoral fellowship.

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