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D. J. Byron[a]; A. S. Matharu[a]; R. C. Wilson[a]
[a] Department of Chemistry and Physics, The Nottingham Trent University, Nottingham, England

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The synthesis and liquid crystal properties of certain 1-(4′-*n*-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)-ethanes and -ethenes

by D. J. BYRON, A. S. MATHARU* and R. C. WILSON
Department of Chemistry and Physics, The Nottingham Trent University,
Clifton Lane, Nottingham NG11 8NS, England

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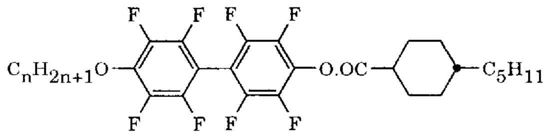
The synthesis and liquid crystal properties of eight members of the homologous series of 1-(4′-*n*-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)-ethanes and eight members of the corresponding -ethanes, which have the *E*-configuration, are reported. These compounds are nematic, the ethenes having a considerably mesophase higher thermal stability than the analogous ethanes.

1. Introduction

In general, the introduction of a lateral substituent into a mesogenic molecule effectively increases molecular breadth and hence increases the separation of the long axes of the molecules in the mesophases to an extent dependent on the size of the substituent. This normally leads to a reduction in the mesophase thermal stability, although other factors, such as the polarity of the substituent, may exert a compensating effect [1].

Only limited studies of the effect on liquid crystal behaviour of polyfluoro-substitution within the molecular core structure have been carried out. This may have been because the systematic, pioneering work of Gray and his co-workers [2] inferred, by intuitive extrapolation, that the presence of a large number of fluoro-substituents would lead to adverse properties. Extensive lateral ring polysubstitution frequently gives rise to compounds which are high melting and non-mesomorphic, and similar disadvantageous behaviour has been assumed even when small fluoro-substituents occupy lateral positions within the molecular core [3].

However, in 1967, Goldmacher and Barton [4] investigated the azomethines derived from 4,4′-diamino-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl and 4-methoxy- and -propyloxy-benzaldehyde. Their results indicated that complete fluorination of the biphenyl core did not drastically alter the liquid crystal characteristics shown by the parent azomethines, which have m.p.s in excess of 250°C and very high N–I transition temperatures in the region of 400°C. Nevertheless, the two cases studied revealed that octafluoro-substitution causes a reduction in m.p. (by 33° and 47°C) and, significantly, in the case of 4-propyloxy compound, induces a short smectic phase, as well as lowering T_{N-I} by 75°C. We have recently reported [5] our work on the synthesis and liquid crystal properties of certain members of a homologous series of 4′-*n*-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl) *trans*-4-*n*-pentylcyclohexane-1-carboxylates (**1**). Contrary to expectation, the increase in molecular breadth due to extensive lateral fluorination coupled with the associated twisting of the biphenyl ring system due to the presence of four *ortho*-substituents does not prevent the formation of mesomorphic compounds. In fact, these compounds are low melting nematogens which possess a moderately wide N–I range and their refractive indices ($n_e = 1{\cdot}5723$, $n_o = 1{\cdot}4499$ [5]) are similar to that of fused silica, although they have a rather high viscosity. It appears that the biphenyl core can tolerate the relatively small lateral fluoro-substituents so that, despite complete lateral fluorination, the octafluorobiphenyl unit does not give rise to high melting non-mesomorphic solids and, in fact, promotes nematic rather than smectic phase formation.



(**1**)

We have now extended this work to investigate the effect of replacing the ester group by a dimethylene linkage (CO.O replaced by CH_2CH_2) in the expectation that the outcome would be the retention of mesomorphic properties in lower melting compounds. We now report the synthesis and liquid crystal transition temperatures of members ($n = 3$–10) of the homologous series

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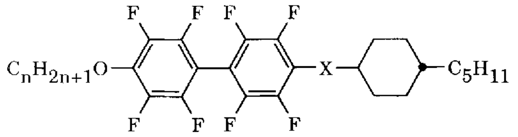
* Author for correspondence.

of symmetrically fluorinated 1-(4′-*n*-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)-ethanes (**3 a–h**) and the corresponding -ethenes (**2 a–h**). We have established that the ethenes, from which the ethanes were obtained by reduction, have the *E*-(*trans*-)configuration.

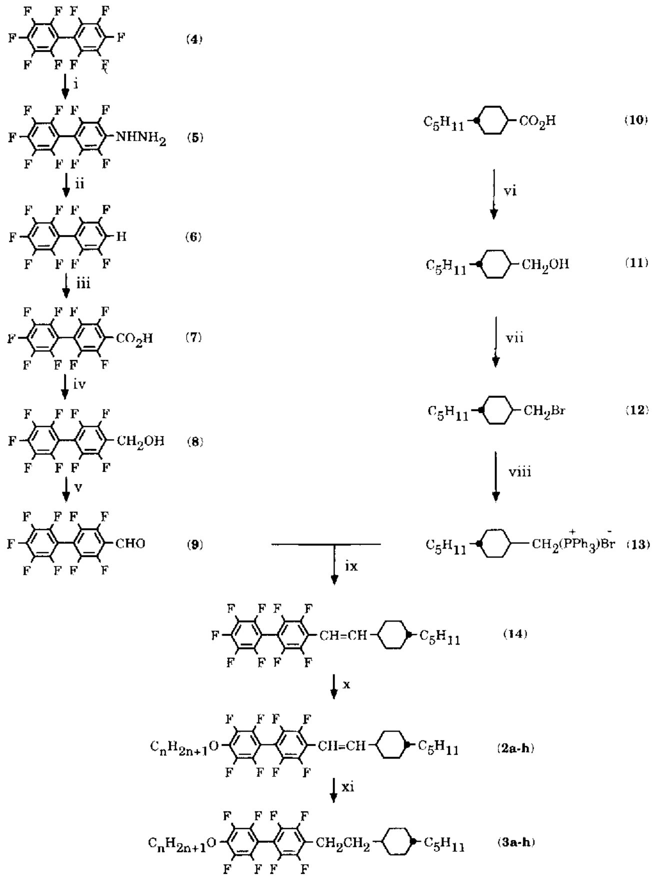


$X =$ *trans*-CH=CH (**2 a–h**); CH_2CH_2 (**3 a–h**)

2. Synthesis of materials

The synthetic route (see the scheme) to the alkylarylethenes (**2 a–h**) [and thence to the corresponding -ethanes (**3 a–h**)] involved the Wittig reaction [6] between the appropriate polyfluoroaromatic aldehyde (**9**) and *trans*-4-*n*-pentylcyclohexyl-1-methyltriphenylphosphonium bromide (**13**). An advantage of the Wittig reaction over alternative alkene-forming reactions is that the carbonyl group is specifically replaced by a carbon–carbon double bond without the formation of structurally isomeric alkenes. In addition, proton NMR evidence, discussed later, is consistent with the product of the Wittig reaction being predominantly or exclusively of the *E*-(*trans*-) configuration, at least in the present work, so that after work-up and purification the *trans*-alkene is the material isolated.

As shown in the scheme, the starting material for the preparation of the desired polyfluoroaromatic aldehyde (**9**) was decafluorobiphenyl (**4**) which is commercially available. Initially, copper (II) sulphate reduction [7] of the 4-hydrazino-compound (**5**) was the method used to prepare the nonafluorobiphenyl (**6**). However, the 4-hydrazino-compound was extremely difficult to separate and purify, as hydrazinolysis of decafluorobiphenyl afforded a mixture of mono-, di- and poly-substituted hydrazino-compounds. Wall *et al.* [8], have reported the preparation of pentafluorobenzene from hexafluorobenzene by a more convenient method involving reduction with $LiAlH_4$ and, on application of this method of decafluorobiphenyl, a mixture of mono- and di-hydro-compounds (2,2′,3,3′,4,5,5′,6,6′-nona- and 2,2′,3,3′,5,5′,6,6′-octa-fluorobiphenyl) and some unchanged starting material in the ratio 5:2:3 was obtained. Lithiation of compound (**6**) at −78°C followed by carbonation afforded the desired nonafluorobiphenyl-4-carboxylic acid (**7**) in high yield. Reduction of the carboxylic acid to the alcohol (**8**) with lithium aluminium hydride was inappropriate because the hydride anion can also compete as a nucleophile and displace the fluoro-substituent located at the 4′-position. Instead, borane dimethyl sulphide (BMS), which is a reducing agent of an electrophilic type, was employed [9].



(i) NH_2NH_2, dioxane. (ii) $CuSO_4$, C_2H_5OH. (iii) 1·6 M *n*BuLi, −78°C, CO_2. (iv) Borane dimethylsulphide, diethyl ether, N_2. (v) Pyridinium chlorochromate, CH_2Cl_2. (vi) $LiAlH_4$, diethyl ether. (vii) H_2SO_4/HBr. (viii) PPh_3. (ix) 1·6 M *n*BuLi, THF. (x) NaH, $C_nH_{2n+1}OH$, pyridine. (xi) H_2, 5 per cent Pd/C, C_2H_5OH.

Scheme

Finally, the resulting alcohol (**8**) was converted into the aldehyde (**9**) by selective oxidation using pyridinium chlorochromate (PCC) [10]. The reaction sequence (**6**)–(**9**) was found to be a much more efficient route to the aldehyde (**9**) than that reported by Wakefield [11], involving treatment of the nonafluorobiphenyl (**6**) with *n*-butyllithium, followed by quenching with dimethylformamide.

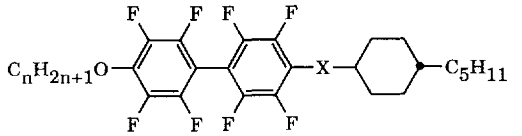
The alkyltriphenylphosphonium bromide (**13**) was obtained from *trans*-4-*n*-pentylcyclohexane-1-carboxylic acid (**10**) as the starting material. The acid was reduced with lithium aluminium hydride and the resulting alcohol (**11**), on treatment with a mixture of concentrated sulphuric acid and hydrobromic acid, gave the bromo-compound (**12**). This, on heating with a large excess of triphenylphosphine and a small quantity of 1,2-dichlorobenzene, which acted as a solvent, provided the desired *trans*-4-*n*-pentylcyclohexyl-1-methyltriphenylphosphonium bromide (**13**).

The alkene (**14**) was formed by the reaction between the aldehyde (**9**) and the phosphonium salt (**13**) in the presence of 1·6 M butyllithium. Nucleophilic displacement of the 4′-fluoro-substituent by the appropriate alkoxide anion then afforded the members of the homologous series of alkylaryl-ethenes (**2 a–h**) which gave the corresponding -ethanes (**3 a–h**) by catalytic hydrogenation at room temperature.

3. Results and discussion

Eight members ($n = 3$–10) of each homologous series were prepared. The liquid crystal transition temperatures of the alkylaryl-ethenes (**2 a–h**) and the corresponding -ethanes (**3 a–h**) are listed in table 1 and shown graphically in figures 1 and 2, respectively, as a plot against n, the number of carbon atoms in the alkyl chain. The members of both series are moderately low melting nematogens which do not give rise to smectic phases. The N–I transition temperatures fall with increasing chain length and also exhibit the expected odd–even alternation, i.e. the curve which correlates the N–I transition temperatures for the even n homologues lies above the corresponding curve for the odd n homologues. The melting points of the ethanes are lower than those of the corresponding ethenes; the differences for various homologues range from 6°C ($n = 5$) to 36°C ($n = 10$). The ethenes also give rise to nematic phases that have a greater thermal stability than the corresponding ethanes (**3 a–h**), the average N–I transition temperature for the ethenes ($n = 3$–10) being

Table 1. Transition temperatures (°C) for members of the homologous series of 1-(4′-*n*-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)-ethenes (**2 a–h**) and -ethanes (**3 a–h**).



$X =$ *trans*-CH=CH (**2 a–h**); CH_2CH_2 (**3 a–h**)

		Alkylarylethenes (**2 a–h**)		Alkylarylethanes (**3 a–h**)		
n		Cr–N	N–I	Cr–I	Cr–N	N–I†
3	**a**	91	135		59	60·5
4	**b**	74	134	66		(63·5)
5	**c**	65	125	59		(54)
6	**d**	62	123		53·5	56·5
7	**e**	68	118		51	52
8	**f**	71	115		41·5	52
9	**g**	73	113		39·5	50·5
10	**h**	76	112		40	50

† Values in brackets denote a monotropic transition.

Symbols have their usual significance: Cr, crystal; N, nematic; I, isotropic. Thus, Cr–N indicates the temperature at which the crystal (Cr) melts to the nematic phase (N).

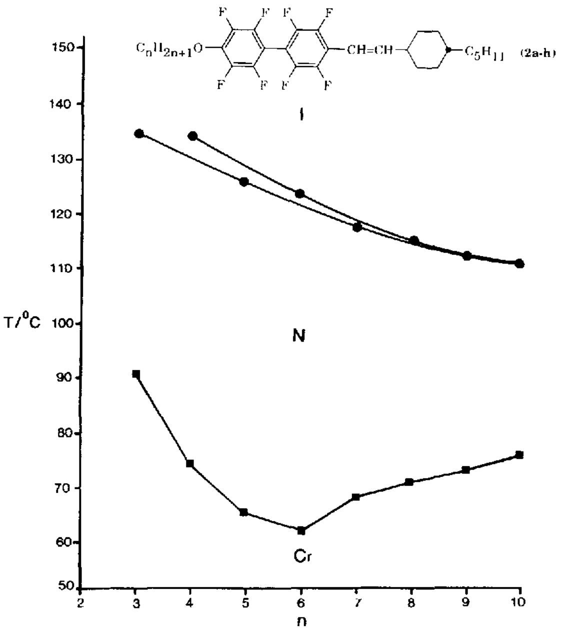


Figure 1. (*E*)-1-(4′-*n*-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethenes (**2 a–h**): transition temperatures against n, the number of carbon atoms in the alkyl group. ■——■ crystal to nematic transition; ●——● nematic to isotropic transition.

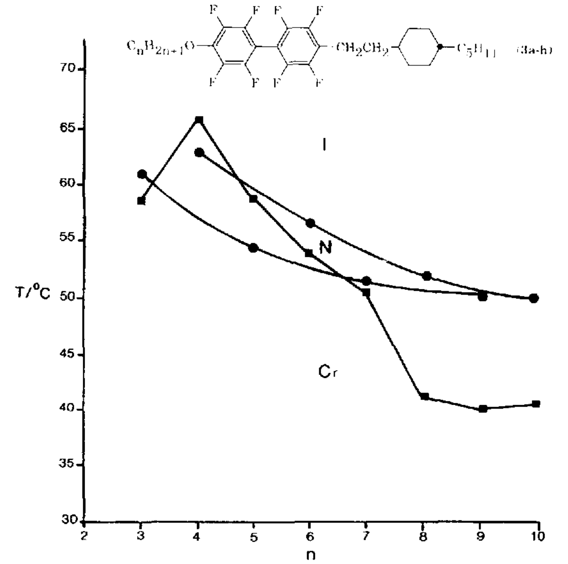
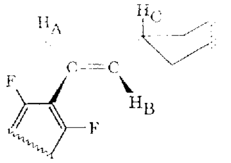


Figure 2. 1-(4′-*n*-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethanes (**3 a–h**): transition temperatures against n, the number of carbon atoms in the alkyl group. ■——■ crystal to nematic transition; ●——● nematic to isotropic transition.

greater by 67·1°C than the corresponding value for the ethanes. In addition, the nematic phase persists over a greater range for the ethenes than for the ethanes (the average values being 49·3°C and 5·4°C for $n = 3$–10).

We have established that the carbon–carbon double bond of the alkylarylethenes (**2 a–h**) has the *E*- (i.e. *trans*-) configuration. This assignment is based on ^{1}H NMR studies (at 270 MHz) of both 1-(4′-*n*-heptyloxy-2,2′, 3,3′, 5,5′, 6,6′-octafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethene and the precursor 1-(2,2′, 3,3′, 4′, 5,5′, 6,6′-nonafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethene. The NMR spectra, are distinctive and unambiguous, consisting of two sets of multiplets in the region 6·3–6·7 ppm (see figure 3). The first set (6·32–6·42 ppm) shows a doublet of doublets which corresponds to the signal of the alkene proton, H$_A$, adjacent to the fluoroaromatic ring, split by coupling with the neighbouring vinylic proton, H$_B$, (J_{AB} = 16 Hz) and the allylic proton, H$_C$, (J_{AC} = 1 Hz). Similarly, the second set of multiplets (6·62–6·72 ppm) also corresponds to a doublet of doublets which arises from coupling of H$_B$, adjacent to the cyclohexyl ring, with the vinylic proton, H$_A$ (J_{AB} = 16 Hz) and with the cyclohexyl ring proton, H$_C$ (J_{BC} = 7 Hz). The large value of the coupling constant, J_{AB} = 16 Hz, is highly characteristic and reliable evidence for a *trans*-alkene [12] and it is on this basis that our assignment of an *E*-(*trans*-) configuration to the alkylarylethenes is made.



The present results are compared in table 2 with those previously reported [5] relating to the esters (**1**) derived from 4-*n*-alkoxy-4′-hydroxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl in order to assess the influence of the three central linking groups on nematic thermal stability. Table 2 lists the N–I transition temperatures and the N–I phase temperature range, ΔT_{N-I}, for four members ($n = 5, 8, 9, 10$) of the series (**1**), (**2**) and (**3**).

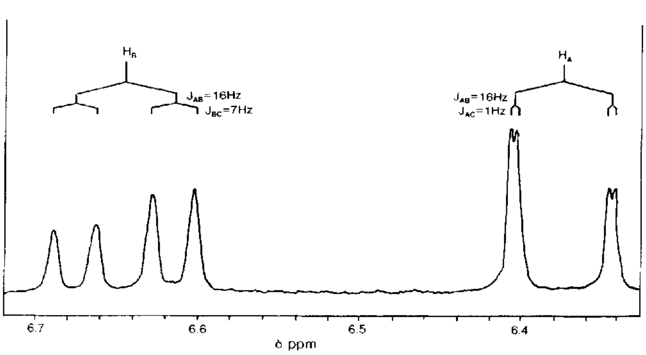
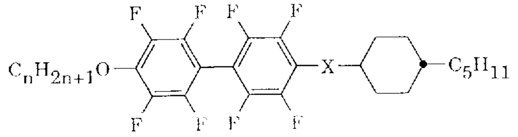


Figure 3. 270 MHz ^{1}H NMR spectrum of (*E*)-1-(2,2′,3,3′,4′, 5, 5′, 6, 6′-nonafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethene showing the absorption signals and coupling associated with the alkene protons H$_A$ and H$_B$.

Table 2. Clearing points (N–I) and nematic temperature ranges (ΔT_{N-I}) (°C) for compounds containing the 4,4′-disubstituted octafluorobiphenyl core.



	X					
	–O.OC– (**1**)		*trans*-CH=CH– (**2**)		–CH$_2$CH$_2$– (**3**)	
n	N–I	ΔT_{N-I}	N–I	ΔT_{N-I}	N–I	ΔT_{N-I}
5	112	69	125	60	54	5
8	99	45	115	44	52	10·5
9	93	40	113	40	50·5	11
10	91	38	112	36	50	10
Average	98·7	48·5	116·2	45	51·6	9·1

The results show the following group order for promoting nematic thermal stability:

$$trans\text{-CH=CH–} > \text{–O.OC–} > \text{–CH}_2\text{CH}_2\text{–}$$

As expected, due to the low molecular polarizability [13] and much reduced rigidity of the system containing sp^3-hybridized carbon atoms, the dimethylene linkage is associated with compounds that give the lowest nematic thermal stability. The intermediate behaviour associated with the ester linkage may be due to two contributing factors. Firstly, conjugation between the oxygen atom of the terminal alkoxy group through the aromatic core portion, with extension into the central linking group, cannot occur [14] when this group is the reversed ester linkage O.OC, but is possible for CH=CH which is a $\pm M$ group. Secondly, the disposition of the fluoro-substituents located at the 3- and 5-positions may cause steric interference with the oxygen atom of the carbonyl group. This will result in some molecular broadening due to steric twisting, so that the fluoro-substituents and the ester group no longer remain in the same plane with respect to each other [15]. The combined influence of the two effects is likely to lead to an overall decrease in the anisotropy of molecular polarizability ($\Delta\alpha$) of the system.

In contrast, a reversed order for the nematic phase temperature range, ΔT_{N-I}, is observed. The ester group is associated with compounds that possess the largest phase range and the ethene group now shows intermediate behaviour.

4. Experimental

4.1. *Analysis*

Structural confirmation of the structures of the intermediates and the products was obtained by ^{1}H NMR spectroscopy (either Hitachi Perkin–Elmer R24-b 60 MHz spectrometer or JEOL FX60Q 270 MHz spectrometer) with tetramethylsilane as internal standard and by 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 polarizing microscope in conjunction with a Mettler FP52 hot stage and FP5 control unit.

4.2. *Synthesis of 4-hydrazino-2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl* (**5**)

To decafluorobiphenyl (20 g, 0·06 mol) in ethanol (150 cm^3), 96 per cent hydrazine hydrate (3·25 g, 0·06 mol) was added, dropwise, under reflux over 15 min. After 1 h the reaction mixture was cooled, poured into water (500 cm^3), and left to stand. The resulting solid was filtered off, dissolved in diethyl ether (100 cm^3), the solution dried (MgSO$_4$), and the solvent removed *in vacuo*. Tlc indicated that the crude product was a mixture containing unchanged starting material, mono-substituted decafluorobiphenyl and poly-substituted decafluorobiphenyls. The starting material was removed by sublimation (70°C/20 mmHg) and the residue was then purified by fractional crystallization from hexane. Insoluble material was removed by hot filtration and the solution set aside to cool. The initial fraction of crystals (polysubstituted compounds) was discarded, but the second fraction corresponded with the desired 4-hydrazino-2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl, 13 g (65 per cent), m.p. 132–135°C (lit. [16] 132–133·5°C).

4.3. *Synthesis of 2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl* (**6**): *Method 1.*

Copper (II) sulphate (30 g, 0·04 mol) was added to a solution of 4-hydrazino-2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl (13 g, 0·04 mol) dissolved in 1 : 1 ethanol : water and gently heated under reflux for 24 h. During this period, nitrogen gas was evolved and copper was deposited. The reaction mixture was then filtered through a funnel loosely packed with glass wool to remove suspended solids. The resulting solution was shaken with diethyl ether (3 × 200 cm^3), and the combined extracts were washed with water (3 × 100 cm^3), dried (MgSO$_4$), and the solvent removed under reduced pressure. Sublimation (50°C/17 mmHg) of the resulting solid gave the pure 2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl, 9 g (71 per cent), as white needles, m.p. 83–84°C (lit. [17] 81–82°C): δ_H (CDCl$_3$) 7·5 (1 H, m, ArH) ppm; ν_{max} (KBr) 3150, 1600, 1530, 1500, 1480, 740, 705 cm^{-1}.

4.4. *Synthesis of 2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl* (**6**): *Method 2*

In an atmosphere of nitrogen, a slurry of LiAlH$_4$ (0·31 g, 0·008 mol) in dry diethyl ether (20 cm^3) was added, dropwise, to a rapidly stirred solution of decafluorobiphenyl (3·6 g, 0·011 mol) in dry diethyl ether (30 cm^3) at such a rate that the ether boiled gently. On completion of the addition, the reaction was heated under reflux for an additional 8 h and then allowed to cool. The excess of LiAlH$_4$ was destroyed by the addition of moist diethyl ether, ethyl acetate, then water (1–2 cm^3) and finally 4 M-aqueous hydrochloric acid. The ether layer was separated and the aqueous layer was shaken with diethyl ether (2 × 50 cm^3). The combined ethereal extracts were dried (MgSO$_4$), and the solvent removed *in vacuo*. Examination of the residue by t.l.c. revealed a mixture containing unchanged starting material and the desired 2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl.

4.5. *Synthesis of 2,2′,3,3′,4′,5,5′,6,6′,-nonafluoro-bi-phenyl-4-carboxylic acid* (**7**)

Commercial butyllithium (20·6 cm^3, 0·033 mol) was added dropwise to a rapidly stirred solution of 2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl (9·5 g, 0·03 mol) in dry 1 : 1 diethyl ether : hexane (150 cm^3) maintained at − 78°C to − 65°C throughout the addition, which took 2 h to complete. After an additional 1 h at − 78°C, the reaction mixture was poured on to powdered solid carbon dioxide, allowed to warm to room temperature and acidified (4 M HCl). The resulting acid was extracted into diethyl ether (2 × 100 cm^3), and the combined ether extracts were dried (MgSO$_4$). The solvent was removed under reduced pressure and the off-white solid then recrystallized from hexane affording the desired 2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl-4-carboxylic acid, 10 g (88 per cent), as a white crystalline solid, m.p. 170–172°C (lit. [18] 175–176°C): δ_H (CDCl$_3$/DMSO) 12·3 (1 H, s, CO$_2$H) ppm; ν_{max} (KBr) 3500, 3300–2750 (O–H str.), 1720 (C=O str.), 1530, 1500, 1480, 725 cm^{-1}.

4.6. *Synthesis of 2,2′,3,3′,4′,5,5′,6,6′-nonafluoro-biphenyl-4-ylmethanol* (**8**)

In an atmosphere of nitrogen, borane dimethylsulphide (4·2 cm^3, 0·044 mol) was added dropwise to a solution of 2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl-4-carboxylic acid (5 g, 0·014 mol) in dry diethyl ether (50 cm^3) causing vigorous effervescence and the ether to boil. On completion of the addition, the mixture was heated under reflux for 2 h. The reaction mixture was then poured into cold methanol (200 cm^3) and allowed to stand overnight before removal of the solvent *in vacuo*. The residue was recrystallized from hexane, affording the pure 2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl-4-ylmethanol 4·8 g (100 per cent), as a white crystalline solid, m.p. 78–80°C: δ_H ($CDCl_3$) 2·5 (1 H, s, OH), 4·9 (2 H, s, CH_2) ppm; ν_{max} (KBr) 3500–3300 (O–H str.), 2975, 1660, 1530, 1500, 1480, 1000, 725 cm^{-1}.

4.7. *Synthesis of 2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl-4-carbaldehyde* (**9**)

2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl-4-ylmethanol (5 g, 0·014 mol) in dry dichloromethane (10 cm^3) was added, in portions, to a rapidly stirred suspension of pyridinium chlorochromate [10] (6 g, 0·027 mol) in dry dichloromethane (100 cm^3). After 24 h dry diethyl ether (100 cm^3) was added and the supernatant liquid was decanted from the black gum which was washed with more dry diethyl ether (2 × 100 cm^3). The ether solutions were combined and filtered through 'Hyflo-supercel', and the solvent was removed under reduced pressure. The resulting dark brown oil was purified by flash chromatography on silica gel eluting with 3:1 light petroleum (b.p. 60–80°C) : chloroform, followed by recrystallization from hexane affording the desired 2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl-4-carbaldehyde, 3·7 g (77 per cent), as a white crystalline solid, m.p. 75–76°C: δ_H ($CDCl_3$) 10·4 (1 H, s, CHO) ppm; ν_{max} (KBr) 2950, 2850, 1710 (C=O str.), 1530, 1500, 1480, 1000, 725 cm^{-1}.

4.8. *Synthesis of* trans-*4-*n-*pentylcyclohexyl-1-methanol* (**11**)

Trans-4-*n*-pentylcyclohexanecarboxylic acid (**10**) (20 g, 0·1 mol) was treated with borane dimethyl sulphide (28 cm^3, 0·3 mol) as described for the preparation of nonafluorobiphenyl (**6**) [Method 2]. Vacuum distillation of the resulting oil afforded the pure *trans*-4-*n*-pentylcyclohexyl-1-methanol, 18 g (97 per cent), as a clear oil, b.p. 100°C/0·5 mmHg (lit. [19] 99°C/0·1 mm Hg).

4.9. *Synthesis of* trans-*4-*n-*pentylcyclohexyl-1-methyl bromide* (**12**)

Trans-4-*n*-pentylcyclohexyl-1-methanol (30 g, 0·16 mol) was added to 3:1 (vol.) 47 per cent hydrobromic acid : concentrated sulphuric acid (50 cm^3). The reaction mixture was heated under reflux for 5 h and then poured on to ice–water (300 cm^3). The aqueous layer was shaken with diethyl ether (4 × 100 cm^3) and the extracts were washed with concentrated hydrochloric acid (30 cm^3), water (2 × 100 cm^3), saturated sodium bicarbonate solution (2 × 100 cm^3), water (100 cm^3), then dried ($MgSO_4$), and the solvent was removed *in vacuo*. Vacuum distillation of the resulting dark residue afforded the pure alkyl bromide, 37 g (95 per cent), as a clear oil, b.p. 90°C/0·1 mmHg (lit. [19] 155°C/15 mmHg).

4.10. *Synthesis of* trans-*4-*n-*pentylcyclohexyl-1-methyltriphenylphosphonium bromide* (**13**)

Triphenylphosphine (47 g, 0·18 mol), *trans*-4-*n*-pentylcyclohexyl-1-methyl bromide (30 g, 0·12 mol) and 1,2-dichlorobenzene (20 cm^3) were heated vigorously under reflux for 30 min. On cooling, the reaction mixture was poured into dry diethyl ether (200 cm^3) and the resulting solid filtered off, washed several times with dry diethyl ether in order to remove any unchanged triphenylphosphine, dried in an oven at 100°C and stored in a vacuum dessicator. The pure phosphonium salt, 40 g (63 per cent), was obtained as a white crystalline solid, m.p. 177–181°C: δ_H ($CDCl_3$/DMSO) 0·8 (3 H, t, CH_3), 1·2 (9 H, br s, alkyl), 1·6 (9 H, m, alkyl), 3·6 (2 H, m, CH_2), 7·1 (15 H, m, ArH) ppm; ν_{max} (KBr) 3100, 3000, 2950, 1605, 1550, 1400, 825 cm^{-1}.

4.11. *Synthesis of* (E)-*1-(2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl-4-yl)-2-*(trans-*4-*n-*pentylcyclohexyl)ethene* (**14**)

In an atmosphere of nitrogen, commercial butyllithium (1·1 mol) was added, dropwise, to a rapidly stirred suspension of *trans*-4-*n*-pentylcyclohexyl-1-methyltriphenylphosphonium bromide (1 mol) in dry tetrahydrofuran (50 cm^3) cooled to − 10°C. On completion of the addition, the dark orange-brown solution was stirred for 1 h at 0°C. 2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl-4-carbaldehyde (1 mol) in dry tetrahydrofuran (10 cm^3) was added and the reaction mixture then stirred at 5°C for 1 h at 0°C. Water (50 cm^3) was added and the reaction mixture shaken with diethyl ether (3 × 50 cm^3). The extracts were combined, washed with water (2 × 75 cm^3), and dried ($MgSO_4$), the solvent was removed and the residue purified by column chromatography on silica gel, eluting with light petroleum (b.p. 60–80°C). The resulting clear oil, on addition of cold ethanol (10–20 cm^3), afforded the desired (*E*)-1-(2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethene (**14**), (65 per cent), as white flakes, m.p. Cr–I, 84–86°C, I–N, (80°), N–C, 46°: Found: C, 60·80; H, 4·76; F, 34·60 per cent. $C_{25}H_{23}F_9$ requires C, 60·73; H, 4·69; F, 34·58 per cent; δ_H ($CDCl_3$) 0·9–1·0 (3 H, m, CH_3), 1·2–1·4 (14 H, br s, alkyl), 1·8–2·0 (4 H, m, alkyl), 6·32–6·42 (1 H, dd, –CH=CH–), 6·62–6·72 (1 H, dd, –CH=CH–) ppm. See the text for coupling constants and assignments.

4.12. *Synthesis of* (E)-*1-(4′-*n-*alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl)-2-*trans-*4-*n-*pentylcyclohexyl)ethenes* (**2 a–h**)

The appropriate sodium alkoxide (1·1 mol), prepared from the alcohol by the addition of the necessary quantity of sodium hydride, was added, dropwise, with stirring, to (*E*)-1-(2,2′,3,3′,4′,5,5′,6,6′-nonafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethene (1 mol) in dry pyridine at − 10°C. The progress of the reaction was monitored by t.l.c. at 10 min intervals as the mixture was slowly allowed to warm to room temperature. The optimum reaction time was determined either by the complete consumption of the starting material or by the formation of undesirable side-products. The reaction mixture was then acidified by pouring into ice-cold 4 M-aqueous hydrochloric acid and the aqueous layer was shaken with diethyl ether ($2 \times 50\,\mathrm{cm}^3$). The ether extracts were combined, washed with water ($50\,\mathrm{cm}^3$), and dried ($MgSO_4$), and the solvent was removed *in vacuo*. The resulting pale yellow liquid was purified by flash chromatography on silica gel eluting with light petroleum (b.p. 60–80°C) followed by recrystallization from ethanol to give the pure (*E*)-1-(4′-*n*-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethene as a white crystalline solid. The yield of the product was normally greater than 90 per cent. M.p.s: propyloxy, C–N, 91°, N–I, 135°; butyloxy, C–N, 74°, N–I, 134°; pentyloxy, C–N, 65°, N–I, 125°; hexyloxy, C–N, 62°, N–I, 123°; heptyloxy, C–N, 68°, N–I, 118°; octyloxy, C–N, 71°, N–I, 115°; nonyloxy, C–N, 73°, N–I, 113°; decyloxy, C–N, 76°, N–I, 112°.

The following data for (*E*)-1-(4′-*n*-heptyloxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethene are representative of the series. Found: C, 65·17; H, 6·60 per cent. $C_{32}H_{38}F_8O$ requires C, 65·08; H, 6·44 per cent; δ_H ($CDCl_3$) 0·9 (6 H, t, $2 \times CH_3$), 1·3 (24 H, br s, alkyl), 1·8–2·0 (4 H, m, alkyl), 4·2 (2 H, t, OCH_2), 6·32–6·42 (1 H, dd, –CH=CH–), 6·62–6·72 (1 H, dd, –CH=CH–) ppm; ν_{max} (KBr) 2950, 2850, 1540, 1480, 1150, 1050, 880 cm^{-1}.

4.13. *Synthesis of* (E)-*1-(4′*-n-*alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl*)-2-(trans-*4*-n-*pentylcyclohexyl*)*ethanes* (**3 a–h**)

1-(4′-*n*-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethene (0·5 g) was added to a stirred suspension of 5 per cent palladium on charcoal (150 mg) in ethanol ($20\,\mathrm{cm}^3$), and hydrogenated at room temperature and atmospheric pressure. After uptake of the appropriate amount of hydrogen (approximately 1 h) the catalyst was filtered off and the filtrate evaporated to dryness. The residue was dissolved in hot ethanol, insoluble material was removed by hot filtration, and the solution then set aside to cool, when the pure 1-(4′-*n*-alkoxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethane (100 per cent) crystallized out as white flakes.

The following data for 1-(4′-*n*-decyloxy-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4-yl)-2-(*trans*-4-*n*-pentylcyclohexyl)ethane are representative of the series. Found: C, 66·66; H, 7·40 per cent; *m*/*z* 634 (29 per cent), 494 (51), 140 (100). $C_{35}H_{46}F_8O$ requires C, 66·25; H, 7·26 per cent; M, 634; δ_H($CDCl_3$) 0·9 (6 H, t, $2 \times CH_3$), 1·3 (30 H, br s, alkyl), 1·8–2·0 (4 H, m, alkyl) 4·2 (2 H, t, OCH_2) ppm; ν_{max} (KBr) 2950, 2850, 1540, 1480, 1150, 1050, 880 cm^{-1}.

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