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The effect of the ferrocene unit on mesomorphic properties

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The synthesis of a number of 1,1′-disubstituted ferrocene-containing compounds is described; the structures of the compounds containing the ferrocene unit are related to those of mesogenic systems containing a 1,4-disubstituted benzene ring or a *trans*-1,4-cyclohexyl ring. Direct comparisons are made between the aryl-, cyclohexyl- and ferrocene-containing compounds in order to assess the effect on transition temperatures of replacing a benzene or cyclohexyl ring with a ferrocene unit. In comparison with conventional ring systems the ferrocene unit causes substantial reductions in clearing temperatures.

1. Introduction

Among the large variety of metal-containing liquid-crystals which are reported in the literature, increasing interest is being shown in systems containing a ferrocene unit. The first ferrocene-containing compound thought to show liquid crystalline properties was ferrocenecarboxaldehyde [1] which was reported to exhibit a liquid crystalline state between 45 and 124·5°C; this compound was later reinvestigated [2, 3] and the mesophase was assigned as a disordered crystal. Truly mesogenic derivatives of ferrocene, with the structures shown in figure 1, were reported by Malthète and Billard [4] and these compounds show a nematic phase.

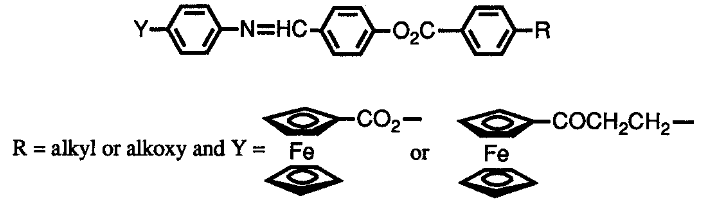

Figure 1. The first liquid crystalline ferrocene derivatives.

More recently, diesters of ferrocene with the structure shown in figure 2(*a*) have been reported [5] and several of the examples show monotropic smectic A or C phases; the monosubstituted ferrocene esters (see figure 2(*b*)) were found to be non-mesomorphic, but similar derivatives with an additional benzene ring (see figure 2(*c*)) show smectic phases. The crystal and molecular structure of the pentyloxy diester (see figure 2(*a*), $R = C_5H_{11}$) have been studied by X-ray diffraction methods [6] which have shown that the molecules adopt the extended ‘S’ geometry, i.e. the two bulky substituents on the ferrocene core point away from each other.

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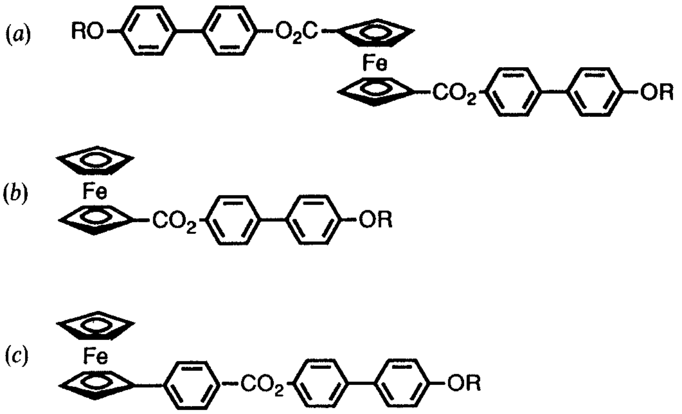


Figure 2. (*a*) Ferrocene diesters, (*b*) monoesters and (*c*) aryl derivatives.

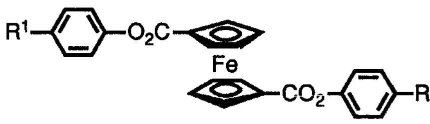


Figure 3. Ferrocene derivatives reported to be mesogenic, $R^1=R^2=OC_7H_{15}$ or $OC_{10}H_{21}$ and $R^1=OC_{10}H_{21}$, $R^2=OH$.

Compounds with the structures shown in figure 3 have recently been reported [7] and are described as being smectogenic when $R^1=R^2=OC_7H_{15}$ and nematogenic when $R^1=R^2=OC_{10}H_{21}$ or $R^1=OCH_{21}$, $R^2=OH$. The clearing temperatures of the mesophases appear not to be reversible and indeed the nematic phase is seen only on considerable supercooling of the isotropic liquid.

An interesting departure from compounds based on a 1,1′-disubstituted ferrocene core has also been considered [8]. Several 1,3-disubstituted ferrocene derivatives with the structures shown in figure 4 show enantiotropic nematic phases, whereas for the corresponding 1,1′-derivatives, only that in which $R=(a)$-hexyloxy shows a nematic phase, which is monotropic.

The aim of the work now described was to investigate the effect on the transition temperatures caused by the replacement of a benzene or a cyclohexyl ring with a 1,1′-ferrocene unit. In order to investigate this matter we have synthesized a number of novel 1-alkyl-1′-substituted ferrocene ester derivatives; examples of ferrocene derivatives described previously and their aryl derivatives are also discussed. From the results obtained, and those drawn from the literature, direct comparisons are made between the 1,4-disubstituted benzene ring and the 1,1′-disubstituted ferrocene unit as a component of a mesogenic core unit. It is found that the ferrocene unit causes marked reductions in clearing points and possible reasons for these reductions are discussed.

The synthetic routes to the ferrocene derivatives and their benzene and cyclohexane analogues are shown in schemes 1 to 5. The 1,1′-alkylferrocenecarboxylic acids were prepared according to the method described by Little *et al.* [9] by Friedel–Crafts

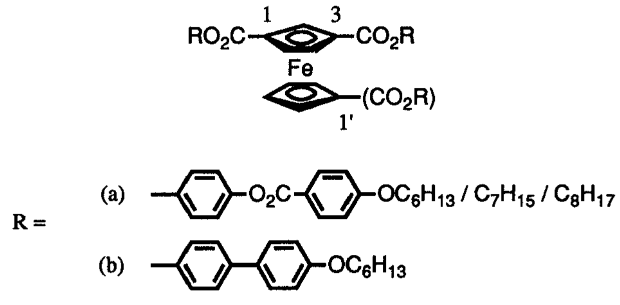
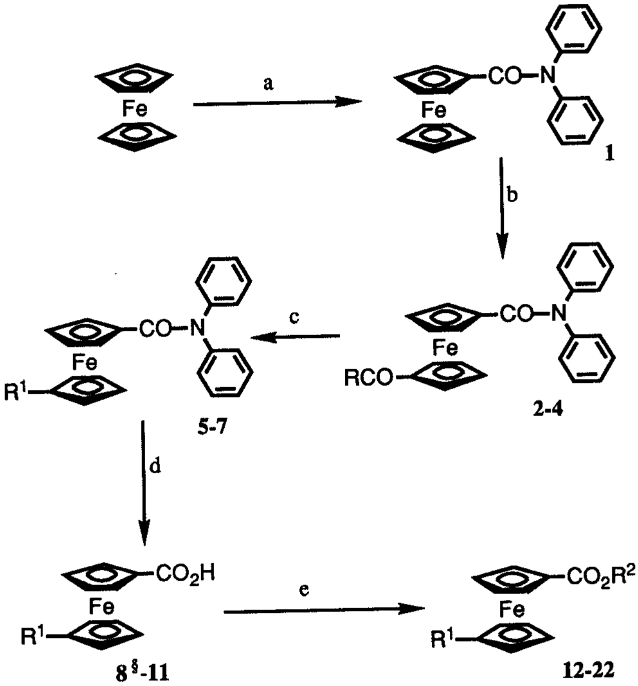
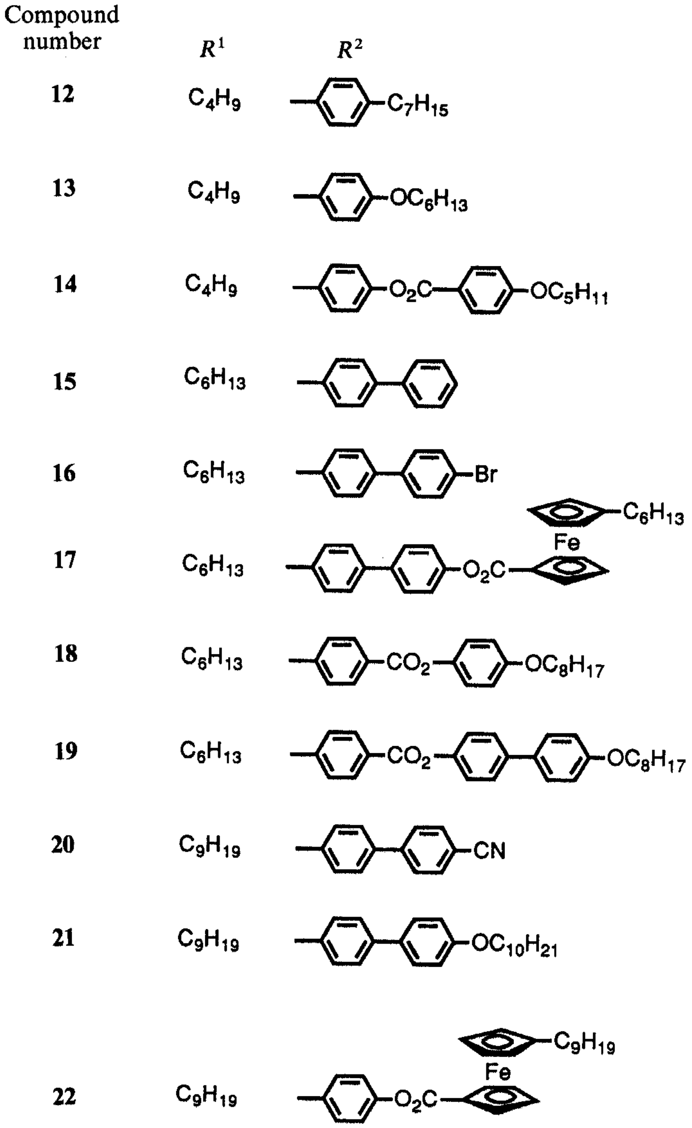


Figure 4. 1,3- and 1,1′-disubstituted ferrocenes.

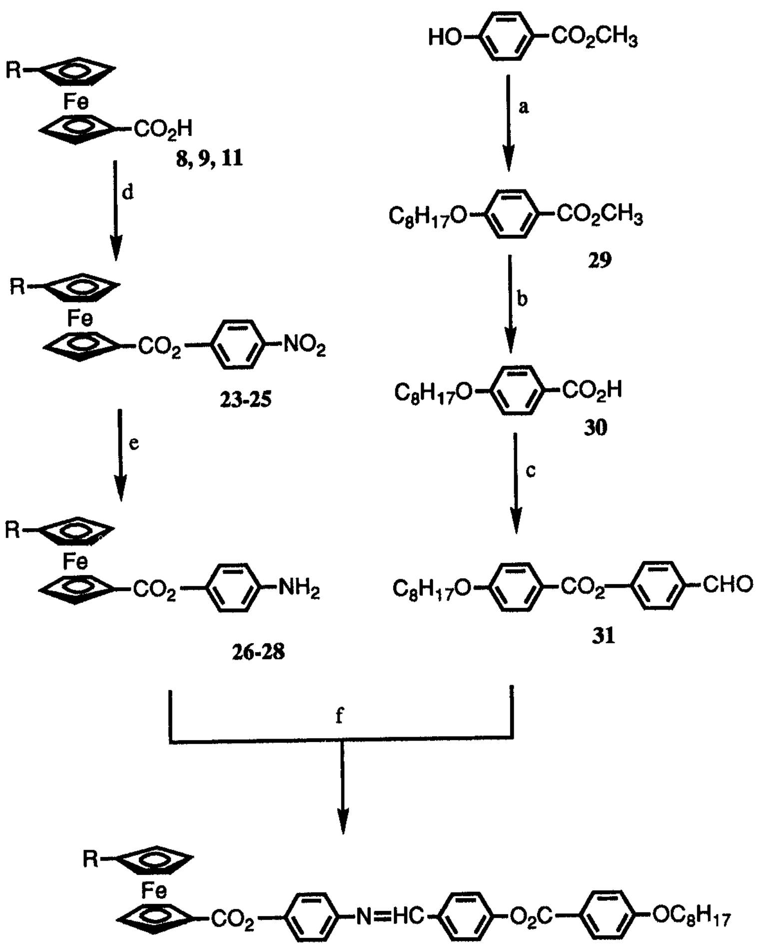
reaction of ferrocene with diphenylcarbamoyl chloride, followed by Friedel–Crafts acylation with an acid chloride. The subsequent reduction of the carbonyl group to give the alkyl substituent was achieved using triethylsilane in trifluoroacetic acid according to the method of West *et al.* [10]. The esters were prepared by reacting the substituted phenol with the ferrocenecarboxylic acid, benzoic acid or cyclohexanecarboxylic acid and dicyclohexylcarbodiimide with 4-(*N*-pyrrolidino)pyridine catalyst [11]. The Schiffs base derivatives were prepared using the method described previously by Malthète and Billard [4].



Scheme 1. (*a*) $AlCl_3/(C_6H_5)_2NCOCl$, (*b*) $AlCl_3/RCOCl$, (*c*) $(C_2H_5)_3SiH/CF_3CO_2H$, (*d*) $KOH/CH_3OCH_2CH_2OH$, (*e*) $DCC/4PP/R^2OH$. §Compound **8** ($R^1 = H$) was prepared directly from compound **1**.

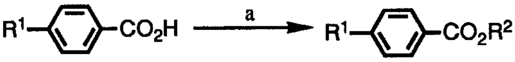

Compound number
R1
R2
12 C4H9 C7H15
13 C4H9 OC6H13
14 C4H9 O2C OC5H11
15 C6H13
16 C6H13 Br
17 C6H13 O2C Fe C6H13
18 C6H13 CO2 OC8H17
19 C6H13 CO2 OC8H17
20 C9H19 CN
21 C9H19 OC10H21
22 C9H19 O2C Fe C9H19

Scheme 1.

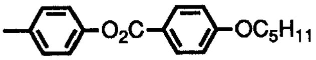
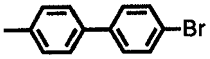
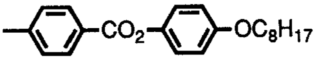
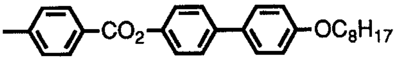


R	Compound number
H	**32**
C_4H_9	**33**
C_9H_{19}	**34**

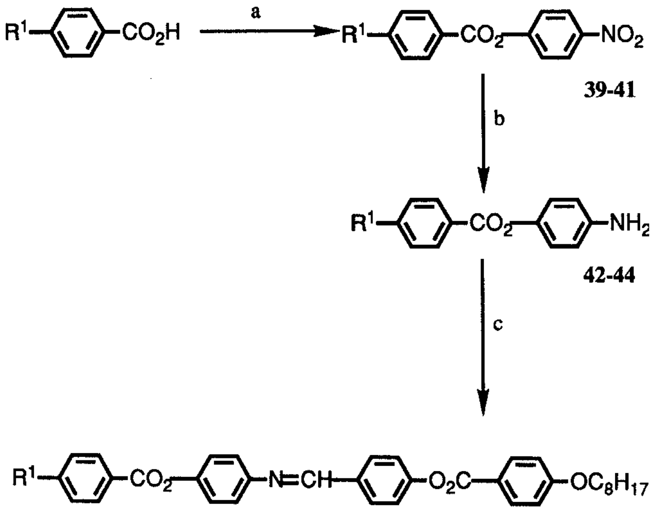
Scheme 2. (*a*) $C_8H_{17}Br/K_2CO_3$/acetone, (*b*) KOH/ethanol/water; acid, (*c*) DCC/4PP/HOC_6H_4CHO, (*d*) DCC/4PP/$HOC_6H_4NO_2$, (*e*) H_2/Pd, (*f*) ethanol, heat.



(*a*) DCC/4PP/R^{2}OH.

Compound number	*R*^{1}	*R*^{2}
35	C_4H_9	
36	C_6H_{13}	
37	C_6H_{13}	
38	C_6H_{13}	

Scheme 3.



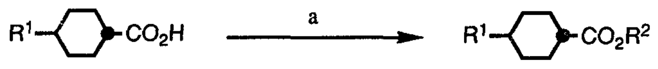
39-41

42-44

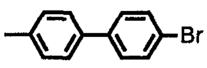
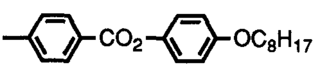
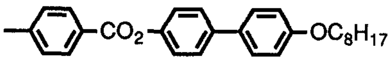
Compound number	*R*^{1}
45	H
46	C_4H_9
47	$C_{10}H_{21}$

(*a*) DCC/4PP/p-$HOC_6H_4NO_2$, (*b*) H_2/Pd, (*c*) compound **31**/ethanol.

Scheme 4.



(*a*) $R^2OH/DCC/4PP$.

Compound number	*R*¹	*R*²
48	C_6H_{13}	
49	C_6H_{13}	
50	C_6H_{13}	

Scheme 5.

2. Results and discussion

The transition temperatures for the ferrocene-based compounds, the benzene-containing analogues and, in certain examples, the cyclohexyl-containing analogues are given in tables 1 to 5. A number of compounds of increasing molecular length were prepared to assess the type of structure and the molecular length required to generate a mesophase for a molecule incorporating a ferrocene core. Table 1 shows the transition temperatures for the compounds with the shortest molecular lengths. Compounds **12** and **13** are both liquids and these do not show liquid crystalline phases on cooling; the corresponding benzene compounds (**51** and **52**) have low melting points and low clearing temperatures; the cyclohexyl analogue of compound **52** (compound **53**) has a higher nematic stability than the benzene analogue (compound **52**) by 22°C.

Table 2 shows two ferrocene compounds (**21** and **14**) with longer molecules; only the benzene analogue of compound **14** has been prepared. The ferrocene-containing compounds (**14** and **21**) are non-mesomorphic crystalline solids. Comparison between the values for compound **14** and its benzene analogue (compound **35**) shows that its nematic clearing temperature has been reduced by at least 180°C, since compound **14** supercools to room temperature in the isotropic state.

Compounds **22** and **17** in table 3 are isolated examples of compounds which contain two ferrocene units and neither is mesomorphic. A virtual T_{NI} value for compound **17** of −28°C was obtained by miscibility with I35 [1-(2'-fluoro-4'-pentylbiphenyl-4-yl)-2-(*trans*-4-propylcyclohexyl)ethane] and this value, although only approximate, indicates a reduction in the nematic clearing temperature of 321°C in comparison with the benzene analogue (compound **55**). This reduction in mesophase stability is extremely large and it seems that the detrimental effect on transition temperatures caused by the inclusion of one ferrocene unit (compounds **14** and **35**) is increased further by the inclusion of a second ferrocene unit.

Table 4 shows the structures and transition temperatures for the most comprehensive set of compounds from which the effect of changing from a cyclohexyl to a benzene to a ferrocene ring can be evaluated. From the transition temperatures shown in table 4, general trends can be seen regarding the melting points and the nematic phase thermal stabilities for compounds with a similar structure. On changing the nature of ring *X*

Table 1. Transition temperatures (°C) of ferrocene and related derivatives with small length-to-breadth ratios.

	$X = 1,1'$-disubstituted ferrocene				$X = 1,4$-disubstituted benzene						$X = trans$-1,4-disubstituted cyclohexane						
Structure	No.	C	N	I	No.	C	S_C	S_A	N	I	No.	C	S_B	S_C	S_A	N	I
$C_4H_9XCO_2PhC_7H_{15}$	**12**	Liquid			**51**†	● 9			● 15	●							
$C_4H_9XCO_2PhOC_6H_{13}$	**13**	Liquid			**52**†	● 31			● 48	●	**53**†	● 25				● 70	●

Table 2. Transition temperatures (°C) of ferrocene and related derivatives with intermediate length-to-breadth ratios.

	$X = 1,1'$-disubstituted ferrocene				$X = 1,4$-disubstituted benzene					
Structure	No.	C	N	I	No.	C	S_C	S_A	N	I
$C_9H_{19}XCO_2PhPhOC_{10}H_{21}$	**21**	● 67		●						
$C_4H_9XCO_2PhO_2CPhOC_5H_{11}$	**14**	● 77		●	**35**	● 115			● 203	●

Table 3. Transition temperatures of ferrocene and related benzene derivatives containing two ring systems (X).

	$X = 1,1'$-disubstituted ferrocene				$X = 1,4$-disubstituted benzene					
Structure	No.	C	N	I	No.	C	S_C	S_A	N	I
$C_9H_{19}XCO_2PhO_2CXC_9H_{19}$	**22**	● 35		●	**54**†	● 112	● 119		● 153	●
$C_6H_{13}XCO_2PhPhO_2CXC_6H_{13}$	**17**	● 84	[● −28]	●	**55**†	● 154	S	● 191	● 293	●

Table 4. Transition temperatures (°C) of ferrocene and related derivatives.

	X = 1,1'-disubstituted ferrocene				X = 1,4-disubstituted benzene						X = *trans*-1,4-disubstituted cyclohexane						
Structure	No.	C	N	I	No.	C	S_C	S_A	N	I	No.	C	S_B	S_C	S_A	N	I
$C_6H_{13}XCO_2PhPhH$	**15**	● 73	[● −85]	●	**56**†	● 130			(● 97)	●	**58**†	● 90				● 129	●
$C_6H_{13}XCO_2PhPhBr$	**16**	● 78	[● −20]	●	**36**	● 135		● 188	● 198	●	**48**	● 82	● 152		● 198	● 212	●
$C_9H_{19}XCO_2PhPhCN$	**20**	● 78	[● −25]	●	**57**†	● 91		● 196	● 210	●	**59**†	● 91			● 179	● 228	●
$C_6H_{13}XCO_2PhCO_2PhOC_8H_{17}$	**18**	● 54	[● −6]	●	**37**	● 88			● 170	●	**49**	● 65	● 88		● 161	● 185	●
$C_6H_{13}XCO_2PhCO_2PhPhOC_8H_{17}$	**19**	● 107	(● 63)	●	**38**	● 138	● 176		● 280	●	**50**	● 98		● 180		● 283	●

Table 5. Transition temperatures (°C) of ferrocene and related Schiffs base compounds.

	X = 1,1'-disubstituted ferrocene				X = 1,4-disubstituted benzene					
Structure	No.	C	N	I	No.	C	S_C	S_A	N	I
$XCO_2PhN{=}CHPhO_2CPhOC_8H_{17}$	**32**‡	● 153	● 167	●	**45**	● 132			● 288	●
$C_4H_9XCO_2PhN{=}CHPhO_2CPhOC_8H_{17}$	**33**	● 96	● 127	●	**46**	● 128			● 299	●
$C_9H_{19}XCO_2PhN{=}CHPhO_2CPhOC_8H_{17}$	**34**	● 83	● 115	●	**47**	● 115			● 267	●

†Transition temperatures obtained from [13].

‡Compound first reported in [4].

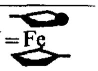
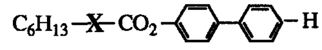
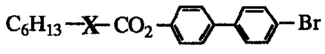
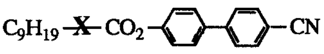
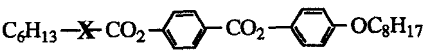
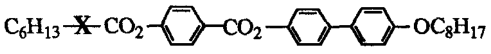
[ ] Virtual transition temperature determined by miscibility with I35 (except for compound **20** for which the cyano-host E7 was used; both hosts were supplied by Merck Ltd (Poole)).

from cyclohexyl to benzene the nematic clearing temperatures are reduced. The reductions range from only 3°C (compare compounds **50** and **38**) up to 32°C (compare compounds **58** and **56**). The melting points, however, tend to increase on changing ring *X* from cyclohexyl to benzene. The melting points increase by up to 53°C (compare compounds **48** and **36**), although in one instance they remain unchanged (compounds **57** and **59**). The changes in melting points and mesophase stabilities for the benzene- and cyclohexyl-containing systems, although adhering to a trend, are not particularly dramatic when compared to the effects which the incorporation of a ferrocene unit has on transition temperatures and melting points. Numerous comparisons are possible between the compounds listed in table 4, but in order to contain the discussion, the ferrocene-based compounds are compared only with the benzene analogues.

From table 4 it can be seen that, compared with the 1,4-disubstituted benzene ring, the 1,1'-disubstituted ferrocene core is particularly poor in stabilizing the nematic mesophase. Indeed only one of the ferrocene-based compounds shown in table 4 actually exhibits a mesophase (compound **19**); the T_{NI} values for the other four ferrocene compounds (compounds **15**, **16**, **18** and **20**) are virtual T_{NI} values. The reliability of these virtual T_{NI} values is not high, but they form the only basis for comparison; the inaccuracy of the virtual T_{NI} values is demonstrated by that for compound **18** which has a value of −6°C, and yet a sample of compound **18**, observed microscopically, does not show a nematic phase even on cooling to −15°C, at which temperature crystallization occurs.

The replacement of a 1,4-disubstituted benzene ring with a 1,1'-disubstituted ferrocene unit causes a moderate decrease in melting point for each of the systems in table 4. The reduction in melting points range from only 13°C (compare compounds **20** and **57**) up to 57°C (compare compounds **15**/**56** and **16**/**36**). The reductions in melting points, however, appear insignificant in comparison with the reductions in clearing points observed. The reductions in nematic phase thermal stabilities are tabulated in figure 5.

The values given in figure 5 show that the reductions caused by the replacement of a benzene ring with a ferrocene unit range from 176 to 235°C. The most reliable comparison within this set, however, is between compounds **38** and **19**, both of which

	T_{NI} (°C)		Reduction in clearing point/°C
	X = 	*X* = 	
	(**56**) 97	(**15**) -85	182
	(**36**) 198	(**16**) -20	218
	(**57**) 210	(**20**) -25	235
	(**37**) 170	(**18**)-6	176
	(**38**) 280	(**19**) 63†	217

† This T_{NI} value is the only non-virtual value.

Figure 5. T_{NI} values for compounds in table 4 and the decreases observed in T_{NI} on changing *X* from 1,4-disubstituted benzene to 1,1'-disubstituted ferrocene.

actually exhibit nematic phases; the decrease in the T_{NI} value in this example is 217°C. The other reductions in figure 5, based on virtual T_{NI} values for the ferrocene compounds, do not appear unreasonable in comparison. From the data presented it is clear that the order for the promotion of nematic phase stability in these systems is cyclohexyl > benzene > > > ferrocene. The 1,1'-disubstituted ferrocene unit causes immense reductions in T_{NI} values when incorporated into linear systems and the possible reasons for this effect are discussed later.

Three Schiffs bases incorporating the ferrocene unit are shown in table 5 along with their benzene analogues. Compound **32** was first reported by Malthête *et al.* [4], and compounds **33** and **34** are alkyl derivatives of this compound. The transition temperatures give three additional direct comparisons between the 1,1'-disubstituted ferrocene unit and the 1,4-disubstituted benzene ring as all of the compounds are nematic. Compounds **32** and **45** show that the melting point is increased by 21°C on changing ring *X* from benzene to ferrocene, but the nematic clearing point is decreased by 121°C. The corresponding change for the butyl-compounds (**33** and **46**) and nonyl-compounds (**34** and **47**) causes the melting points to decrease by 32°C in each case and the clearing temperatures to decrease by 172°C and 152°C, respectively.

In conclusion, the incorporation of a 1,1'-disubstituted ferrocene unit into linear liquid crystalline systems causes severe reductions in mesophase thermal stability. This finding is contrary to that presented by Singh *et al.* [7] who stated that 'the ferrocene unit can be an effective component of a mesogen'. From the results presented in tables 1 to 5 it can be seen that the ferrocene unit is hardly an effective component although it can be tolerated within linear systems, provided that the molecule is sufficiently long to offset the reduction in mesogenic properties caused by its inclusion; see compounds **19**, and **32**–**34**.

The reasons for the reduction of T_{NI} values caused by the incorporation of the ferrocene unit in comparison to other common ring systems (for example, benzene and cyclohexyl) are open to speculation. In their paper, Singh *et al.* [7] described the ferrocene unit as having the ability to impart both rigidity and collinearity to a system. However, when a model of the ferrocene unit is considered, it seems likely that these two reasons are invalid, and indeed it is more likely that the lack of collinearity and the lack of rigidity conferred by the ferrocene unit is responsible for the reduced mesogenic character.

The structure of a 1,1'-disubstituted ferrocene system is represented in figure 6 which shows a side elevation of the molecule, and it is clear that the ferrocene unit

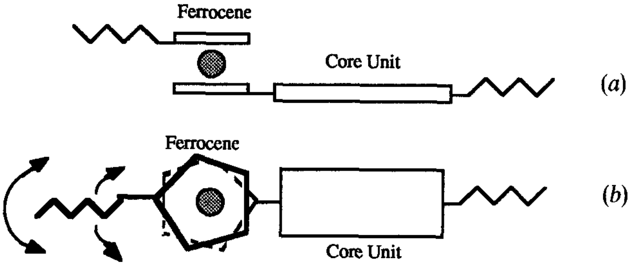
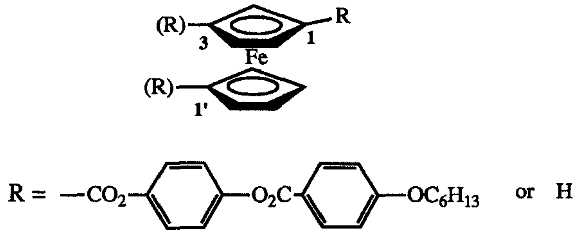


Figure 6. Side (*a*) and plan (*b*) elevations of a 1,1-disubstituted ferrocene showing how the cyclopentadienyl rings can rotate. The cyclopentadienyl ring below the plane of the paper is shown with dotted lines.

imparts a 'step' into the structure. As a consequence of this step, the alkyl chain cannot be coplanar with the major core system of the molecule. The interplanar distance between the two cyclopentadienyl rings is between 3 and 5Å [12]. In addition to the lack of coplanarity, it is possible that a lack of rigidity is conferred on the system by the inclusion of the ferrocene unit.

Khan *et al.* [6] have determined that the ferrocene diesters exist in the fully extended 'S' geometry. This appears to be a reasonable geometry for the molecules to adopt rather than the alternative 'U' geometry which would lead to the substituents in each of the cyclopentadienyl rings coming into close contact. The internal energy for the rotation of the cyclopentadienyl rings in ferrocene [12] is only ~4 kJ mol^{-1} and it is likely that, in a disubstituted system, some degree of rotation occurs (as shown by the arrows in figure 6(*b*)). Such rotations would decrease the rigidity of the system in comparison with a similarly substituted benzene or cyclohexyl ring. These reasons may explain why all of the systems studied to date which incorporate a 1,1′-disubstituted ferrocene core give, at best, mesophases of low thermal stability [4, 5]. In contrast, 1,3-disubstituted ferrocene derivatives, in which rotation of the cyclopentadienyl rings will not affect the rigidity of the system, all form enantiotropic nematic phases. Figure 7 shows examples [8] of 1,1′- and 1,3-disubstituted ferrocenes to illustrate this point.



1,3-disubstituted derivative C 184°C N 248°C I
1,1′-disubstituted derivative C 172°C (N 153°C) I

Figure 7. Transition temperatures for 1,1′ and 1,3-disubstituted ferrocene derivatives [8].

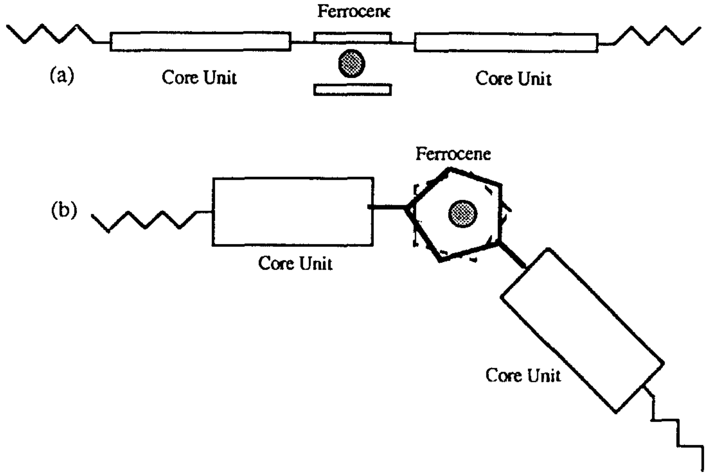


Figure 8. Side (*a*) and plan (*b*) elevations of a 1,3-disubstituted ferrocene system. The cyclopentadienyl ring below the plane of the paper is shown with dotted lines.

From the example shown in figure 7, it can be seen that the change from 1,1'- to 1,3-disubstituted ferrocene causes an increase in clearing temperature of 95°C. The 1,3-disubstituted derivative, although containing a central bulky ferrocene unit, will not suffer from the rotational or non-collinear effects discussed previously. The molecule is bent (see figure 8 (*b*)), but it will be both rigid and will not contain a 'stepped' structure in which the two core units constitute the 'step' (see figure 8 (*a*)).

3. Experimental

The transition temperatures and natures of the phases were determined using an Olympus BH2 polarizing microscope fitted with a Mettler FP52 heating stage and temperature controller. The transition temperatures were confirmed using a Perkin–Elmer DSC-2C differential scanning calorimeter, calibrated with a pure indium sample. ^{1}H NMR spectra were obtained using a JEOL JNM-GX270 spectrometer, infrared spectra were obtained using a Perkin–Elmer 457 grating spectrophotometer and mass spectra were obtained using a Finnigan-MAT 1020GC/MS spectrometer. The progress of reactions was monitored by thin layer chromatography (Merck, silica gel 60 F_{254} coated on aluminium sheets). Compounds were purified, where specified, by column chromatography using silica gel 60–120 mesh or by flash chromatography using Sorbsil C60 silica.

3.1. *N,N-Diphenylcarbamoylferrocene* (**1**)

Powdered aluminium chloride (44·0 g, 32 mmol) was added to a cooled (0°C), stirred solution of diphenylcarbamoyl chloride (62·2 g, 27 mmol) in dry 1,2-dichloroethane (150 ml). A solution of ferrocene (50·0 g, 27 mmol) in dry 1,2-dichloroethane (350 ml) was added dropwise to the mixture during 1 h. The reaction mixture was stirred and heated under reflux for a further 10 h and allowed to cool. Water (150 ml) was added to the mixture and the organic layer was washed with 10 per cent aqueous sodium hydroxide (100 ml) and then repeatedly with water (200 ml) until the aqueous washings were neutral. The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane : petroleum spirit [bp 40–60°C], 1 : 1). The eluent was changed (dichloromethane : ethyl acetate, 10 : 1) after the unreacted ferrocene had been eluted and the product was obtained as orange/brown crystals. Yield 77·8 g, 76 per cent; mp 178–179°C; ^{1}H NMR ($CDCl_3$), δ 4·17(d,2 H), 4·19(d,2 H), 4·25(s,5 H), 7·24(m,6 H), 7·35 ppm (m,4 H); ν_{max} 1732, 1645, 1600, 1490, 1445, 1340, 1270, 830, 765, 698 cm^{-1}; (*m*/*z*) 381(M^+), 213(100 per cent), 185, 129, 121.

3.2. *1-Butanoyl-1'-N,N-diphenylcarbamoylferrocene* (**2**)

Powdered aluminium chloride (3·58 g, 26·2 mmol) was added to a cooled (0°C), stirred solution of compound **1** (5·0 g, 13·1 mmol) in dry 1,2-dichloroethane (50 ml). A solution of butanoyl chloride (1·4 g, 13·1 mmol) in dry 1,2-dichloroethane (20 ml) was added dropwise to the mixture during 1 h. The reaction mixture was allowed to reach room temperature and stirred for a further 4 h. Water (100 ml) was added to the mixture and the organic layer was washed with 10 per cent aqueous sodium hydroxide (50 ml) and then repeatedly with water (150 ml) until the aqueous washings were neutral. The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane) to give the product as an orange/brown semi-solid. Yield 2·4 g, 40 per cent;

^{1}H NMR (CDCl$_3$) δ 0·98(t,3 H), 1·74(m,2 H), 2·72(t,2 H), 4·18(m,4 H), 4·58(s,2 H), 4·80(s,2 H), 7·20(m,6 H), 7·35 ppm(m,4 H); ν_{max} 2950, 2890, 1730, 1700, 1630, 1590, 1490, 1345, 1280, 835 cm^{-1}; (*m*/*z*) 451 (M$^+$), 283(100 per cent), 213, 185, 167.

The following compounds were prepared by using a similar procedure to that described for compound **2**.

3.3. *1-Hexanoyl-1′-N,N-diphenylcarbamoylferrocene* (**3**)

An orange/brown semi-solid from compound **1** and hexanoyl chloride; yield 15·6 g, 62 per cent; ^{1}H NMR(CDCl$_3$) δ 0·90(t,3 H), 1·34(m,4 H), 1·68(m,2 H), 2·72(t,2 H), 4·18(tt, 4 H), 4·57(t,2 H), 4·80(t,2 H), 7·25(m,6 H), 7·36 ppm(m,4 H); ν_{max} 2950, 2890, 1730, 1705, 1635, 1600, 1495, 1348, 1290, 840 cm^{-1}; (*m*/*z*) 479(M$^+$), 311(100 per cent), 212, 184, 168.

3.4. *1-Nonanoyl-1′-N,N-diphenylcarbamoylferrocene* (**4**)

An orange/brown semi-solid from compound **1** and octanoyl chloride; yield 14·3 g, 87 per cent; ^{1}H NMR(CDCl$_3$) δ 0·90(t,3 H), 1·30(m,10 H), 1·70(m,2 H), 2·70(t,2 H), 4·18(m,4 H), 4·58(s,2 H), 4·80(t,2 H), 7·25(m,6 H), 7·35 ppm(m,4 H); ν_{max} 2950, 2890, 1728, 1710, 1640, 1600, 1490, 1350, 1290, 830 cm^{-1}; (*m*/*z*) 521(M$^+$), 353(100 per cent), 212, 184, 168.

3.5. *1-Butyl-1′-N,N-diphenylcarbamoylferrocene* (**5**)

Triethylsilane (1·33 g, 11·4 mmol) was added dropwise over 30 min to a cooled (0°C), stirred solution of compound **2** (2·36 g, 5·2 mmol) in trifluoroacetic acid (6·0 g, 52 mmol) and dry dichloromethane (150 ml). The reaction mixture was allowed to reach room temperature and stirred for a further 3 h. Portions of saturated aqueous sodium bicarbonate were added carefully to the reaction mixture until the evolution of carbon dioxide had ceased. The organic material was extracted into dichloromethane (2 × 50 ml) and the combined extracts were washed with water (2 × 50 ml) and dried (MgSO$_4$). The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, dichloromethane) to give an orange/brown oil. Yield 1·23 g, 54 per cent; ^{1}H NMR(CDCl$_3$) δ 0·90(t,3 H), 1·45(m,4 H), 2·28(t,2 H), 4·20(m,8 H), 7·22(m,6 H), 7·35 ppm(m,4 H); ν_{max} 2950, 2880, 1650, 1590, 1490, 1448, 1378, 1320, 1290, 760 cm^{-1}; (*m*/*z*) 437(M$^+$), 268(100 per cent), 212, 198, 167.

The following compounds were prepared by using a similar procedure to that described for compound **5**.

3.6. *1-Hexyl-1′-N,N-diphenylcarbamoylferrocene* (**6**)

An orange/brown semi-solid from compound **3**; yield 3·75 g, 59 per cent; ^{1}H NMR(CDCl$_3$), δ 0·90(t,3 H), 1·32(m,6 H), 1·50(m,2 H), 2·35(t,2 H), 4·08(m,4 H), 4·12(t,2 H), 4·15(t,2 H), 7·23(m,6 H), 7·34 ppm(m,4 H); ν_{max} 2930, 2870, 1630, 1592, 1442, 1300, 1012, 830, 735, 695 cm^{-1}; (*m*/*z*) 465(M$^+$), 297, 199, 55(100 per cent).

3.7. *1-Nonyl-1′-N,N-diphenylcarbamoylferrocene* (**7**)

An orange/brown semi-solid from compound **4**; yield 7·3 g, 53 per cent; ^{1}H NMR(CDCl$_3$), δ 0·90(t,3 H), 1·27(m,12 H), 1·50(m,2 H), 2·35(t, 2 H), 4·08(m,4 H), 4·14(m,4 H), 7·22(m,6 H), 7·35 ppm(m,4 H); ν_{max} 2930, 2870, 1648, 1595, 1495, 1448, 1380, 1302, 760, 700 cm^{-1}; (*m*/*z*) 507(M$^+$, 100 per cent), 339, 199, 166, 120.

3.8. *Ferrocenecarboxylic acid* (**8**)

Compound **1** (5·0 g, 13·1 mmol) was added to a homogeneous mixture of potassium hydroxide (6·0 g, 107 mmol) in 2-methoxyethanol (150 ml) and water (10 ml). The reaction mixture was heated under reflux for 24 h, allowed to cool to room temperature and acidified with concentrated hydrochloric acid. The organic material was extracted into ether (2 × 100 ml) and the combined ethereal extracts were washed with water (200 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the crude acid was purified by column chromatography (silica gel, dichloromethane) to give brown crystals. Yield 2·14 g, 71 per cent; mp 205–206°C; ^{1}H NMR($CDCl_3$), δ 4·30(s,5 H), 4·50(s,2 H), 4·90 ppm(s,2 H) the acid proton was not detected; ν_{max} 3120–2560, 1660, 1480, 1402, 1285, 1160, 1035, 942, 838, 742 cm^{-1}; (*m/z*) 230(M$^+$), 165, 138(100 per cent), 73, 56.

The following compounds were prepared by using a similar procedure to that described for compound **8**.

3.9. *1′-Butylferrocene-1-carboxylic acid* (**9**)

Orange/brown crystals from compound **5**; yield 0·52 g, 80 per cent; mp 130–132°C; ^{1}H NMR($CDCl_3$), δ 0·90(t,3 H), 1·40(m,4 H), 2·25(m,2 H), 4·25(s,4 H), 4·50(s,2 H), 4·85 ppm(s,2 H), the acid proton was not detected; ν_{max} 3300–2500, 1668, 1480, 1298, 1162, 1030, 930, 820, 744 cm^{-1}; (*m/z*) 286(M$^+$), 174, 165, 148, 81(100 per cent).

3.10. *1′-Hexylferrocene-1-carboxylic acid* (**10**)

Orange/brown crystals from compound **6**; yield 0·85 g, 60 per cent; mp 115–118°C; ^{1}H NMR($CDCl_3$), δ 0·90(t,3 H), 1·26(m,6 H), 1·45(m,2 H), 2·26(t,2 H), 4·14(s,4 H), 4·43(s,2 H), 4·80 ppm(s,2 H), the acid proton was not detected; ν_{max} 3100–2560, 2940, 2870, 1672, 1480, 1300, 1170, 1030, 828 cm^{-1}; (*m/z*) 314(M$^+$, 100 per cent), 243, 200, 165, 73.

3.11. *1′-Nonylferrocene-1-carboxylic acid* (**11**)

Orange/brown crystals from compound **7**; yield 1·7 g, 62 per cent; mp 61–62°C; ^{1}H NMR($CDCl_3$), δ 0·90(t,3 H), 1·30(m,10 H), 1·45(m,2 H), 1·65(m,2 H), 2·40(t,2 H), 4·12(s,4 H), 4·44(s,2 H), 4·78 ppm(s,2 H), the acid proton was not detected; ν_{max} 3080, 2930, 2860, 1700, 1678, 1480, 1292, 1170, 1030, 820 cm^{-1}; (*m/z*) 356(M$^+$,100 per cent), 242, 165.

3.12. *4-Heptylphenyl 1′-butylferrocene-1-carboxylate* (**12**)

Dicyclohexylcarbodiimide (0·57 g, 2·8 mmol) and 4-(*N*-pyrrolidino)pyridine (0·1 g) were added to a stirred solution of compound **9** (0·70 g, 2·5 mmol) and 4-heptylphenol (0·47 g, 2·5 mmol) in dry dichloromethane (50 ml). The reaction mixture was stirred at room temperature for 6 h. The dicyclohexylurea was filtered off and the solvent from the filtrate was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane) to give an orange/brown liquid. Yield 1·05 g, 92 per cent; ^{1}H NMR($CDCl_3$), δ 0·90(2 × t,6 H), 1·34(m,10 H), 1·48(m,2 H), 1·64(m,2 H), 2·32(t,2 H), 2·62(t,2 H), 4·20(s,4 H), 4·45(s,2 H), 4·90(s,2 H), 7·08(d,2 H), 7·20 ppm(d,2 H); ν_{max} 2960, 2940, 1730, 1455, 1270, 1198, 1168, 1100, 1020, 912 cm^{-1}; (*m/z*) 460(M$^+$), 269(100 per cent), 192, 121, 107.

The following compounds were prepared by using a similar procedure to that described for compound **12**.

3.13. *4-Hexyloxyphenyl 1'-butylferrocene-1-carboxylate* (**13**)

An orange/red liquid from compound **9** and 4-hexyloxyphenol; yield 0·77 g, 87 per cent; ^{1}H NMR(CDCl$_3$), δ 0·90(t,3 H), 0·92(t,3 H), 1·35(m,10 H), 1·46(m,2 H), 2·34(t,2 H), 3·95(t,2 H), 4·15(2 × s,4 H), 4·45(s,2 H), 4·86(s,2 H), 6·92(d,2 H), 7·09 ppm(d,2 H); ν_{max} 2930, 2860, 1730, 1610, 1465, 1272, 1196, 1102, 1025, 912 cm^{-1}; (*m/z*) 462(M$^+$), 269(100 per cent), 199, 121, 110.

3.14. *4-(4-Pentyloxybenzoyloxy)phenyl 1'-butylferrocene-1-carboxylate* (**14**)

Orange crystals from compound **9** and 4-(4-pentyloxybenzoyloxy)phenol; yield 0·35 g, 90 per cent; mp 76–77°C; ^{1}H NMR(CDCl$_3$), δ 0·90(t,3 H), 0·95(t,3 H), 1·35(m,2 H), 1·45(m,6 H), 1·84(m,2 H), 2·35(t,2 H), 4·05(t,2 H), 4·18(s,4 H), 4·47(s,2 H), 4·88(s,2 H), 6·98(d,2 H), 7·25(2 × s,4 H), 8·15 ppm(d,2 H); ν_{max} 2930, 2860, 1738, 1720, 1610, 1455, 1260, 1134, 1108, 1070 cm^{-1}; (*m/z*) 568(M$^+$), 268, 198, 191, 120(100 per cent).

3.15. *Biphenyl-4-yl 1'-hexylferrocene-1-carboxylate* (**15**)

Orange crystals from compound **10** and 4-hydroxybiphenyl; yield 0·25 g, 83 per cent; mp 72–73°C; ^{1}H NMR(CDCl$_3$), δ 0·90(t,3 H), 1·28(m,6 H), 1·46(m,2 H), 2·80(t,2 H), 4·24(s,4 H), 4·48(s,2 H), 4·94(s,2 H), 7.24(d,2 H), 7·35(d,2 H), 7·35(m,1 H), 7·45(t,2 H), 7·59(d,2 H), 7·62 ppm(d,2 H); ν_{max} 2920, 2850, 1716, 1480, 1448, 1265, 1200, 1165, 1100, 1005 cm^{-1}; (*m/z*) 466(M$^+$), 297(100 per cent), 199, 141, 115.

3.16. *4'Bromobiphenyl-4-yl 1'-hexylferrocene-1-carboxylate* (**16**)

Orange crystals from compound **10** and 4-bromo-4'-hydroxybiphenyl; yield 0·28 g, 78 per cent; mp 77–78°C; ^{1}H NMR(CDCl$_3$), δ 0·86(t,3 H), 1·30(m,6 H), 1·49(m,2 H), 2·32(t,2 H), 4·19(m,4 H), 4·46(s,2 H), 4·90(s,2 H), 7·26(d,2 H), 7·45(d,2 H), 7·57(d,2 H), 7·59 ppm(d,2 H); ν_{max} 2920, 2850, 1725, 1478, 1442, 1270, 1200, 1092, 1000, 830 cm^{-1}; (*m/z*) 545, 544(M$^+$), 465, 464, 297(100 per cent), 115.

3·17. *4,4'-Di-(1'-hexylferrocene-1-carbonyloxy)biphenyl* (**17**)

Orange crystals from compound **10** and 4,4'-dihydroxybiphenyl; yield 0·15 g, 60 per cent; mp 83–84°C; ^{1}H NMR(CDCl$_3$), δ 0·88(t,6 H), 1·30(m,12 H), 1·50(m,4 H), 2·35(t,4 H), 4·20(s,8 H), 4·46(s,4 H), 4·90(s,4 H), 7·26(d,4 H), 7·64 ppm(d,4 H); ν_{max} 2920, 2850, 1715, 1448, 1268, 1202, 1168, 1110 cm^{-1}; (*m/z*) 778(M$^+$), 297(100 per cent), 268, 227, 199.

3.18. *4-(4-Octyloxyphenyloxycarbonyl)phenyl 1'-hexylferrocene-1-carboxylate* (**18**)

Orange crystals from compound **10** and 4-(4-octyloxyphenyloxycarbonyl)phenol; yield 0·26 g, 85 per cent; mp 53–54°C; ^{1}H NMR(CDCl$_3$), δ 0·90(2 × t,6 H), 1·30(m,12 H), 1·48(m,4 H), 1·75(m,2 H), 1·92(m,2 H), 2·32(t,2 H), 3·96(t,2 H), 4·20(s,4 H), 4·49(s,2 H), 4·90(s,2 H), 6·94(d,2 H), 7·12(d,2 H), 7·35(d,2 H), 7·37 ppm(d,2 H); ν_{max} 2920, 2840, 1720, 1600, 1502, 1450, 1262, 1186, 1156, 1062 cm^{-1}; (*m/z*) 638(M$^+$), 297(100 per cent), 199, 121.

3.19. *4-[(4'-Octyloxybiphenyl-4-yl)oxycarbonyl]phenyl 1'-hexylferrocene-1-carboxylate* (**19**)

Orange crystals from compound **10** and 4-[(4'-octyloxybiphenyl-4-yl)oxycarbonyl]phenol; yield 0·28 g, 82 per cent; transitions C 107°C (N 63°C) I; ^{1}H NMR(CDCl$_3$), δ 0·90(2 × t,6 H), 1·30(m,12 H), 1·48(m,4 H),1·75(m,2 H), 1·92(m,2 H), 2·34(t,2 H), 4·00(t,2 H), 4·20(s,4 H), 4·48(s,2 H), 4·90(s,2 H), 6·94(d,2 H), 7·26(d,2 H),7·35(d,2 H),7·52(d,2 H), 7·60(d,2 H), 8·30(d,2 H); ν_{max} 2920, 2845, 1730, 1718, 1492, 1268, 1208, 1160, 1070 cm^{-1}; (*m*/*z*) 714(M$^+$), 297(100 per cent), 121.

3.20. *4′-Cyanobiphenyl-4-yl 1′-nonylferrocene-1-carboxylate* (**20**)

Orange crystals from compound **11** and 4-cyano-4′-hydroxybiphenyl; yield 0·62 g, 84 per cent; mp 77–78°C; ^{1}H NMR(CDCl$_3$), δ 0·85(t,3 H), 1·24(m,10 H), 1·48(m,2 H), 2·32(t,2 H), 4·18(d,4 H), 4·46(t,2 H), 4·90(t,2 H), 7·31(d,2 H), 7·65(d,2 H), 7·68(d,2 H), 7·76 ppm(d,2 H); ν_{max} 2930, 2860, 2230, 1725, 1610, 1550, 1458, 1280, 1205, 1110 cm^{-1}; (*m*/*z*) 533(M$^+$), 339(100 per cent), 239, 199, 121.

3.21. *4′-Decyloxybiphenyl-4-yl 1′-nonylferrocene-1-carboxylate* (**21**)

Orange crystals from compound **11** and 4-hydroxy-4′-decyloxybiphenyl; yield 0·86 g, 93 per cent; mp 66–67°C; ^{1}H NMR(CDCl$_3$), δ 0·88(2 × t,6 H), 1·28(m,24 H), 1·45(m,4 H), 1·70(m,2 H), 2·12(m,2 H), 4·00(t,2 H), 4·60(m,6 H), 5·12(m,2 H), 6·96(d,2 H), 7·16(d,2 H), 7·52 ppm(2 × d,4 H); ν_{max} 2930, 2860, 1732, 1612, 1502, 1280, 1210, 1172, 1104, 838 cm^{-1}; (*m*/*z*) 664(M$^+$), 339, 199, 185, 57(100 per cent).

3.22. *1,4-Di-(1′-nonylferrocene-1-carbonyloxy)benzene* (**22**)

Orange crystals from compound **11** and hydroquinone; yield 0·36 g, 75 per cent; mp 34–36°C; ^{1}H NMR(CDCl$_3$), δ 0·90(t,6 H), 1·28(m,24 H), 1·50(m,4 H), 2·34(m,4 H), 4·18(m,8 H), 4·45(s,4 H), 4·88(s,4 H), 7·24 ppm(s,4 H); ν_{max} 2930, 2860, 1730, 1505, 1452, 1380, 1275, 1188, 1102, 835 cm^{-1}; (*m*/*z*) 786(M$^+$), 588, 339, 198, 140(100 per cent).

3.23. *4-Nitrophenyl ferrocenecarboxylate* (**23**)

Orange crystals from compound **8** and 4-nitrophenol; yield 1·98 g, 98 per cent; mp 142–143°C; ^{1}H NMR(CDCl$_3$), δ 4·30(s,5 H), 4·56(s,2 H), 4·98(s,2 H), 7·40(d,2 H), 8·30 ppm (d,2 H); ν_{max} 1740, 1598, 1518, 1450, 1342, 1210, 1090, 1022, 912, 760 cm^{-1}; (*m*/*z*) 351(M$^+$,100 per cent), 213, 185.

3.24. *4-Nitrophenyl 1′-butylferrocene-1-carboxylate* (**24**)

Orange crystals from compound **9** and 4-nitrophenol; yield 1·2 g, 85 per cent; mp 128–129°C; ^{1}H NMR(CDCl$_3$), δ 0·90(t,3 H), 1·32(m,2 H), 1·50(m,2 H), 2·30(t,2 H), 4·20(s,4 H), 4·50(s,2 H), 4·90(s,2 H), 7·40(d,2 H), 8·30 ppm (d,2 H);ν_{max} 2930, 2860, 1740, 1599, 1520, 1450, 1345, 1210, 1090, 860 cm^{-1}; (*m*/*z*) 407(M$^+$,100 per cent), 269.

3.25. *4-Nitrophenyl 1′-nonylferrocene-1-carboxylate* (**25**)

Orange crystals from compound **11** and 4-nitrophenol; yield 1·25 g, 93 per cent; mp 110–111°C; ^{1}H NMR(CDCl$_3$), δ 0·88(t,3 H), 1·28(m,12 H), 1·50(m,2 H), 2·30(t,2 H), 4·18(s,4 H), 4·50(s,2 H) 4·88(s,2 H), 7·40(d,2 H), 8·32 ppm (d,2 H); ν_{max} 2930, 2860, 1740, 1598, 1526, 1452, 1348, 1208, 1090, 862 cm^{-1}; (*m*/*z*) 477(M$^+$,100 per cent), 339.

3.26. *4-Aminophenyl ferrocenecarboxylate* (**26**)

A stirred solution of compound **23** (1·8 g, 5·1 mmol) in THF (80 ml) was hydrogenated over a palladium/charcoal catalyst. After the calculated volume of hydrogen had been taken up the catalyst was filtered off (Hyflo Supercel) and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane) to give orange crystals. Yield 0·63 g, 38 per cent; mp 151–152°C; ^{1}H NMR(CDCl$_3$), δ 3·35(s,2 H), 4·30(s,5 H), 4·48(s,2 H), 4·95(s,2 H), 6·75(d,2 H), 7·00 ppm (d,2 H); ν_{max} 3380, 3350, 1715, 1620, 1510, 1452, 1280, 1195, 1116, 825 cm^{-1}; (*m*/*z*) 321(M$^+$), 114, 80, 69, 54(100 per cent).

The following compounds were prepared by using a similar procedure to that described for compound **26**.

3.27. *4-Aminophenyl 1′-butylferrocene-1-carboxylate* (**27**)

Orange oil from compound **24**; yield 0·76 g, 68 per cent; ^{1}H NMR(CDCl$_3$), δ 0·90(t,3 H), 1·34(m,2 H), 1·45(m,2 H), 2·34(t,2 H), 3·65(s,2 H), 4·15(s,4 H), 4·42(s,2 H), 4·85(s,2 H), 6·70(d,2 H), 6·96 ppm(d,2 H); ν_{max} 3460, 3370, 2940, 1720, 1630, 1515, 1455, 1275, 1196, 1110 cm^{-1}; (*m*/*z*) 377(M$^+$,100 per cent), 269, 199, 108.

3.28. *4-Aminophenyl 1′-nonylferrocene-1-carboxylate* (**28**)

Orange oil from compound **25**; yield 0·70 g, 70 per cent; ^{1}H NMR(CDCl$_3$), δ 0·89(t,3 H), 1·26(m,12 H), 1·49(m,2 H), 2·33(t,2 H), 3·65(s,2 H), 4·16(s,4 H), 4·42(s,2 H), 4·85(s,2 H), 6·72(d,2 H), 7·12 ppm(d,2 H); ν_{max} 3960, 3380, 2930, 2860, 1720, 1630, 1517, 1452, 1196, 1110 cm^{-1}; (*m*/*z*) 447(M$^+$,100 per cent), 339, 108.

3.29. *Methyl 4-octyloxybenzoate* (**29**)

A solution of 1-bromo-octane (22·9 g, 118·4 mmol) in acetone (50 ml) was added dropwise during 1 h to a vigorously stirred mixture of methyl 4-hydroxybenzoate (15·0 g, 98 mmol) and potassium carbonate (27·3 g, 197 mmol) in acetone (300 ml). The mixture was heated under reflux for 72 h and allowed to cool to room temperature. The organic material was extracted into ether (2 x 300 ml) and the combined ethereal extracts were washed with water (400 ml) and dried (MgSO$_4$). The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, dichloromethane : petroleum spirit [bp 40–60°C], 1 : 1) to give colourless crystals. Yield 7·06 g, 27 per cent; mp 35–36°C; ^{1}H NMR(CDCl$_3$), δ 0·90(t,3 H), 1·30(m,8 H), 1·45(m,2 H), 1·80(m,2 H), 3·88(s,3 H), 4·00(t,2 H), 6·90(d,2 H), 7·96 ppm(d,2 H); ν_{max} 2920, 2860, 1730, 1612, 1440, 1288, 1258, 1172, 1112, 850 cm^{-1}; (*m*/*z*) 264(M$^+$,100 per cent), 152, 121, 113.

3.30. *4-Octyloxybenzoic acid* (**30**)

Compound **29** (5·0 g, 19 mmol) was added to a homogeneous mixture of potassium hydroxide (1·10 g, 19·6 mmol) in ethanol (100 ml) and water (10 ml) and the reaction mixture was heated under reflux for 8 h. The reaction mixture was allowed to cool to room temperature and the excess of ethanol was removed under reduced pressure. The salt of the required acid was taken up in water (200 ml) and washed with ether (100 ml). The aqueous layer was acidified with sulphuric acid and the resulting precipitate was filtered off and washed with water. The crude product was purified by recrystallization (petroleum spirit [bp 40–60°C]) to give colourless needles. Yield 4·6 g, 97 per cent; transitions C 101°C S$_C$ 108°C S$_A$ 143°C I; ^{1}H NMR(CDCl$_3$), δ 0·90(t,3 H), 1·30(m,8 H), 1·45(m,2 H), 1·80(m,2 H), 4·02(t,2 H), 6·95(d,2 H), 8·05(d,2 H), 12·15 ppm(s,1 H); ν_{max} 2930, 2850, 2600, 1690, 1610, 1430, 1252, 1170, 930, 850 cm^{-1}; (*m*/*z*) 250(M$^+$), 138, 71, 57, 43(100 per cent).

3.31. *4-(4-Octyloxybenzoyloxy)benzaldehyde* (**31**)

This compound was prepared as colourless crystals from compound **30** and 4-hydroxybenzaldehyde by using a similar procedure to that described for compound **12**. Yield 3·93 g, 92 per cent; transitions C 56°C N 126°C I; ^{1}H NMR($CDCl_3$), δ 0·90(t,3 H), 1·34(m,8 H), 1·50(m,2 H), 1·85(m,2 H), 4·05(t,2 H), 6·98(d,2 H), 7·40(d,2 H), 7·95(d,2 H), 8·12(d,2 H), 10·02 ppm(s,1 H);ν_{max} 2935, 2855, 1735, 1704, 1608, 1516, 1270, 1218, 1170, 1075 cm^{-1}; (*m*/*z*) 354(M^+), 233(100 per cent), 120, 93.

3.32. *1-(Ferrocenecarbonyloxy)-4-[4-(4-octyloxybenzoyloxy) benzylideneamino]benzene* (**32**)

A mixture of compound **31** (0·57 g, 1·6 mmol) and compound **26** (0·52 g, 1·6 mmol) in ethanol was heated under reflux for 10 h. The mixture was allowed to cool and the product crystallized as orange plates. The precipitate was filtered off and recrystallized (ethanol). Yield 0·68 g, 55 per cent; transitions C 154°C N 168°C I; ^{1}H NMR($CDCl_3$), δ 0·90(t,3 H), 1·34(m,8 H), 1·48(m,2 H), 1·85(m,2 H), 4·05(t,2 H), 4·30(m,5 H), 4·50(m,2 H), 4·98(m,2 H), 7·00(d,2 H), 7·22(d,2 H), 7·30(d,2 H), 7·36(d,2 H), 8·00(d,2 H), 8·15(d,2 H), 8·50 ppm(s,1 H); ν_{max} 2930, 2860, 1730, 1610, 1512, 1260, 1195, 1168, 1102, 1060 cm^{-1}; (*m*/*z*) 657(M^+), 520, 393, 321(100 per cent), 213.

The following compounds were prepared by using a similar procedure to that described for compound **32**.

3.33. *1-(1'-Butylferrocene-1-carbonyloxy)-4-[4-(4-octyloxybenzoyloxy)benzylideneamino]benzene* (**33**)

Orange plates from compounds **31** and **27**; yield 0·71 g, 50 per cent; transitions C 96°C N 127°C I; ^{1}H NMR($CDCl_3$), δ 0·90(t,6 H), 1·30(m, 10 H), 1·48(m,4 H), 1·84(m,2 H), 2·35(t,2 H), 4·05(t,2 H), 4·18(m,4 H), 4·46(s,2 H), 4·90(s,2 H), 7·08(d,2 H), 7·25(d,2 H), 7·30(d,2 H), 7·36(d,2 H), 7·95(d,2 H), 8·16(d,2 H), 8·60 ppm(s,1 H); ν_{max} 2930, 2860, 1730, 1720, 1604, 1510, 1260, 1195, 1102, 1060 cm^{-1}; (*m*/*z*) 713(M^+), 268, 233, 199, 121(100 per cent).

3.34. *1-(1'-Nonylferrocene-1-carbonyloxy)-4-[4-(4-octyloxybenzoyloxy)benzylideneamino]benzene* (**34**)

Orange plates from compounds **31** and **28**; yield 0·57 g, 52 per cent; transitions C 83°C N 115°C I; ^{1}H NMR($CDCl_3$), δ 0·90(tt,6 H), 1·30(m,20 H), 1·46(m,4 H), 1·82(m,2 H), 2·34(t,2 H), 4·05(t,2 H), 4·20(m,4 H), 4·45(s,2 H), 4·90(s,2 H), 6·97(d,2 H), 7·25(d,2 H), 7·30(d,2 H), 7·35(d,2 H), 7·95(d,2 H), 8·15(d,2 H),8·60 ppm(s,1 H); ν_{max} 2930, 2860, 1730, 1720, 1610, 1512, 1260, 1195, 1165, 1060 cm^{-1}; (*m*/*z*) 783(M^+), 712, 552, 446, 356(100 per cent).

The following compounds were prepared by using a similar procedure to that described for compound **12**.

3.35. *4-(4-Pentyloxybenzoyloxy)phenyl 4-butylbenzoate* (**35**)

Colourless crystals from 4-butylbenzoic acid and 4-(4-pentyloxybenzoyloxy)phenol; yield 2·3 g, 92 per cent; transitions C 115°C N 203°C I; ^{1}H NMR($CDCl_3$), δ 0·95(2 × t,6 H), 1·44(m,6 H), 1·66(m,2 H), 1·85(m,2 H), 2·72(m,2 H), 4·05(t,2 H), 6·97(d,2 H), 7·25(s,4 H), 7·34(d,2 H), 8·12(d,2 H), 8·20 ppm(d,2 H); ν_{max} 2940, 2860, 1740, 1730, 1608, 1512, 1270, 1258, 1168, 1072 cm^{-1}; (*m*/*z*) 460(M^+), 190(100 per cent), 160, 120.

3.36. *4′-Bromobiphenyl-4-yl 4-hexylbenzoate* (**36**)

Colourless crystals from 4-hexylbenzoic acid and 4′-bromo-4-hydroxybiphenyl; yield 0·39 g, 90 per cent; transitions C 135°C S_A 188°C N 198°C I; ^{1}H NMR($CDCl_3$), δ 0·90(t,3 H), 1·32(m,6 H), 1·67(m,2 H), 2·70(t,2 H), 7·28(d,2 H), 7·33(d,2 H), 7·46(d,2 H), 7·57(d,2 H), 7·60(d,2 H), 8·13 ppm(d,2 H); ν_{max} 2930, 2860, 1730, 1628, 1605, 1290, 1275, 1210, 1070, 1005 cm^{-1}; (*m*/*z*) 437(M$^+$), 189, 94(100 per cent).

3.37. *4-(4-Octyloxyphenyloxycarbonyl)phenyl 4-hexylbenzoate* (**37**)

Colourless crystals from 4-hexylbenzoic acid and 4-(4-octyloxyphenyloxycarbonyl)phenol; yield 0·45 g, 86 per cent; transitions C 88°C N 170°C I; ^{1}H NMR($CDCl_3$), δ 0·90(t,6 H), 1·32(m,14 H), 1·45(m,2 H), 1·65(m,2 H), 1·78(m,2 H), 2·72(t,2 H), 3·96(t,2 H), 6·93(d,2 H), 7·12(d,2 H), 7·32(d,2 H), 7·36(d,2 H), 8·12(d,2 H), 8·28 ppm(d,2 H); ν_{max} 2930, 2860, 1742, 1732, 1600, 1510, 1268, 1165, 1062 cm^{-1}; (*m*/*z*) 530(M$^+$), 309, 189(100 per cent), 110, 94.

3.38. *4-(4′-Octyloxybiphenyl-4-yloxycarbonyl)phenyl 4-hexylbenzoate* (**38**)

Colourless crystals from 4-hexylbenzoic acid and 4-(4′-octyloxybiphenyl-4-yloxycarbonyl)phenol; yield 0·49 g, 82 per cent; transitions C 138°C S_C 176°C N 280°C I; ^{1}H NMR($CDCl_3$), δ 0·90(t,6 H), 1·34(m,14 H), 1·49(m,2 H), 1·67(m,2 H), 1·82(m,2 H), 2·72(t,2 H), 4·00(t,2 H), 6·99(d,2 H), 7·27(d,2 H), 7·34(d,2 H), 7·39(d,2 H), 7·51(d,2 H), 7·60(d,2 H), 8·13(d,2 H), 8·30 ppm(d,2 H); ν_{max} 2930, 2860, 1748, 1740, 1600, 1500, 1280, 1222, 1165, 1070 ppm; (*m*/*z*) 606(M$^+$), 298, 189(100 per cent), 121.

3.39. *4-Nitrophenyl benzoate* (**39**)

Colourless crystals from benzoic acid and 4-nitrophenol; yield 3·85 g, 99 per cent; mp 143–144°C; ^{1}H NMR($CDCl_3$), δ 7·42(d,2 H), 7·55(m,2 H), 7·68(m,1 H), 8·20(d,2 H), 8·34 ppm(d,2 H); ν_{max} 1745, 1592, 1522, 1350, 1270, 1252, 1210, 1175, 1060, 715 cm^{-1}; (*m*/*z*) 243(M$^+$), 105(100 per cent), 77.

3.40. *4-Nitrophenyl 4-butylbenzoate* (**40**)

Colourless crystals from 4-butylbenzoic acid and 4-nitrophenol; yield 1·54 g, 96 per cent; mp 43–44°C; ^{1}H NMR($CDCl_3$), δ 0·96(t,3 H), 1·40(m,2 H), 1·66(m,2 H), 2·74(t,2 H), 7·35(d,2 H), 7·42(d,2 H), 8·12(d,2 H), 8·34 ppm(d,2 H); ν_{max} 2940, 2865, 1730, 1598, 1522, 1350, 1275, 1230, 1075, 752 cm^{-1}; (*m*/*z*) 299(M$^+$), 161(100 per cent), 91.

3.41. *4-Nitrophenyl 4-decylbenzoate* (**41**)

Colourless crystals from 4-decylbenzoic acid and 4-nitrophenol; yield 0·25 g, 50 per cent; transitions C 50°C (S_A 43°C) I; ^{1}H NMR($CDCl_3$), δ 0·96(t,3 H), 1·30(m,14 H), 1·66(m,2 H), 2·72(t,2 H), 7·35(d,2 H), 7·42(d,2 H), 8·10(d,2 H), 8·33 ppm(d,2 H); ν_{max} 2920, 2860, 1730, 1605, 1525, 1350, 1280, 1225, 1080, 750 cm^{-1}; (*m*/*z*) 383(M$^+$), 262, 256, 245(100 per cent).

The following compounds were prepared by using a similar procedure to that described for compound **26**.

3.42. *4-Aminophenyl benzoate* (**42**)

Colourless crystals from compound **39**; yield 1·83 g, 60 per cent; mp 156–157°C; ^{1}H NMR($CDCl_3$), δ 3·68(s,2 H), 6·72(d,2 H), 7·00(d,2 H), 7·50(m,2 H), 7·62(m,1 H), 8·20 ppm(d,2 H); ν_{max} 3460, 3380, 1718, 1638, 1512, 1455, 1278, 1195, 1090, 712 cm^{-1}; (*m*/*z*) 213(M$^+$), 105(100 per cent), 77, 51.

3.43. *4-Aminophenyl 4-butylbenzoate* (**43**)

Colourless crystals from compound **40**; yield 1·02 g, 78 per cent; mp 77–78°C; ^{1}H NMR(CDCl$_3$), δ 0·95(t,3 H), 1·38(m,2 H), 1·65(m,2 H), 2·70(t,2 H), 3·68(s,2 H), 6·72(d,2 H), 7·00(d,2 H), 7·32(m,2 H), 8·10 ppm(d,2 H); ν_{max} 3490, 3400, 1725, 1635, 1612, 1512, 1278, 1190, 1178, 750 cm^{-1}; (*m*/*z*) 269(M$^+$), 161(100 per cent), 91.

3.44. *4-Aminophenyl 4-decylbenzoate* (**44**)

Colourless crystals from compound **41**; yield 0·13 g, 72 per cent; mp 55–56°C; ^{1}H NMR(CDCl$_3$), δ 0·90(t,3 H), 1·30(m,14 H), 1·64(m,2 H), 2·68(t,2 H), 3·72(s,2 H), 6·72(d,2 H), 6·98(d,2 H), 7·28(d,2 H), 8·08 ppm(d,2 H); ν_{max} 3400, 3330, 2930, 2860, 1728, 1612, 1512, 1280, 1196, 1080 cm^{-1}; (*m*/*z*) 253(M$^+$), 245(100 per cent), 131, 91.

3.45. *1-Benzoyloxy-4-[4-(4-octyloxybenzoyloxy)benzylideneamino]benzene* (**45**)

A mixture of compound **42** (1·13 g, 5·3 mmol) and compound **31** (1·87 g, 5·3 mmol) in ethanol was heated under reflux for 10 h. The reaction mixture was allowed to cool and the product crystallized as colourless plates. The product was filtered off and recrystallized (ethanol). Yield 1·6 g, 56 per cent; transitions C 132°C N 287°C I; ^{1}H NMR(CDCl$_3$), δ 0·90(t,3 H), 1·35(m,8 H), 1·50(m,2 H), 1·84(m,2 H), 4·05(t,2 H), 6·98(d,2 H), 7·26(d,2 H), 7·32(d,2 H), 7·35(d,2 H), 7·52(t,2 H), 7·65(t,1 H), 8·00(d,2 H), 8·16(d,2 H), 8·23(d,2 H), 8·50 ppm(s,1 H); ν_{max} 2930, 2860, 1735, 1602, 1515, 1290, 1260, 1210, 1065, 705 cm^{-1}; (*m*/*z*) 549(M$^+$), 233, 191(100 per cent), 160, 120.

The following compounds were prepared by using a similar procedure to that described for compound **45**.

3.46. *1-(4-Butylbenzoyloxy)-4-[4-(4-octyloxybenzoyloxy)benzylideneamino]benzene* (**46**)

Colourless plates from compounds **43** and **31**; yield 0·27 g, 70 per cent; transitions C 128°C N 299°C I; ^{1}H NMR(CDCl$_3$), δ 0·90(t,3 H), 0·95(t,3 H), 1·35(m,10 H), 1·52(m,2 H), 1·65(m,2 H), 1·84(m,2 H), 2·75(t,2 H), 4·05(t,2 H), 6·98(d,2 H), 7·26(dd,4 H), 7·32(d,2 H), 7·35(d,2 H), 7·99(d,2 H), 8·12(d,2 H),8·16(d,2 H),8·50 ppm(s,1 H); ν_{max} 2925, 2860, 1735, 1632, 1605, 1515, 1250, 1200, 1162, 1072 cm^{-1}; (*m*/*z*) 605(M$^+$), 233, 161, 121(100 per cent), 91.

3.47. *1-(4-Decylbenzoyloxy)-4-[4-(4-octyloxybenzoyloxy)benzylideneamino]benzene* (**47**)

Colourless plates from compounds **44** and **31**; yield 0·12 g, 62 per cent; transitions C 115°C N 267°C I; ^{1}H NMR(CDCl$_3$), δ 0·90(tt,6 H), 1·30(m,22 H), 1·50(m,2 H), 1·65(m,2 H), 1·82(m,2 H), 2·70(t,2 H), 4·05(t,2 H), 6·99(d,2 H), 7·27(dd,4 H), 7·36(d,2 H), 8·00(d,2 H), 8·12(d,2 H), 8·17(d,2 H), 8·50 ppm(s,1 H); ν_{max} 2925, 2860, 1738, 1605, 1510, 1252, 1200, 1178, 1162, 1072 cm^{-1}; (*m*/*z*) 689(M$^+$), 245, 233(100 per cent), 121, 91.

The following compounds were prepared by using a similar procedure to that described for compound **12**.

3.48. *4′-Bromobiphenyl-4-yl* trans-*4-hexylcyclohexanecarboxylate* (**48**)

Colourless crystals from *trans*-4-hexylcyclohexanecarboxylic acid and 4′-bromo-4-hydroxybiphenyl; yield 0·96 g, 92 per cent; transitions C 82°C S$_B$ 152°C S$_A$ 198°C N 212°C I; ^{1}H NMR(CDCl$_3$), δ 0·90(t,3 H), 1·02(m,1 H), 1·28(m,12 H), 1·58(m,2 H), 1·90(d,2 H), 2·15(d,2 H), 2·50(m,1 H), 7·13(d,2 H), 7·42(d,2 H), 7·54 ppm(2 × d,4 H); ν_{max} 2925, 2860, 1752, 1482, 1378, 1190, 1162, 1130, 1000, 812 cm^{-1}; (m/z) 445, 444(M$^+$), 327, 248(100 per cent), 219, 139.

3.49. *4-(4-Octyloxyphenyloxycarbonyl)phenyl* trans-*4-hexylcyclohexanecarboxylate* (**49**)

Colourless crystals from *trans*-4-hexylcyclohexanecarboxylic acid and 4-(4-octyloxyphenyloxycarbonyl)phenol; yield 1·11 g, 88 per cent; transitions C 65°C S_B 88°C S_A 161°C N 185°C I; ^{1}H NMR(CDCl$_3$), δ 0·90(t,6 H), 1·00(m,1 H), 1·30(m,20 H), 1·55(m,4 H), 1·85(m,4 H), 2·15(d, 2 H), 2·50(m,1 H), 3·90(t,2 H), 6·92(d,2 H), 7·12(d,2 H), 7·20(d,2 H), 8·22 ppm(d,2 H); ν_{max} 2930, 2860, 1752, 1735, 1605, 1510, 1280, 1200, 1162, 1080 cm^{-1}; (m/z) 537(M$^+$), 315(100 per cent), 121.

3.50. *4-(4'-Octyloxybiphenyl-4-yloxycarbonyl)phenyl* trans-*4-hexylcyclohexanecarboxylate* (**50**)

Colourless crystals from *trans*-4-hexylcyclohexanecarboxylic acid and 4-(4'-octyloxybiphenyl-4-yloxycarbonyl)phenol; yield 1·36 g, 94 per cent; transitions C 98°C S_C 180°C N 283°C I; ^{1}H NMR(CDCl$_3$), δ 0·90(t,6 H), 1·00(m,1 H), 1·30(m,20 H), 1·55(m,4 H), 1·85(m,4 H), 2·15(d,2 H), 2·50(m,1 H), 4·00(t,2 H), 6·96(d,2 H), 7·24(2 × d,4 H), 7·50(d,2 H), 7·58(d,2 H), 8·25 ppm(d,2 H); ν_{max} 2930, 2860, 1758, 1738, 1605, 1495, 1275, 1206, 1110, 1080 cm^{-1}; (m/z) 612(M$^+$,100 per cent), 315, 297, 185, 121.

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