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The effect of fluorinated terminal chains on the mesomorphic properties of 4,4′-disubstituted phenyl benzoates

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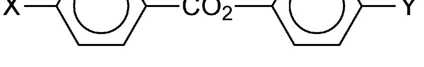
A variety of 4,4′-disubstituted phenyl benzoates having a terminal chain containing multi-fluorine atoms, attached directly to the benzene ring or through an ester group, have been synthesized and their mesomorphic properties determined by hot stage polarizing optical microscopy. These properties were compared to those of the corresponding hydrogenated esters and to other esters containing rigid terminal chains. Usually transition temperatures were higher and mesophase ranges wider than those observed for the parent compounds but no nematic phases were found. Any mesophase seen was usually a smectic A phase sometimes accompanied by a smectic C phase. Crystal E phases were found along with the smectic A phase in alkyl or alkoxy esters having a $C_9F_{19}CO_2$ chain on the acid side. A first order smectic A–smectic C transition was observed in the ester with CN on the acid side and $O_2CC_7F_{15}$ on the phenol side. A comparison of the effect of a terminal fluorinated chain and a lateral fluorine group on one set of esters is also included.

1. Introduction

In earlier studies of the effect of a variety of terminal chains on the mesomorphic properties of 4,4′-disubstituted phenyl benzoates and phenyl thiobenzoates, we found that chains with increased flexibility or more *gauche* conformers, such as carbonyl-containing chains, usually produced poorer mesomorphic properties than those found in compounds having straight hydrocarbon chains [1]. Terminal chains having a rigid linkage such as C=C or C≡C gave mixed results. Olefin chains attached directly to the benzene ring in diphenyldiacetylenes produced wider range nematic phases than those found in their hydrocarbon chain analogues [2]. This is also true in the 1-olefinphenyl benzoates (table 1). Unfortunately, transition temperatures also increased. However, attaching a triple bond directly to the benzene ring in the phenyl benzoates usually did not increase the mesophase temperature range [5]. Clearing temperatures did not change significantly and the effect on melting temperatures varied.

Much of the improvement in the mesomorphic properties for the 1-olefin compounds can be attributed to increased conjugation which yields a longer core; this is known to often improve the mesomorphic properties. However, the increase in the nematic ranges for some of the 2-olefin diacetylenes, albeit less than that of the 1-olefins, suggests that rigidity might play some role in improving these properties. Still, both the olefin chain and the alkynyl chain have adjacent C–C bonds around which free rotation is possible leading to more *gauche* conformers than those found in the hydrocarbon chain. This is more so in the alkynyl chains, possibly explaining their poorer properties. Of course, these two functional groups could also affect electronic interactions between the chains and it becomes quite clear that finding a rigid group that changes only the rigidity of the chain is not easy.

We felt it worthwhile to study the effects of a perfluorinated chain. With the slightly larger van der Waals radius of the fluorine atom (1.35 Å) as compared with the hydrogen atom (1.20 Å), rotation around the single carbon–carbon bonds is more hindered, making the perfluoro chain more rigid than the hydrocarbon chain. This increased rigidity has been confirmed by X-ray studies of the crystalline phase of some mesogens having a perfluorinated chain [6, 7]. We chose to prepare several of the perfluorinated chain esters **1**



1

where *X* or *Y* is a perfluorinated chain. By using the phenyl benzoates, we could minimize the amount of

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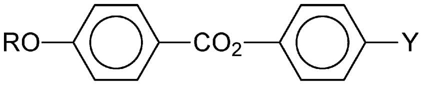
Table 1. Transition temperatures (°C) for structures listed.



	$Y=C_5H_{11}$[a]				$Y=CH=CHC_3H_7$[b]			
R	SmA[c]	N	I	ΔN	SmA	N	I	ΔT/°C
CH_3		29.9	42.5	12.6		88	130	42.0
C_2H_5		(68.1)	72.9			99	138	39.0
C_4H_9		(61.6)	67.5			93.5	127	33.5
C_7H_{15}	46.7	44.1	60.9	14.2		71.5	111.5	40.0
C_8H_{17}	55.8	56.6	66.2	10.4	77	83	114	37.0

[a] Data are from ref. [3].
[b] Data are from ref. [4].
[c] SmA=smectic A, N=nematic, I=isotropic liquid, ΔT is mesophase temperature range and parenthesis indicate a monotropic phase.

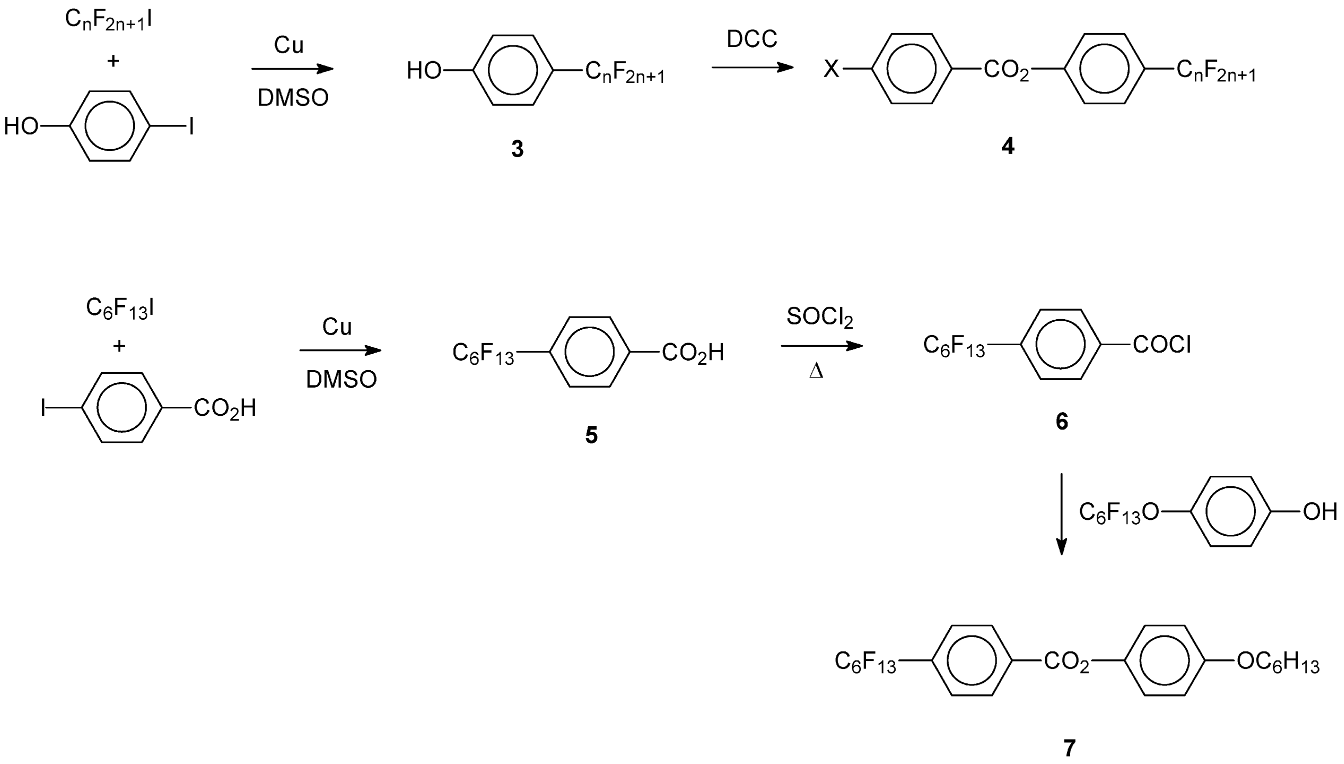
synthesis required, since data for many of the parent esters were already available from our earlier work. Additionally, we still had many of the hydrogenated chain acids and phenols that would be needed to esterify the perfluorinated chain intermediates. Combinations such as $X=R$, RO; $Y=R_F$, O_2CR_F and $X=R_FCO_2$ $Y=R$, OR were prepared along with several esters with $Y=CO_2CH_2R_F$. This latter chain was also used to prepare an ester **2** with an additional lateral fluorine atom to study the additional effect of both chain and ring fluorine atoms on mesomorphic properties.

During the course of this work, we also prepared the ester **1** with $X=C_6F_{13}$, $Y=OC_6H_{13}$ for another project. The synthesis and properties of this compound are included. Mesomorphic properties for several members of this series with $X=R_F$, $Y=OR$ [4, 8] and the dialkoxy series $X=R_FO$, $Y=OR$ [4] were reported earlier. With these and the new compounds, we have sufficient data to discuss the effect of the fluorinated chains on these properties.

2. Synthesis

The synthesis routes for the fluorinated chain esters prepared are given in reaction schemes 1–5. Perfluorinated alkyl chains attached directly to the benzene ring either on the phenolic side (**4**) or the acid side (**7**) were prepared by copper catalysed coupling [8] of the perfluorinated iodide with either 4-iodophenol or 4-iodobenzoic acid to give the phenol **3** and the acid **5**, respectively, which were esterified to the esters (scheme 1). Some of these types of intermediates and esters were prepared earlier by others [9–13], usually by the same methods. Our workup procedures varied from these and usually different chain lengths were prepared. Synthesis of the acid **5** and its properties were reported earlier. Our melting temperature (189–192°C) was higher than that reported by Matsui *et al.* (168–170°C) [12] but agreed with the values reported by others [13–15]. Additionally, their ^{1}H NMR chemical shifts (δ, PPM) of 7.31 and 7.47 do not agree with either our data or other reported data (7.87 and 8.30) [15]. From our experience, the aromatic protons *ortho* to the acid group in 4-alkylbenzoic acids occur at about $\delta=8$. These should not shift much in the fluorinated acid so that the 8.30 value is more reasonable. The protons *ortho* to the perfluorinated chain would be expected to show a large shift from the 7.1 value observed for the hydrocarbon analogue and this should be to a higher value making 7.87 seem more reasonable. The mass spectral data of Matsui *et al.* appears to be correct so it seems likely the errors are not because the acid was not isolated. No mesophases were observed in this acid, in agreement with data reported for a series of these acids [14]. The phenols **3** were esterified with the 4-substituted benzoic acids using the carbodiimide method [16] to obtain the esters **4**. This method is well documented in the literature and therefore no further description is needed in this paper. The acid **5** was esterified using the well known acid chloride method to give the ester **7**.

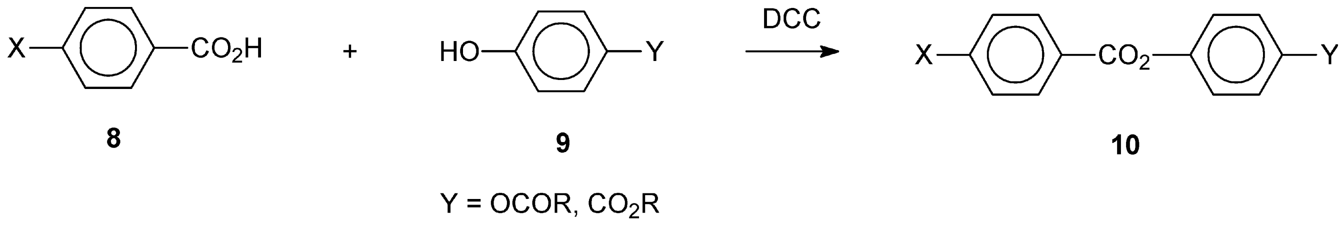
Earlier, we reported the synthesis of the esters **10** having the phenolic ester chains $Y=OCOR$ and CO_2R by the esterification of the acids **8** with the phenols **9** (scheme 2) [16, 17]. There was no difficulty in preparing the $Y=CO_2R$ esters in this manner but the $Y=OCOR$ esters isolated often were impure and difficult to purify. We have come to realize that this was probably due to the occurrence of *trans*-esterification [5]. At the time of



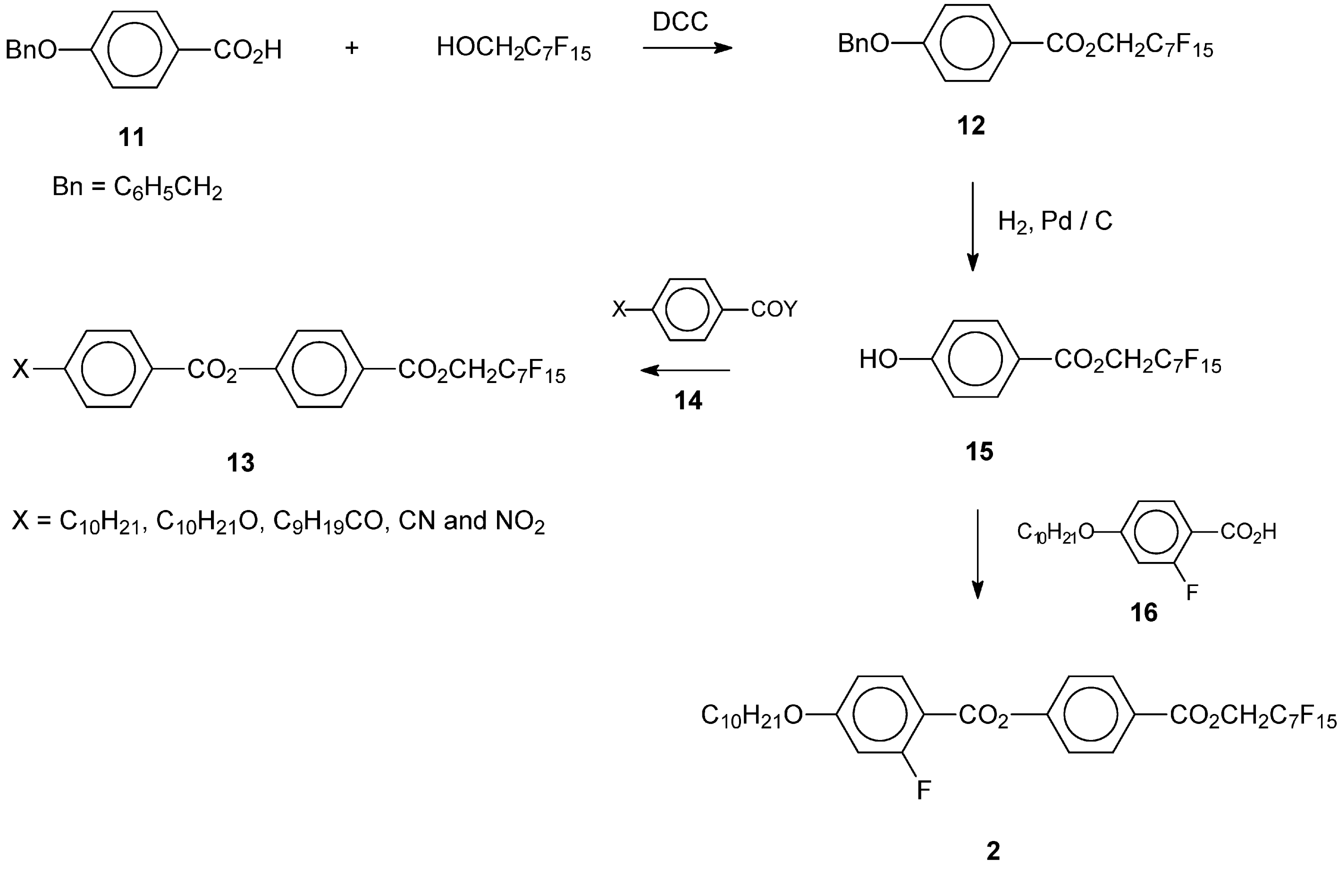
Scheme 1

this work, however, we were unaware of this and proceeded to use this approach to prepare the fluorinated esters. As before, we were able to prepare the esters **13** and **2** using this method (scheme 3). The phenol **15** was synthesized by hydrogenating the protected phenol **12** obtained from the esterification of the acid **11** with the fluorinated alcohol using the carbodiimide method [18]. However, ester exchange was so extensive when we tried to prepare the esters **19** (X=$C_{10}H_{21}$, $C_{10}H_{21}O$) that these were never isolated, the predominate product being the phenol **18** (scheme 4). This phenol could also be prepared by treating excess hydroquinone with the benzoyl chloride [19] but some of the diester **20** (X=$C_{10}H_{21}$, $C_{10}H_{21}O$) was also formed, contaminating the phenol. These could be separated and the phenol acylated to give the ester **19**. No diester was isolated in the synthesis of the phenol **17**. As we found for the corresponding alkynyl chain esters [5], a better approach is first to prepare a protected phenol ester **23,** then remove the protecting group to obtain the phenol and esterify this with the fluorinated acid chloride to obtain the esters **25** (scheme 5). We found that the final products were easier to purify and yields were higher, despite the addition of two steps, confirming the reports of others [20]. With the fluorinated esters **25**, the yields appeared to be higher when the phenol **24** was added to the acid chloride rather than the reverse sequence.

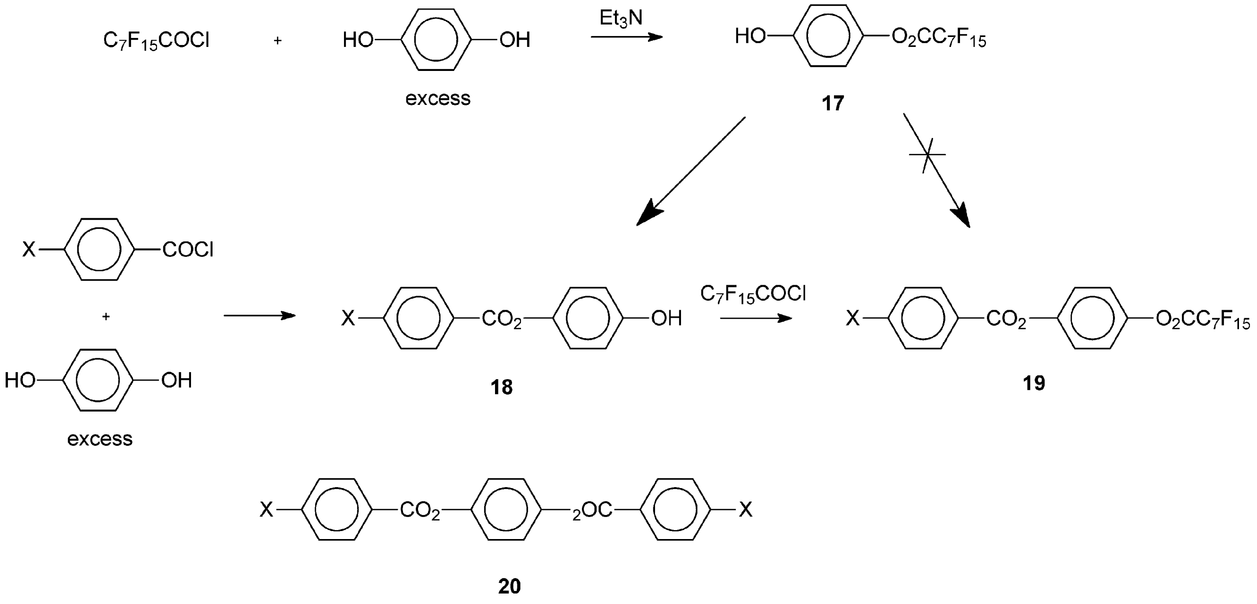
However, over a period of time of storage in bottles, both esters **19** and **25** hydrolysed back to the phenol. This was discovered when they were studied again by microscopy. The melting temperature for the ester **25** with Y=$C_{10}H_{21}$ was now in the range of that for the phenol **24**. This was confirmed by a mixture melting



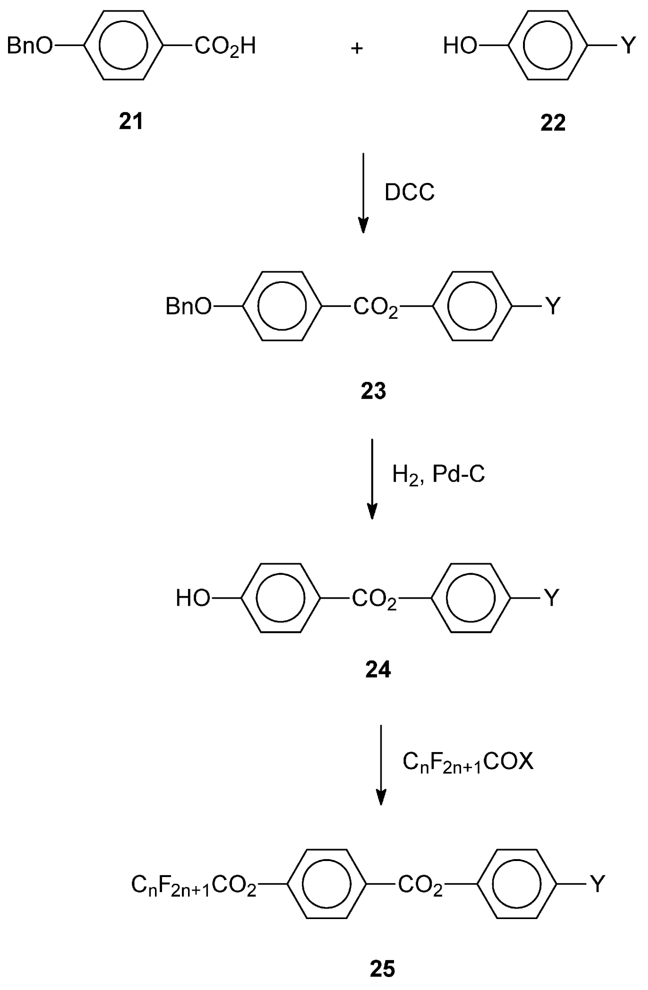
Scheme 2



Scheme 3



Scheme 4



Scheme 5

point with the phenol which showed no depression. New IR spectra for some of the esters **19** showed a hydroxyl peak which was not present in the freshly prepared material and TLC showed two spots instead of the original one. We had hoped to repeat at least one synthesis trying to maintain anhydrous conditions as much as possible, including storing the final esters under anhydrous conditions, but have been unable to do so. We report here the information collected initially; some of the materials are less pure than we would wish.

3. Mesomorphic properties

Mesomorphic properties for the fluorinated chain esters prepared were determined by hot stage polarizing optical microscopy and are given in tables 2 and 3. No nematic phases were observed, even though these were seen in many of the parent hydrogenated compounds. This preference for smectic phases has also been observed in a variety of other structures having highly fluorinated terminal chains. In a few instances crystal E [21–24] and smectic B [23, 24] phases have been reported in some mixed fluorinated-hydrogen chain mesogens. Most of our esters showed smectic A and C phases but a crystal smectic E phase was seen in the esters **1** with X=$C_9F_{19}CO_2$ and Y=$C_{10}H_{21}$ or $OC_{10}H_{21}$ (nos. 18 and 19, table 3). This phase was identified by the conversion of the typical focal-conic smectic A fan texture to that with arcs across the fans which did not disappear (see the figure) and by X-ray crystallographic studies which showed the multi-center ring pattern of the crystal smectic E phase when Y=$C_{10}H_{21}$. The X-ray diffraction pattern at 103°C showed four reflections at small angles. Three of these were multiples of the primary reflection suggesting that the layers are very well defined. The large angle reflection was also sharp indicating in-plane ordering of the molecules. These observations rule out the possibility of it being the smectic A or smectic C phase. On the other hand, the diffraction pattern at room temperature has many reflections like those found in crystalline phases.

The smectic C–smectic A transition for the cyano-ester no. 15 (table 2) was found by DSC to be a first order transition: T=117.8°C, ΔH=33.75 kJ mol^{-1} (crystal to smectic C), T=136.1°C, ΔH=1.34 kJ mol^{-1} (smectic C to smectic A) and T=138.8°C, ΔH=2.84 kJ mol^{-1}. Microscopic studies showed little variation of the smectic C texture with temperature, the texture appearing either as a typical grey schlieren texture or a highly coloured schlieren texture more typical of those seen in the first order smectic C to nematic transition. Our colleague, S. Kumar, has found first order SmC–SmA transitions in other fluorinated mesogens. Our cyano-ester represents only one of very few mesogens having a cyano group which shows a smectic C phase. Unfortunately, the fluorinated ester

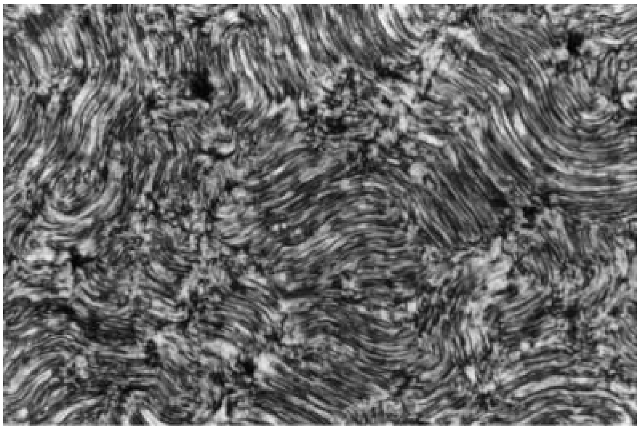
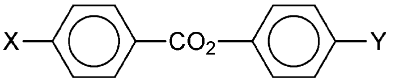


Figure. Crystal E phase in the ester **1** with X=$C_9F_{19}CO_2$, Y=$C_{10}H_{21}$.

chain in this compound hydrolysed too readily for more studies to be done. In rechecking some of the other fluorinated esters, we found that most of those having either *X* or Y=OCOR_F had undergone at least partial hydrolysis of the fluorinated ester chain.

Comparisons of the transition temperatures of our new fluorinated esters with those for the parent compounds shows that these temperatures always increased in the fluorinated ester (tables 2 and 3). This trend was also observed in some *R*-OR_F esters reported earlier (table 4) but some variation in the melting temperatures were found in two *R*O-O*R* series (table 5). In our X=R_FCO$_2$ series, the clearing temperatures increased more than the melting temperatures, giving wider mesophase ranges. This trend can also be seen in data reported for the *Y*=olefin chain series (table 1) and in our 1-olefin diacetylenes [2]. Usually mesophase ranges increased in all the fluorinated esters. A decrease in the melting temperature was observed in only a few *R*O-OR_F esters (table 5). Table 6 shows a comparison of the effect of a fluorinated chain with that for a lateral fluorine group. A fluorinated chain increased the clearing temperature considerably more than the melting temperature, giving a much wider total mesophase range and adding a smectic A phase range. Incorporating both fluorinated groups into the molecule decreases the transition temperatures a little when compared with the ester containing only a fluorinated chain, while increasing slightly the total mesophase range and increasing the smectic A phase range at the expense of the smectic C range. Considerably more similar comparisons will be needed to establish reliable trends.

Table 2. A comparison of transition temperatures (°C) for the structures listed.



X	*Y*	Cr[a]	SmC	SmA[b]	N	I	No.	*Y*	Cr	SmC	SmA	I
$C_{10}H_{21}$	C_3H_7	24.0			(29.5)	57.4	1	C_3F_7	44.8			53.9
$C_{10}H_{21}$	C_8H_{17}	38.0[c]			(40.7)	50.1	2	C_8F_{17}	93.2(Cr_2)[d]			101.0(Cr_1) 99.9(Cr_2)
$C_{10}H_{21}$	$C_{10}H_{21}$	47.6[c]				52.8	3	$C_{10}F_{21}$	113.9			116.7
$C_{10}H_{21}O$	C_3H_7			59.5[c]	62.5	66.0	4	C_3F_7	40.8		60.1	66.1
$C_{10}H_{21}O$	C_7H_{15}	41.1[c]		55.6		71.2	5	C_8F_{17}	93.5	(102.8)	107.6	109.7
	C_9H_{19}			60.0[c]		73.0						
$C_{10}H_{21}O$	$C_{10}H_{21}$	46.1[c]		66.6		75.1	6	$C_{10}F_{21}$	100.2(Cr_2)[e]	(110.9)	113.4(Cr_1)	125.5
$C_{10}H_{21}$	$CO_2C_9H_{19}$	64.8[f]				69.8	7	$CO_2CH_2C_7F_{15}$	82.9	(85.8)	87.8	92.4
$C_{10}H_{21}O$	$CO_2C_7H_{15}$	47.8[f]		64.7		75.2	8	$CO_2CH_2C_7F_{15}$	71.6	76.5	113.2	120.3
	$CO_2C_9H_{19}$	51.5[f]		69.4		74.7						
$C_6H_5CH_2O$							9	$CO_2CH_2C_7F_{15}$	125.7		143.9	183.0
$C_9H_{19}CO$	$CO_2C_9H_{19}$	87.8[g]		97.3		105.4	10	$CO_2CH_2C_7F_{15}$	112.0	124.2	137.0	191.4
NC	$CO_2C_9H_{19}$	49.3[g]			(61.1)	65.1	11	$O_2CCH_2C_7F_{15}$	114.8	127.3		135.1
O_2N	$CO_2C_9H_{19}$	40.9[g]				58.8	12	$O_2CCH_2C_7F_{15}$	83.2		103.5	117.4
$C_{10}H_{21}$	$OCOC_7H_{15}$	60.7[h]	(61.7)		69.0	70.4	13	$O_2CCH_2C_7F_{15}$	80.5		84.8	97.3
$C_{10}H_{21}O$	$OCOC_7H_{15}$	36[h,i]	73.6		85.0	94.9	14	$O_2CCH_2C_7F_{15}$	73.1	81.8	102.1	123.9
NC	$OCOC_9H_{19}$	76.4[g]		82.1	102.1	105.8	15	$O_2CCH_2C_7F_{15}$	114.5	118.4	138.2	141.0
O_2N	$OCOC_9H_{19}$	64.3[g]		70.5	88.9	91.4	16	$O_2CCH_2C_7F_{15}$	128.5			130.8

[a] Cr=crystallization temperature obtained by cooling the melt at 2° min^{-1}, (SmA=smectic A, SmC=smectic C, N=nematic and I=isotropic liquid. Parenthesis indicate a monotropic phase.

[b] Mesophase transitions usually had ranges of 0.3–0.4°. Only the end of the transition is given here.

[c] Data from ref. [3].

[d] When the crystallized melt (Cr_1) was heated immediately after forming, it melted at 99.9°. If allowed to cool to 97.6°, Cr_2 crystals formed which melted at 100.5°.

[e] The crystallized melt (Cr_2) converted to Cr_1 on cooling to 99.9°. Cr_1 melted to the smectic A phase.

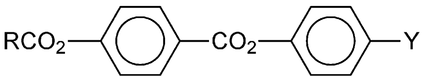
[f] Data from ref. [17].

[g] Data from ref. [2].

[h] Data from ref. [16].

[i] Also showed a monotropic smectic B at 64.1°.

Table 3. A Comparison of transition temperatures (°C) for the structures listed.



	R=C_nH_{2n+1}						R=C_nF_{2n+1}						
Y	n	Cr[a]	SmC	SmA	N	I	No.	n	Cr	E	SmC	SmA	I
C_9H_{19}	7	43.0	52.4		55.1	67.5	17	7	70.1			80.5	114.8
$C_{10}H_{21}$	9	39.5[b]	58.8[c]	71.2		74.1	18	9	83.4	99.3		104.3	124.7
$OC_{10}H_{21}$	9	65.1[b]	74.7		87.3	90.3	19	9	111.0	114.4		118.7	146.9
$(CH_2)_2CO_2C_7H_{15}$	9	35.1[d]				47.7	20	9	89.1			91.5	120.5
CN	9	60.8[d]		67.1	73.8	87.0	21	9	123.2[e]		128.8	129.8	184.6
COC_9H_{19}	9	107.0		118.2		126.5	22	9	134[e]			140.5	168

[a] Cr=crystallization temperature obtained on cooling the melt at 2° min^{-1}, E denotes crystal E, smectics are SmA=smectic A, SmC=smectic C, N=nematic, I=isotropic liquid. Mesophase transitions usually had a range of 0.3–0.4°. Only the end temperature is given here.

[b] Data from ref. [25].

[c] A monotropic smectic B phase also occurred at 50.7°.

[d] Data from ref. [1]. [e] Sample contained trace amounts of impurities.

4. Conclusions

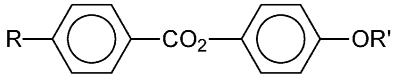
A variety of chain fluorinated phenyl benzoates have been synthesized, their mesomorphic properties determined and compared with those for the hydrogenated parent compounds and some 1-olefin phenyl benzoates. Transition temperatures were always higher in the fluorinated esters and mesophase ranges were wider. Only smectic phases were observed, usually smectic A but sometimes with a smectic C or crystal E phase. With a fluorinated ester chain on the acid side of the phenyl benzoates, the clearing temperature increased considerably more than the melting temperature, giving wide range mesophases. This trend was also reported in the 1-olefin esters and diphenyldiacetylenes, and appears to be a result of increased rigidity in the fluorinated chain. One ester **1** (*X*=NC, *Y*=$O_2CC_7F_{15}$) showed a first order smectic C–smectic A phase transition.

5. Experimental

5.1. *Characterization*

TLC data were obtained using Anal-Tech silica gel GHLF Uniplates with UV light and I_2 as detectors. A Hewlett Packard 5890 instrument equipped with a HP

Table 4. Transition temperatures (°C) for the structures listed.

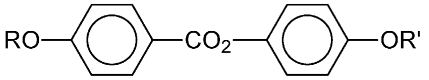


R	*R*[a]	N[b]	I	Δ*T*/°C	*R*	SmA	N	I	Δ*T*/°C	Ref.
CH_3	C_5H_{11}		62.0	0	CF_3			79	0	[4]
CH_3	C_6H_{13}	48.0	51.7	3.7	CF_3			84	0	[4]
C_4H_9	C_5H_{11}	(39.1)	39.8		C_4F_9		72	86	14	[4]
C_4H_9	C_6H_{13}	29.4	48.8	19.4	C_4F_9		74	82	8	[4]
C_6H_{13}	C_6H_{13}	44.9	53.1	8.2	C_6F_{13}	94.0		107.8	13.8	
C_7H_{15}	C_6H_{13}	41.7	61.0	19.3	C_7F_{15}	108		117	9	[11]
C_8H_{17}	CH_3				C_8F_{17}	126		133	7	[11]
$C_{10}H_{21}$	C_6H_{13}	(43.1)	58.1		$C_{10}F_{21}$	134		143	9	[11]

[a] Data for this parent series from ref. [3].

[b] SmA=smectic A, N=nematic, I=isotropic liquid, Δ*T*=total mesophase temperature range and parenthesis indicate a monotropic phase.

Table 5. Transition temperatures (°C) for the structures listed.



R	*R*[a]	SmA[b]	N	I	ΔT/°C	*R*	Sm	SmC	SmA	I	ΔT/°C	Ref.
C_6H_{13}	C_4H_9		64.5	90.5	26	$C_3F_7CH_2$		58	63	93	35	[26]
C_8H_{17}	C_4H_9		67.0	86.0	19	$C_3F_7CH_2$		46	61	90	44	[26]
C_8H_{17}	C_7H_{15}		68.6	86.5	17.9	$C_5F_{11}CH_2$		44	84	107	63	[26]
C_8H_{17}	C_9H_{19}	60.7	61.1	88.1	27.4	$C_7F_{15}CH_2$		76	88	125	49	[26]
C_5H_{11}	C_4H_9		72.0	86.5	14.5	C_4F_9	63			91	28	[27]
C_6H_{13}	C_4H_9		64.5	90.5	26	C_4F_9	65			124	59	[27]
C_6H_{13}	C_5H_{11}		56.3	84.3	28	C_5F_{11}	64			134	70	[27]
C_6H_{13}	C_7H_{15}	(51.4)	66.1	86.4	26.3	C_7F_{15}	84			100	16	[27]

[a] Data for this parent series from ref. [3].

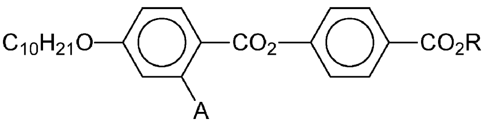
[b] SmA=smectic A, N=nematic, I=isotropic liquid, ΔT=mesophase temperature range and parenthesis indicate a monotropic phase.

3395 integrator and a FID detector, a Hewlett Packard 5 mm methylsilicone gum column was used for capillary GC analyses. Melting points were determined using a Hoover-Thomas melting point apparatus and are corrected. These are not reported for compounds for which the more accurate transition temperatures are given.

Infrared spectral data (cm^{-1}) were collected using either a Pye Unicam 3-200 or a Nicolet Magna FTIR instrument and NaCl plates. ^{1}H and ^{13}C NMR spectra were determined in $CDCl_3$ containing TMS as the internal standard, using a Varian Gemini–200 spectrometer equipped with a VXR-400 data station at 200 and 50 MHz, respectively. Chemical shifts are given in δ units (PPM) and coupling constants in Hz. Data for ^{1}H spectra are given in the order of multiplicity, number of protons, coupling constant and identification. ^{13}C NMR chemical shifts compared favourably with those values calculated using a Softshell ^{13}C NMR module.

Transition temperatures (°C) were determined using a Leitz Laborlux 12 POL polarizing microscope fitted with a modified and calibrated FP-2 heating stage at a heating rate of 2°C min^{-1} to the isotropic liquid. This liquid was then cooled at 2°C min^{-1} until crystals formed, to determine the crystallization temperature and to ensure that all mesophases occurring before this temperature were observed. These crystals were reheated to obtain the melting temperature and to confirm that these were not mesophases. All transition temperatures reported here were obtained from a heating run, including those for monotropic mesophases. Mesophase textures were identified by comparison with known textures [29–31]; procedural details are given in ref. [31]. DSC scans were obtained using a

Table 6. A Comparison of mesomorphic properties for the structures listed.



	R=C_9H_{19}					*R*=$CH_2C_7F_{15}$						
	Transition temperature/°C				SmA phase	Transition temperature/°C				Phase range/°C		
A	Cr	SmA[a]	I	Ref.	range/°C	Cr	SmC	SmA	I	SmC	SmA	Total
H	51.6	69.4	74.7	[17]	5.3	71.6	76.5	113.2	120.3	36.7	7.1	43.8
F	34.6	54.6	62.2	[28]	7.6	54.2	66.6	94.9	111.5	28.3	16.6	44.9

[a] Cr=crystallization temperature obtained by cooling the melt at 2° min^{-1}; SmA=smectic A, SmC=smectic C, I=isotropic liquid.

Perkin Elmer DSC 7 equipped with a TAC 7/PC instrument controller at a rate of 5°C min^{-1} which had been calibrated using indium. Three runs were performed: heating the virgin crystals to the isotropic liquid, cooling this liquid to crystals, and reheating. Enthalpy values were taken only from the first run since this is known to give the best value for the melting transition.

5.2. *Synthesis*

Commercially available starting materials were used without purification unless otherwise noted. The following intermediates were synthesized using previously described methods: 4-benzyloxybenoic acid [32], 4-alkylbenzoic acids and acid chlorides [33], 4-alkylphenols [34], 4-(keto)benzoic acids [35], 4-hexyloxyphenol [36], 4-(ester)phenols [17] and 2-F-4-decyloxybenzoic acid [28]. Anhydrous reactions were run in flame-dried glassware using solvents dried over Linde #4A molecular sieves. All reactions using iodides were protected from light. Organic extracts were dried over anhydrous Na_2SO_4. Flash chromatography [37] and silica gel filtrations were performed using Mallincrodt silica gel (200–400 mesh).

5.2.1. 4-(Heptafluoropropyl)phenol 3 (*n*=3). To a stirred solution of 4-iodophenol (3.05 g, 13.9 mmol) in DMSO (26 ml) containing Cu powder (2.96 g, 46.6 mmol) perfluoropropyl iodide (5.13 g, 17.3 mmol) was added quickly. The reaction mixture was heated at 110°C for 1 h, cooled to r.t., poured into H_2O (150 ml) and extracted with Et_2O (4×150 ml). The Et_2O extract was washed with H_2O (150 ml), dried and filtered. Removal of the solvent *in vacuo* gave the crude product (4.04 g). This material was purified by flash chromatography using 5–10% EtOAc/hexane as the eluant to give 3.08 g (84.7%) of the phenol **3** ($n=3$) as a yellow liquid. TLC (10% EtOAc/hexane) $R_F=0.25$, GC $t_R=0.69$ (100%). IR (film) 3381 (str br, OH), 1615 (str d, Ar), 1220 (str br, C–F) and 1175 (str, C–F). ^{1}H NMR 7.48 (d, 2, $J=8.71$, ArH *ortho* to R_F), 6.94 (d, 2, $J=8.14$, ArH *ortho* to OH) and 5.26 (s, 1, OH).

The following phenols **3** were prepared in the same manner: $n=8$ purified yield=63.4%, yellow solid, m.p. 68.1–71.6°C; $n=10$ purified yield=69.7%, colourless solid, m.p. 94.5–96.5°C.

5.2.2. 4-(Tridecafluorohexyl)benzoic acid 5. This acid was prepared by treating 4-iodobenzoic acid with tridecafluorohexyl iodide in the same manner as for the phenol **3** [10, 13]. The crude product was recrystallized from abs EtOH to give the acid **5** as a colourless solid: m.p. 189–192°C (lit [4] 193°C). IR (Nujol) 3100–2560 (br med, acid OH), 1696 (str, acid carbonyl), 1584 (wk, Ar), 1515 (wk, Ar), 1200, 1240 (str br, CF) and 1140 (str, C–F). ^{1}H NMR 8.18 (d, 2, $J=7.00$, ArH *ortho* to CO_2H) and 7.85 (d, 2, $J=7.00$, ArH *ortho* to R_F).

5.2.3. 4-(Tridecafluorohexyl)benzoyl chloride 6. A solution of the acid **5** (10.0 g, 0.023 mol) in $SOCl_2$ (60 ml) was heated under reflux for 24 h and then cooled to r.t. Excess $SOCl_2$ was removed by vacuum distillation to give the crude acid chloride **6**: yield=98.2%. IR (film) 1785, 1748 (str d, COCl) and 1616 (wk, Ar). This material was used without further purification.

The subsequent esterifications were carried out using the standard carbodiimide or acid chloride methods [16]. The first sequence of esters described below were prepared by the *carbodiimide method*.

5.2.4. 4-(Heptafluoropropyl)phenyl 4-decylbenzoate 4 (*X*=$C_{10}H_{21}$, *n*=3). Purification: chromatography using 15% $CHCl_2$/hexane followed by recrystallization from abs EtOH; yield=57.9%, colourless solid, TLC ($CHCl_3$) $R_F=0.81$. IR (Nujol) 1749 (med, ester), 1615 (wk, Ar), 1200 (str br, C–F) and 1152 (str, C–F). ^{1}H NMR 8.12 (d, 2, $J=8.34$, ArH *ortho* to CO_2), 7.67 (d, 2, $J=8.81$, ArH *ortho* to C_3F_7), 7.38 (d, 2, $J=9.16$, ArH *ortho* to O_2C), 7.34 (d, 2, $J=8.43$, ArH *ortho* to C_{10}), 2.71 (t, 2, $J=7.68$, α-CH_2), 1.69–1.62 (m, 2, β-CH_2), 1.40–1.21 (m, 14, 7 CH_2) and 0.88 (t, 3, $J=6.23$, CH_3). A COSY 2-D spectrum was run to identify the 7.38 and 7.34 peaks. Spectra for the other esters **4** having $X=C_mH_{2m+1}$ were similar.

$X=C_{10}H_{21}$, $n=8$. Purified by chromatography using 20% EtOAc/hexane, yield=50.9%.

$X=C_{10}H_{21}$, $n=10$. Purified by recrystallization from abs EtOH, yield=35.7%.

$X=C_{10}H_{21}O$, $n=3$. Purified by chromatography using 15% CH_2Cl_2/hexane followed by recrystallization from abs EtOH, yield=44.9%. IR was similar to that for the esters with $X=C_{10}H_{21}$. ^{1}H NMR 8.15 (d, 2, $J=8.95$, ArH *ortho* to CO_2), 7.67 (d, 2, $J=8.71$, ArH *ortho* to R_F), 7.38 (d, 2, $J=8.50$, ArH *ortho* to O_2C), 6.99 (d, 2, $J=9.03$, ArH *ortho* to OC_{10}), 4.06 (t, 2, $J=6.45$, α–CH_2), 1.84 (quint, 2, $J=7.14$, β-CH_2), 1.48–1.22 (m, 14, 7 CH_2) and 0.89 (t, 3, $J=6.41$, CH_3). Spectral data were similar for the other $X=OC_mH_{2m+1}$ esters.

$X=C_{10}H_{21}O$, $n=8$. Chromatography solvent was 20%EtOAc/hexane, yield=67.6%.

$X=C_{10}H_{21}O$, $n=10$. Purification was by recrystallization from abs EtOH, yield=61.6%.

5.2.5. 4-(2H, 2H-Pentadecafluorooctyloxycarbonyl) benzyloxyphenol 12. Purified by recrystallization from abs EtOH: yield=59.8%, TLC ($CHCl_3$) $R_F=0.72$. IR (Nujol) 1720 (str, ester) and 1620 (med, Ar). ^{1}H NMR

8.02 (d, 2, J=8.83, ArH *ortho* to CO_2Ar), 7.49–7.31 (m, 5, C_6H_5), 7.03 (d, 2, J=8.92, ArH *ortho* to O), 5.14 (s, 2, OCH_2) and 4.79 (t, 2, J=13.4, CO_2CH_2). Transition temperatures (°C) 142.8–142.9 (Cr–SmA), 181.1–183.0 (SmA–I) and 125.7 (SmA–Cr).

5.2.6. Esters 13. *X*=$C_{10}H_{21}O$. Purification was by recrystallization from abs EtOH: yield=72.8%, TLC (5% EtOAc/hexane) R_F=0.25. IR (Nujol) 1739 (str, aliphatic ester), 1724 (str, aromatic ester), 1608 (med, Ar), 1202 (str br, C–F) and 1130 (str, C–F). ^1H NMR 8.15 (d, 4, J=8.54, ArH *ortho* to both $ArCO_2$), 7.35 (d, 2, J=8.75, ArH *ortho* to O_2C), 6.99 (d, 2, J=8.91, ArH *ortho* to OC_{10}), 4.85 (t, 2, J=13.91, OCH_2CF_2), 4.06 (t, 2, J=6.60, $ArOCH_2$), 1.82 (quint, 2, J=7.98, β-CH_2), 1.41–1.23 (m, 14, 7CH_2) and 0.84 (t, 3, J=6.37, CH_3).

X=$C_9H_{19}CO$. Purification was by recrystallization from abs EtOH to give a colourless solid: yield=41.6%, TLC ($CHCl_3$) R_F=0.39. IR (Nujol) 1735 (str, aliphatic ester), 1724 (str, aromatic ester), 1684 (str, ketone), 1603 (wk, Ar), 1205 (str br, C–F) and 1146 (str, C–F). ^1H NMR 8.30 (d, 2, J=8.43, ArH *ortho* to CO_2Ar), 8.18 (d, 2, J=8.47, ArH *ortho* to $ArCO_2R$), 8.09 (d, 2, J=8.10, ArH *ortho* to COR), 7.38 (d, 2, J=8.79, ArH *ortho* to O_2CAr), 4.86 (t, 2, J=13.53, CO_2CH_2), 3.03 (t, 2, J=7.25, $COCH_2$), 1.77–1.73 (m, 2, β-CH_2), 1.36–1.20 (m, 12, 6 CH_2) and 0.89 (t, 3, J=6.68, CH_3).

5.2.7. Ester 2. Prepared using the acid **16** and phenol **15**. Purification was by flash chromatography using 30% hexane in $CHCl_3$ followed by recrystallization from abs EtOH: yield=71.5%, TLC ($CHCl_3$) R_F=0.75. IR 1720 (str with sh, esters), 1620 (med, Ar), 1220 (str db, C–F) and 1150 (str, C–F). ^1H NMR 8.14 (d, 2, J=8.42, ArH *ortho* to CO_2R), 8.04 (d, 1, J=8.71, ArH *ortho* to CO_2Ar), 7.35 (d, 2, J=9.31, ArH *ortho* to O_2CAr), 6.79 (dd, 1, J=7.31, 2.40, ArH *ortho* to O*R*), 6.70 (dd, 1, J=10.62, 2.20, ArH *ortho* to F), 4.84 (t, 2, J=13.27, CO_2CH_2), 4.03 (t, 2, J=6.24, OCH_2), 1.83 (quint, 2, J=6.50, β-CH_2), 1.50–1.10 (m, 14, 7 CH_2) and 0.89 (t, 3, J=6.22, CH_3).

5.2.8. Esters 23. *Y*=$C_{10}H_{21}$. Purification was by recrystallization from EtOAc/EtOH to give a colourless solid: yield=71.2%, TLC ($CHCl_3$) R_F=0.69. IR (Nujol) 1720 (str, ester) and 1620 (str, Ar). ^1H NMR 8.15 (d, 2, J=8.88, ArH *ortho* to CO_2Ar), 7.50–7.34 (m, 5, C_6H_5), 7.22 (d, 2, J=8.43, ArH *ortho* to C_{10}), 7.09 (d, 2, J not determined, ArH *ortho* to OCOAr), 7.05 (d, 2, J=8.79, ArH *ortho* to OBn), 5.16 (s, 2, $C_6H_5CH_2$), 2.62 (t, 2, J=7.55, $ArCH_2$), 1.71–1.50 (m, 2, β-CH_2), 1.27 (br s, 14, 7 CH_2) and 0.88 (t, 3, J=6.35, CH_3). Transition temperatures (°C) 113.3–115.3 (Cr–I) and 86.9 (I–Cr).

Y=$C_{10}H_{21}O$. Recrystallized from CH_3CN: yield=82.9%, TLC ($CHCl_3$) R_F=0.62. IR (Nujol) 1720 (str, ester), 1610 (med, Ar) and 1520 (med, Ar). ^1H NMR 8.14 (d, 2, J=8.63, ArH *ortho* to CO_2Ar), 7.54–7.30 (m, 5, C_6H_5), 7.09 (d, 2, J=9.04, ArH *ortho* to O_2CAr), 7.05 (d, 2, J=8.71, ArH *ortho* to Bn), 6.91 (d, 2, J=8.95, ArH *ortho* to OC_{10}), 5.15 (s, 2, $C_6H_5CH_2$), 3.95 (t, 2, J=6.45, OCH_2), 1.79 (quint, 2, J not determined, β-CH_2), 1.55–1.18 (m, 14, 7 CH_2) and 0.88 (t, 3, J=6.03, CH_3). Transition temperatures (°C) 109.3–111.9 (Cr_2–Cr_1), 122.9–123.8 (Cr–I), 104.1–104.2 (N–I, not always seen) and 88.2 (N–Cr). The nematic phase was seen only when the liquid was cooled very fast. Reheating the nematic phase immediately gave the N–I transition (lit [20] m.p.=122°C). Our NMR data also agrees with the literature values [20].

Y=COC_9H_{19}. The DCC reaction was run in THF for 17 h. Purification was by flash chromatography using 70% CH_2Cl_2/hexane to give a colourless solid: yield=69.2%, TLC ($CHCl_3$) R_F=0.36. IR (Nujol) 1739 (str, ester) 1681 (str, ketone) and 1612 (med d, Ar). ^1H NMR 8.16 (d, 2, J=8.83, ArH *ortho* to CO_2Ar), 8.04 (d, 2, J=8.79, ArH *ortho* to COC_9), 7.44–7.38 (m, 5, C_6H_5), 7.30 (d, 2, J=8.59, ArH *ortho* to O_2C), 7.07 (d, 2, J=8.84, ArH *ortho* to OBn), 5.17 (s, 2, $ArCH_2$), 2.97 (t, 2, J=7.38, $COCH_2$), 1.74–1.71 (m, 2, β-CH_2), 1.35–1.20 (m, 12, 6 CH_2) and 0.90 (t, 3, J=6.25, CH_3). Transition temperatures (°C): 129.3–129.7 (Cr_2–Cr_1), 140.5–141.5 (Cr_1–SmA), 141.3–141.9 (SmA–I) and 108.6 (SmA–Cr_2).

Y=$CO_2CH_2C_7F_{15}$. Purification was by flash chromatography using 20% hexane/CH_2Cl_2 (the sample was added to the column in $CHCl_3$) followed by recrystallization from CH_3CN: yield=79.0%, TLC ($CHCl_3$) R_F=0.62. IR 1740 (str with sh, ester), 1600 (wk, Ar), 1200 (str br, C–F) and 1140 (str, C–F). ^1H NMR 8.16 (d, 2, J=8.99, ArH *ortho* to CO_2Ar), 8.14 (d, 2, J=8.83, $ArCO_2R_F$), 7.50–7.37 (m, 5, C_6H_5), 7.34 (d, 2, J=8.79, ArH *ortho* to O_2CAr), 7.07 (d, 2, J=8.99, ArH *ortho* to OBn), 5.17 (s, 2, $C_6H_5CH_2$) and 4.84 (t, 2, J=13.21, CH_2R_F). Transition temperatures (°C) 142–143.9 (Cr–SmA), 181.1–183.0 (SmA–I) and 125.7 (SmA–Cr).

Y=$CH_2CH_2CO_2C_7H_{15}$. Recrystallized from abs EtOH: yield=70.2%, TLC ($CHCl_3$) R_F=0.42. IR (Nujol) 1745 (str, ester), 1620 (wk, Ar), 1200 (str br, C–F) and 1140 (str, C–F). ^1H NMR 8.14 (d, 2, J=9.04, ArH *ortho* to CO_2Ar), 7.50–7.33 (m, 5, C_6H_5), 7.25 (d, 2, J=8.71, ArH *ortho* to O_2CAr), 7.11 (d, 2, J=8.55, ArH *ortho* to CH_2), 7.05 (d, 2, J=8.99, ArH *ortho* to OBn), 5.16 (s, 2, $BnCH_2$), 4.07 (t, 2, J=6.68, CO_2CH_2), 2.97 (t, 2, J=7.74, $ArCH_2$), 2.63 (t, 2, J=7.66, CH_2CO_2), 1.70–1.49 (m, 2, β-CH_2), 1.41–1.15 (m, 8, 4CH_2) and 0.88 (t, 3, J=6.46, ArH ortho to O_2CAr).

Y=CN. Recrystallized from CH_3CN: yield=77.8%, m.p. 174.5–175.5°C, TLC ($CHCl_3$) R_F=0.39. IR (Nujol) 2200 (wk, CN), 1710 (str, ester) and 1600 (med, Ar). ^1H NMR 8.14 (d, 2, *J*=9.03, ArH *ortho* to CO_2Ar), 7.72 (d, 2, *J*=8.83, ArH *ortho* to CN), 7.50–7.30 (m, 7, C_6H_5 and ArH *ortho* to O_2CAr), 7.07 (d, 2, *J*=8.71, ArH *ortho* to OBn) and 5.17 (s, 2, CH_2O).

The second sequence of esters were prepared by the acid chloride method using Et_3N and CH_2Cl_2.

5.2.9. Ester 7. Recrystallized from abs EtOH: yield=86.8%; TLC ($CHCl_3$) R_F=0.74. IR (Nujol) 1749 (sh), 1739 (str, ester), 1596 (wk, Ar), 1511 (str, Ar), 1200 (str m, C–F) and 1150 (str, C–F). ^1H NMR 8.34 (d, 2, *J*=8.42, ArH *ortho* to CO_2Ar), 7.76 (d, 2, *J*=8.43, ArH *ortho* to C_6F_{13}), 7.13 (d, 2, *J*=9.08, ArH *ortho* to O_2CAr), 6.94 (d, 2, *J*=9.12, ArH *ortho* to OC_6), 3.97 (t, 2, *J*=6.54, OCH_2), 1.80 (quint, 2, *J*=7.14, β-CH_2), 1.57–1.25 (m, 6, 3 CH_2) and 0.92 (t, 3, *J*=6.55, CH_3). ^{13}C NMR 164.0, 157.2, 144, 133.5, 133.2, 130.3, 127.4, 127.2, 127.1, 122.2, 115.6, 115.2, 68.5, 31.6, 29.3, 25.8, 22.6 and 14.1.

5.2.10. Esters 13. *X=*$C_{10}H_{21}$. Purification was by flash chromatography using 1% EtOAc/hexane followed by recrystallization from abs EtOH: yield=61.9%. IR (Nujol) 1715 (str, esters), 1695 (med, Ar), 1200 (str m, C–F) and 1140 (str, C–F). ^1H NMR 8.15 (d, 2, *J*=8.87, ArH *ortho* to CO_2Ar), 8.11 (d, 2, *J*=7.41, ArH *ortho* to CO_2R), 7.34 (d, 2, *J*=8.75, ArH *ortho* to O_2CAr), 7.33 (d, 2, *J*=8.30, ArH *ortho* to C_{10}), 4.84 (t, 2, *J*=13.29, CO_2CH_2), 2.71 (t, 2, *J*=7.55, $ArCH_2$), 1.66 (quint, 2, *J*=7.43, β-CH_2), 1.27 (m, 14, 7 CH_2) and 0.88 (t, 3, *J*=4.27, CH_3).

X=NC. Recrystallized from abs EtOH: yield=44.8%, TLC ($CHCl_3$) R_F=0.51. IR (Nujol) 2225 (med, CN), 1740 (str, esters) and 1600 (med, Ar). ^1H NMR 8.32 (d, 2, *J*=8.46, ArH *ortho* to CO_2Ar), 8.18 (d, 2, *J*=8.67, ArH *ortho* to CO_2R), 7.85 (d, 2, *J*=7.97, ArH *ortho* to CN), 7.37 (d, 2, *J*=8.95, ArH *ortho* to O_2CAr) and 4.85 (t, 2, *J*=13.23, OCH_2).

X=O_2N. Recrystallized from abs EtOH: yield=27.6%, TLC ($CHCl_3$) R_F=0.62. IR (Nujol) 1740 (str, esters), 1600 (med, Ar), 1200 (str br, C–F) and 1140 (str, C–F). ^1H NMR 8.39 (s, 4, nitro ArH), 8.19 (d, 2, *J*=8.83, ArH *ortho* to CO_2R), 7.38 (d, 2, *J*=8.83, ArH *ortho* to O_2CAr) and 4.85 (t, 2, *J*=13.21, OCH_2).

5.2.11. Esters 19. Prepared by the esterification of the phenols **18** with pentadecaflurooctanoyl chloride.

X=$C_{10}H_{21}$. Recrystallized from hexane and then CH_3CN: yield=38.1%, TLC (CH_2Cl_2) R_F=0.12. IR (Nujol) 1799 (str, R_F ester), 1733 (str, Ar ester), 1208 (str br, C–F) and 1150 (str, C–F). ^1H NMR 8.10 (d, 2, *J*=8.22, ArH *ortho* to CO_2Ar), 7.32 (d, 2, *J*=8.35, ArH *ortho* to O_2CAr), 7.30 (d, 2, *J*=8.54, ArH *ortho* to C_{10}), 7.28 (d, 2, *J*=6.71, ArH *ortho* to $O_2CC_7F_{15}$), 2.70 (t, 2, *J*=6.49, $ArCH_2$), 1.75–1.60 (m, 2, β-CH_2), 1.40–1.20 (m, 14, 7 CH_2) and 0.88 (t, 3, *J*=6.37, CH_3).

X=$C_{10}H_{21}O$. Recrystallized from CH_3CN: yield=33.3%; TLC (CH_2Cl_2) R_F=0.11. IR (Nujol) 1797 (str, R_F ester), 1733 (str, Ar ester), 1610 (wk Ar), 1214 (str br, C–F) and 1150 (str, C–F). ^1H NMR 8.11 (d, 2, *J*=8.83, ArH *ortho* to CO_2Ar), 7.34 (d, 2, *J*=~8.02, ArH *ortho* to O_2CAr), 7.28 (d, 2, *J*=~7.13, ArH *ortho* to O_2CR_F), 4.07 (t, 2, *J*=6.45, OCH_2), 1.83 (quint, 2, *J* not recorded, β-CH_2), 1.60–1.15 (m, 14, 7 CH_2) and 0.89 (t, 3, *J*=6.41, CH_3).

X=NC. Recrystallized from CH_3CN: yield=30.8%, TLC (CH_2Cl_2) R_F=0.11. IR (Nujol) 1802 (str, R_F ester), 1733 (str, Ar ester), 1611 (med, Ar), 1214 (str br, C–F), 1150 (str, C–F). ^1H NMR 8.31 (d, 2, *J*=14, ArH *ortho* to CO_2Ar), 7.84 (d, 2, *J*=8.10, ArH *ortho* to CN) and 7.32 (s, 4, ArH *ortho* to OCOAr and R_F).

X=O_2N. Recrystallized from CH_3CN: yield=54.9%; TLC (CH_2Cl_2) R_F=0.11. IR (Nujol) 1790 (str, R_F ester), 1730 (str, Ar ester), 1620 (med, Ar), 1210 (str br, C–F) and 1160 (str, C–F). ^1H NMR 8.39 (s, 4, O_2NArH), 7.39 (d, 2, *J*=9.72, ArH *ortho* to OCOAr) and 7.32 (d, 2, *J*=8.80, ArH *ortho* to O_2CR_F).

5.2.12. Esters 25. *n=9, Y=*$C_{10}H_{21}$. The crude product (reaction time=48 h) was dissolved in hexane by heating; this solution was cooled to r.t. and the precipitated solid (unreacted phenol) removed by filtration. The filtrate consisted of two liquids. The lighter one was decanted and the solvent removed from the heavier one *in vacuo*. The remaining material was recrystallized twice from hexane: yield=57.9%; TLC ($CHCl_3$) R_F=0.07. IR (Nujol) 1790 (str, R_F ester), 1740 (str, Ar ester), 1600 (wk, Ar), 1500 (med, Ar), 1200 (str br, C–F) and 1140 (str, C–F). ^1H NMR 8.31 (d, 2, *J*=8.79, ArH *ortho* to CO_2Ar), 7.36 (d, 2, *J*=8.51, ArH *ortho* to CO_2Ar), 7.24 (d, 2, *J*=8.47, ArH *ortho* to C_{10}), 7.11 (d, 2, *J*=8.87, ArH *ortho* to CO_2R_F), 2.63 (t, 2, *J*=7.41, $ArCH_2$), 1.76–1.60 (m, 2, β-CH_2), 1.46–1.20 (m, 14, 7 CH_2) and 0.88 (t, 3, *J*=6.51, CH_3).

n=9, Y=$C_{10}H_{21}O$. Recrystallized from EtOAc: yield=51.5%; TLC ($CHCl_3$) R_F=0.10. IR (Nujol) 1790 (str, R_F ester), 1720 (str, Ar ester), 1600 (med, Ar), 1520 (str, Ar), 1200 (str br, C–F) and 1150 (str, C–F). ^1H NMR 8.31 (d, 2, *J*=8.59, ArH *ortho* to CO_2Ar), 7.35 (d, 2, *J*=8.79, ArH *ortho* to O_2CR_F), 7.11 (d, 2, *J*=8.96, ArH *ortho* to O_2CAr), 6.93 (d, 2, *J*=9.03, ArH *ortho* to OC_{10}), 3.96 (t, 2, *J*=6.51, OCH_2), 1.80 (quint, 2, *J*=7.18, β-CH_2), 1.52–1.18 (m, 14, 7 CH_2) and 0.89 (t, 3, *J*=6.18, CH_3).

n=7, Y=C₉H₁₉. Recrystallized from CH_3CN, yield=29.0%; characterization data were similiar to those for *n*=9, $Y=C_{10}H_{21}$.

n=9, Y=CN. Recrystallized from CH_3CN: yield=7.3%; TLC ($CHCl_3$) $R_F=0.09$. IR (Nujol) 2230 (wk, CN), 1790 (str, R_F ester), 1740, 1720 (med and str, CO_2Ar), 1610 (med, Ar), 1210 (str br, C–F) and 1180 (str, C–F). ^1H NMR 8.31 (d, 2, *J*=8.27, ArH *ortho* to CO_2Ar), 7.77 (d, 2, *J*=8.18, ArH *ortho* to CN), 7.39 (d, 2, *J*=8.58, ArH *ortho* to O_2CR_F) and 7.38 (d, 2, *J*=8.42, ArH *ortho* to O_2CAr).

n=9, $Y=(CH_2)_2CO_2C_7H_{15}$. Recrystallized from CH_3CN: yield=29.2%. IR (Nujol) 1800 (str, R_F ester), 1750 (str, Ar ester), 1600 (wk, Ar), 1200 (str br, C–F) and 1150 (str, C–F). ^1H NMR 8.31 (d, 2, *J*=8.91, ArH *ortho* to CO_2Ar), 7.36 (d, 2, *J*=8.87, ArH *ortho* to O_2CR_F), 7.28 (d, 2, *J*=8.59, ArH *ortho* to CH_2), 7.13 (d, 2, *J*=8.59, ArH *ortho* to O_2CAr), 4.08 (t, 2, *J*=6.68, OCH_2), 2.99 (t, 2, *J*=7.69, $ArCH_2$), 2.64 (t, 2, *J*=7.83, CH_2CO_2), 1.74–1.52 (m, 2, β-CH_2), 1.42–1.19 (m, 8, 4 CH_2) and 0.88 (t, 3, *J*=6.45, CH_3).

n=9, $Y=COC_9H_{19}$. Prepared using pyridine as the solvent and base (8 ml, 0.79 mmol), heating to reflux for 3 h and removing the solvent *in vacuo*. Purification was by flash chromatography using 15% EtOAc/hexane followed by recrystallization from abs EtOH; yield 4.4% of material still containing some impurities: TLC (10% EtOAc/hexane) $R_F=0.05$. IR (Nujol) 1797 (str, R_F ester), 1741 (str, Ar ester) 1682 (str, ketone), 1599 (med, Ar), 1200 (str br, C–F) and 1140 (str, C–F). ^1H NMR 8.33 (d, 2, *J*=8.83, ArH *ortho* to $ArCO_2$), 8.07 (d, 2, *J*=8.71, ArH *ortho* to COC_9), 7.39 (d, 2, *J*=8.87, ArH *ortho* to O_2CR_F), 7.33 (d, 2, *J*=8.79, ArH *ortho* to O_2C), 2.98 (t, 2, *J*=7.47, $COCH_2$), 1.79–1.64 (m, 2, β-CH_2), 1.40–1.21 (m, 12, 6 CH_2) and 0.88 (t, 3, *J*=5.84, CH_3).

n=9, $Y=CO_2CH_2C_7F_{15}$. We were unable to isolate any of this ester.

5.2.13. Nonadecafluorodecanoyl chloride. Problems were encountered in the preparation of this acid chloride by treating the acid with an excess of $SOCl_2$. Even when heated to reflux, this acid did not dissolve. Several solvents were added in an attempt to obtain a solution: CH_2Cl_2, pyridine and Et_2O. Only a combination of pyridine and Et_2O was effective. A solution of $C_{10}F_{21}CO_2H$ (5.0 g, 0.010 mol), $SOCl_2$ (10 ml), pyridine (4 drops), CH_2Cl_2 (2 ml) and Et_2O (2–4 ml) was heated at reflux for 5 h, cooled to r.t. and stirred for 17 h. The layers were separated and the lower layer found to be the acid chloride (4.64 g, 89.6%). IR (film) 1800 (str, COCl), 1200 (str br, C–F) and 1140 (str, C–F). This material was used without further purification. The C_7 acid chloride ($C_7F_{15}COCl$) was commercially available.

5.2.14. 4-(2H, 2H-Pentadecafluorooctyloxycarbonyl)-phenol 15. A solution of the benzyl ether **14** (5.39 g, 8.00 mmol) in THF (200 ml) containing 2 drops of dil HCl was hydrogenated at 50 lb in^{-2} for 17 h and then vacuum filtered through Celite. Removal of the solvent *in vacuo* gave 6.39 g of the crude product. Recrystallization of this material from hexane gave 3.15 g (75.7%) of the phenol **15** as a colourless solid: m.p. 106.4–109.9°; TLC (hexane) $R_F=0.14$. IR (Nujol) 3275 (wk br, OH), 1700 (str, ester), 1620, 1600 (str, Ar), 1240 (str br, C–F) and 1170 (str, C–F). ^1H NMR 7.99 (d, 2, *J*=8.79, ArH *ortho* to CO_2R_F), 6.89 (d, 2, *J*=8.88, ArH *ortho* to OH), 5.53 (s, 1, OH) and 4.79 (t, 2, *J*=13.35, CH_2). Our data are similar to those reported for the C_6F_{13} analog [18].

5.2.15. Phenols 24. These were prepared in the same manner as phenol **15**.

$Y=C_{10}H_{21}$. Purified by flash chromatography using 10% hexane/CH_2Cl_2 followed by recrystallization from hexane: yield=47.8%, TLC ($CHCl_3$) $R_F=0.11$. IR (Nujol) 3360, 3450 (wk med, OH), 1740, 1720 (str d, ester) and 1600 (wk, Ar). ^1H NMR 8.10 (d, 2, *J*=8.75, ArH *ortho* to CO_2Ar), 7.22 (d, 2, *J*=8.58, ArH *ortho* to C_{10}), 7.09 (d, 2, *J*=8.50, ArH *ortho* to O_2CAr), 6.89 (d, 2, *J*=8.87, ArH *ortho* to OH), 2.61 (t, 2, *J*=7.65, $ArCH_2$) 1.61 (quint, 2, *J* not determined, β-CH_2), 1.26 (br s, 14, 7 CH_2) and 0.88 (t, 3, *J*=6.37, CH_3). Transition temperatures (°C) 116.1–117.5 (Cr–I), 113.4 (I–Cr).

$Y=C_{10}H_{21}O$. Recrystallized from CCl_4: yield=89.4%; TLC ($CHCl_3$), $R_F=0.08$. IR (Nujol) 3425, 3325 (med, OH), 1730, 1710 (str, ester) and 1600, 1590 (wk, Ar). ^1H NMR agreed with the literature data [38] except that the OH peak was observed at 5.96. Transition temperatures (°C): 146.2–147.0 (Cr–I) and 142.4 (I–Cr), lit [38] m.p.=144.7°.

$Y=COC_9H_{19}$. Hydrogenation was performed in a solution of 21.4% abs EtOH, 35.7% EtOAc and 57.1% THF for 1.5 h. Purification was by flash chromatography using 15–20% EtOAc/hexane to give a colourless solid: yield=26.7%, TLC ($CHCl_3$) $R_F=0.04$. IR (Nujol) 3434 (wk, br, OH) 1731 (str, ester), 1687 (str, ketone) and 1604 (med d, Ar). ^1H NMR 8.14 (d, 2, *J*=8.75, ArH *ortho* to CO_2Ar), 8.05 (d, 2, *J*=8.75, ArH *ortho* to COC_9), 7.32 (d, 2, *J*=8.71, ArH *ortho* to O_2CAr), 6.95 (d, 2, *J*=8.87, ArH *ortho* to OH), 5.41 (s, 1, OH), 2.98 (t, 2, *J*=7.37, α-CH_2), 1.75–1.72 (m, 2, β-CH_2), 1.35–1.20 (m, 12, 6 CH_2) and 0.89 (t, 3, *J*=6.42, CH_3). Transition temperatures (°C) 120.1–123.3 (Cr–I) and 116.8–114.3 (I–Cr).

$Y=CO_2CH_2C_7F_{15}$. Hydrogenation seemed incomplete after 48 h at r.t.; repeated at 35–40° for 17 h. The product was recrystallized from CCl_4 to give a colourless solid: yield=40.8%; TLC ($CHCl_3$) R_F=0.14. IR (Nujol) 3400 (str br, OH), 1700 (str, ester), 1200 (str, C–F) and 1150 (str, C–F). ^{1}H NMR 8.14 (d, 2, J=8.50, ArH *ortho* to $CO_2CH_2R_F$), 8.06 (d, 2, J=8.43, ArH *ortho* to CO_2Ar), 7.34 (d, 2, J=8.79, ArH *ortho* to OCOAr), 6.94 (d, 2, J=8.58, ArH *ortho* to OH), 4.88 (t, 2, J=13.19, CO_2CH_2) and 3.59 (br s, 1, OH). Transition temperatures (°C) 167.2–168.5° (Cr–I) and 158.2 (I–Cr).

$Y=CH_2CH_2CO_2C_7H_{15}$. Recrystallized from CH_3CN: yield=36.9% and IR (Nujol) 3270 (br med, OH), 1760, 1720 (str, ester), 1590, 1570 (str, Ar). ^{1}H 8.09 (d, 2, J=8.66, ArH *ortho* to CO_2Ar), 7.25 (d, 2, J=7.86, ArH *ortho* to CH_2), 7.11 (d, 2, J=8.14, ArH *ortho* to O_2CAr), 6.88 (d, 2, J=8.42, ArH *ortho* to OH), 6.08 (1, s, OH), 4.08 (t, 2, J=6.64, CO_2CH_2), 2.98 (t, 2, J=7.66, $ArCH_2$), 2.65 (t, 2, J=7.63, CH_2CO_2), 1.75–1.50 (m, 2, β-CH_2), 1.45–1.15 (m, 8, 4 CH_2) and 0.88 (t, 3, J=6.19, CH_3).

$Y=CN$. Recrystallized from EtOAc/hexane: yield=52.6%; m.p.=187.5–188.0, lit [4] 186–190°C; TLC ($CHCl_3$) R_F=0.04. IR (Nujol) 3275 (br med, OH), 2200 (med, CN), 1720 (str, ester) and 1600 (med d, Ar). ^{1}H NMR 9.78 (br s, 1, OH), 8.04 (d, 2, J=8.75, ArH *ortho* to CO_2Ar), 7.73 (d, 2, J=8.43, ArH *ortho* to CN), 7.35 (d, 2, J=8.14, ArH *ortho* to O_2CAr) and 6.95 (d, 2, J=8.79, ArH *ortho* to OH).

5.2.16. 4-(Pentadecafluoroctanoyloxy)phenol 17. To a refluxing solution of hydroquinone (2.54 g, 23.1 mmol) and Et_3N (1.65 ml) in CH_2Cl_2 (35 ml) was added dropwise pentadecafluorooctanoyl chloride (5.00 g, 11.6 mmol). This mixture was heated at reflux for 2 h, cooled to r.t. and CH_2Cl_2 (100 ml) added. After washing with H_2O (3 × 150 ml), the organic layer was dried, filtered and the solvent removed to give 4.25 g (72.4%) of the crude product. Recrystallization of this material from $CHCl_3$/hexane gave 3.06 g (52.1%) of the phenol **17**: m.p. 91.5–92.5°C, TLC (CH_2Cl_2) R_F=0.15. IR (Nujol) 3500–3200 (med, OH), 1790 (str, ester) and 1600 with sh at 1585 (str, Ar). ^{1}H NMR 7.06 (d, 2, J=8.92, ArH *ortho* to OCOR), 6.86 (d, 2, J=6.86, ArH *ortho* to OH) and 5.00 (br s, 1, OH).

5.2.17. 4-Hydroxyphenyl 4-cyanobenzoate 18 (X=CN). To a stirred solution of hydroquinone (5.98 g, 54.4 mmol) in CH_2Cl_2 (100 ml) containing Et_3N at r.t. was added dropwise a solution of 4-cyanobenzoyl chloride (2.0 g, 12.1 mmol, obtained by treating the acid with $SOCl_2$ in 30 ml CH_2Cl_2). This mixture was heated at reflux for 10 h, cooled to r.t. and washed with H_2O. The organic layer was separated, dried, filtered and the solvent removed *in vacuo* to give 2.0 g (69.2%) of the crude product. TLC (CH_2Cl_2) showed 3 spots with R_F=0, 0.14 and 0.75. Separation of these spots could not be achieved by recrystallization from CH_2Cl_2. Flash chromatography on silica gel in CH_2Cl_2 gave two fractions. The first fraction was eluted with CH_2Cl_2: 570 mg, m.p.>300°, TLC (CH_2Cl_2) R_F=0.50, IR (Nujol) 2242 (med, CN) and 1736 (str, ester). ^{1}H NMR showed only 3 sets of aromatic protons: 8.33 (d, 4, J=8.18, ArH *ortho* to CN), 7.88 (d, 4, J=8.43, ArH *ortho* to CO_2Ar) and 7.36 (d, 4, J=10.34, ArH *ortho* to OCOAr), supporting the diester structure **20** (X=CN). This compound was reported earlier to have the following transition temperatures (°C): 331.5 (Cr–N) and 353.5 (N–I) [39], higher temperatures than we could achieve. The weight represents a yield of 26.0% (28.5% of the crude product).

A second fraction was eluted with Et_2O: 1.22 g (43.6% yield, 61.0% of the crude product), TLC (CH_2Cl_2) R_F=0.13, IR (Nujol) 3400 (med, OH) and 1710 (str, ester). ^{1}H NMR 8.30 (d, 2, J=8.75, ArH *ortho* to CO_2Ar), 7.82 (d, 2, J=8.76, ArH *ortho* to CN), 7.08 (d, 2, J=9.03, ArH *ortho* to CO_2Ar), 6.87 (d, 2, J=8.96, *ortho* to ArOH) and 5.01 (s, 1, OH), supporting the phenol structure **18**.

$X=CN$. Recrystallization of this material from $CHCl_3$/hexane gave a solid with m.p. 182.0–185.0°C, which agrees with the literature [19] m.p. 186°C for this phenol.

$X=NO_2$. This form of phenol **18** was prepared in the same manner. Flash chromatography gave 1.18 g (46.4%) of the diester **20** (X=NO_2); TLC (CH_2Cl_2) R_F=0.57. IR (Nujol) 1740 (str, ester) and 1620 (med, Ar) and mp 259–261°C [lit [39] transition temperatures (°C): 262 (Cr–N) and 281 (N–I)]. ^{1}H NMR 8.40 (s, 8, nitro ArH) and 7.42 (d, 4, J=25.5, ArH *ortho* to O_2CAr) and 1.30 g (51.2%) of the phenol **18** (X=NO_2): TLC (CH_2Cl_2) R_F=0.11 and IR (Nujol) 3400 (med br, OH), 1720 (str, ester) and 1590 (med, Ar). This material was recrystallized from CH_2Cl_2 to give the purified phenol: m.p. 192–195°C (lit [40] 197°). ^{1}H NMR 8.26 (slightly split s, 4, nitro ArH), 6.93 (d, 2, J=9.07, ArH *ortho* to O_2CAr) and 6.81 (d, 2, J=8.79, ArH *ortho* to OH).

5.2.18. Attempts at esterifying the phenol 17 with 4-substituted benzoic acids. $X=C_{10}H_{21}$. The carbodiimide method [16] was used with a reflux time of 4 h and an excess (1.25 equiv) of the acid. Purification was by chromatography on silica gel with CH_2Cl_2 followed by recrystallization from 95% EtOH to give a colourless solid: TLC (CH_2Cl_2) R_F=0.56. IR (Nujol) 1735 (str, Ar ester) and no R_F ester at 1797, supporting the diester structure **20** (X=$C_{10}H_{21}$). ^{1}H NMR 8.04 (d, 4, J=8.22, ArH *ortho* to CO_2Ar), 7.25 (d, 4, $J=8.22$, ArH *ortho* to CH_2), 7.20 (s, 4, ArH *ortho* to O_2CAr), 2.63 (t, 4, $J=7.69$, $ArCH_2$), 1.70–1.50 (m, 4, β-CH_2), 1.40–1.10 (m, 28, 14 CH_2) and 0.81 (t, 6, $J=6.41$, CH_3). Transition temperatures (°C): 79.7–80.4 (Cr–S_{mosaic}), 112.4–112.7 (S_{mosaic}–SmC), 122.2–124.1 (SmC–N), 145.1–145.3 (N–I) and 72.5 (S_{mosaic}–Cr).

Fraction 2 from the chromatography and the recrystallization solvent were combined, the solvent removed *in vacuo* and the remaining material recrystallized from hexane to give a colourless solid shown to be the phenol **18** ($X=C_{10}H_{21}$): m.p. 104–105°C, TLC (CH_2Cl_2) $R_F=0.03$, (Et_2O) $R_F=0.83$. Both IR and ^1H NMR data agreed with those reported for this phenol [5].

$X=C_{10}H_{21}O$. Similar results were obtained using this acid. Characterization data for the isolated phenol agreed with our earlier data [5]. Data for the diester **20** ($X=C_{10}H_{21}O$) are: IR (Nujol) 1727 (sh, CO_2R), 1618, 1509 (med, Ar). ^1H NMR 8.14 (d, 4, $J=9.12$, ArH *ortho* to CO_2Ar), 7.26 (s, 4, ArH *ortho* to OCOAr), 6.97 (d, 4, $J=9.04$, ArH *ortho* to O*R*), 4.05 (t, 4, $J=6.48$, OCH_2), 1.83 (quint, 4, $J=7.14$, β-CH_2), 1.60–1.10 (m, 14, 7 CH_2) and 0.89 (t, 3, $J=6.52$, CH_3). Transition temperatures (°C) 123.0–126.1 (Cr–SmC), 126.7–127.5 (SmC–N), 175.3–178.7 (N–I) and 113.8 (SmC–Cr) agree with those reported [41].

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