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The synthesis and mesomorphic behaviour of the 1,2,4,5-tetra-substituted benzenes with (4-tridecyloxyphenyl)ethynyl and (4-tridecyloxyphenyl)carbonyloxy substituents

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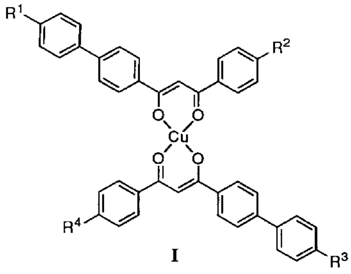
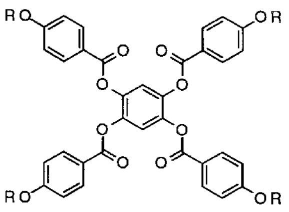
The synthesis, mesophase morphology and transition temperatures of a series of 1,2,4,5-tetra-substituted benzenes are described. The compounds have (4-tridecyloxyphenyl)carbonyloxy or (4-tridecyloxyphenyl)ethynyl as the peripheral substituents in all possible combinations ranging from the tetra-ester to the tetra-alkyne. Both the substituents used have similar structural dimensions but the greater rigidity of the alkynyl unit ensures that it projects more directly from the central core than does the more flexible ester unit. All of the seven compounds are nematogenic and five show a smectic C phase; the differences observed in the transition temperatures of the compounds are discussed in terms of molecular shape and the relationship of the compounds to appropriate calamitic and discotic systems. Molecular modelling indicates that π–π interactions of peripheral phenyl groups can lead to molecules with calamitic shapes.

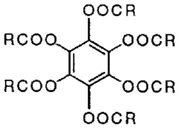
1. Introduction



I



II
a, $R = C_{13}H_{27}$



III

Thermotropic liquid crystal materials are normally classified as calamitic, sanidic or discotic compounds and the respective molecular shapes of lath-like, board-like and disc-like structures give an immediate, although superficial, appreciation of how such structures can generate mesophases [1]. In addition to these three distinct molecular shapes for mesogens, there are many examples of mesogenic compounds with molecular structures that are not rod-, board- or disc-shaped [2]. For example, copper(II) complexes of *β*-diketones (e.g. **I**) with a cross-shaped structure are mesomorphic, showing calamitic nematic and smectic phases, and for several years studies have been made of the way in which the nature of the cross members affect the mesogenicity of the complexes [3–8]. The molecular shape of the 1,2,4,5-tetra-(4-alkyloxybenzoyloxy)benzenes (**II**) [9, 10] is closely related to that of compounds **I** in terms of the mutual position of the cross-members, but they have a more compact central region; these tetra-esters also show nematic and smectic mesophases. An additional point of interest in compounds **II** is that they are related to the discotic 1,2,3,4,5,6-hexa-(4-alkanoyloxy)benzenes (**III**) [11–13] and so the change from tetra- to hexa-substituted benzene systems of this type changes the type of liquid crystal from calamitic to discotic. Other classes of mesogenic compounds which have unusual shapes and are relevant to the compounds considered in this work are 1,2-disubstituted benzenes [14, 15] and 1,3-disubstituted benzenes [16–18]; both of these types of system are related to the 1,2,4,5-tetra-substituted benzenes in that the substitution pattern of the 1,2-disubstituted compounds is like that of the left- and right-hand side of structure **II**, and the substitution pattern of the

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1,3-disubstituted benzenes is like the top and bottom parts of structure **II**.

Recently we started to examine the borderline between calamitic and discotic systems, with the possibility of generating biaxial nematic compounds, by varying the nature, number and flexibility of the substituents on the central benzene ring of compounds of type **II** [10]. The tetra-esters **II** ($R = C_3H_7$ to $C_{16}H_{33}$ and $C_{18}H_{37}$) were initially considered and it was found that for R from C_3H_7 to $C_{10}H_{21}$, the compounds show only a nematic phase, for $R = C_{11}H_{23}$ to $C_{14}H_{29}$ nematic and smectic C phases are seen and for $R = C_{15}H_{31}$ onwards only a smectic C phase is produced; the refractive indices for the aligned nematic phase of compound **II**, $R = C_{10}H_{21}$, show that the nematic phase is positive uniaxial [10].

A further step in the examination of the effect of molecular structure on the mesogenicity of cross-shaped compounds involves varying the rigidity of the linkage between the central core and the four peripheral units, and here results are reported for compounds (**1**–**6**) related to compound **IIa** in which the ester linkages have been systematically replaced in all possible combinations by an alkynyl unit. Although the esters **II** are calamitic, rotation around the bonds in the ester groups can give a structure in which the substituents are not disposed as the formal cross-shape shown, but the *ortho*-related lateral groups interact with each other to generate a lath-like structure. In this case, increasing the rigidity of the cross-shaped framework by using alkynyl links should lead to reduced mesogenicity for a calamitic system. The terminal substituent chosen for the series of compounds was the 4-tridecyloxy group which in the tetra-ester (**II**, $R = C_{13}H_{27}$) gave smectic C and nematic phases, and so with this terminal group, the effect of structural changes on both these mesophase stabilities could be evaluated. The alkyne link used to replace the ester is rigid and linear and maintains the direction in which the substituent group extends from the core; the dimensions of the alkynyl unit are similar to those of the ester group, as can be seen for the values given in figure 1. For these reasons all the compounds in this series have almost the same diameter both for the inner core region and for the whole molecule.

2. Experimental discussion

The full series of esters and alkynes consists of seven compounds (**IIa** and **1**–**6**) and the results for one of these (**IIa**) have been reported previously [10]. The synthetic routes to the further six compounds are shown in schemes 1 and 2 and are principally based on protection of hydroxy groups (where necessary) with *t*-butyldimethylsilyl chloride, coupling of the appropriate bromo compounds or triflates with (4-tridecyloxyphenyl)-ethynylzinc chloride, and esterification of hydroxy groups with 4-tridecyloxybenzoyl chloride.

3. Discussion of results

3.1. *General discussion of transition temperatures*

The melting points, transition temperatures and mesophase types for the series of compounds **IIa** and **1**–**6** are given in table 1; the results are first of all summarized and discussed comparatively and then some molecular modelling studies on the structures of these compounds are presented to give a further insight into the nature of the molecular shape.

The general impression from the melting points and transition temperatures is that they are broadly similar throughout the series, with an overall range in melting points, smectic C–nematic and nematic–isotropic liquid transition temperatures of 39·2, 27·5 and 29·5°C, respectively. Optical polarizing microscopy shows that throughout the series the defect textures for smectic C phases are identical to each other, and this is also the case for the nematic phase textures. Both textures are typical of those for calamitic systems with the smectic C phase showing regions of focal conic and schlieren textures and the nematic phase showing schlieren and threaded textures. It has been suggested that only two-brush disclinations are seen in the textures of biaxial nematic liquid crystals [19], but both two- and four-brush disclinations are seen for the compounds reported here. As expected, both mesophases are more viscous than

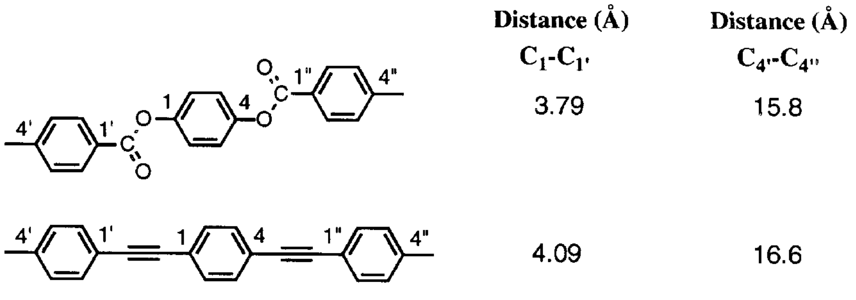
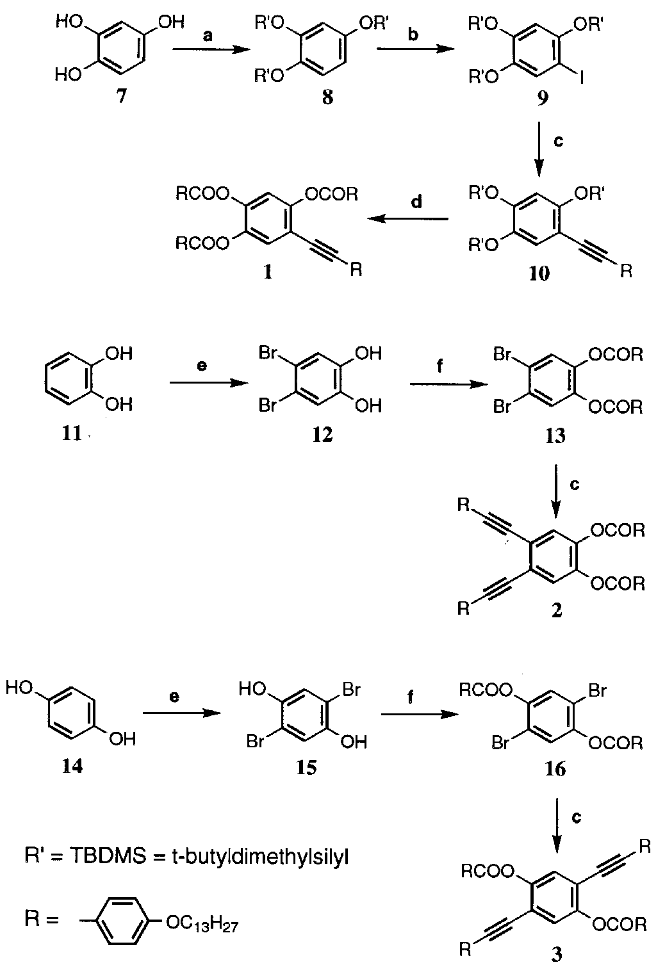
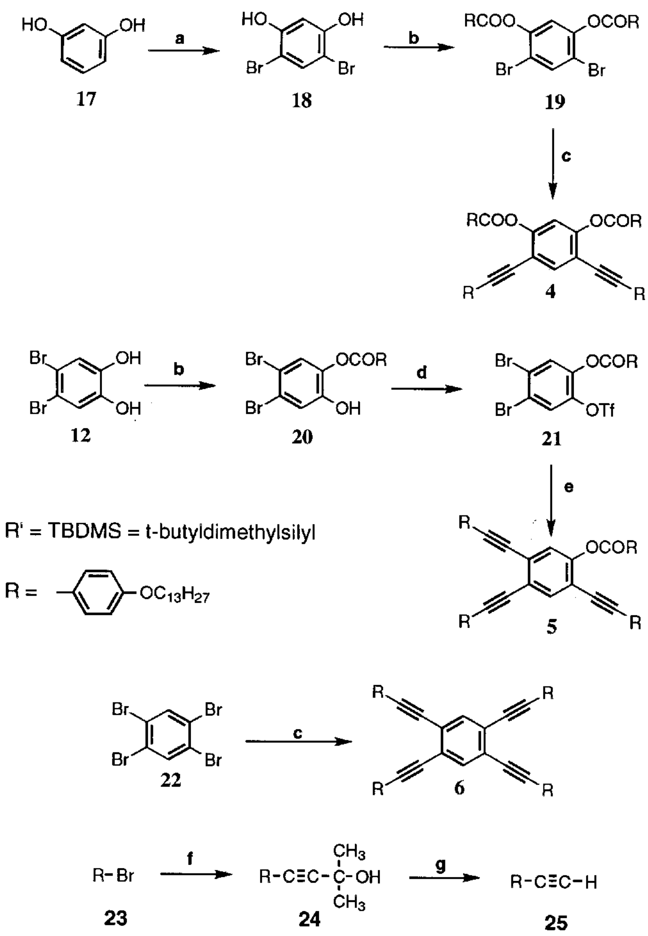


Figure 1. A comparison of molecular dimensions in esters and alkynes.



a ...TBDMSCl/K_2CO_3, butanone, reflux, 18 h
b....CF_3CO_2Ag /I_2 , $CHCl_3$, r.t.
c....RC≡CZnCl/Pd$(PPh_3)_4$, THF, reflux
d....Bu_4NF, RCOCl, THF, r.t., 18 h
e....Br_2/AcOH, 0 °C, 1 h
f.....RCOCl, Et_3N, CH_2Cl_2, r.t., 2 h

Scheme 1. Synthetic routes to the ester- and alkyne-linked 1,2,4,5-tetra-substituted benzenes (**1**–**3**).

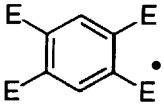
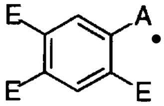
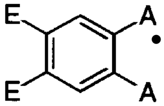
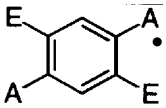
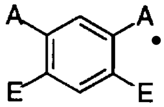
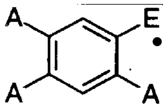
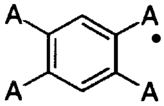


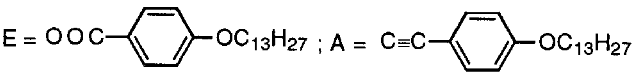
a....Br_2/AcOH, 0 °C, 1 h
b....RCOCl, Et_3N, CH_2Cl_2, r.t., 2 h
c....RC≡CZnCl/Pd$(PPh_3)_4$, THF, reflux
d....$PhNTf_2$, CH_2Cl_2, - 78 °C to r.t., 18 h
e....reagents c and LiCl
f....$PdCl_2(PPh_3)_2$, 2-methylbut-3-yn-2-ol, CuI, Et_3N, THF, 60 °C, 18 h
g....KOH, toluene, reflux, 2 h

Scheme 2. Synthetic routes to the ester- and alkyne-linked 1,2,4,5-tetra-substituted benzenes (**4**–**6**).

those for normal calamitic systems. Although there is no evidence for a dramatic decrease in mesogenicity arising from the introduction of the more rigid alkyne link, the general trend is for the presence of an increasing number of alkyne units to lead to lower mesophase stability and to depress the transition temperature for smectic C–nematic more than for nematic–isotropic liquid. With 0, 1, 2, 3 and 4 alkyne substituents present, the smectic C–nematic transitions, where observed, gradually decrease [94·3, 90·5, (74·9, absent, 89·5), 66·8, absent °C for compounds **IIa** and **1**–**6**, respectively]; the diester/di-alkyne compounds have three positional isomers and their temperatures are shown in parentheses (). Similarly, the T_{NI} values broadly decrease [100, 100·6, (88·6, 98·2, 103·7), 85·8, 74·2°C, respectively] with increasing numbers of alkyne substituents (compounds **IIa** and **1**–**6**, respectively). In normal calamitic systems the differences in clearing points for ester and alkyne linked compounds are also small, but the alkyne compounds usually have the higher values because of their greater linearity and polarisability (see **IV**–**VII**) [20, 21]; the alkyne systems also show reduced smectic C character. The closest comparison of the effect of ester and alkyne linking groups in discotic systems is provided by compounds **VIII** and **IX** where the link is between the

Table 1. Mesophase morphology and transition temperatures (°C) for ester- and alkyne-linked 1,2,4,5-tetra-substituted benzenes.

Compound		Cr		SmC		N		I
IIa		•	97·8	(•	94·3)	•	100	•
			[58·3][a]		[6·3]		[2·3]	
1		•	84·5	•	90·5	•	100·6	•
			[63·8]		[5·8]		[2·4]	
2		•	**75·3**	(•	74·9)	•	88·6	•
			[50·7]		[3·1]		[1·6]	
3		•	110·5[b]	—	—	(•	98·2)	•
			[95·1]				[1·0]	
4		•	107	(•	89·5	•	103·7)	•
			[89·5]		[4·2]		[1·2]	
5		•	71·3	(•	66·8)	•	85·8	•
			[74·6]		[3·5]		[1·6]	
6		•	96[c]	—	—	(•	74·2[d])	•
			[77·7]				[ ][e]	



[a] [ ] Enthalpies of transition in kJ mol^{-1}.

[b] Recrystallised at 94°C (DSC).

[c] Recrystallised at 84°C (DSC).

[d] Monotropic transition observed by polarizing microscopy on small regions.

[e] Not detected by DSC.

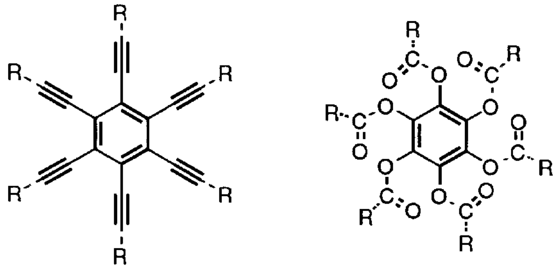


Figure 2. A comparison of alkyne- and ester-linked discotic systems to show the greater space-filling achieved by ester substituents.

central benzene core and an alkyl group; here, in contrast to the calamitic compounds, the ester-containing compound has a much higher clearing point than the compound with alkynyl links [11, 13, 22]. There are several plausible explanations for the marked difference in the effect caused by alkyne and ester links in discotic and calamitic systems. For example, the alkyne unit in **IX** is less effective in its space-filling ability around the central benzene core than is the ester unit (see figure 2) whereas for calamitic systems, the linear nature of alkynes allows more effective intermolecular associations. Alternatively, the greater polarity of the six-ester region may give greater inter-disk attractions than for the alkynes.

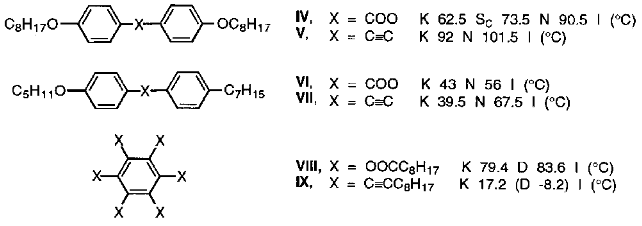
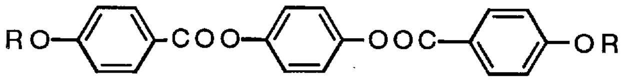


Table 2 shows the transition temperatures for a few 1,4-di-(4-alkoxybenzoyloxy)benzenes [23] and some of the compounds in table 1 can be regarded as having lateral substituents present in these reference parent di-esters; the values for the equivalent parent di-alkynes are not available. Because the overall effects on transition temperatures caused by interchanging ester and alkyne groups are small, detailed analysis of the structural reasons for these small changes is not particularly fruitful, but some further observations can be made on the values for the transition temperatures shown in table 1 in relation to those shown in table 2:

(*a*) The clearing points for compounds **IIa**, **1** and **3** are almost identical (100, 100·6 and 98·2°C, respectively) showing that if the 1,4-di-(4-alkoxybenzoyloxy)benzenes **X**–**XII** given in table 2 are taken as the point of reference, then the inclusion of two esters, one ester and one alkyne or two alkynes as lateral 2,5-substituents

Table 2. Mesophase morphology and transition temperatures (°C) for some 1,4-di-(4-alkoxybenzoyloxy)benzenes.



R		Cr		SmC		N		I
$C_{11}H_{23}$	**X**	•	111·0	•	151·1	•	175	•
$C_{12}H_{25}$	**XI**	•	109·1	•	155·7	•	171·5	•
$C_{14}H_{29}$	**XII**	•	105·4	•	157·3	•	162·5	•

has almost the same effect. Introducing one alkyne unit into the tetra-ester has a negligible effect on the clearing point (compare compounds **IIa** and **1**; T_{NI} values 100 and 100·6°C, respectively) and a second alkyne also has a very small effect on clearing point if positioned either to preserve the linearity of the two rigid alkyne groups (see compound **3**; T_{NI} value 98·2°C) or to give an obtuse angle between *meta*-alkynes as in compound **4** (T_{NI} value 103·7°C). It is somewhat surprising that compound **4** has a higher clearing point than compound **3**, and indeed it has the highest clearing point of the series. The possibilities for intramolecular interactions between ester and alkyne units are the same in compounds **3** and **4** where the groups are *ortho* to each other.

(*b*) The clearing points are lower when two alkyne substituents are *ortho* to each other (compounds **2** and **5** with values of 88·6 and 85·8°C, respectively) and the lowest value of 74·2°C arises when this relationship occurs twice within the molecule for compound **6**. The formal angle between the alkyne substituents in the *ortho* arrangement is 60° and is more acute than when the rigid alkynes are *meta* disposed to each other giving an angle of 120°; the more linear arrangement in the *meta* case leads to higher clearing points as seen for compound **4** (103·7°C), in comparison with compound **2** (88·6°C).

(*c*) The smectic C to nematic transition temperature is gradually depressed relative to the nematic to isotropic transition as alkyne groups are introduced; the initial difference of 5·7°C between these transition temperatures for **IIa** increases to 10·1°C (one alkyne, **1**), to 13·7 and 14·2°C (two alkynes, **2** and **4**), to 19·9°C (three alkynes, **5**).

3.2. *Molecular modelling*

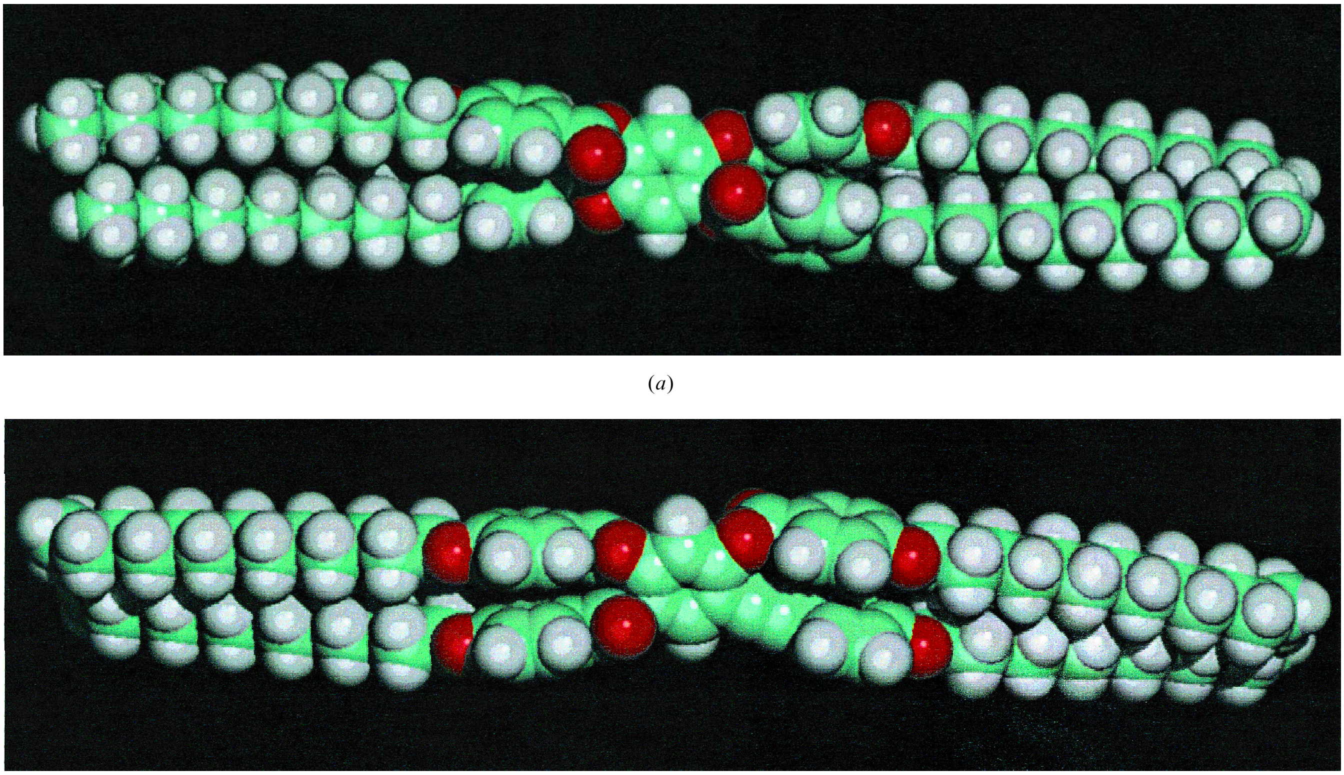
All the structures shown in table 1 were modelled using Cerius^2 (BIOSYM/Molecular Simulations) (for a single molecule at 0 K in the gas phase) with tridecyloxy terminal groups (to give a constant basis for comparison, the terminal groups were used in the fully extended zig-zag form in all cases, although it is acknowledged that crystal structure analysis, for example, sometimes shows that alkyl chains are distorted from the fully extended form [24–26]). For each compound, initial structures were used with the ester groups in the plane of the central ring, perpendicular to the plane of the central ring, with the carbonyl oxygen atoms pointing in each of the two possible directions and in all possible relationships with respect to the carbonyl oxygen atoms in the other ester groups. The peripheral benzene rings were also considered in the plane of, and perpendicular to, the central ring and the energies of the structures were minimized to a termination criterion of 0·1 kcal mol^{-1} Å^{-1} starting from each of these initial arrangements.

The minimum energy structure to emerge from modelling of the tetra-ester **IIa** is that shown in figure 3 (*a*) for which the main features are a face-to-face relationship of the 1,2- and 4,5-benzene rings which are rotated approximately 30° with respect to each other about the axis joining the ring centres, with the carbonyl groups of the esters at the 1,2-positions opposed, as is the case for the carbonyl groups in a 4,5- and 2,4-relationship.

All the low energy structures which were generated show that the π–π interactions of the peripheral benzene rings are the major feature and the orientation of the carbonyl oxygen atoms in the ester groups is less significant. For example, the minimum energy structure shown in figure 3 is 1·02 kcal mol^{-1} more stable than the second lowest energy conformer which has the carbonyl groups of the esters at the 1,2- and 4,5-positions opposed, but those at the 2,4- (and 1,5-) positions pointing in the same direction; the energies for cross-shaped structures where π–π interactions do not occur are approximately 37·4 kcal mol^{-1} higher. This analysis shows that with flexible ester linking groups, π–π interactions of the outer rings in **IIa** can create a structure with calamitic characteristics (see figure 3 (*a*)) rather than one with a planar, discotic appearance.

Similar modelling of the compounds with all combinations of esters and alkyne units was also carried out. When an ester and an alkyne are *ortho* to each other (e.g. compound **1**), then π–π interaction of the benzene rings in the ester and alkyne arm is still possible (see figure 3 (*b*)). When two alkyne units are *ortho* to each other (e.g. compound **2**), the π–π approach of the benzene rings in the *ortho*-dialkyne region is less feasible but it appears to occur slightly at the expense of distortion from linearity of the alkyne region. The two bonds attached to the alkyne unit are bent approximately 9° and 7° with respect to the alkyne bond giving a total deviation from linearity of 16° in each case to allow interaction of the benzene rings, and giving a separation of 4·37 and 4·94 Å between the C_1 and C_4 atoms in the splayed benzene rings, respectively (see figure 4). The corresponding separations shown in figure 4 for two *ortho*-esters are 3·42 and 3·75 Å, respectively, and for *ortho*-ester/alkynes the separations are 3·67 and 3·85 Å, respectively, with angles around the alkyne bond of 176° in each case.

Several X-ray crystallographic studies have shown that an alkyne bond can deviate appreciably from linearity both when the triple bond is part of a ring system (e.g. the C_{aryl}–C≡C angle in *sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne is 156° [27]) and when it is in an open-chain structure (e.g. angles of 169°/178° and 176°



(*a*)

(*b*)

Figure 3. Minimum energy structures from molecular modelling of (*a*) compound **IIa**, (*b*) compound **1**.

occur in 4-butyl-4′-methoxytolane for the $\mathrm{C_{aryl}}$–C≡C angle at the methoxyphenyl and butylphenyl ring, respectively [28]).

A comprehensive analysis of π–π interactions has been developed [29] in which the interplanar separation of the aryl rings in molecules associating by intermolecular π–π interactions is typically 3·4–3·6 Å, but for intramolecular π–π interactions the separation of the benzene rings will obviously depend on the structural constraints imposed by the molecular geometry. The values of 3·45–3·75, 3·67–3·85 and 4·37–4·94 Å obtained in this work for a 1,2-diester, a 1,2-alkyne/ester and a 1,2-dialkyne system, respectively, show that in the first two cases a strong π–π interaction should arise and even in the last case the benzene rings may still be attracted slightly. A further feature of the proposed model for π–π interactions [29] is that an offset or slipped geometry of the π regions [29, 30] or a face-to-face geometry with an offset rotation about the principal axis [31] is preferred and π–π interactions between two π-deficient aromatic systems are particularly favourable.

An X-ray crystallographic study of 1,2,4,5-tetra-(4-butyloxyphenylcarbonyloxy)benzene has been carried out [32] which reveals an offset π–π stacking of the aromatic rings from one molecule to the next rather than intramolecularly. Although the compounds considered in this work can generate intramolecular or intermolecular π–π interactions there are good reasons why in the solid state the intermolecular effects are more significant and these reasons will be discussed in another paper [32].

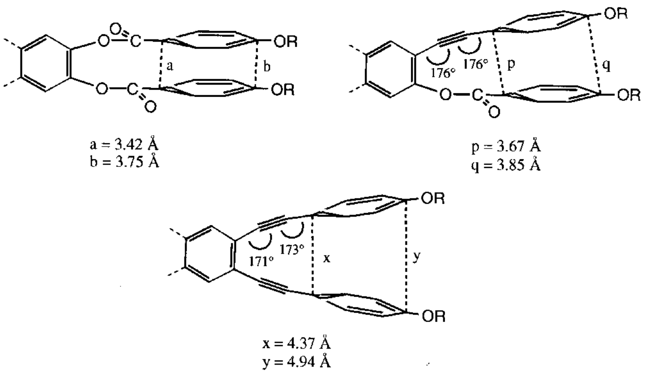
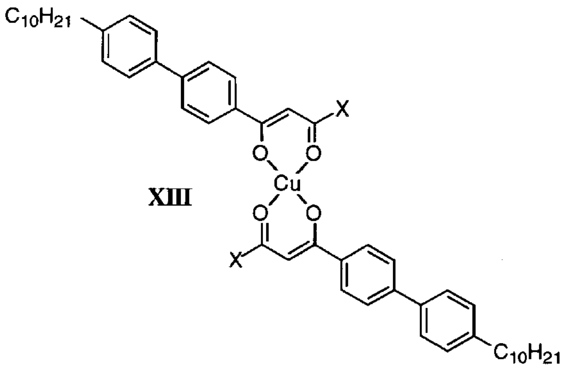


Figure 4. Diagram to show the distances separating the benzene rings in 1,2-diesters (e.g. **IIa**), 1,2-ester/alkynes (e.g. compound **1**) and 1,2-dialkynes (e.g. compound **2**).

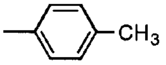
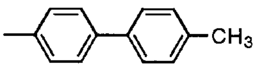
The modelling reported here on a single molecule is quite remote from the macroscopic situation experienced by molecules in a crystal or mesophase and should not therefore be treated as convincing proof for the situation in such assemblies of molecules. None-the-less, the results briefly described do seem to be compatible with the trends in mesophase stabilities revealed in table 1 in the following ways. The clearing points are highest for compounds which have *ortho*-diesters or *ortho*-ester/alkynes on both sides of the molecule (100, 100·6, 98·2 and 103·7°C for **IIa**, **1**, **3** and **4**, respectively). In all of these situations, each side of the molecule can bring the *ortho*-substituents towards each other by π–π interactions and so help to create a lath-like, calamitic structure. For compounds **2** and **5**, the substituents on only one side of the molecule can be brought together, giving a somewhat Y-shaped molecule with clearing points of 88·6 and 85·8°C, respectively. Finally, with compound **6**, a more X-shaped molecule exists and this has the lowest clearing point of 74·2°C. The ease with which the *ortho*-substituents can interact with each other to give a lath-like structure appears to be the major factor in determining the mesogenicities of the molecules.

Molecules with the shape generated by π–π interactions of the peripheral benzene rings (i.e. as shown in figure 3) can then be involved in normal calamitic intermolecular associations and the result is effectively a 'double-molecule' unit with two alkoxy terminal chains at each end.

Several aspects of the relationship between molecular structure and mesogenicity for laterally substituted molecules and cross-shaped molecules are, at the moment, still difficult to rationalize. Many examples of lateral substitution at the 2-position in 1,4-disubstituted benzenes have been examined [2] and both for compounds with lateral alkyl groups [33, 34] and for those with lateral groups containing ring systems [35, 36] the general view is that the lateral substituent stretches along the molecular long axis, as defined by the rest of the molecule, to give an effective rod-like shape. It therefore seems compatible with those views that the *ortho*-groups in the compounds presented here could also interact with each other and produce a rod-like shape. However, the mesogenicity of metal β-diketonates cannot be justified in this way. Although **I** and **II** have the common feature of a cross-shaped structure (see earlier comments), they are quite different in so far as it is impossible for the *ortho*-related substituents in **I** to associate by π–π interactions. Certain structural changes to **I** and **II** also give quite different effects on the mesogenicity of the compounds. Removing two diagonally related substituents in **IIa** to give compounds such as **X**–**XII** leads to an increase in mesogenicity (see tables 1 and 2), but for compounds **XIII**, decreasing the length of the 'lateral' X group decreases the temperature of clearing [5, 7]; for these reasons there does not appear to be a common explanation for mesogenicity of systems **I** and **II**.



XIII

<u>X</u>	<u>N - I</u> (°C)
H	160 (decomp.)
CH_3	[160] virtual value
	(167) monotropic value
	206

4. Conclusions

The major conclusion drawn from the transition temperatures for compounds prepared in this work (see table 1) is that ester functions in 1,2,4,5-tetra-substituted benzenes enhance mesophase thermal stability relative to alkyne units. Superficially this result seems more in keeping with a discotic nature for '1,2,4,5-' systems, but the results of birefringence measurements [10], molecular modelling and optical polarizing microscopy studies on single compounds and binary mixtures [37] are more compatible with calamitic structures. The flexibility of the ester links allows the peripheral phenyl groups in 1,2-diesters and 1,2-ester/alkynes to come close enough together for π–π interactions to occur and give the molecules a calamitic shape; this effect may operate, but less effectively, in 1,2-dialkynes.

5. Experimental

Compounds **7**, **11**, **14**, **17** and **22** are commercially available. Confirmation of the structures of intermediates and products was obtained by a combination of ^{1}H NMR spectroscopy (JEOL JNM-GX270 spectrometer), infrared spectroscopy (Perkin-Elmer 457 grating spectrophotometer) and mass spectrometry (Finnigan 1020 GC-MS spectrometer). The progress of reactions was monitored frequently by thin layer chromatography using aluminium-backed silica gel plates (60 F254 Merck) and flash chromatography was performed using Merck silica gel 60 (230–400 mesh). The phase assignments and transition temperatures were determined by thermal polarizing light microscopy (Olympus BH2 polarizing microscope) in conjunction with a Mettler FP5 hot-stage and control unit. Differential scanning calorimetry (Perkin-Elmer DSC-7 and IBM data station) was used to determine the enthalpies of the transitions; the instrument was previously calibrated against an indium standard (measured $\Delta H = 28{\cdot}35\,\mathrm{J\,g^{-1}}$, literature $28{\cdot}45\,\mathrm{J\,g^{-1}}$ [38]) and all values are quoted in $\mathrm{kJ\,mol^{-1}}$.

5.1. *1,2,4-Tri-(t-butyldimethylsiloxy)benzene* (**8**)

1,2,4-Trihydroxybenzene (3·0 g, 23·8 mmol) and *t*-butyldimethylchlorosilane (11·0 g, 72·5 mmol) were suspended in dry THF (25 ml); triethylamine (10·2 ml, 72·5 mmol) and 4-pyrrolidinopyridine (0·10 g, 0·67 mmol) were added and the mixture was stirred at room temperature for 24 h. The reaction mixture was diluted with ether (150 ml) and washed with water (2 × 50 ml), dilute hydrochloric acid (2 × 50 ml) and water (50 ml); the ether solution was dried ($MgSO_4$) and the ether removed to give a thick brown oil which was purified by chromatography on silica using dichloromethane : light petroleum (b.p. 40–60°C) (1 : 1) followed by distillation to give a colourless oil. Yield 10·0 g, 87%, b.p. 152°C at 0·01 mmHg. δ_H (270 MHz; $CDCl_3$; TMS): 0·14 and 0·15 (18 H, 2 × s), 1·00 (27 H, bs), 6·26 (2 H, m), 6·65 (1 H, d).

5.2. *1,2,4-Tri-(t-butyldimethylsiloxy)-5-iodobenzene* (**9**)

Dry silver trifluoroacetate (2·60 g, 11·73 mmol) [39] was placed in a dry, single-necked flask fitted with a pressure-equalizing funnel protected with a guard tube, and compound **8** (5·82 g, 11·73 mmol) was added. A solution of iodine (3·00 g, 11·73 mmol) in chloroform (50 ml) was added dropwise during 2 h to the stirred suspension at room temperature. The mixture was stirred for a further 1 h, filtered and the filter pad washed with chloroform (25 ml). The combined filtrates were washed successively with water, sodium thiosulphate solution, and dilute hydrochloric acid, dried ($MgSO_4$) and concentrated *in vacuo* to give a brown oil which was purified by column chromatography on silica using dichloromethane : light petroleum (b.p. 40–60°C) (8 : 92) to give a viscous colourless oil. Yield 3·5 g, 50%. δ_H (270 MHz; $CDCl_3$; TMS): 0·16 (6 H, s), 0·19 (6 H, s), 0·24 (6 H, s), 0·96 (18 H, s), 1·04 (9 H, s), 6·39 (1 H, s), 7·15 (1 H, s); *m/z* 595 (M^+).

5.3. *1,2,4-Tri-(t-butyldimethylsiloxy)-5-(4-tridecyloxyphenylethynyl)benzene* (**10**)

Compound **9** (0·630 g, 1·06 mmol) was added to the zinc chloride derivative of (4-tridecyloxyphenyl)ethyne [prepared from the ethyne (0·954 g, 3·18 mmol) and butyllithium (1·3 ml, 2·5 M in hexane, 3·18 mmol) at −40°C, followed by addition of zinc chloride (6·4 ml, 0·5 M in THF, 3·18 mmol) at −40°C and the solution then allowed to warm to 0°C] and tetrakis(triphenylphosphine)palladium(0) (0·100 g) at room temperature. The reaction mixture was heated under reflux for 18 h, filtered and the filtrate concentrated *in vacuo*. The residue was taken up in the minimum volume of ethyl acetate and the solution was triturated with ethanol until a precipitate formed. The solid was collected and purified by column chromatography [silica; eluent light petroleum (b.p. 40–60°C) : dichloromethane, 9 : 1] and recrystallization (ethyl acetate) to give the product. Yield 0·50 g, 62%, m.p. 71°C. δ_H (270 MHz; $CDCl_3$; TMS): 0·18–0·21 (18 H, m, $6 \times SiCH_3$), 0·88 (3 H, t, CCH_3), 0·97–1·02 (27 H, m, tBu), 1·25 (20 H, m, $10 \times CH_2$), 1·78 (2 H, m, CH_2), 3·95 (2 H, t, OCH_2), 6·35 (1 H, s, ArH), 6·83 (2 H, d, ArH), 6·87 (1 H, s, ArH), 7·41 (2 H, d, ArH); *m/z* 769 $(M+3)^+$, 528, 469, 355.

5.4. *1,2,4-Tri-(4-tridecyloxyphenylcarbonyloxy)-5-(4-tridecyloxyphenylethynyl)benzene* (**1**)

Compound **10** (0·200 g, 0·26 mmol) was dissolved in dry THF (10 ml) and cooled to 0°C under nitrogen. Tetrabutylammonium fluoride (0·8 ml, 1 M solution in THF, 3·05 equiv) was added, followed by 4-tridecyloxybenzoyl chloride (0·60 g, 1·8 mmol, see the preparation of compound **19**), and the reaction mixture was stirred at 0°C for 1 h and then allowed to warm to room temperature; additional tetrabutylammonium fluoride in THF (6 ml) was added followed by the acid chloride (0·20 g, 0·59 mmol); TLC analysis showed the disappearance of starting material. Ether was added until an oil separated and the mixture was cooled (liquid nitrogen) so that the oil became a semi-solid. The ether layer was decanted and this process was repeated until oil formation no longer occurred. The ether solution was concentrated *in vacuo* to give a viscous yellow oil which was triturated with ethanol and the precipitate formed was filtered off and purified by column chromatography [silica; eluent light petroleum (b.p. 40–60°C) : dichloromethane, 9 : 1] and recrystallization (ethyl acetate) to give compound **1**. Yield 0·060 g, 5%. δ_H (270 MHz; $CDCl_3$; TMS): 0·88 (12 H, t, $4 \times CH_3$), 1·26–1·45 (80 H, m, $10 \times CH_2$), 1·54–1·85 (8 H, m, $4 \times CH_2$), 3·88–4·07 (8 H, m, $4 \times OCH_2$), 6·74 (2 H, d, ArH), 6·83 (2 H, d, ArH), 6·85 (2 H, d, ArH), 6·97 (2 H, d, ArH), 7·15 (2 H, d, ArH), 7·42 (1 H, s, ArH), 7·57 (1 H, s ArH), 7·98 (2 H, d, ArH), 8·02 (2 H, d, ArH), 8·23 (2 H, d, ArH). ν_{max} 2920, 2840, 2115, 1725, 1600, 1508, 1245, 1165, 1152, 1145, 1060, 1030, 1005, 845, 760 $\mathrm{cm^{-1}}$. Elemental analysis calculated for $C_{87}H_{126}O_{10}$: C, 78·45; H, 9·53. Found: C, 78·77; H, 9·86%.

5.5. *4,5-Dibromocatechol* (**12**)

Compound **12** was prepared following the procedure reported by Kohn [40].

5.6. *1,2-Dibromo-4,5-di-(4-tridecyloxyphenylcarbonyloxy)benzene* (**13**)

This compound was prepared from compound **12** by following the procedure given for compound **16** and stirring the reaction mixture at room temperature for 18 h. The crude product was a viscous brown oil which was purified by column chromatography (silica; dichloromethane); the diester was eluted first, followed by the monoester. Compound **13** was recrystallized (acetone). Yield 49%, m.p. 97°C. δ_H (270 MHz; $CDCl_3$; TMS): 0·85 (6 H, t), 1·26–1·44 (40 H, bm, $20\times CH_2$), 1·55–2·17 (4 H, m, $2\times CH_2$), 3·97 (4 H, t, $2\times OCH_2$), 6·82 (4 H, d, ArH), 7·66 (2 H, s, ArH), 7·97 (4 H, d, ArH).

The monoester [1,2-dibromo-4-hydroxy-5-(4-tridecyloxyphenylcarbonyloxy)benzene] (**20**) was obtained in 15% yield after recrystallization (acetone).

5.7. *1,2-Di-(4-tridecyloxyphenylcarbonyloxy)-4,5-(4-tridecyloxyphenylethynyl)benzene* (**2**)

Compound **2** was prepared from compound **13** and compound **25** by following the procedure described for compound **3**. Compound **2** was obtained as colourless needles, yield 30%. δ_H (270 MHz; $CDCl_3$; TMS): 0·88 (12 H, t, $4\times CH_3$), 1·18–1·54 (80 H, m, $40\times CH_2$), 1·73–1·81 (8 H, m, $4\times CH_2$), 3·97 (8 H, t, $4\times OCH_2$), 6·85 (2×4 H, $2\times$d, ArH), 7·48 (4 H, d, ArH), 7·52 (2 H, s, ArH), 8·00 (4 H, d, ArH). ν_{max} 2920, 2840, 2200, 1730, 1600, 1510, 1465, 1250, 1220, 1170, 1160, 1130, 890, 830 cm^{-1}. Elemental analysis calculated for $C_{88}H_{126}O_8$: C, 80·56; H, 9·68. Found: C, 80·96; H, 10·14%.

5.8. *2,5-Dibromoquinol* (**15**)

Compound **15** was prepared by adapting a reported procedure [40]; m.p. 184°C (lit. [41] 183–185°C).

5.9. *1,4-Dibromo-2,5-di-(4-tridecyloxyphenylcarbonyloxy)benzene* (**16**)

Compound **15** (2·00 g, 7·46 mmol), 4-tridecyloxybenzoyl chloride (5·56 g, 16·42 mmol; see preparation of compound **19**) and triethylamine (2·29 ml, 16·42 mmol) were suspended in dichloromethane (30 ml) and stirred for 2 h. Chloroform (50 ml) was added and the organic phase was washed with water (2×20 ml), 1M hydrochloric acid (2×20 ml), saturated sodium hydrogen carbonate (2×20 ml) and water (2×20 ml), and then dried ($MgSO_4$). The solvents were removed under reduced pressure to give an off-white solid which was purified by column chromatography [silica; light petroleum (b.p. 40–60°C): dichloromethane, 1 : 1] and recrystallization (acetone) to give compound **16**. Yield 5·20 g, 83%, m.p. 127°C. δ_H (270 MHz; $CDCl_3$; TMS): 0·88 (6 H, t, $2\times CH_3$), 1·26–1·57 (40 H, m, $20\times CH_2$), 1·70 (4 H, m, $2\times CH_2$), 4·04 (4 H, t, $2\times OCH_2$), 7·00 (4 H, d, ArH), 7·59 (2 H, s, ArH), 8·16 (4 H, d, ArH).

5.10. *4-(4-Tridecyloxyphenyl)-2-methylbut-3-yn-2-ol* (**24**)

A solution of 4-tridecyloxybromobenzene (21·5 g, 60·5 mmol, prepared by a standard method from 4-bromophenol and 1-bromotridecane [42]; the sample had m.p. 39·8°C), bis(triphenylphosphine)palladium(II) chloride (0·212 g, 0·30 mmol, 0·5%), 2-methylbut-3-yn-2-ol (5·6 g, 66·5 mmol), triphenylphosphine (0·396 g, 1·5 mmol, 2·5%), and copper(I) iodide (0·230 g, 1·21 mmol, 2%) in THF (150 ml) and triethylamine (50 ml) was stirred at 60°C under nitrogen for 18 h. The reaction mixture was filtered through 'Hyflo Supercel' and the filtrate was evaporated to give a viscous brown oil (crystallized on standing) which was purified by column chromatography [silica; eluent light petroleum (b.p. 40–60°C):dichloromethane, 3 : 7] to give compound **24** as an off-white solid. Yield 7·0 g, 33% (based on total starting material; 69·5% allowing for recovered starting material [11·16 g]), m.p. 56°C. δ_H (270 MHz; $CDCl_3$; TMS): 0·88 (3 H, t, CH_3), 1·20–1·42 (20 H, bs, $10\times CH_2$), 1·60 (6 H, s, $2\times CH_3$), 1·73 (2 H, m, CH_2), 3·93 (2 H, t, OCH_2), 6·80 (2 H, d, ArH), 7·33 (2 H, d, ArH); *m/z* 358 (M^+), 343, 161.

5.11. *4-Tridecyloxyphenylethyne* (**25**)

Compound **24** (15·6 g, 43·5 mmol) and potassium hydroxide (2·92 g, 52·2 mmol) in toluene (150 ml) were stirred and heated under reflux under nitrogen for 2 h. The cooled reaction mixture was poured into water (250 ml) and the organic layer was separated; the aqueous layer was neutralized with 0·01M hydrochloric acid to pH 7 and washed with ether (2×100 ml). The combined organic layers were washed with a saturated solution of sodium chloride, dried ($MgSO_4$), decolourized with charcoal and the solvents removed to leave a viscous yellow oil. The oil was purified by column chromatography [silica; light petroleum (b.p. 40–60°C): dichloromethane, 1 : 1] to give compound **25** as an off-white solid. Yield 10·0 g, 77%, m.p. 40·5°C. δ_H (270 MHz; $CDCl_3$; TMS): 0·88 (3 H, t, CH_3), 1·36–1·53 (20 H, m, $10\times CH_2$), 1·74 (2 H, m, CH_2), 2·98 (1 H, s, $C{\equiv}CH$), 3·94 (2 H, t, OCH_2), 6·82 (2 H, d, ArH), 7·41 (2 H, d, ArH); *m/z* 300 (M^+), 118.

5.12. *1,4-Di-(4-tridecyloxyphenylcarbonyloxy)-2,5-(4-tridecyloxyphenylethynyl)benzene* (**3**)

4-Tridecyloxyphenylethyne (0·904 g, 3·0 mmol) was placed in a 100 ml three-necked flask fitted with a septum, condenser, thermometer, and addition funnel. The apparatus was several times heated with a heat gun (the acetylene melted), evacuated with a pump and flushed with nitrogen. Dry THF (10 ml) was added and the system was degassed at −40°C; nitrogen was introduced and butyllithium (1·4 ml, 3·5 mmol; 2·5M solution in hexane) was added dropwise keeping the temperature below 0°C. The mixture was kept at 0°C for 15 min and then cooled to −40°C and anhydrous zinc chloride (0·477 g, 3·5 mmol) in dry THF (20 ml) was added and the mixture allowed to warm to room temperature and stirred for 30 min. Compound **16** (0·1 g, 1·2 mmol) and tetrakis(triphenylphosphine)palladiun(0) (0·10 g, 0·08 mmol, 2·47%) were added and the reaction mixture was heated under reflux for 2 days. The THF was removed *in vacuo*, ether (50 ml) was added, the mixture was filtered, and the precipitate recrystallized (ethyl acetate) to give compound **3**. Yield 0·570 g, 36%. δ_H (270 MHz; $CDCl_3$; TMS): 0·88 (12 H, m, $4\times CH_3$), 1·55–1·26 (80 H, bm, $40\times CH_2$), 1·86–1·69 (8 H, m, $4\times CH_2$), 3·90 (4 H, t, $2\times OCH_2$), 4·05 (4 H, t, $2\times OCH_2$), 6·73 (4 H, d, ArH), 6·98 (4 H, d, ArH), 7·13 (4 H, d, ArH), 7·48 (2 H, s, ArH), 8·22 (4 H, d, ArH). ν_{max} 2920, 2840, 2210, 1780, 1600, 1510, 1465, 1240, 1155, 1055, 900, 830 cm^{-1}. Elemental analysis calculated for $C_{88}H_{126}O_8$: C, 80·56; H, 9·68. Found: C, 81·17; H, 10·14%.

5.13. *4,6-Dibromoresorcinol* (**18**)

Bromine (11 ml) in glacial acetic acid (50 ml) was added dropwise to resorcinol (11·0 g, 0·1 mol) dissolved in cold glacial acetic acid (50 ml). The solvent was removed by distillation under reduced pressure and the residue was quenched with ice/water (350 g). The mixture was washed with ether (3 × 30 ml), the washings were dried ($MgSO_4$) and the ether was removed to leave a viscous brown oil which formed a solid after trituration with toluene and then being left for a few days. The solid was filtered off and dried *in vacuo* at 25°C to give compound **18**. Yield 4·50 g, 16·8%, m.p. 114–116°C (lit. [43] 109–110°C). δ_H (270 MHz; $CDCl_3$; TMS): 6·69 (1 H, ArH), 7·48 (1 H, ArH).

5.14. *1,5-Dibromo-2,4-di-(4-tridecyloxyphenylcarbonyloxy)benzene* (**19**)

4-Tridecyloxybenzoic acid [10] (4·4 g, 13·7 mmol) was suspended in thionyl chloride (20 ml) and heated under reflux for 2 h; the excess of thionyl chloride was removed under reduced pressure, dry benzene (10 ml) was added and then removed under reduced pressure. The residue was dried *in vacuo* then dissolved in dry dichloromethane (20 ml) and compound **18** (2·1 ml, 14·9 mmol) was added and the mixture stirred for 2 h. The reaction mixture was poured into water and the organic layer washed with 1M hydrochloric acid (20 ml), saturated sodium hydrogen carbonate solution (2 × 20 ml) and water (2 × 20 ml), and then dried ($MgSO_4$). The solvent was removed to leave an off-white solid which was purified by column chromatography [silica; eluent light petroleum (b.p. 40–60°C): dichloromethane, 4 : 1] and recrystallization (acetone) to give compound **19**. Yield 2·9 g, 66%, m.p. 55·5–56·7°C. δ_H (270 MHz; $CDCl_3$; TMS): 0·88 (6 H, t, $2\times CH_3$), 1·26–1·47 (40 H, bm, $20\times CH_2$), 1·76–1·86 (4 H, m, $2\times CH_2$), 4·04 (4 H, t, $2\times OCH_2$), 6·96 (4 H, d, ArH), 7·34 (1 H, s, ArH), 7·91 (1 H, s, ArH), 8·16 (4 H, d, ArH).

5.15. *1,5-Di-(4-tridecyloxyphenylcarbonyloxy)-2,4-di-(4-tridecyloxyphenylethynyl)benzene* (**4**)

Compound **4** was prepared from compounds **19** and **25** by following the procedure described for compound **3**. The reaction was continued for four days and then the solvent was evaporated under reduced pressure. The residue was triturated with ether (10 ml) and the mixture filtered; the filter pad was washed with ether until the washings were colourless. The white precipitate contained the product and zinc halides, and washing the pad with dichloromethane gave a solution of the product; removal of the solvent and recrystallization (ethyl acetate) gave compound **4**. Yield 0·310 g, 20%. δ_H (270 MHz; $CDCl_3$; TMS): 0·88 (12 H, t, $4\times CH_3$), 1·26–1·54 (80 H, bm, $40\times CH_2$), 1·70–1·85 (8 H, m, $4\times CH_2$), 3·91 (4 H, t, $2\times OCH_2$), 4·04 (4 H, t, $2\times OCH_2$), 6·74 (4 H, d, ArH), 6·96 (4 H, d, ArH), 7·17 (4 H, d, ArH), 7·36 (1 H, s, ArH), 7·77 (1 H, s, ArH), 8·21 (4 H, d, ArH). ν_{max} 2920, 2840, 2110, 1720, 1600, 1508, 1250, 1160, 1140, 1075, 1060, 1030, 1005, 845, 830, 765 cm^{-1}. Elemental analysis calculated for $C_{88}H_{126}O_8$: C, 80·56; H, 9·68. Found: C, 81·06; H, 10·17%.

5.16. *1,2-Dibromo-4-hydroxy-5-(4-tridecyloxyphenylcarbonyloxy)benzene* (**20**)

Compound **20** was prepared following the procedure described for compound **16**, using compound **12** (2·0 g, 7·46 mmol), 4-tridecyloxybenzoyl chloride (2·53 g, 7·46 mmol; see preparation of compound **19**), and triethylamine (1 ml, 7·46 mmol) in dichloromethane (30 ml) at room temperature overnight. Yield 0·89 g, 20%, m.p. 103·3°C. δ_H (270 MHz; $CDCl_3$; TMS): 0·88 (3 H, t, CH_3), 1·26–1·47 (20 H, bm, $10\times CH_2$), 1·77–1·87 (2 H, m, CH_2), 4·04 (2 H, t, OCH_2), 5·92 (1 H, bs, OH), 6·98 (2 H, d, ArH), 7·32 (1 H, s, ArH), 7·44 (1 H, s, ArH), 8·10 (2 H, d, ArH); *m/z* 303, 121.

5.17. *1,2-Dibromo-4-(4-tridecyloxyphenylcarbonyloxy)-5-trifluoromethylsulphonylbenzene* (**21**)

Compound **20** (1·0 g, 1·75 mmol) and triethylamine (0·50 ml) were dissolved in dichloromethane (20 ml) and the solution was cooled to −78°C. *N*-Phenyltrifluoromethanesulphonimide (0·630 g, 1·76 mmol) in dichloromethane (10 ml) was added dropwise and the solution allowed to rise to room temperature and stirred overnight. The reaction mixture was poured into water and the organic phase was washed with water (2 × 20 ml), 1M hydrochloric acid (2 × 20 ml) and water (2 × 20 ml), and then dried ($MgSO_4$). The solvent was evaporated to give a colourless oil which solidified on standing. The solid was purified by column chromatography [silica gel; light petroleum (b.p. 40–60°C): dichloromethane, 4:1] and recrystallization (light petroleum, b.p. 40–60°C) to give compound **21** as colourless needles. Yield 0·80 g, 68%, m.p. 47·5°C. δ_H (270 MHz; $CDCl_3$; TMS): 0·88 (3 H, t, CH_3), 1·26–1·53 (20 H, m, 10 × CH_2), 1·76–1·84 (2 H, m, CH_2), 4·04 (2 H, t, OCH_2), 6·97 (2 H, d, ArH), 7·63 (1 H, s, ArH), 7·76 (1 H, s, ArH), 8·10 (2 H, d, ArH); *m/z* 700 (M^+), 303, 121.

5.18. *1-(4-Tridecyloxyphenylcarbonyloxy)-2,4,5-tri-(4-tridecyloxyphenylethynyl)benzene* (**5**)

Compound **21** (0·800 g, 1·14 mmol) was added to a mixture of 4-(tridecyloxyphenyl)ethynylzinc chloride [prepared from the ethyne **25** (1·05 g, 3·5 mmol) and butyllithium (1·5 ml, 2·5M in hexane, 3·56 mmol) at −40°C, followed by addition of zinc chloride (0·500 g) at −40°C and the solution then allowed to warm to 0°C], tetrakis(triphenylphosphine)palladium(0) (0·100 g) and lithium chloride (0·148 g, 3·5 mmol) at room temperature. The mixture was heated under reflux for three days and after the usual work-up the product was purified by column chromatography [silica; light petroleum (b.p. 40–60°C): ether, 19:1]. Yield 0·300 g, 20%. δ_H (270 MHz; $CDCl_3$; TMS): 0·88 (12 H, m, CH_3), 1·26–1·54 (80 H, bm, CH_2), 1·76–1·79 (8 H, m, CH_2), 3·88–4·08 (8 H, m, 4 × OCH_2), 6·73 (2 H, d, ArH), 6·84–6·88 (4 H, 2 × d, ArH), 7·10 (2 H, d, ArH), 7·13 (2 H, d, ArH), 7·45–7·51 (5 H, 2 × d and s, ArH), 7·72 (1 H, s, ArH), 8·22 (2 H, d, ArH). ν_{max} 2920, 2840, 2200, 1760, 1500, 1465, 1245, 1190, 1165, 1140, 1080, 1015, 896, 830 cm^{-1}. Elemental analysis calculated for $C_{89}H_{126}O_6$: C, 82·74; H, 9·83. Found: C, 83·03; H, 10·25%.

5.19. *1,2,4,5-Tetra-(4-tridecyloxyphenylethynyl)benzene* (**6**)

Butyllithium (6·7 ml, 2·5M solution in hexane, 16·7 mmol) was added to a solution of 4-tridecyloxyphenylethyne **25** (4·57 g, 15·2 mmol) in dry THF (20 ml) at −40°C. The reaction mixture was stirred for 10 min and a solution of zinc chloride (3·10 g, 22·8 mmol) in THF (10 ml) was added dropwise keeping the temperature below 0°C. The reaction mixture was then stirred at room temperature for 15 min and compound **22** (1·0 g, 2·5 mmol) and tetrakis(triphenylphosphine)palladium(0) (0·10 g, 0·09 mmol) were added and the mixture was heated under reflux at 60°C for three days. The reaction mixture was concentrated *in vacuo* to give a viscous brown oil which on trituration with ether gave a white solid; recrystallization (ethyl acetate) gave compound **6**. Yield 1·84 g, 57%. δ_H (270 MHz; $CDCl_3$; TMS): 0·88 (12 H, t, 4 × CH_3), 1·26–1·54 (80 H, bm, 40 × CH_2), 1·76 (8 H, m, 4 × CH_2), 3·97 (8 H, t, 4 × OCH_2), 6·85 (8 H, d, ArH), 7·48 (8 H, d, ArH), 7·68 (2 H, s, ArH). ν_{max} 2920, 2840, 2200, 1600, 1508, 1240, 1170, 1130, 1105, 1015, 890, 830, 720 cm^{-1}. Elemental analysis calculated for $C_{90}H_{126}O_4$: C, 84·98; H, 9·98. Found: C, 85·20; H, 10·37%.

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