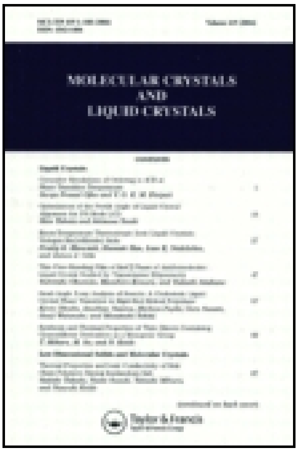

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Liquid Crystalline Polymesomorphism in Copper(II) Complexes of β-Diketones: The Effect of the Position of a Polar Substituent

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Liquid Crystalline Polymesomorphism in Copper(II) Complexes of β-Diketones: The Effect of the Position of a Polar Substituent

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We have shown previously that smectic phase thermal stability in copper(II) complexes of 1-(4′-decylbiphenyl-4-yl)-3-(biphenyl-4-yl)propane-1,3-diones is considerably enhanced by the introduction of polar substituents (F, Br and CF_3) into the 4′-position of the lateral biphenyl unit. The preparation of a new series of complexes is described and the transition temperatures of the ligands and complexes reveal the effect on mesophase type and stability of a polar substituent at different positions in the molecule. The effects which fluoro-substituents have on the transition temperatures of the β-diketone ligands and the complexes are also compared with the effects produced by similar fluoro-substitution in terphenyl systems.

Keywords: copper(II) complexes, β-diketones, metallo-mesogens, polymesomorphism

INTRODUCTION

Research in the field of metal-containing liquid crystals has flourished during the past decade. A wide variety of metallo-mesogens are now known and the reader is referred to a recently published review of this field.[1] Many examples of liquid-crystalline copper(II) complexes of β-diketones have been reported over the years and many of these are discussed in the review mentioned above and in our previous communications.[2,3] We have recently described the enhancement of smectic character induced by the introduction of polar substituents (R = F, Br and CF_3) into complexes with the structure shown in Figure 1.[3] Those complexes shown in Figure 1 in which R is non-polar (i.e., R = H or CH_3) are purely nematogenic, but when halogen substituents are introduced into the 4′-position the complexes are purely smectogenic, exhibiting enantiotropic smectic A and monotropic smectic C phases. One possible explanation for the enhancement of smectic character is that the polarity of these substituents increases the lateral interactions between the molecules leading to a layered arrangement. If the shape of the molecule in Figure 1 is considered by viewing molecular models, it can be seen that the molecule is cross-shaped with the polar substituents in an almost lateral disposition with respect to the long molecular axis; i.e., that which incorporates the two decyl chains. In order to investigate the nature of such lateral interactions between the molecules,

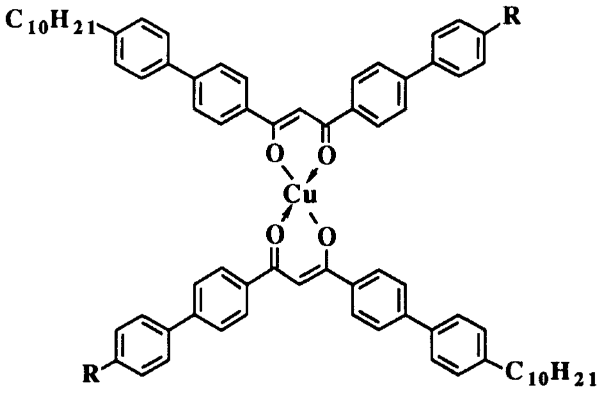


FIGURE 1 Copper(II) complex structure.

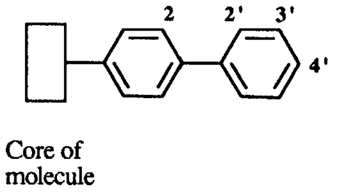
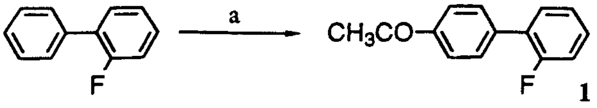


FIGURE 2 Positions of fluoro substitution in the lateral biphenyl unit.

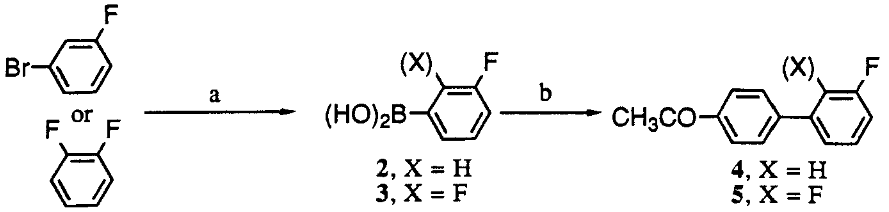
a new series of complexes was prepared in which the position of a polar substituent, fluorine, was altered in order to alter the direction and magnitude of the lateral dipole. It was expected that as the fluoro-substituent was moved to the 3'-position (see Figure 2) the overall lateral polarity with respect to the long molecular axis would decrease, possibly leading to a decrease in smectic phase thermal stability. A fluoro-substituent in the 2'-position would not give a lateral dipole pointing away from the long molecular axis and also, by increasing the inter-annular twisting of the biphenyl unit, it should further reduce, or even eliminate, smectic character. A fluoro-substituent in the 2-position would give a lateral dipole component similar to that of the 3'-fluoro-substituent, but its effectiveness in allowing inter-molecular associations would be reduced in comparison with compounds having a fluoro-substituent in the outer ring of the biphenyl unit; the 2-fluoro-substituted compound would therefore be less conducive to smectic phase formation than 3'- or 4'-substituted compounds. The fluorine in the 2-position, however, would be expected to be better than a fluorine in the 2'-substituted compound by virtue of its outward lateral dipole. An added factor with fluorination in the 2- and 2'-position is the effect of twisting in the biphenyl unit. The result of such twisting in these systems is uncertain, although in calamitic systems inter-annular twisting causes an increase in molecular breadth and usually adversely affects mesophase stability. A difluoro complex with fluoro-substituents at the 2'- and 3'-positions has also been prepared to assess the effect on phase nature and transition temperatures of two dipoles, acting towards and away from the molecular centre. The synthetic routes for the preparation of the ligands and the complexes are outlined in Schemes I, II and III.



1

a ... CH_3COCl / $AlCl_3$

SCHEME I



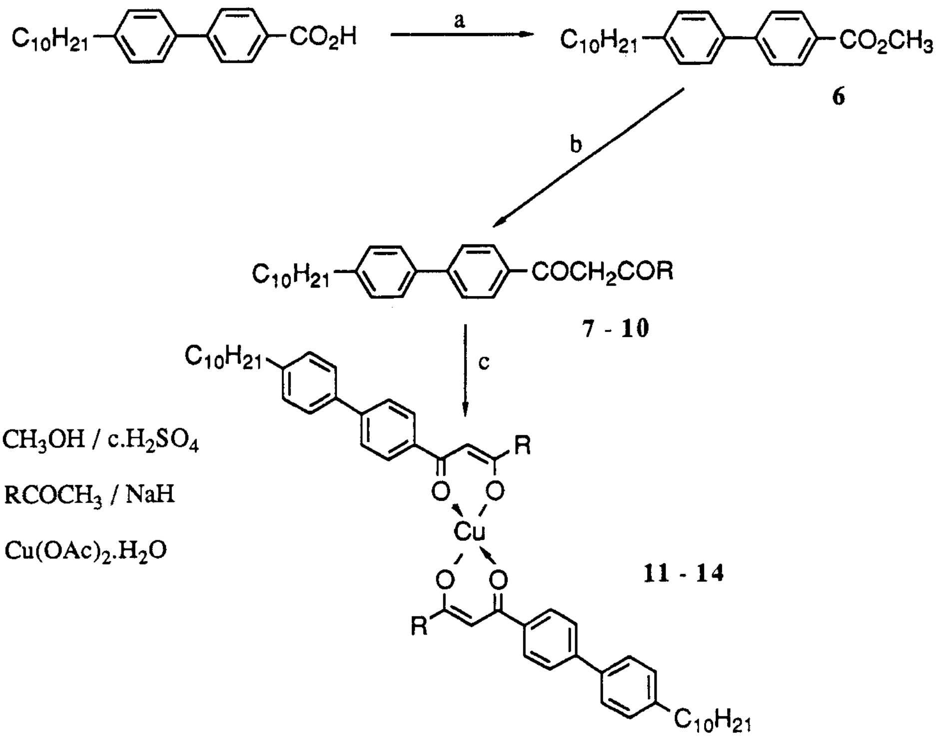
2, X = H
3, X = F

4, X = H
5, X = F

a ... *n*BuLi, (*i*PrO)$_3$B, -78 °C

b ... $CH_3COC_6H_4Br$, $[(C_6H_5)_3P]_4Pd$

SCHEME II



6

7 - 10

11 - 14

a ... CH_3OH / c.H_2SO_4

b ... $RCOCH_3$ / NaH

c ... $Cu(OAc)_2.H_2O$

SCHEME III

The ligands were synthesized by reacting methyl 4'-decylbiphenyl-4-carboxylate (**6**) with an appropriately substituted methyl ketone. The methyl ketones were prepared either by Friedel-Crafts acetylation of the appropriately substituted biphenyl (Scheme I) or by a boronic acid coupling reaction[4] with tetrakistriphenylphosphinepalladium(0)[5] as catalyst (Scheme II). All of the copper(II) complexes were prepared by reaction of the β-diketone ligand with copper(II) acetate monohydrate in a tetrahydrofuran (THF) solution (Scheme III) and the crude complexes were purified by recrystallisation from THF/acetone mixtures. ^{1}H nmr spectra are not quoted for the complexes because of the paramagnetic nature of the copper centre. Mass spectral values for the complexes are also not quoted because decomposition of the samples in the spectrometer leads to spectra similar to those obtained for the ligands.

RESULTS AND DISCUSSION

The melting point and transition temperatures of the β-diketone ligands are shown in Table II. In our previous communications[2,3] we have reported a number of β-diketones with the structure shown in Figure 3 bearing a variety of 4'-substituents. All of the compounds reported were high melting and non-mesogenic, with the

TABLE I

Transition temperatures (°C) for ligands with increasing size of substituent. (Bz = 1,4-disubstituted benzene ring)

Number	Structure	K_1	K_2	E	S_B	S_A	I
I	$C_{10}H_{21}BzBzCOCH_2COCH_3$	*86		*97	*107	*135	*
II	$C_{10}H_{21}BzBzCOCH_2COBzCH_3$	*84	*97			(*93)	*
III	$C_{10}H_{21}BzBzCOCH_2COBzBzCH_3$	*186				[*106]	*

TABLE II

Transition temperature (°C) for β-dicarbonyl ligands and their copper(II) complexes

Ligand Structure.	Ligand No.	Transition Temperatures of Ligands.			Complex No.	Transition Temperatures of Complexes.				
		K	S_A	I		K	S_C	S_A	N	I
$C_{10}H_{21}BzBzCOCH_2COBz.BzH$§	a	*163	[* 113]	*	A†	* 193/208			* 195	*
$C_{10}H_{21}BzBzCOCH_2COBz.(4'\text{-}FBz)$§	b	* 199	[* 135]	*	B	* 155	(* 122)	* 250		*
$C_{10}H_{21}BzBzCOCH_2COBz.(3'\text{-}FBz)$	7	* 156	(* 154)	*	11	* 176		* 209		*
$C_{10}H_{21}BzBzCOCH_2COBz.(2'\text{-}FBz)$	8†	* 95/109	* 105	*	12	* 180			(* 165)	*
$C_{10}H_{21}BzBzCOCH_2CO(2\text{-}FBz).BzH$	9	* 121	* 133	*	13	* 170	(* 150)	* 179	* 188	*
$C_{10}H_{21}BzBzCOCH_2COBz.(2'\text{-}F,3'\text{-}FBz)$	10	* 70	* 78	*	14	* 172				*

Bz = 1,4-disubstituted benzene ring; ( )...monotropic transition temperature; [ ] ... virtual transition temperature.

An entry such as 95/109 denotes two crystal forms melting at 95 and 109 °C respectively.

§ Previously reported in reference 2. † Two crystal forms are evident; the mesophase is monotropic with respect to the higher melting form.

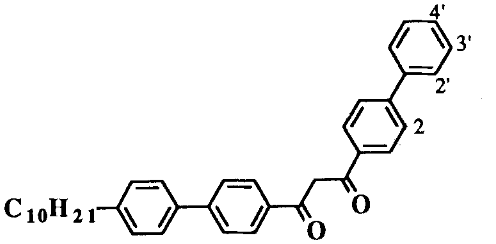


FIGURE 3 General structure of the ligands.

exception of the cyano-substituted compound which showed smectic A and E phases. The non-mesogenic β-diketones gave virtual smectic A to isotropic transition temperatures, obtained by miscibility with 4-pentyl-4″-octyloxyterphenyl (K 194 S_B 211 S_A 221 I), which were below the temperatures at which they crystallised on cooling, and the relatively low virtual transition temperatures appear to arise from the 'banana-like' molecular shape being unfavourable for lamellar smectic packing. In this article we report a number of similar compounds containing fluoro-substituents which do show smectic A phases, generally as a consequence of lower melting points, and still have relatively low clearing points.

The parent, non-fluorinated system (**a**) melts at 163°C and has a virtual smectic A to isotropic transition temperature of 113°C. The terminally fluorinated compound (**b**) has an increased melting point by 36°C and an increased virtual smectic A phase thermal stability, by 22°C. This increase in smectic A thermal stability is consistent with the effect of terminal fluoro-substitution in linear systems which often leads to an increase in smectic character.[6] All of the β-diketone ligands which contain lateral fluoro-substituents (compounds **7**, **8**, **9** and **10**) have lower melting points than compounds **a** and **b** and, as a consequence of the lower melting points, the smectic A phases can be detected enantiotropically or monotropically in each case. It is interesting to note that none of these compounds show nematic mesophases, and indeed the only nematogenic β-diketones which we have prepared contain either a cyclohexyl ring, a long alkoxy chain or, in one case, a lateral fluoro-substituent in the decyl-substituted biphenyl unit[2]; Eidenschink and Pohl have also reported nematogenic β-diketones incorporating a cyclohexyl unit.[7] All other β-diketone systems which we have studied are smectogenic and, although the role of the β-diketone core unit in influencing smectic character is not known, it is possible that the significant dipole associated with it is responsible for the predominance of smectic phases. The smectic A phase thermal stabilities of β-diketones in general are markedly influenced by their bent molecular geometry in comparison with related linear terphenyl or quaterphenyl systems. Increasing the size of the substituent group, *X*, (in the direction shown by the arrow in Figure 4) has drastic effects on mesophase formation and a series of compounds to illustrate the effects is shown in Table I.

The ligand with the smallest substituent (CH_3, compound **I**) exhibits orthogonal smectic phases with the smectic A phase clearing at 135°C. The ligand (**II**), with a larger substituent present, also shows a smectic A phase but its clearing point is 42°C lower than that of compound **I**. This decrease is smectic phase thermal stability

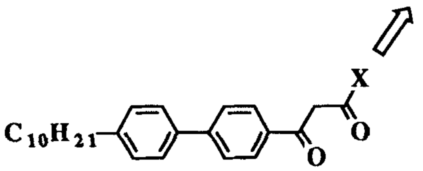


FIGURE 4 Bent molecular shape of ligands with increasing size of group X.

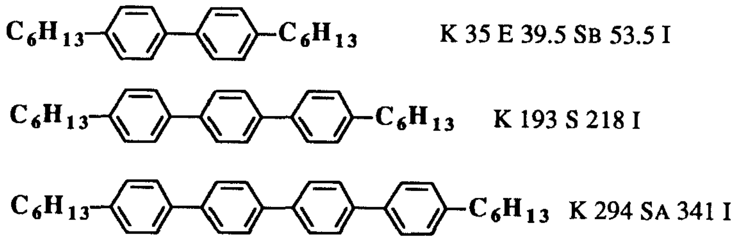
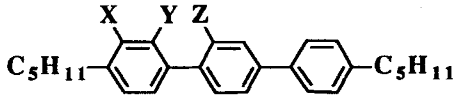


FIGURE 5 Extension of core unit in linear systems and its effect on transition temperatures (°C).

is initially quite surprising since the addition of an extra benzene ring in linear systems would cause a dramatic increase in smectic A phase thermal stability (see examples in Figure 5). With the ligands, however, the smectic A phase stability is reduced and to explain this the changes in the molecular geometry must be taken into account.

Compound **I** is essentially a linear molecule and packing of this type of molecule in an orthogonal layered structure will not cause problems. With compound **II**, the extra benzene ring is held in such a manner that it can be considered as a semi-lateral/semi-terminal group (Figure 4). The addition of an extra benzene ring in a linear system, i.e. in the change from biphenyl to terphenyl (Figure 5), increases clearing points significantly and an increase in T_{S-I} of 164.5°C results. The semi-lateral nature of the extra ring in the ligands, causing a bent molecular shape, will disrupt the close packing of the molecules, especially within a layered structure, and so a *decrease* in the smectic phase thermal stability is seen (42°C). The addition of yet another benzene ring into the system (compound **III**) to make the molecule even more banana-like, leads to a high melting crystalline solid; a virtual smectic A to isotropic transition temperature of 106°C for this compound was obtained by miscibility with 4-pentyl-4″-octyloxyterphenyl. This virtual value shows an increase of only 13°C compared with the monotropic value for compound **II**, and can be compared with an increase in clearing point of 123°C for the change from terphenyl to quaterphenyl. Although there is an apparent increase in T_{SA-I} value for the ligands, it is minute compared with the increase found in linear systems. This is once again a consequence of the molecular shape which is unfavourable for lamellar packing.

The effects of mono-fluorosubstitution in terphenyl systems have been studied in detail and several examples of such compounds are shown in Figure 6; detailed comparisons between the transition temperatures for the fluoro-substituted ligands and those for the compounds shown in Figure 6 are, however, tenuous because of the major differences in the natures of the systems. The values in Figure 6 are



IV

(i) X = Y = Z = H	K 192 S_A 213.0 I
(ii) X = F, Z = Y = H	K ? G 156.5 S_A 185.5 I
(iii) Y = F, Y = Z = H	K 72.5 S_C 80.0 N 136.0 I
(iv) Z = F, X = Y = H	K 51.5 S_B 62.0 S_A 109.5 N 136.5 I
(v) X = Y = F, Z = H	K 81 S_C 115.5 S_A 131.5 N 142.0 I

FIGURE 6 Transition temperatures (°C) of some mono- and di-fluoroterphenyls.[8,9]

provided to highlight the dramatic differences caused by fluoro-substitution at various positions in terphenyl systems and to exemplify the contrast with fluoro-substitution in the β-diketone ligands.

Melting points of the ligands are reduced on introduction of lateral fluoro-substituents on the core of the molecules and compound **7** has a lower melting point than compound **a** by 7°C and shows a monotropic smectic A phase which clears 41°C higher than the virtual value for compound **a**. The increase in smectic A phase thermal stability in compound **7** compared with compound **a** is unusual in that lateral fluoro-substituents tend to decrease mesophase stability along with melting points. It must be stressed, however, that the smectic A phase clearing point for compound **a** is a virtual value and so no firm conclusions can be drawn on this basis.

Compounds **8** and **9** both contain fluoro-substituents at the inter-annular positions of the biphenyl unit and it is known that fluoro-substituents occupying the inter-annular positions cause increased out of plane twisting of the biphenyl unit which increases the molecular breadth and this effect causes a reduction in the mesophase stabilities and melting points (see **IV(iii)** and **IV(iv)** in Figure 6); compounds **8** and **9** both show lower melting points than compound **a** by 54/68°C and 42°C respectively and these reductions appear consistent with those seen in terphenyl systems. The direction of the fluoro-substituent appears to be an important factor in determining smectic mesophase stability in these two β-diketones, and in compound **8**, with the fluoro-substituent pointing inwards to the central core of the molecule, the smectic A phase clears at 105°C whereas in compound **9**, with the substituent pointing outwards to the blunt end of the molecule, the smectic A phase clears at the higher temperature of 133°C. This trend is once again similar to that seen in the terphenyl systems shown in Figure 6. The compound in which the inter-annular fluorine points in towards the molecular core [compound **IV(iii)**] does not show a smectic A phase, but the compound in which the fluorine points away from the molecular centre [compound **IV(iv)**] has a smectic A phase clearing at 109.5°C, i.e., 29.5°C higher than the smectic C phase in compound **IV(iii)**; this trend has also been noted in similar fluorinated biphenyl systems.[10,11] Compound **10**, containing two fluoro-substituents on the end ring, has a vastly reduced melting point and a decreased smectic thermal stability compared to the parent system **a**; this is in keeping with the trend for the terphenyl systems shown by comparison of **IV(v)** with **IV(i)**. However, the difluoro-substituted systems show different relative effects on smectic A phase thermal stabilities in comparison with the mono-substituted analogues. In the terphenyl systems the difluoro-substituted compound **IV(v)** has a relatively high smectic A thermal stability but in the diketone system, compound **10** has a lower smectic A stability than all of the mono-fluoro analogues listed. The introduction of fluoro-substituents in the inter-annular positions are detrimental to the smectic phase stability, revealing nematic mesophases in the terphenyl systems; in the β-diketone systems nematic phases are not observed and the predominance of layered phases is thought to be due to the effect of the dipole of the diketone core unit. The direction of the inter-annular fluoro-substituent is an important factor in each system with similar effects on smectic phase stability observed in each case.

The melting points and transition temperatures of the complexes are also given in Table II. In our previous communication[3] we reported the enhanced smectogenicity of complexes bearing polar substituents in the 4′-position (Figure 7) in comparison with their non-polar analogues (H, CH_3) which are purely nematogenic. The enhancement in smectic character could be caused by the polarity of the 4′-substituents acting laterally (shown by the arrows in Figure 7) and increasing the lateral interactions between the molecules, leading to lamellar smectic phases. The enhancement of smectic character is, however, also analogous to the increased smectic tendencies found in linear systems with terminal polar substituents, although it is difficult to see how the complex molecules resemble linear systems. In the systems which we describe here the position of the polar substituent, in this case fluorine, has been altered around the biphenyl ‘arms’ of the molecule in the positions shown in Figure 7, in order to see what effect the position of the substituent has on the types of mesophase and transition temperatures.

Compound **A** is typical of the non-polar substituted complexes of this type and is purely nematogenic. Compound **B** has a smectic A phase which clears at 250°C and a monotropic smectic C phase at 122°C and we shall use these two compounds as the systems for comparison with the other complexes under consideration. Complex **B** is remarkable among all the complexes we have studied in that its melting point is *lower* than that of its ligand (**b**) and yet its smectic A phase clearing point

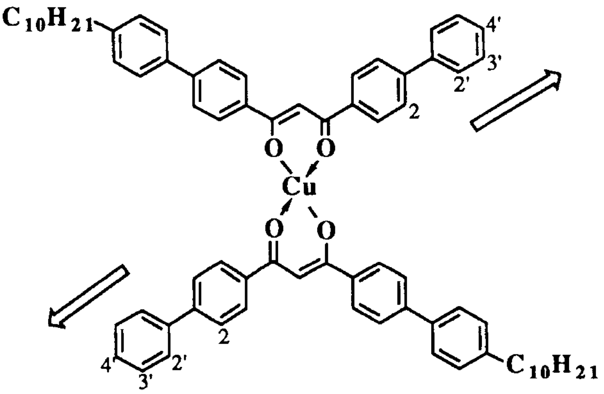


FIGURE 7 General structure of the complexes.

is considerably higher, and is indeed higher than any of the complexes reported here. In contrast, for ligands **7**, **8** and **9**, the transformation to the complex leads to *higher* melting points with only moderate increases in clearing points of 50–60°C. The consequence of these diverging effects is that complex **B** has a very large smectic 'window.' A similar situation occurs with the corresponding 4′-bromo-substituted ligand and complex.[3] On moving the fluoro-substituent to the 3′-position, to give compound **11**, the melting point is decreased by 17/32°C and the smectic A phase stability is increased by at least 64°C compared to the parent complex, **A** (compound **A** supercools to ~145°C in the nematic phase before crystallisation). In compound **11** the fluoro-substituent will have the effect of slightly broadening the biphenyl arms of the molecule (van der Waals radii for hydrogen and fluorine are 1.20 and 1.47 Å respectively[12]) but it will still have a dipole component, although reduced with respect to that in compound **B**, in the direction away from the molecular centre and therefore the decrease in smectic phase stability, relative to **B**, is not unexpected. Compound **12** has a fluoro-substituent in the 2′-position and so has a dipole component acting inwards, *towards* the molecular core. The fluoro-substituent in the 2′-inter-annular position will also cause increased twisting in the biphenyl arms of the molecule and so would be expected to further reduce mesophase stability and indeed smectic character has been eliminated in this system and the compound is nematogenic. It is interesting to note that in comparison with compound **A** the melting point is lower by 13/28°C and the nematic thermal stability is lower by 30°C; in calamitic systems, similar reductions would be expected on the introduction of lateral fluoro-substituents of this type.

Compound **13** also has a fluoro-substituent in an inter-annular twisting position (2-position) but its dipole again points outwards, away from the molecular centre. In comparison with the parent compound **A** the melting point is decreased by 23/38°C and the nematic phase thermal stability has been reduced by 7°C, the smectic A phase stability, however, has been enhanced by at least 34°C (compound **A** supercools to ~145°C in the nematic phase before crystallisation). In comparison with compound **12**, compound **13** has a higher T_{N-I} by 23°C and once again the smectic A phase stability has been enhanced (by at least 39°C); compound **12** supercools to ~140°C in the nematic phase before crystallisation. Both compounds **12** and **13** have a fluoro-substituent in an inter-annular twisting position and so the direction of the dipole appears to be an important factor for smectic phase formation. Compound **13** represents the first complex which we have studied which shows N-S_A-S_C polymesomorphism. Compound **14**, containing two opposing dipoles towards and away from the molecular centre is non-mesogenic and supercools to ~150°C without exhibiting a mesophase; this constitutes a reduction in nematic phase stability of at least 45°C in comparison with compound **A**.

The three compounds which show smectic A phases all have dipoles which point away from the molecular centre and their stabilities decrease as the fluoro-substituent is moved away from the terminal position and placed closer to the molecular centre. As the fluoro-substituent is moved from the 4′- to the 3′- or the 2-position, the effectiveness of the dipole component in a lateral direction away from the molecular long axis is reduced, and this will diminish the magnitude of the lateral interactions between the molecules, and consequently decreases in smectic A phase clearing points are observed. A further factor of inter-annular twisting arises with compound **13** and this causes a further reduction (30°C) in smectic A phase thermal stability relative to that for compound **11**. It appears important that the polar substituent should point away from the molecular centre for smectic phase formation; the only mono-fluoro compound which is not smectogenic (compound **12**) has the fluoro-substituent directed inwards towards the molecular centre. If we consider the terphenyl systems discussed previously (Figure 4), some of the trends observed in the complexes are also consistent with those observed in the terphenyl systems, although, as we have mentioned earlier, the relevance of such comparisons are questionable because of the very different molecular structures of the complexes and the terphenyls. The similarities occur when the fluoro-substituents are situated at the 3′-, 2′- or 2-positions in the complexes (compounds **11**, **12** and **13**). The relative smectic A phase thermal stabilities are similar to those in the terphenyl compounds **IV(ii)**, **IV(iii)** and **IV(iv)** in that in the inter-annular substituted compounds the smectic A phases are considerably lower, as would be expected, and the smectic A phase stability shows a similar dependence on the orientation of the substituent with respect to the molecular centre; the complex with the substituent in the 2′-position (cf. compound **IV(iii)** in the terphenyls) has a considerably lower smectic A thermal stability than the complex with the fluoro-substituent in the 2-position (cf, compound **IV(iv)** in the terphenyls). The compounds containing a fluoro-substituent on the outer edge [compounds **11** and **IV(ii)**] have higher smectic thermal stabilities than the inter-annular substituted compounds described above. Despite these similarities, many anomalies are also apparent, especially regarding the difluorinated systems [compounds **14** and **IV(v)**] in which the copper(II) complex is non-mesogenic and the terphenyl system is relatively unaffected by the introduction of an extra fluorine.

EXPERIMENTAL

The transition temperatures and natures of the phases were determined using an Olympus BH2 polarising microscope fitted with a Mettler FP 52 heating stage and temperature controller. The transition temperatures were confirmed using a Perkin Elmer DSC-2C differential scanning calorimeter, calibrated with a pure indium sample. ^1H nmr spectra were obtained using a JEOL JNM-GX270 spectrometer, infrared spectra were obtained using a Perkin-Elmer 457 grating spectrophotometer and mass spectra were obtained using a Finnigan-MAT 1020 GC/MS spectrometer. The progress of reactions was monitored by thin layer chromatography (Merck, silica gel 60 F_{254} coated on aluminum sheets) or by gas chromatography (Perkin-Elmer 8310 capillary gas chromatograph fitted with a 12 m QC2/BP1-1.0 SGE column). Compounds were purified, where specified, by column chromatography using silica gel 60–120 mesh or by flash chromatography using silica gel 200–400 mesh.

4-Acetyl-2′-fluorobiphenyl (1)

Powdered aluminum chloride (7.87 g, 57 mmol) was added to a cooled (0°C), stirred solution of 2-fluorobiphenyl (8.00 g, 47 mmol) in dry dichloromethane (150

ml). A solution of acetyl chloride (3.75 g, 47 mmol) in dry dichloromethane (50 ml) was added dropwise during 1 hour. The reaction mixture was allowed to reach room temperature and stirred for 10 hours. The mixture was poured onto ice and the organic material was extracted into ether (2 × 100 ml). The combined ethereal extracts were washed with water (100 ml), 10% aqueous sodium hydroxide solution (50 ml) and water until the aqueous washings were neutral. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel/dichloromethane:petroleum spirit [bp 40–60°C], 1:1).
Yield 8.76 g, 87%; melting point 78–80°C; ^{1}H nmr($CDCl_3$) δ 2.65(s, 3H), 7.20(m, 2H), 7.40(m, 2H), 7.65(d, 2H), 8.05(d, 2H); ir (KCl)ν_{max} cm^{-1} 1680, 1608, 1484, 1405, 1270, 1252, 1208, 828, 765, 600; mass spectrum (*m*/*z*) 214 (M^+), 199(100%), 170, 85, 75.

3-Fluorophenylboronic acid (2)

n-Butyllithium (1.6 M, 17.9 ml, 28.6 mmol) was added slowly to a cooled (−78°C) stirred solution of 3-fluorobromobenzene (5.0 g, 28.6 mmol) in dry THF (20 ml) under a nitrogen atmosphere. The reaction mixture was stirred at −78°C for 20 minutes and a solution of tri-isopropyl borate (10.75 g, 8.76 ml, 57.2 mmol) in dry THF (30 ml) was added dropwise so as to maintain the temperature at −78°C. The mixture was allowed to reach room temperature and stirred overnight. 10% Aqueous hydrochloric acid (100 ml) was added and the mixture was stirred for a further 1 hour. The organic material was extracted into ether (2 × 200 ml), the combined ethereal extracts were washed with water (100 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure to give a pale yellow solid which was used without purification.
Yield 3.4 g, 85%; melting point 185–187°C; ^{1}H nmr($CDCl_3$) δ 7.04(s, 2H), 7.10(m, 1H), 7.35(m, 1H), 7.55(m, 1H), 7.68 (d, 1H); ir (KCl) ν_{max} cm^{-1} 3420, 1622, 1590, 1492, 1440, 1350, 1320, 1200, 808, 735; mass spectrum (*m*/*z*) 366 (100%), 244, 200, 183, 122.

2,3-Difluorophenylboronic acid (3)

This compound was prepared using the method described in the literature.[8]

4-Acetyl-3′-fluorobiphenyl (4)

Compound **2** (1.20 g, 8.7 mmol) and tetrakis(triphenylphosphine)palladium(0) (1.0 g) were added to a stirred, degassed mixture of 4-bromoacetophenone (1.44 g, 7.2 mmol) in dimethoxyethane (50 ml) and 15% aqueous sodium carbonate solution (50 ml) under nitrogen. The reaction mixture was heated under reflux for 4 hours and stirred overnight at room temperature. Water (50 ml) and ether (50 ml) were added and the organic material was extracted into ether (2 × 50 ml). The combined ethereal extracts were washed with saturated aqueous sodium chloride solution (2 × 50 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel/petroleum spirit [bp 40–60°C]: dichloromethane, 1:1).
Yield 1.1 g, 70%; melting point 90–91°C; ^{1}H nmr($CDCl_3$) δ 2.65(s, 3H), 7.10(m,

1H), 7.32(m, 1H), 7.42(m, 2H), 7.67(d, 2H), 8.04(d, 2H); ir (KCl)ν_{max} cm^{-1} 1685, 1608, 1590, 1482, 1368, 1272, 1190, 965, 795, 602; mass spectrum (*m*/*z*) 214 (M$^+$), 199 (100%), 170.

4-Acetyl-2′,3′-difluorobiphenyl (5)

This compound was prepared using the same method as described for compound **4**, by reacting compound **3** (1.98 g, 12.5 mmol) with 4-bromoacetophenone (2.08 g, 10.4 mmol) and tetrakis(triphenylphosphine)palladium(0) (1.0 g).
Yield 1.27 g, 53%; ^{1}H nmr(CDCl$_3$) δ 2.65(s, 3H), 7.22(m, 3H), 7.65(d, 2H), 8.05(d, 2H); ir (KCl)ν_{max} cm^{-1} 1678, 1605, 1482, 1402, 1355, 1270, 895, 835, 794, 745; mass spectrum (*m*/*z*) 232 (M$^+$), 217 (100%), 188, 169, 94.

Methyl 4′-decylbiphenyl-4-carboxylate (6)

A mixture of 4′-decylbiphenyl-4-carboxylic acid (10.0 g, 30 mmol), concentrated sulphuric acid (3 ml) and methanol (300 ml) was heated under reflux for 4 hours. The mixture was allowed to cool and the excess of methanol was removed under reduced pressure. The organic material was extracted into chloroform (2 × 150 ml) and the combined organic extracts were washed with saturated aqueous sodium bicarbonate (200 ml) (the washing was repeated until evolution of carbon dioxide had ceased) and then with water (2 × 200 ml). The organic layer was dried (MgSO$_4$) and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel/dichloromethane) to give colourless crystals.
Yield 9.80 g, 90%; melting point 79–80°C; ^{1}H nmr(CDCl$_3$) δ 0.85(t, 3H), 1.30(m, 14H), 1.65(m, 2H), 2.65(t, 2H), 3.95(s, 3H), 7.28(d, 2H), 7.54(d, 2H), 7.66(d, 2H), 8.10(d, 2H); ir (KCl)ν_{max} cm^{-1} 2920, 2850, 1722, 1610, 1470, 1440, 1290, 1278, 1115, 770; mass spectrum (*m*/*z*) 352 (M$^+$), 225 (100%).

1-(4′-Decylbiphenyl-4-yl)-3-(3′-fluorobiphenyl-4-yl)propane-1,3-dione (7)

Sodium hydride (60% in oil, 0.25 g, 6.4 mmol) was added to a stirred solution of compound **6** (1.12 g, 3.2 mmol) and compound **4** (0.68 g, 3.2 mmol) in dry 1,2-dimethoxyethane (90 ml). The reaction mixture was heated under reflux for 3 hours under nitrogen and allowed to cool to room temperature. A few drops of water were added cautiously followed by concentrated hydrochloric acid (3 ml) and water (150 ml). The organic material was extracted into chloroform (3 × 250 ml) and the combined organic extracts were washed with water (2 × 150 ml). The organic layer was dried (MgSO$_4$) and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel/petroleum spirit [bp 40–60°C]:dichloromethane 1:1) to give pale yellow crystals.
Yield 0.95 g, 55%; transition temperatures (°C) K 156 (S$_A$ 154) I; ^{1}H nmr(CDCl$_3$) δ 0.90(t, 3H), 1.30(m, 14H), 1.68(m, 2H), 3.68(t, 2H), 6.93(s, 1H), 7.10(m, 1H), 7.30(d, 2H), 7.35(m, 1H), 7.43(m, 2H), 7.58(d, 2H), 7.72(2xd, 4H), 8.08(2xd, 4H), 16.95(s, 1H); ir (KCl)ν_{max} cm^{-1} 2918, 2842, 1610, 1582, 1482, 1468, 1290, 1188, 835, 775; mass spectrum (*m*/*z*) 534 (M$^+$), 407, 199 (100%), 167, 147.

1-(4′-Decylbiphenyl-4-yl)-3-(2′-fluorobiphenyl-4-yl)propane-1,3-dione (8)

This compound was prepared using the same procedure as described for compound **7**, by reacting compound **6** (3.72 g, 11 mmol) with compound **1** (2.35 g, 11 mmol) and sodium hydride (60% in oil, 0.88 g, 22 mmol). The crude product was purified by column chromatography (silica gel/dichloromethane:petroleum spirit [bp 40–60°C], 1:1) to give pale yellow crystals.
Yield 3.3 g, 56%; transition temperatures (°C) K_1 95 and K_2 109 (S_A 105) I; ^{1}H nmr(CDCl$_3$) δ 0.90(t, 3H), 1.30(m, 14H), 1.65(m, 2H), 2.70(t, 2H), 6.92(s, 1H), 7.20(m, 2H), 7.29(d, 2H), 7.37(m, 1H), 7.49(m, 1H), 7.58(d, 2H), 7.70(2xd, 4H), 8.08(2xd, 4H), 16.92(s, 1H); ir (KCl)ν_{max} cm^{-1} 2930, 2860, 1608, 1588, 1482, 1305, 1230, 1010, 795, 758; mass spectrum (*m*/*z*) 534 (M$^+$), 407, 321, 199, 69 (100%).

1-(4′-Decylbiphenyl-4-yl)-3-(2-fluorobiphenyl-4-yl)propane-1,3-dione (9)

This compound was prepared using the same procedure as described for compound **7**, by reacting compound **6** (4.50 g, 12.8 mmol) with 4-acetyl-2-fluorobiphenyl (2.74 g, 12.8 mmol) and sodium hydride (60% in oil, 1.02 g, 25.6 mmol). The crude product was purified by flash column chromatography (silica gel/dichloromethane:petroleum spirit [bp 40–60°C], 1:1) to give pale yellow crystals.
Yield 2.91 g, 42%; transition temperatures (°C) K 121 S_A 133 I; ^{1}H nmr(CDCl$_3$) δ 0.90(t, 3H), 1.30(m, 14H), 1.70(m, 2H), 2.70(t, 2H), 6.90(s, 1H), 7.30(d, 2H), 7.46 (m, 3H), 7.60(m, 5H), 7.72(d, 2H), 7.83(m, 2H), 8.07(d, 2H), 16.90(s, 1H); ir (KCl)ν_{max} cm^{-1} 2920, 2850, 1608, 1465, 1258, 1190, 1008, 800, 780, 700; mass spectrum (*m*/*z*) 534 (M$^+$), 321, 200, 167, 69 (100%).

1-(4′-Decylbiphenyl-4-yl)-3-(2′,3′-difluorobiphenyl-4-yl)propane-1,3-dione (10)

This compound was prepared using the same procedure as described for compound **7**, by reacting compound **6** (1.52 g, 4.3 mmol) with compound **5** (1.0 g, 4.3 mmol) and sodium hydride (60% in oil, 0.35 g, 8.6 mmol). The crude product was purified by column chromatography (silica gel/dichloromethane:petroleum spirit [bp 40–60°C], 1:1) to give pale yellow crystals.
Yield 1.40 g, 60%; transition temperatures (°C) K 70 S_A 78 I; ^{1}H nmr(CDCl$_3$) δ 0.90(t, 3H), 1.30(m, 14H), 1.68(m, 2H), 2.65(t, 2H), 6.95(s, 1H), 7.15(m, 3H), 7.29(d, 2H), 7.58(d, 2H), 7.66(d, 2H), 7.72(d, 2H), 8.06(2xd, 4H), 16.95(s, 1H); ir (KCl)ν_{max} cm^{-1} 2930, 2860, 1608, 1584, 1470, 1262, 1230, 1004, 892, 778; mass spectrum (*m*/*z*) 552 (M$^+$), 460, 229, 217, 69 (100%).

Bis-[1-(4′-decylbiphenyl-4-yl)-3-(3′-fluorobiphenyl-4-yl)propane-1,3-dionato]copper(II) (11)

A solution of copper(II) acetate monohydrate (0.15 g, 0.75 mmol) in warm THF (40 ml) was added rapidly to a stirred solution of compound **7** (0.08 g, 1.5 mmol) in THF (20 ml). The mixture was stirred at room temperature for 4 hours and the solvent was removed under reduced pressure. The crude product was recrystallised (THF/acetone) to give green crystals.
Yield 0.53 g, 62%; transition temperatures (°C) K 176 S_A 209 I; ir (KCl)ν_{max} cm^{-1} 2930, 2860, 1604, 1582, 1535, 1482, 1412, 1215, 1185, 780.

Bis-[1-(4′-decylbiphenyl-4-yl)-3-(2′-fluorobiphenyl-4-yl)propane-1,3-dionato]copper(II) (12)

This compound was prepared using the same procedure as described for compound **11**, by reacting compound **8** (1.4 g, 2.6 mmol) with copper(II) acetate monohydrate (0.26 g, 1.3 mmol) in THF. The crude product was recrystallised (THF/acetone) to give green crystals.
Yield 1.87 g, 63%; transition temperatures (°C) K 180 (N 165) I; ir (KCl)ν_{max} cm^{-1} 2920, 2850, 1602, 1585, 1530, 1480, 1382, 1315, 1002, 780.

Bis-[1-(4′-decylbiphenyl-4-yl)-3-(2-fluorobiphenyl-4-yl)propane-1,3-dionato]copper(II) (13)

This compound was prepared using the same procedure as described for compound **11**, by reacting compound **9** (0.10 g, 0.19 mmol) with copper(II) acetate monohydrate (0.02 g, 0.09 mmol) in THF. The crude product was recrystallised (THF/acetone) to give green crystals.
Yield 0.14 g, 65%; transition temperatures (°C); K 170 (S_C 150) S_A 179 N 188 I; ir (KCl)ν_{max} cm^{-1} 2920, 2850, 1606, 1582, 1530, 1484, 1430, 1382, 1002, 780.

Bis-[1-(4′-decylbiphenyl-4-yl)-3-(2′,3′-difluorobiphenyl-4-yl)propane-1,3-dionato]-copper(II) (14)

This compound was prepared using the same procedure as described for compound **11**, by reacting compound **10** (1.2 g, 2.2 mmol) with copper(II) acetate monohydrate (0.21 g, 1.1 mmol) in THF. The crude product was recrystallised (THF/acetone) to give green crystals.
Yield 0.6 g, 48%; melting point 171–172°C; ir (KCl)ν_{max} cm^{-1} 2930, 2860, 1605, 1585, 1535, 1428, 1410, 1315, 1006, 780.

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