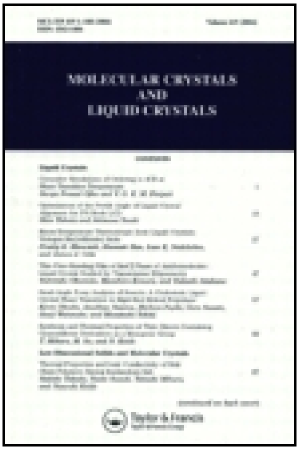

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Liquid-Crystalline Polymesomorphism in Copper(II) Complexes of β-Diketones

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Version of record first published: 24 Sep 2006.

To cite this article: Neil J. Thompson, John W. Goodby & Kenneth J. Toyne (1992): Liquid-Crystalline Polymesomorphism in Copper(II) Complexes of β-Diketones, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 213:1, 187-205

To link to this article: http://dx.doi.org/10.1080/10587259208028730

Mol. Cryst. Liq. Cryst., 1992, Vol. 213, pp. 187–205
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Printed in the United States of America

Liquid-Crystalline Polymesomorphism in Copper(II) Complexes of β-Diketones†

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(Received July 15, 1991)

The preparation of a number of copper(II) complexes of β-diketones is described. Following the unexpected discovery of a smectic A phase in bis-[1-(4′-decylbiphenyl-4-yl)-3-(4′-fluorobiphenyl-4-yl)propane-1,3-dionato]copper(II), two series of novel copper(II) complexes were prepared; one series is based on 1-biphenyl-3-phenylpropane-1,3-dione and the other on 1,3-di-(biphenyl)propane-1,3-dione and each incorporates polar terminal substituents in the lateral benzene and biphenyl units respectively. Many of the complexes containing polar substituents show enhanced smectic character in comparison with their non-polar analogues. Four further examples of complexes exhibiting polymesomorphism (S_A, N and S_C, S_A) are described and the occurrence of an S_C phase in three of the complexes are the first such examples. The liquid-crystalline properties of the β-diketone ligands are also discussed.

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

INTRODUCTION

Over the past ten years a wide variety of metallo-mesogens containing different metal atoms has been reported, and although many of the compounds show discotic mesophases others show phases which appear typically nematic or smectic. Copper(II) complexes of β-diketones are one of the most widely studied types of metallo-mesogen. Ohta *et al.*[1,2] first reported multiple melting behaviour in complexes with the structure shown in Figure 1, and many liquid-crystalline complexes have since been discovered. Discotic mesophases have been reported in symmetrical copper(II) complexes, shown in Figure 2, by Giroud *et al.*[3,5] and by Ohta *et al.*[4,6] The complex in which R = $C_{12}H_{25}O$, (R) = H[7] (see Figure 2) has been studied by X-ray diffraction[8] and its discotic phase is described as a discotic lamellar phase. The phase shows layered characteristics but there is no columnar ordering within the layers, which appear to be slightly tilted.

An interesting departure from discotic mesomorphism was described by Chandrasekhar *et al.*[9–11] for complexes with the structure shown in Figure 3. These complexes exhibit monotropic nematic phases which show typical *schlieren* micro-

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† Presented at the Annual Conference of the British Liquid Crystal Society, Reading, England, 25–27th March 1991.

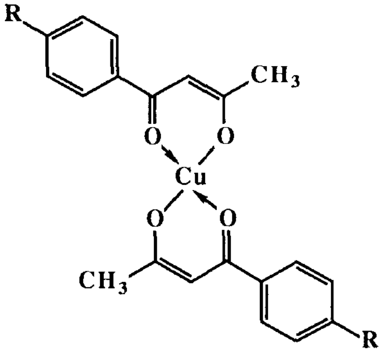


FIGURE 1 Complexes exhibiting multiple melting behaviour (R = CH_3–$C_{12}H_{25}$).

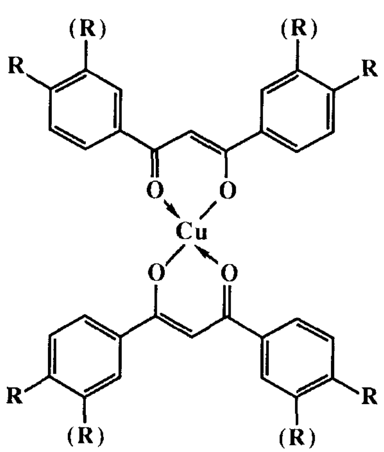


FIGURE 2 Discotic copper(II) complexes [R = alkyl or alkoxy, (R) = H, alkyl or alkoxy].

scopic textures. Furthermore, the nematic phase is described as being biaxial and is apparently continuously miscible with the nematic phase of 4-cyano-4″-pentylterphenyl (5CT), a calamitic nematogen. Complexes with a similar structure to that shown in Figure 3 (long chain = $C_{12}H_{25}$, R = CH_3, C_2H_5, OCH_3, OC_2H_5, Cl, Br and CN) have been reported very recently[12] and these complexes will be considered in greater detail in the discussion. Muhlberger *et al.*[13] have reported complexes, shown in Figure 4a, which also exhibit monotropic nematic phases and in our previous communication,[14] we reported that enantiotropic nematic phases can be obtained by altering the structure of the complexes shown in Figure 3, to make the molecule more ‘disc-like’ (see Figure 5). For the broadened complexes related to the general structure shown in Figure 5, enantiotropic nematic phases were observed in all of the examples which we prepared with one exception (R = F and n = 10 in Figure 5),[15] which showed a monotropic smectic C phase and an enantiotropic smectic A phase which persisted over a large temperature range; enantiotropic nematic phases in similar compounds have also been described by Sadashiva *et al.*[16] (Figure 5b). Ohta *et al.* have recently reported complexes with the structures shown in Figure 4b[17] and Figure 4c[18]; complexes with R′ = alkyl

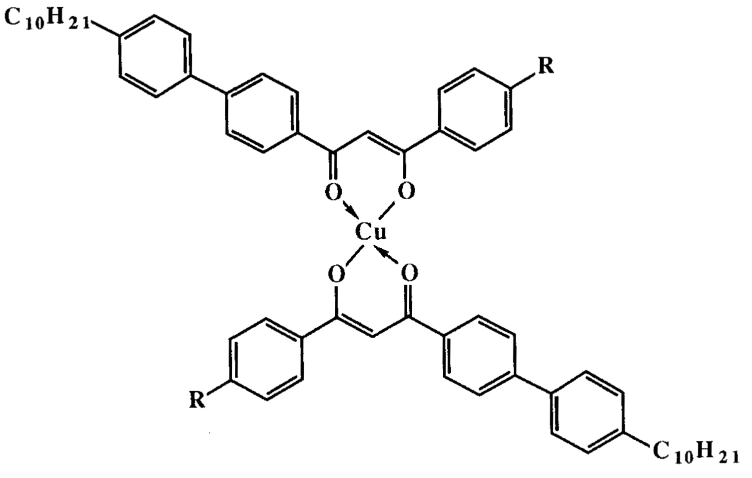
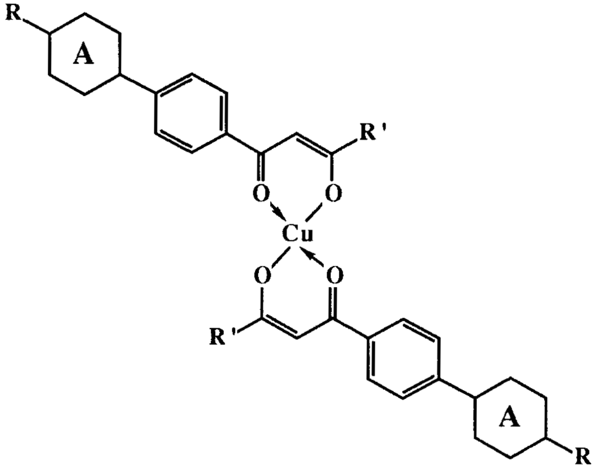


FIGURE 3 Nematogenic (monotropic) complexes (R = short alkyl or alkoxy).



(a) R = CH_3, C_5H_{11}, C_7H_{15}, A=cyclohexyl, R'=C_3H_7-C_5H_{11}, C_7H_{15} and C_8H_{17}

(b) R = $C_8H_{17}O$-$C_{12}H_{25}O$, $C_{16}H_{33}O$, A = 1,4-disubstituted benzene, R' = CH_3

(c) R = C_4H_9O, $C_8H_{17}O$, $C_{12}H_{25}O$, A = 1,4-disubstituted benzene, R' = C_4H_9, C_8H_{17} and $C_{12}H_{25}$

FIGURE 4 Complexes exhibiting nematic or discotic rectangular columnar phases.

show enantiotropic nematic phases, whereas those shown in Figure 4b (R = CH_3) exhibit a discotic rectangular columnar phase. The generation of the discotic phase is thought to be due to dimerisation of the complex molecules which is hindered when R′ is a sufficiently long alkyl chain.

The aim of the work described in this article was to investigate the structural reasons for the generation of smectic character which was apparent for the complex

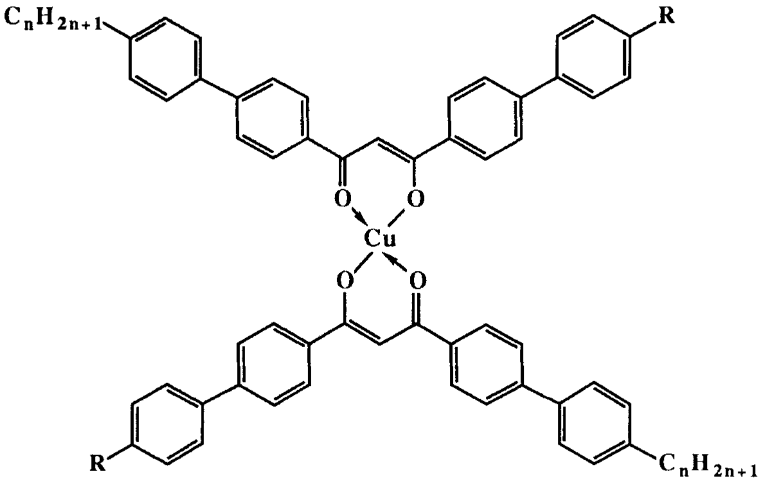


FIGURE 5 Complexes exhibiting enantiotropic nematic phases. (a) R = CH_3 and C_2H_5; n = 10. (b) R = CN, CH_3O and C_2H_5; n = 10, 11 and 12.

with the structure shown in Figure 5 (R = F and n = 10). The small, polar fluoro-substituent appears to be responsible for the formation of the smectic A and C phases since other complexes represented by the structure shown in Figure 5 with alkyl, alkoxyl or indeed a cyano substituent[16] show only nematic mesophases. In order to investigate the effect of polar substituents a number of complexes were prepared with R = F, Br, CN and CF_3 so that comparisons could be made between the phase nature and the transition temperatures of these complexes and those complexes reported previously[14] with R = H, CH_3 and OCH_3.

It was found that smectic character was enhanced in all of the polar substituted complexes apart from the one containing a cyano-substituent. A relationship was also observed between the structure of the molecules and the monotropic or enantiotropic nature of the phases. Those complexes based on the structure shown in Figure 3 gave monotropic mesophases, whereas complexes based on the structure shown in Figure 5 gave enantiotropic phases, with polymesomorphism appearing monotropically. Five examples of polymesomorphism were found in the complexes we report here.

RESULTS AND DISCUSSION

The β-diketone ligands were prepared by reaction of the appropriate methyl ketone and ester with sodium hydride according to the method of Kopecky *et al.*[19] (see Scheme I). The methyl ketones which were not commercially available were prepared using a variety of methods which are described in the experimental section (see Schemes II and III). 4-Acetyl-4′-bromobiphenyl was prepared by acetylation of 4-bromobiphenyl although the yield was much lower than that for the preparation of 4-acetyl-4′-fluorobiphenyl[14] using a similar procedure. A mixture of several compounds was obtained from the reaction of 4-bromobiphenyl but the individual components of the mixture were not completely separated or identified. It is likely that the mixture consisted of biphenyls in which dehalogenation and/or bromine migration had taken place since it is known that Friedel-Crafts catalysts may catalyse such proccesses[20] for iodo-, bromo- and chloro-aryl halides although the problem is not encountered with aryl fluorides. 4′-Acetyl-4-cyanobiphenyl was prepared by cyanation of 4-acetyl-4′-bromobiphenyl[21] and 4-acetyl-4′-trifluoromethylbiphenyl was prepared by coupling[22] 4-trifluoromethylphenylboronic acid with 4-bromoacetophenone using tetrakis(triphenylphosphine)palladium(0)[23] as catalyst.

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 and the crude complexes were purified by recrystallisation from THF/acetone mixtures. ^1H 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.

The melting points and transition temperatures of the β-diketone ligands are shown in the Table. The ligands which contain only three aromatic rings all show smectic A mesophases and those ligands which contain polar substituents (**c**, **6**, **7** and **8**) have higher clearing points and higher melting points than the parent compound **a**. The relative elevation of melting points and clearing temperatures for the ligands containing polar substituents is such that the smectic A phase has a reduced temperature range and in the case of compound **7** has become monotropic. In addition to a smectic A phase, compound **6** also shows a monotropic E phase. In our previous communication[14] we also reported smectic characteristics for ligands based on three-ring systems although several compounds in that report showed nematic phases. Some similar ligands have been reported recently[12] which also show smectic A character; the chloro and bromo substituted ligands with a $C_{12}H_{25}$ terminal chain both show E and smectic A phases. The clearing points in the two compounds are similar but the bromo-substituted compound has a higher melting point and a higher E to smectic A transition temperature. The two halogen-substituted ligands which we report here (**c**, F) and (**6**, Br) conform to this trend. The bromo compound has a higher melting point and a higher E to smectic A transition (compound **c** does not show an E phase) and also has a higher smectic A clearing point than the fluoro-substituted compound **c**. A homologous series of such chloro-substituted ligands with the long chain length varying from C_5H_{11} to $C_{12}H_{25}$ have also been reported recently[24] and the decyl-substituted ligand has transition temperatures of K 133 S_A 145 I. Comparison between this compound and the bromo ligand (**6**) shows similar smectic A phase clearing points and a slightly lower melting point for the chloro compound. The bromo ligand, however, shows a monotropic E phase which is only observed in the higher homologues of the chloro-substituted ligands and then with somewhat lower E to smectic A transition temperatures.

The ligands based on a four-ring structure (compounds **9**, **d e**, **10**, **11** and **12**) give high melting crystals which are not mesogenic, with the exception of the cyano-substituted compound (**12**) which shows smectic A and E phases. In our previous communication[14] we reported that ligands containing two biphenyl units separated by a diketone moiety were essentially banana-shaped and that we would expect

TABLE

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

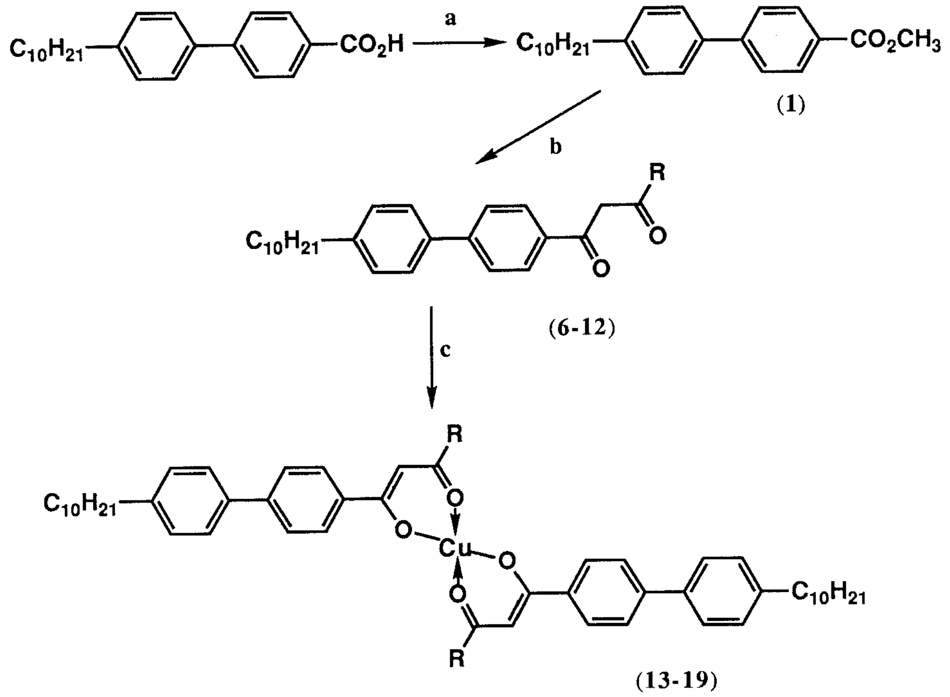
Ligand Structure.	Ligand No.	Transition Temperatures of Ligands.						Complex No.	Transition Temperatures of Complexes.				
		K_1	K_2	E	S_A	N	I		K	S_C	S_A	N	I
$C_{10}H_{21}BzBzCOCH_2COBzH^§$	**a**	* 60			* 98		*	**A**	* 198			(* 156)	*
$C_{10}H_{21}BzBzCOCH_2COBzCH_3{}^§$	**b**	* 84	*97		(* 93)		*	**B**	* 197/221			(* 167)	*
$C_{10}H_{21}BzBzCOCH_2COBzF^§$	**c**	* 88			* 122		*	**C**	* 189/193			(* 175)	*
$C_{10}H_{21}BzBzCOCH_2COBzBr$	**6**	* 138		(*130)	* 145		*	**13**	* 205/212		(*182	* 183)	*
$C_{10}H_{21}BzBzCOCH_2COBzCF_3$	**7**	* 128	*138		(* 128)		*	**14**	* 188		(*131	* 132)	*
$C_{10}H_{21}BzBzCOCH_2COBzCN$	**8**	* 126			* 145		*	**15**	* 230		(* 203)		*
$C_{10}H_{21}BzBzCOCH_2COBzBzH$	**9**	* 163			[* 113]		*	**16**†	* 193/208			* 195	*
$C_{10}H_{21}BzBzCOCH_2COBzBzCH_3{}^§$	**d**	* 186			[* 106]		*	**D**	* 195			* 206	*
$C_{10}H_{21}BzBzCOCH_2COBzBzF^§$	**e**	* 199			[* 135]		*	**E**[15]	* 155	(* 122)	* 250		*
$C_{10}H_{21}BzBzCOCH_2COBzBzBr$	**10**	* 182					*	**17**	* 150	(* 141)	* 260		*
$C_{10}H_{21}BzBzCOCH_2COBzBzCF_3$	**11**	* 218			[* 161]		*	**18**	* 228	(* 203)	* 265		*
$C_{10}H_{21}BzBzCOCH_2COBzBzCN$	**12**¶	* 105		* 180	* 198		*	**19**¶	* 259			* 273	*

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

An entry such as 197/221 denotes two crystal forms melting at 197 and 221 °C respectively.

§ Previously reported in reference 14.† Two crystal forms are evident; the nematic phase is monotropic with respect to the higher melting form.

¶ Also reported in reference 16.



a ... CH_3OH/H_2SO_4

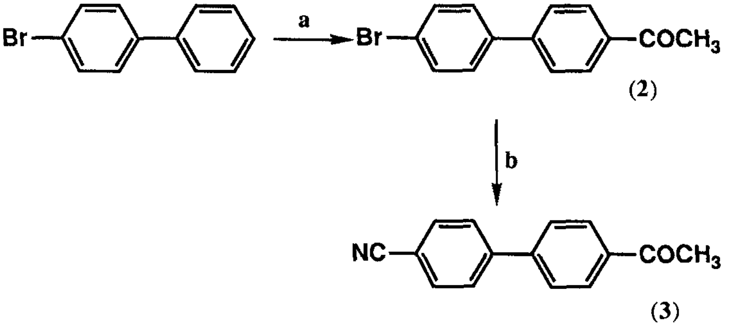
b ... $RCOCH_3/NaH$

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

R	Ligand	Complex	R	Ligand	Complex
$C_6H_4.Br$	**6**	**13**	$C_6H_4.C_6H_4.H$	**9**	**16**
$C_6H_4.CF_3$	**7**	**14**	$C_6H_4.C_6H_4.Br$	**10**	**17**
$C_6H_4.CN$	**8**	**15**	$C_6H_4.C_6H_4.CF_3$	**11**	**18**
			$C_6H_4.C_6H_4.CN$	**12**	**19**

SCHEME I

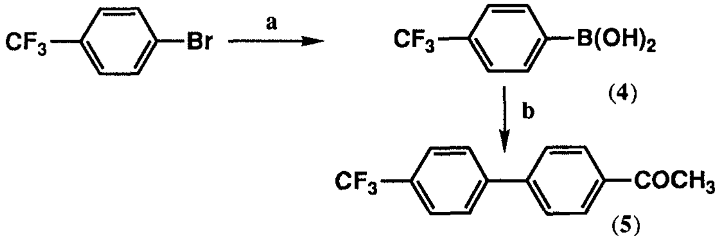
systems with this geometry to be less likely to pack in a layered smectic phase than more linear molecules. Although smectic mesophases are not observed in these systems, virtual smectic A to isotropic liquid transition temperatures have been obtained by miscibility with 4-pentyl-4″-octyloxyterphenyl (K 194 S_B 211 S_A 221 I). By comparison of the transition temperatures of the ligands containing three benzene rings with the virtual values for the four-ring systems containing the same substituent we can see that in each case the smectic A phase thermal stability is higher in the four ring systems. The addition of an extra benzene ring into a linear molecule (e.g. the change from biphenyl to terphenyl) would be expected to in-



a ... $CH_3COCl/AlCl_3$

b ... Cu(I)CN

SCHEME II



a ... (i) BuLi, -78 °C (ii) $(i\text{-}PrO)_3B$ (iii) H^+

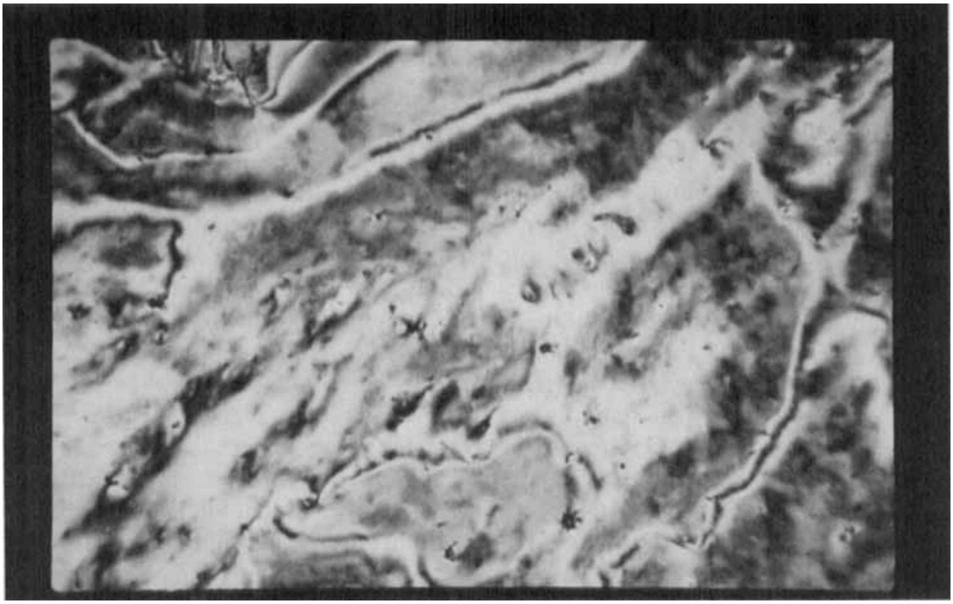
b ... $[(C_6H_5)_3P]_4Pd(0)$, $CH_3COC_6H_4Br$

SCHEME III

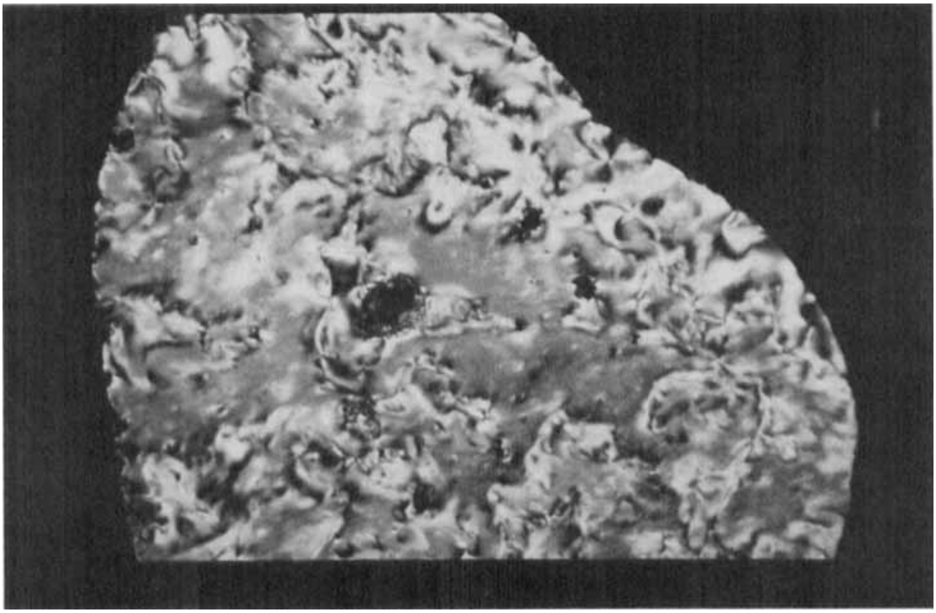
crease mesophase clearing temperatures and melting points considerably but in the β-diketone systems the increases in smectic A phase clearing points induced by the addition of a benzene ring range from only 13°C (compare compounds **b**/**d** and **c**/**e**) to 33°C for compounds **7** and **11**. These increases in mesophase stability are far less than one would expect and are a consequence of the molecular shape, which is unfavourable for a lamellar packing arrangement and offsets the advantage gained by addition of an extra benzene ring. The melting point in each case has increased sharply. The cyano-substituted ligands (compounds **8** and **12**) are exceptional in this series in that both the three- and four-ring ligands show smectic phases. Compound **12** has a higher smectic A clearing point by 53°C in comparison with compound **8**. It is possible that in the cyano-systems antiparallel type correlations occur which would lead to a molecular pair with a more linear shape than that of a single ligand molecule in the other systems.

The transition temperatures of the complexes are also given in the Table. If we compare the phase behaviour of complexes which have a structure similar to that shown in Figure 3 (i.e. compounds **A**, **B**, **C**, **13**, **14**, and **15**, all of which are nematogenic apart from the cyano substituted complex, **15**) we can see the effect which each substituent has in relation to the parent compound **A** and the results are less regular than those seen for the corresponding ligands. For example, the methyl substituent (compound **B**) increases both melting point (23°C) and nematic clearing point (11°C) whereas the fluoro-substituted complex (compound **C**) has a reduced melting point (5°C) and enhanced nematic phase stability (19°C). The bromo substituted complex (compound **13**) provides the first example of smectic A/nematic polymesomorphism in unsymmetrical copper(II) complexes. The effect of bromine has been to increase smectic thermal stability by at least 30°C since complex **A** supercools to 152°C before cystallisation occurs without a smectic phase being observed. Bromo- and chloro-substituted complexes with a similar structure ($C_{12}H_{25}$ instead of $C_{10}H_{21}$ as the long chain) have recently been reported[12] and the chloro compound is nematogenic (monotropic) whereas the bromo compound shows a smectic A phase which, again, is monotropic. Similarly, in the systems we report here the fluoro compound is nematogenic and the bromo compound shows nematic/ smectic A polymesomorphism. It appears therefore that the smectic A character is enhanced in the order Br > Cl > F. The replacement of hydrogen with a trifluoromethyl group (compound **14**) has reduced the melting point by 10°C and has also had a detrimental effect on phase stability so that the nematic clearing point is reduced by 24°C. In this complex, a monotropic smectic A phase has also been generated, although it only exists briefly before crystallisation occurs at 130°C. The effect of a cyano-substituent (compound **15**) is to increase both melting point (32°C) and smectic A phase thermal stability to such an extent that the nematic phase is eliminated. In all of the complexes with the structure shown in Figure 3 the mesophases, as expected,[14] are monotropic. All of the substituents, with the exception of trifluoromethyl, are superior to hydrogen in enhancing clearing temperatures and interestingly, the bromo and cyano substituents increase smectic thermal stability markedly.

The promotion of smectic character is more marked for complexes having a structure similar to that shown in Figure 5 (i.e. compounds **E**, **17** and **18**). If we again consider the effects of each substituent in comparison to hydrogen (compound **16**) we see that all of the substituents, including trifluoromethyl, promote mesogenicity and all of the complexes show enantiotropic phases apart from complex **16**, which has two crystal forms. Both halogen substituents have a dramatic effect on smectic phase stability. Complex **16** (R = H) supercools in the nematic phase to ~130°C before crystallisation, and therefore the fluoro substituent (compound E) enhances smectic phase stability by at least 120°C and the bromo substituent (compound **17**) similarly enhances it by at least 130°C. Both of these compounds also exhibit monotropic smectic C phases. In complex **18**, which contains a trifluoromethyl group the smectic A phase has been promoted by a similar extent to that of the two halogeno substituted complexes and once again in addition to the smectic A phase, a monotropic smectic C phase is observed. Textures of the smectic C phase formed on cooling the homeotropic regions of the smectic A phase of compound **18** are shown in photomicrographs I and II. The cyano-substituted complex (compound **19**) is anomalous in the trend observed for the other polar substituted complexes since smectic phases are not observed, despite the polarity



PHOTOMICROGRAPH I. Compound **18** in the smectic C phase at 202°C. See Color Plate II.



PHOTOMICROGRAPH II. Compound **18** in the smectic C phase at 198°C. See Color Plate III.

of the nitrile group, with crystallization occurring at ~220°C on cooling. The nitrile substituent, however, increases the nematic thermal stability by 78°C, in comparison to the parent compound, **16**.

From the values given in the Table we can also make direct comparisons of the transition temperatures for complexes with the same substituents, but with six or eight aromatic rings in the molecule (see Figures 3 and 5). In each case, the broader complex (see Figure 5) has significantly higher transition temperatures, although often the melting points are lower. The melting points for complexes **16** (-H), **18** (-CF_3) and **19** (-CN) are, however, higher than those for the analogous six-ring systems (**A**, **14** and **15**). Three of the broader complexes (**16**, **D** and **19**) are nematogenic and increases in nematic thermal stabilities of 39, 39 and at least 70°C respectively arise on broadening the complex. The cyano-substituted complexes **15** and **19** highlight a peculiarity in the trend observed previously, in that the six-ring system is purely smectogenic but the eight-ring system is nematogenic with no smectic phases observed on cooling to ~220°C, at which point crystallisation occurs. The maximum possible increase in smectic A phase thermal stability for the cyano compound is therefore only 17°C compared with increases of 78 and 134°C for the bromo (**17** and **13**) and trifluoromethyl (**18** and **14**) substituted compounds respectively. The low clearing point of the six-ring trifluoromethyl complex (**14**) is in stark contrast to the high clearing point of the analogous eight-ring system (**18**).

The dramatically increased smectic character of compounds **E**, **17** and **18** in comparison with compounds **16** and **D**, appears to be due to the inclusion of a polar substituent in the 4′-position of the laterally attached biphenyl units (R in Figure 5). The increases are also apparent in complexes based on the structure shown in Figure 3 but are far more marked in the broader complexes. The cyano-substituent, although polar, does not appear to enhance smectic phase thermal stability significantly in the broader complex and the reasons for this curious deviation are uncertain.

In calamitic systems the introduction of large lateral substituents decreases the nematic phase thermal stability regardless of the polarity of the substituent. Smectic phase thermal stability is also adversely affected in such systems on introduction of large lateral substituents but there is evidence[25] that the polarity of the substituent is an important factor. Two opposing effects appear to be in operation. The steric effect causes a reduction in the smectic phase stability by increasing the separation between the long molecular axes. In extreme cases, however, such as when the substituent is highly polar (e.g. NO_2), the reduction in smectic stability is countered to some degree by the increased lateral interactions between the molecules due to the dipolar nature of the lateral substituent. The combination of these two effects usually leads to decreased smectic phase thermal stability, but not to the extent expected. The lateral nitro substituent appears to enhance smectic phase stability significantly relative to the methyl, fluoro, bromo, chloro and iodo substituents[25]; however, some enhancement of smectic character may occur for the polar halogeno substituents but this is masked by the steric effect which causes a large decrease in mesophase stability.

In the copper(II) complex systems in question, if the 4-substituted phenyl or biphenyl units are regarded as lateral substituents, the increase in molecular breadth from 4-phenyl to 4′-biphenyl does not reduce nematic phase stability as in calamitic systems. It can clearly be seen (compare compounds **A** and **16** and **B** with **D**) that increasing the size of the 'lateral substituent' considerably enhances nematic phase thermal stability. The two opposing effects (steric and polarity) described for calamitic systems become two complementary effects for the copper(II) complexes. The increase in substituent size enhances mesophase stability and the increase in lateral polarity increases smectic phase stability. The result is that in the broader eight ring systems purely smectogenic complexes are obtained with high temperature mesophases. The narrower six ring systems do show some enhanced smectic character (compounds **13** and **15**, see previous discussion) but not to the same extent as the broader analogues. The structures of the complexes, as shown in Figures 3 and 5, and as seen from molecular models, obviously are not like those of simple calamitic systems and here the broadening of the molecules leads to increased mesophase thermal stability.

An anomaly arises with the cyano-substituted complexes **15** and **19** in which a smectic A phase is observed in the six-ring system (**15**) but remarkably the broader complex (**19**) is purely nematogenic with no significant rise in smectic phase thermal stability induced on broadening the complex. The reasons for this deviation are uncertain although anti-parallel correlations are a common complication encountered with cyano systems whch lead to pairwise association of molecules which contain one nitrile function. In the eight-ring copper(II) complex systems each molecule has two exposed nitrile groups and potentially such associations, if they were to occur, could lead to association of more than two molecules. In the six-ring systems the nitrile groups, by virtue of the shorter phenyl lateral group, are less exposed and it is feasible that anti-parallel correlations could be sterically unfavourable. It is not known whether such associations occur in these systems.

The behaviour seen in the broader copper(II) complex systems described above is, however, consistent with certain trends observed in calamitic liquid-crystals if the polar substituents are considered to be terminally attached. The halogen substituents are polar by virtue of their high electronegativity and they attract electron density from the benzene ring to which they are attached through the σ framework of the molecule and a similar effect occurs for the trifluoromethyl group. Halogen substituents also have a lone pair of electrons which are capable of conjugative interaction with the ring. The cyano-substituent is significantly different from both trifluoromethyl and halogen substituents since, in addition to the electron attraction *via* the σ bond, the nitrile group is also capable of electron withdrawal *via* π interactions with the adjacent benzene ring and its effect may be transmitted throughout the molecule. The π interactions increase the polarisability of the system and in this respect the nitrile group differs greatly from halogen substituents. The effect of terminal polar substituents can be seen in calamitic systems such as the 4-substituted-phenyl 4′-octyloxybiphenyl-4-yl-carboxylates[26] and 4-alkoxybenzylidene-4′-substituted anilines,[27] in which it is common for terminal polar substituents, such as halogens and trifluoromethyl, to promote smectic phases, but for the cyano substituted compounds to be purely nematogenic with relatively high clearing points. This is consistent with the polar substituents in the eight-ring copper(II) complexes being regarded as terminal substituents. The observation that the substituent groups

(R in Figure 5) behave as typical terminal substituents in conventional calamitic systems is also in keeping with the results reported previously[14] that the addition of further benzene units (i.e., the change from the structures shown in Figure 3 to those shown in Figure 5) has the same effect as the extension of the molecular core. It is difficult to perceive how these groups can be regarded as being terminally attached in the complexes in the same sense as they are in the calamitic systems, since the biphenyl-R units in Figure 5 could be regarded as being lateral substituents on the alternative, longer molecular core.

EXPERIMENTAL

The transition temperatures and natures of the phases were determined using an Olympus BH 2 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. ^{1}H nmr spectra were obtained using a JEOL JNM-GX270 spectrometer, infrared spectra were obtained using a Perkin-Elmer 457 grating spectrophotometer and mass spectra were obtained using a Finnigan-MAT 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.

Methyl 4′-decylbiphenyl-4-carboxylate (1)

A mixture of 4′-decylbiphenyl-4-carboxylic acid (10.00 g, 30 mmol), concentrated sulphuric acid (3 ml) and methanol (300 ml) was heated under reflux for 4 h. 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%; mp 79–80.5°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) υ_{max} cm^{-1} 2920, 2850, 1722, 1610, 1470, 1440, 1290, 1278, 1115, 770; mass spectrum (*m/z*) 352 (M^+), 225 (100%).

4-Acetyl-4′-bromobiphenyl (2)

Powdered aluminium chloride (17.58 g, 129 mmol) was added to a cooled (0°C), stirred solution of 4-bromobiphenyl (25.0 g, 107 mmol) in dry dichloromethane

(150 ml). A solution of acetyl chloride (8.42 g, 107 mmol) in dry dichloromethane (100 ml) was added dropwise during 1.5 h. The reaction mixture was allowed to reach room temperature and was stirred for a further 24 h. The mixture was poured onto ice and the organic material was extracted into ether (2 × 200 ml). The combined ethereal extracts were washed with water (100 ml), 10% aqueous sodium hydroxide (100 ml) and repeatedly with water until the aqueous washings were neutral. The crude product was purified by column chromatography (silica gel/dichloromethane:petroleum spirit [bp 40–60°C], 3:2).
Yield 5.57 g, 19%; mp 82.1–83.8°C; ^{1}H nmr ($CDCl_3$) δ 2.65 (s, 3H), 7.50 (d, 2H), 7.60 (d, 2H), 7.65 (d, 2H), 8.05 (d, 2H); ir (KCl) υ_{max} cm^{-1} 1680, 1610, 1392, 1360, 1270, 1080, 1008, 962, 818, 770; mass spectrum (*m*/*z*) 276, 274 (M$^+$), 261, 259, 219, 152 (100%).

4′-Acetyl-4-cyanobiphenyl (3)

A solution of compound **2** (5.0 g, 18.2 mmol) in dry *N*-methylpyrrolidin-2-one (50 ml) was added to a stirred suspension of dried copper(I) cyanide in dry *N*-methylpyrrolidin-2-one (15 ml). The reaction mixture was heated at 185°C for 4 h and allowed to cool to room temperature. The mixture was filtered and water (500 ml) was added to the filtrate; the precipitate which formed was filtered off. The filtrate was washed with ether (2 × 300 ml) and the combined ethereal extracts were washed with water (300 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue, combined with the precipitate collected previously was purified by column chromatography (silica gel/dichloromethane).
Yield 2.40 g, 60%; ^{1}H nmr ($CDCl_3$) δ 2.65 (s, 3H), 7.70 (d, 2H), 7.74 (d, 2H), 7.76 (d, 2H), 8.07 (d, 2H); ir (KCl) υ_{max} cm^{-1} 2228, 1690, 1608, 1420, 1400, 1362, 1275, 960, 820, 562; mass spectrum (*m*/*z*) 221 (M$^+$), 206 (100%), 178, 151, 75.

4-Trifluoromethylphenylboronic acid (4)

n-Butyllithium (1.6 M, 30.5 ml, 48.8 mmol) was added slowly to a cooled (−78°C) stirred solution of 4-trifluoromethylbromobenzene (10.0 g, 44.4 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 triisopropyl borate (16.69 g, 20 ml, 88.8 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 h. 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 7.55 g, 89%; mp 203.3–209.2 and 240.5–243.8°C; ^{1}H nmr ($CDCl_3$) δ 7.60 (d, 2H), 8.00 (d, 2H) the OH protons were not detected; ir (KCl) υ_{max} cm^{-1} 3330, 1520, 1410, 1370, 1325, 1305, 1162, 1130, 1108, 1020; mass spectrum (*m*/*z*) 190 (M$^+$), 162, 145, 126 (100%), 95.

4-Acetyl-4′-trifluoromethylbiphenyl (5)

Compound **4** (5.00 g, 26.3 mmol) and tetrakistriphenylphosphinepalladium(0) (1.0 g) were added to a stirred, degassed mixture of 4-bromoacetophenone (4.36 g, 21.9 mmol) in dimethoxyethane (50 ml) and 15% aqueous sodium carbonate solution (50 ml) under nitrogen. The reaction mixture was heated under reflux for 4 h 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 3.77 g, 66%; mp 117.7–118.9°C; ^1H nmr ($CDCl_3$) δ 2.65 (s, 3H), 7.70 (d, 2H), 7.75 (dd, 4H), 8.08 (d, 2H); ir (KCl) υ_{max} cm^{-1} 1688, 1610, 1398, 1360, 1322, 1262, 1132, 1072, 825, 605; mass spectrum (*m/z*) 264 (M^+), 249 (100%), 201, 152.

1-(4′-Decylbiphenyl-4-yl)-3-(4-bromophenyl)propane-1,3-dione (6)

Sodium hydride (60% in oil, 0.91 g, 22.7 mmol) was added to a stirred solution of compound **1** (4.0 g, 11.4 mmol) and 4-bromoacetophenone (2.26 g, 11.4 mmol) in dry 1,2-dimethoxyethane (250 ml). The reaction mixture was heated under reflux for 3 h under nitrogen and allowed to cool to room temperature. A few drops of water were added cautiously followed by concentrated hydrochloric acid (10 ml) and water (200 ml). The organic material was extracted into dichloromethane (2 × 150 ml) and the combined organic extracts were washed with water (2 × 100 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:petroleum spirit [bp 40–60°C], 1:1) to give pale yellow crystals.

Yield 3.42 g, 58%; transition temperatures (°C) K 138 (E 130) S_A 145 I; ^1H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.30 (m, 14H), 1.65 (m, 2H), 2.68 (t, 2H), 6.52 (s, 1H), 6.95 (d, 2H), 7.23 (d, 2H), 7.30 (d, 2H), 7.38 (d, 2H), 7.54 (d, 2H), 7.71 (d, 2H), 16.90 (s, 1H); ir (KCl) υ_{max} cm^{-1} 2930, 2860, 1682, 1612, 1475, 1430, 1302, 950, 822, 772; mass spectrum (*m/z*) 520, 518 (M^+, 100%), 393, 391, 211, 165.

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

This was prepared using the same procedure as described for compound **6**, by reacting compound **1** (2.0 g, 5.7 mmol) with 4-trifluoromethylacetophenone (1.07 g, 5.7 mmol) and sodium hydride (60% in oil, 0.46 g, 11.4 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 1.8 g, 62%; transition temperatures (°C) $K_1$128 K_2 138 (S_A 128) I; ^1H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.30 (m, 14H), 1.70 (m, 2H), 2.65 (t, 2H), 6.92 (s, 1H), 7.30 (d, 2H), 7.58 (d, 2H), 7.73 (d, 2H), 7.76 (d, 2H), 8.08 (d, 2H), 8.10 (d, 2H), 16.82 (s, 1H); ir (KCl) υ_{max} cm^{-1} 2930, 2860, 1600, 1570, 1540, 1332, 1178, 1132, 1082, 792; mass spectrum (*m/z*) 508 (M^+), 470, 454 (100%), 321.

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

This was prepared using the same procedure as described for compound **6**, by reacting compound **1** (5.0 g, 14.2 mmol) with 4-cyanoacetophenone (2.06 g, 14.2 mmol) and sodium hydride (60% in oil, 1.14 g, 28.4 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 2.45 g, 35%; transition temperatures (°C) K 126 S_A 145 I; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.30 (m, 14H), 1.65 (m, 2H), 2.70 (t, 2H), 6.90 (s, 1H), 7.30 (d, 2H), 7.57 (d, 2H), 7.72 (d, 2H), 7.80 (d, 2H), 8.06 (d, 2H), 8.09 (d, 2H), 16.90 (s, 1H); ir (KCl) υ_{max} cm^{-1} 2925, 2860, 2240, 1587, 1533, 1490, 1432, 1390, 1312, 780; mass spectrum (*m*/*z*) 465 (M^+, 100%), 338, 321, 165, 69.

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

This was prepared using the same procedure as described for compound **6**, by reacting compound **1** (3.15 g, 8.9 mmol) with 4-acetylbiphenyl (1.75 g, 8.9 mmol) and sodium hydride (60% in oil, 0.71 g, 17.8 mmol). The crude product was purified by column chromatography (silica gel/petroleum spirit [bp 40–60°C]:dichloromethane, 6:1) to give pale yellow crystals.
Yield 2.11 g, 46%; mp 162.3–162.9°C; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.30 (m, 14H), 1.65 (m, 2H), 2.70 (t, 2H), 6.94 (s, 1H), 7.30 (d, 2H), 7.48 (m, 3H), 7.58 (d, 2H), 7.66 (d, 2H), 7.72 (d, 4H), 8.08 (dd, 4H), 17.00 (s, 1H); ir (KCl) υ_{max} cm^{-1} 2930, 2860, 1605, 1570, 1505, 1485, 1310, 845, 790, 770; mass spectrum (*m*/*z*) 516 (M^+), 389, 321, 194, 181, 69 (100%).

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

This was prepared using the same procedure as described for compound **6**, by reacting compound **1** (1.98 g, 5.6 mmol) with compound **2** (1.55 g, 5.6 mmol) and sodium hydride (60% in oil, 0.45 g, 11.2 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 1.52 g, 46%; mp 181.5–182°C; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.30 (m, 14H), 1.65 (m, 2H), 2.70 (t, 2H), 6.93 (s, 1H), 7.29 (d, 2H), 7.52 (d, 2H), 7.57 (d, 2H), 7.63 (d, 2H), 7.68 (d, 2H), 7.72 (d, 2H), 8.07 (dd, 4H), 16.95 (s, 1H); ir (KCl) υ_{max} cm^{-1} 2940, 2880, 1618, 1595, 1540, 1490, 1398, 1325, 1010, 790; mass spectrum (*m*/*z*) 596, 594 (M^+), 469, 467, 165.

1-(4′-Decylbiphenyl-4-yl)-3-(4′-trifluoromethylbiphenyl-4-yl)propane-1,3-dione (11)

This was prepared using the same procedure as described for compound **6**, by reacting compound **1** (2.0 g, 5.7 mmol) with compound **5** (1.5 g, 5.7 mmol) and sodium hydride (60% in oil, 0.46 g, 11.4 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 1.8 g, 54%; mp 217.8–218.3°C; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.30 (m, 14H), 1.68 (m, 2H), 2.68 (t, 2H), 6.95 (s, 1H), 7.30 (t, 2H), 7.58 (d, 2H), 7.75

(d, 2H), 8.10 (m, 8H), 8.12 (d, 2H), 16.93 (s, 1H); ir (KCl) υ_{max} cm^{-1} 2940, 2870, 1622, 1610, 1340, 1180, 1135, 1082, 845, 798; mass spectrum (*m/z*) 584 (M$^+$, 100%), 457, 321, 249, 228.

1-(4′-Decylbiphenyl-4-yl)-3-(4′-cyanobiphenyl-4-yl)propane-1,3-dione (12)

This was prepared using the same procedure as described for compound **6**, by reacting compound **1** (1.02 g, 2.9 mmol) with compound **3** (0.64 g, 2.9 mmol) and sodium hydride (60% in oil, 0.23 g, 5.8 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 0.65 g, 42%; transition temperatures (°C) K 105 E 180 S_A 198 I; ^{1}H nmr (CDCl$_3$) δ 0.90 (t, 3H), 1.30 (m, 14H), 1.68 (m, 2H), 2.68 (t, 2H), 6.94 (s, 1H), 7.30 (d, 2H), 7.58 (d, 2H), 7.75 (m, 8H), 8.08 (d, 2H), 8.12 (d, 2H), 16.92 (s, 1H); ir (KCl) υ_{max} cm^{-1} 2940, 2860, 2240, 1610, 1565, 1493, 1470, 1400, 838, 790; mass spectrum (*m/z*) 541 (M$^+$), 482, 240, 206, 183 (100%).

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

A solution of copper(II) acetate monohydrate (0.19 g, 0.95 mmol) in warm THF (60 ml) was added rapidly to a stirred solution of compound **6** (1.0 g, 1.9 mmol) in THF (50 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 0.39 g, 38%; transition temperatures (°C) K_1 205 and K_2 212 (S_A 182 N 183) I; ir (KCl) υ_{max} cm^{-1} 2930, 2860, 1588, 1535, 1480, 1430, 1410, 1384, 1010, 780.

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

This was prepared as described for compound **13**, by reacting compound **7** (0.3 g, 0.6 mmol) with copper(II) acetate monohydrate (0.06 g, 0.3 mmol) in THF. The crude product was recrystallised (THF/acetone) to give green crystals.

Yield 0.4 g, 62%; transition temperatures (°C) K 188 (S_A 131 N 132) I; ir (KCl) υ_{max} cm^{-1} 2940, 2860, 1600, 1570, 1540, 1332, 1178, 1132, 1082, 792.

Bis-[1-(4′-decylbiphenyl-4-yl)-3-(4-cyanophenyl)propane-1,3-dionato]copper(II) (15)

This was prepared as described for compound **13**, by reacting compound **8** (0.72 g, 1.6 mmol) with copper(II) acetate monohydrate (0.16 g, 0.8 mmol) in THF. The crude product was recrystallised (THF/acetone) to give green crystals.

Yield 0.66 g, 83%; transition temperatures (°C) K 230 (S_A 203) I; ir (KCl) υ_{max} cm^{-1} 2925, 2860, 2240, 1587, 1533, 1490, 1432, 1390, 1312, 780.

Bis-[1-(4′-decylbiphenyl-4-yl)-3-(biphenyl-4-yl)propane-1,3-dionato]copper(II) (16)

This was prepared as described for compound **13**, by reacting compound **9** (0.33 g, 0.6 mmol) with copper(II) acetate monohydrate (0.06 g, 0.3 mmol) in THF. The crude product was recrystallised (THF/acetone) to give green crystals.

Yield 0.30 g, 85%; transition temperatures (°C) K 193/208 N 195 I; ir (KCl) υ_{max} cm^{-1} 2925, 2860, 1590, 1533, 1495, 1390, 1310, 770.

Bis-[1-(4′-decylbiphenyl-4-yl)-3-(4′-bromobiphenyl-4-yl)propane-1,3-dionato]copper(II) (17)

This was prepared as described for compound **13**, by reacting compound **10** (1.0 g, 1.9 mmol) with copper(II) acetate monohydrate (0.19 g, 0.95 mmol) in THF. The crude product was recrystallised (THF/acetone) to give green crystals. Yield 0.46 g, 46%; transition temperatures (°C) K 150 (S_C 141) S_A 260 I; ir (KCl) υ_{max} cm^{-1} 2940, 2860, 1600, 1590, 1540, 1485, 1430, 1400, 1390, 1012, 790.

Bis-[1-(4′-decylbiphenyl-4-yl)-3-(4′-trifluoromethylbiphenyl-4-yl)propane-1,3-dionato]copper(II) (18)

This was prepared as described for compound **13**, by reacting compound **11** (1.5 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 0.87 g, 55%; transition temperatures (°C) K 228 (S_C 203) S_A 265 I; ir (KCl) υ_{max} cm^{-1} 2940, 2880, 1618, 1598, 1540, 1498, 1335, 1135, 1080, 790.

Bis-[1-(4′-decylbiphenyl-4-yl)-3-(4′-cyanobiphenyl-4-yl)propane-1,3-dionato]copper(II) (19)

This was prepared as described for compound **13**, by reacting compound **12** (0.16 g, 0.3 mmol) with copper(II) acetate monohydrate (0.03 g, 0.15 mmol) in THF. The crude product was recrystallised (THF/acetone) to give green crystals. Yield 0.13 g, 76%; transition temperatures (°C) K 259 N 273 I; ir (KCl) υ_{max} cm^{-1} 2940, 2870, 2245, 1612, 1598, 1540, 1498, 1395, 1012, 790.

Acknowledgment

This work is published by permission of the Director, HMSO and was funded by the Ministry of Defence. We would like to thank Dr. D. F. Ewing, Mrs. B. Worthington, Mr. R. Knight and Mr. A. D. Roberts for spectroscopic measurements and Dr. M. Hird for providing a sample of 4-pentyl-4″-octyloxyterphenyl.

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