

## Mesogenic $\beta$ -diketones and metallonematogens

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**Abstract.** Several new liquid-crystalline materials have been synthesized and their properties investigated. These belong to a series of  $\beta$ -diketones containing different terminal substituents. Mesophases of the smectic C, smectic A and nematic types have been observed in these  $\beta$ -diketones. Using these ligands many copper(II) and palladium(II) complexes have also been synthesized and their mesogenic behaviour characterized. Microscopic observations and differential scanning calorimetric measurements show that these chelates exhibit the nematic phase. The DSC data also indicate that the nematic phase of the ligands and complexes is associated with very low clearing transition enthalpies. All the metallonematogens reported are enantiotropic in nature.

**Keywords.** Mesogen; smectic; nematic;  $\beta$ -diketone; metallonematogen; chelate.

### 1. Introduction

Many aryl  $\beta$ -diketones which are easily synthesized are useful derivatives and some of these have been reported to exhibit liquid-crystalline properties (Eidenschink and Pohl 1980; Giroud-Godquin and Billard 1981, 1983; Ohta *et al* 1984, 1985, 1986; Veena Prasad and Sadashiva 1991). It has been found that compounds containing a  $\beta$ -diketone moiety between two *p*-alkyl/alkoxy-substituted phenyl rings exhibited phases which have not been conclusively identified. However, replacement of the phenyl rings by a biphenyl or a phenylcyclohexyl moiety changes the nature of the mesophase completely. For example, a series of [1-(*p*-*n*-alkylbiphenyl)-3-(phenyl)propane]-1,3-diones exhibit the classical nematic and smectic A phases (Sadashiva *et al* 1989).

Substituted  $\beta$ -diketones were synthesized in an effort to obtain metallomesogens by chelating them with suitable metal ions. With this in view, copper(II) complexes of many  $\beta$ -diketones have been examined extensively (Giroud-Godquin *et al* 1983, 1984, 1986; Ohta *et al* 1984, 1985, 1986). Sakashita *et al* (1988) carried out detailed X-ray diffraction measurements on a series of disc-like *bis*[1,3-*di*(*p*-*n*-alkoxyphenyl)propane-1,3-dionato]copper(II) complexes. They showed that each of these complexes exhibited a lamellar phase which was immiscible with all other classical mesophases. They designated this as discotic lamellar phase.

The first  $\beta$ -diketonato metal complex containing a biphenyl moiety, viz. *bis*[1-(*p*-*n*-decylbiphenyl)-3-(*p*-methoxyphenyl)propane-1,3-dionato]copper(II) complex and its ethoxy derivative exhibited a monotropic nematic phase (Chandrasekhar *et al* 1986). These represent the first examples of paramagnetic nematic liquid crystals. Since then a number of different metal  $\beta$ -diketonates exhibiting nematic phases have been reported (Muhlberger and Haase 1989; Ohta *et al* 1991; Sadashiva *et al* 1991; Thompson *et al* 1991, 1992a, b).

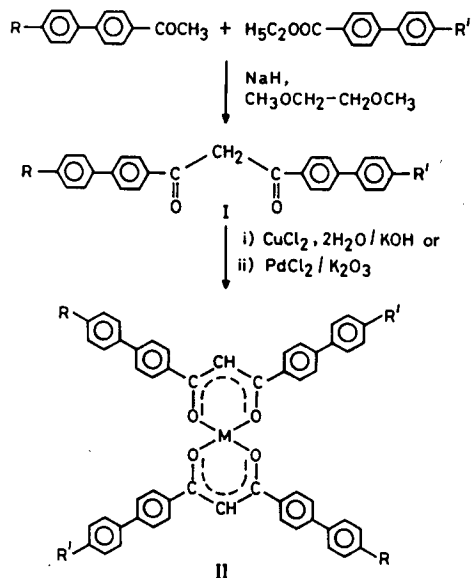
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In this paper, we examine the effect of different terminal substituents on the mesomorphic properties of a series of  $\beta$ -diketones. Using these as ligands a number of copper(II) and palladium(II) complexes have also been prepared and their mesomorphic behaviour studied. Differential scanning calorimetric studies have been carried out to determine the enthalpies of various transitions.

## 2. Experimental

4-*n*-Alkyloxy-4'-acetylbiphenyls and ethyl 4-methoxybiphenyl-4'-carboxylate were prepared following a procedure described in the literature (Gray *et al* 1955). 4-*n*-Alkyl-4'-acetylbiphenyls and 4-cyano-4'-acetylbiphenyl were prepared as described by us previously (Sadashiva *et al* 1989). Ethyl 4-cyanobiphenyl-4'-carboxylate was prepared from 4-bromo-4'-acetylbiphenyl in three steps: first, by sodium hypobromite oxidation to the corresponding carboxylic acid, followed by esterification using ethanol and sulphuric acid; finally the bromo group was replaced by a cyano group using anhydrous cuprous cyanide in refluxing *N,N*-dimethylformamide.

All the  $\beta$ -diketones and their metal chelates were synthesized according to the general scheme shown in figure 1. A typical detailed procedure adopted is described below.



R =  $\text{C}_n\text{H}_{2n+1}$  or  $\text{OC}_n\text{H}_{2n+1}$ ;  $n = 4, 5, 6, \dots, 12$

R' = CN, OCH<sub>3</sub>, OC<sub>2</sub>H<sub>5</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub> or C<sub>4</sub>H<sub>9</sub>

M = Cu or Pd.

**Figure 1.** Synthetic scheme for the preparation of  $\beta$ -diketones and their Cu(II) and Pd(II) chelates.

2.1 [1-(4-*n*-Undecylbiphenyl)-3-(4'''-methoxybiphenyl)propane]-1,3-dione, *I*,  $R = n\text{-}C_{11}H_{23}$ ,  $R' = OCH_3$

A mixture of 4-*n*-undecyl-4'-acetyl biphenyl (1.16 g, 3.3 mmol), ethyl 4-methoxybiphenyl-4'-carboxylate (0.85 g, 3.3 mmol) and anhydrous 1,2-dimethoxyethane (100 ml) was placed in a 250 ml two-necked round bottom flask fitted with a reflux condenser carrying a calcium chloride guard tube and an inlet tube for dry nitrogen. To this was added sodium hydride (0.198 g, 6.6 mmol, 80% dispersed in oil), and the whole mixture was refluxed under nitrogen for 10 h and left at room temperature overnight. The reaction mixture was then cooled in ice and while stirring dilute hydrochloric acid was added until it became acidic. The solid material so obtained was filtered and washed with water until the washings were neutral to litmus. This was dried and chromatographed over silica gel and the pale yellow product thus obtained was recrystallized from butan-2-one several times until the melting point was constant.

Yield 1 g, 38%; m.p. 210.5°C; IR (nujol) 1608, 1585, 1230, 820 and 780  $\text{cm}^{-1}$ ; UV-vis  $\lambda_{\text{max}}(\epsilon)$  375 (56,800) 243 (22,100), 308 (18,400).

Found: C, 83.89; H, 7.98%.  $C_{39}H_{44}O_3$  requires C, 83.57; H, 7.85%.

2.2 [1-(4-*n*-Undecylbiphenyl)-3-(4'''-cyanobiphenyl)propane]-1,3-dione, *I*,  $R = n\text{-}C_{11}H_{23}$ ,  $R' = CN$

This was prepared from 4-*n*-undecyl-4'-acetyl biphenyl (1.2 g, 3.4 mmol), ethyl 4-cyanobiphenyl-4'-carboxylate (0.86 g, 3.4 mmol), anhydrous 1,2-dimethoxyethane (150 ml) and sodium hydride (0.2 g, 6.8 mmol, 80% dispersed in oil) by following a procedure similar to the one described above.

Yield 1.8 g, 34%; m.p. 180.0°C; IR (nujol) 2230, 1606, 1590, 1230, 825 and 780  $\text{cm}^{-1}$ ; UV-vis  $\lambda_{\text{max}}(\epsilon)$  371 (49,800), 285 (22,100), 305 (19,950); NMR ( $\text{CDCl}_3$ )  $\delta$  0.89 (*t*, 3H,  $-\text{CH}_3$ ), 1-1.85 (*m*, 18H,  $9 \times -\text{CH}_2$ ), 2.62 (*t*, 2H,  $\text{ArCH}_2$ ), 6.92 (*s*, 1H,  $-\text{C}=\text{CH}-$ ), 7.85-8.65 (*m*, 16H,  $\text{ArH}$ ), and 16.9 (*s*, 1H, enol OH).

Found: C, 84.63; H, 7.45; N, 2.47%.  $C_{39}H_{41}O_2N$  requires C, 84.32; H, 7.38; N, 2.52%.

2.3 [1-(4-*n*-Undecyloxybiphenyl)-3-(4'''-methoxybiphenyl)propane]-1,3-dione, *I*,  $R = n\text{-}OC_{11}H_{23}$ ,  $R' = OCH_3$

This compound was prepared from 4-*n*-undecyloxy-4'-acetyl biphenyl (1.83 g, 5 mmol), ethyl 4-methoxybiphenyl-4'-carboxylate (1.28 g, 5 mmol), anhydrous 1,2-dimethoxyethane (150 ml) and sodium hydride (0.3 g, 10 mmol, 80% dispersed in oil) using a procedure as described above.

Yield 36.5%; m.p. 233.5°C; IR (nujol) 1608, 1585, 1230, 825, 780  $\text{cm}^{-1}$ .

Found: C, 81.49; H, 7.73%.  $C_{39}H_{44}O_4$  requires C, 81.25; H, 7.63%.

2.4 [1-(4-*n*-Undecyloxybiphenyl)-3-(4'''-cyanobiphenyl)propane]-1,3-dione, *I*,  $R = n\text{-}OC_{11}H_{23}$ ,  $R' = CN$

This compound was prepared from 4-*n*-undecyloxy-4'-acetyl biphenyl (2.81 g, 7.6 mmol), ethyl 4-cyanobiphenyl-4'-carboxylate (1.93 g, 7.6 mmol), dry 1,2-dimethoxyethane

(100 ml) and sodium hydride (0.45 g, 15 mmol, 80% dispersed in oil) using a procedure similar to the one described above.

Yield, 1.5 g, 34%; m.p. 212.5°C; IR (nujol) 2250, 1608, 1580, 1200, 825, 780  $\text{cm}^{-1}$ ; UV-vis  $\lambda_{\text{max}}(\epsilon)$  375 (49,800), 280 (25,950).

Found: C, 81.83; H, 7.26; N, 2.1%.  $\text{C}_{39}\text{H}_{41}\text{O}_3\text{N}$  requires C, 81.96; H, 7.26; N, 2.1%.

2.5 *Bis*[1-(4-*n*-undecylbiphenyl)-3-(4''-methoxybiphenyl)propane-1,3-dionato]copper(II), II,  $R = n\text{-C}_{11}\text{H}_{23}$ ,  $R' = \text{OCH}_3$ ,  $M = \text{Cu}$

To a stirred solution of [1-(4-*n*-undecylbiphenyl)-3-(4''-methoxybiphenyl)propane]-1,3-dione (0.2 g, 0.35 mmol) in warm THF (50 ml) was added a solution of potassium hydroxide (0.019 g, 0.35 mmol) in ethanol (8 ml). To this was added a solution of cupric chloride dihydrate (0.029 g, 0.17 mmol) in ethanol (8 ml). The reaction mixture turned dark green in colour. This was refluxed for 4 h and cooled. The greenish precipitate was filtered and washed with ethanol. This precipitate was dissolved in chloroform (100 ml) and washed with water (3  $\times$  75 ml) and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of solvent and crystallization of the product repeatedly from butan-2-one gave green shining crystals.

Yield, 40%; m.p. 210°C; IR (nujol) 1610, 1585, 1230, 825 and 780  $\text{cm}^{-1}$ ; UV-vis  $\lambda_{\text{max}}(\epsilon)$  373 (88,600), 327 (56,500), 243 (48,100).

Found: C, 79.20; H, 7.73%.  $\text{C}_{78}\text{H}_{86}\text{O}_6\text{Cu}$  requires C, 79.19; H, 7.32%.

2.6 *Bis*[1-(4-*n*-undecyloxybiphenyl)-3-(4''-methoxybiphenyl)propane-1,3-dionato]copper(II), II,  $R = n\text{-OC}_{11}\text{H}_{23}$ ,  $R' = \text{OCH}_3$ ,  $M = \text{Cu}$

This complex was prepared from [1-(4-*n*-undecyloxybiphenyl)-3-(4''-methoxybiphenyl)propane]-1,3-dione (0.32 g, 0.55 mmol), potassium hydroxide (0.031 g, 0.55 mmol), cupric chloride dihydrate (0.047 g, 0.29 mmol) and ethanol (15 ml) by following a procedure similar to the one described above.

Yield, 35%; m.p. 225.0°C; IR (nujol) 1610, 1580, 1250, 830 and 780  $\text{cm}^{-1}$ ; UV-vis  $\lambda_{\text{max}}(\epsilon)$  376.5 (81,000), 336.5 (60,700), 244 (51,900).

Found: C, 77.65; H, 7.17%.  $\text{C}_{78}\text{H}_{86}\text{O}_8\text{Cu}$  requires C, 77.13; H, 7.08%.

2.7 *Bis*[1-(4-*n*-undecyloxybiphenyl)-3-(4''-cyanobiphenyl)propane-1,3-dionato]copper(II), II,  $R = n\text{-OC}_{11}\text{H}_{23}$ ,  $R' = \text{CN}$ ,  $M = \text{Cu}$

This complex was prepared from [1-(4-*n*-undecyloxybiphenyl)-3-(4''-cyanobiphenyl)propane]-1,3-dione (0.22 g, 0.38 mmol), potassium hydroxide (0.022 g, 0.39 mmol), cupric chloride dihydrate (0.034 g, 0.19 mmol) and ethanol (10 ml) by following a procedure similar to the one described above.

Yield, 40%; m.p. 230°C; IR (nujol) 2230, 1610, 1585, 1250, 825 and 780  $\text{cm}^{-1}$ ; UV-vis  $\lambda_{\text{max}}(\epsilon)$  375 (89,800), 300 (61,000), 244 (40,200).

Found: C, 77.57; H, 6.19; N, 2.71%.  $\text{C}_{78}\text{H}_{80}\text{O}_6\text{N}_2\text{Cu}$  requires C, 77.77; H, 6.64; N, 2.32%.

2.8 Bis[1-(4-*n*-undecylbiphenyl)-3-(4''-cyanobiphenyl)propane-1,3-dionato]copper(II), II,  $R = n\text{-C}_{11}\text{H}_{23}$ ,  $R' = \text{CN}$ ,  $M = \text{Cu}$

This was prepared from [1-(4-*n*-undecylbiphenyl)-3-(4'-cyanobiphenyl)propane]-1,3-dione (0.2 g, 0.36 mmol), potassium hydroxide (0.02 g, 0.36 mmol), cupric chloride dihydrate (0.031 g, 0.18 mmol) and ethanol (8 ml) by following a procedure similar to the one described above.

Yield 40%, m.p. 252°C; IR (nujol) 2225, 1610, 1580, 1225, 830 and 780  $\text{cm}^{-1}$ ; UV-vis  $\lambda_{\text{max}}(\epsilon)$  371 (69,600), 307 (54,900), 242 (44,800). Found: C, 84.63; H, 7.45; N, 2.47%.  $\text{C}_{78}\text{H}_{80}\text{O}_4\text{N}_2\text{Cu}$  requires C, 84.32; H, 7.38; N, 2.52%.

2.9 Bis[1-(4-*n*-undecylbiphenyl)-3-(4''-methoxybiphenyl)propane-1,3-dionato]palladium(II), II,  $R = n\text{-C}_{11}\text{H}_{23}$ ,  $R' = \text{OCH}_3$ ,  $M = \text{Pd}$

A mixture of [1-(3-*n*-undecylbiphenyl)-3-(4''-methoxybiphenyl)propane]-1,3-dione (0.254 g, 0.45 mmol), palladium chloride (0.044 g, 0.24 mmol), dry acetonitrile (50 ml) and anhydrous potassium carbonate (0.094 g, 0.68 mmol) was stirred and heated at 80°C for 20 h. The cooled reaction mixture was filtered and the solid material was washed with acetonitrile (50 ml). This was taken up in chloroform (100 ml) and washed with water (3  $\times$  50 ml) and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of solvent afforded a yellow product which was crystallized from butan-2-one several times until the melting point was constant.

Yield, 38%; m.p. 227.5°C; IR (nujol) 1610, 1585, 1250, 825 and 785  $\text{cm}^{-1}$ ; UV-vis  $\lambda_{\text{max}}(\epsilon)$  384 (55,100), 336 (81,800), 246 (69,500); NMR ( $\text{CDCl}_3$ ),  $\delta$  0.88 (t, 6H,  $2 \times -\text{CH}_3$ ), 1.2-2.21 [m, 36H, ( $9 \times -\text{CH}_2$ )<sub>2</sub>], 2.66 (t, 4H,  $2 \times \text{ArCH}_2$ ), 3.8 [s, 6H, ( $2 \times -\text{OCH}_3$ )], 6.9 [s, 2H, ( $-\text{C}=\text{CH}-$ )<sub>2</sub>], 7-8.2 (m, 32H, ArH). Found: C, 76.45; H, 7.11%.  $\text{C}_{78}\text{H}_{86}\text{O}_6\text{Pd}$  requires C, 76.44; H, 7.02%.

2.10 Bis[1-(4-*n*-undecylbiphenyl)-3-(4''-cyanobiphenyl)propane-1,3-dionato] palladium(II), II,  $R = n\text{-C}_{11}\text{H}_{23}$ ,  $R' = \text{CN}$ ,  $M = \text{Pd}$

This complex was prepared from [1-(4-*n*-undecylbiphenyl)-3-(4''-cyanobiphenyl)propane]-1,3-dione (0.194 g, 0.34 mmol), palladium chloride (0.043 g, 0.19 mmol), anhydrous potassium carbonate (0.072 g, 0.52 mmol) and dry acetonitrile (50 ml) following a procedure similar to the one described above.

Yield, 60%; m.p. 269.5°C; IR (nujol) 2230, 1610, 1580, 1250, 825 and 770  $\text{cm}^{-1}$ ; UV-vis  $\lambda_{\text{max}}(\epsilon)$  384 (51,100), 326 (90,200), 260 (55,900); NMR ( $\text{CDCl}_3$ )  $\delta$  0.84 (t, 6H  $2 \times \text{CH}_3$ ), 1.07-1.62 [m, 36H, ( $9 \times -\text{CH}_2$ )<sub>2</sub>], 2.7 [t, 4H, ( $\text{ArCH}_2$ )<sub>2</sub>], 6.8 [s, 2H, ( $-\text{C}=\text{CH}-$ )<sub>2</sub>], 7.15-8.22 (m, 32H, ArH). Found: C, 76.80; H, 6.69; N, 1.88%.  $\text{C}_{78}\text{H}_{80}\text{O}_4\text{N}_2\text{Pd}$  requires C, 77.07; H, 6.58; N, 2.30%.

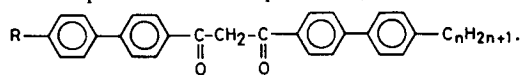
The purity of the compounds synthesized was checked by spectroscopic and microanalytical methods. The transition temperatures and nature of the phases were determined using a Leitz Laborlux 12 POL polarizing microscope equipped with a

Mettler FP52 heating stage and a FP5 controller, and from thermograms obtained on a Perkin-Elmer model DSC-2 differential scanning calorimeter. The enthalpies of transitions were determined from thermograms obtained on a Perkin-Elmer model DSC-4 differential scanning calorimeter. Both calorimeters were calibrated using pure indium as standard. The heating and cooling rates were 5°C/min. The infrared and electronic absorption spectra were recorded on a Shimadzu IR-435 and a Hitachi U-3200 spectrophotometers respectively. The PMR spectra were obtained on a Bruker WP80SY FT-NMR spectrometer in deuteriochloroform with tetramethylsilane as an internal standard. Satisfactory elemental analyses were obtained for all the compounds on a Carlo-Erba 1106 elemental analyser.

### 3. Results and discussion

The transition temperatures and the associated enthalpies for [1-(4-*n*-alkylbiphenyl)-3-(4''-cyanobiphenyl)propane]-1,3-diones are given in table 1. It is seen that all the

Table 1. Mesomorphic transition temperatures (°C) and enthalpies (kcal/mol) of



Compound number	<i>n</i>	R	C	S <sub>C</sub>	S <sub>A</sub>	N	I
1	4	CN	·	198.5 6.29	—	—	(184.0) <sup>†</sup> ·
2	5	CN	·	196.5 7.32	—	—	197.5 <sup>⊙</sup> ·
3	6	CN	·	190.5 9.01	—	—	194.0 0.03 ·
4	7	CN	·	186.5 6.49	—	—	196.5 0.03 ·
5	8	CN	·	183.5 5.49	—	192.0 0.10	195.0 0.03 ·
6	9	CN	·	185.5 5.49	—	199.5 0.51	— ·
7	10	CN	·	182.0 8.28	—	204.0 0.51	— ·
8	11	CN	·	180.0 6.86	181.5 <sup>⊙</sup>	207.0 0.77	— ·
9	12	CN	·	179.5 6.7	182.5 <sup>⊙</sup>	209.5 1.03	— ·
10	10	OCH <sub>3</sub>	·	210.5 11.10	—	—	— ·
11	11	OCH <sub>3</sub>	·	211.5 13.05	—	—	— ·
12	12	OCH <sub>3</sub>	·	207.5 12.58	—	—	— ·

<sup>†</sup>The enthalpy could not be determined because of immediate onset of crystallization.

<sup>⊙</sup>The enthalpy could not be determined.



Figure 2. Focal-conic texture of the smectic A phase of compound 9 at 190°C.

nine compounds exhibit mesophases. The first four lower homologues are purely nematogenic though the *n*-butyl derivative exhibits a monotropic phase. Smectic phase appears from the *n*-octyl derivative with a small temperature range of the nematic phase. The smectic phase of this and the other higher homologues show a simple fan-shaped texture and a photomicrograph of this is shown in figure 2. This smectic phase has been characterized as smectic A. The remaining higher homologues exhibit a very small range of smectic C phase in addition to the  $S_A$  phase. It can also be seen from this table that the three methoxy-substituted derivatives (compounds 10, 11 and 12) are non-mesogenic.

A plot of the transition temperatures vs the number of carbon atoms in the alkyl chain for [1-(4-*n*-alkylbiphenyl)-3-(4''-cyanobiphenyl)propane]-1,3-diones is shown in figure 3. There is alternation in the N→I transition points whereas the S<sub>A</sub>→I transition points rise with increasing length of alkyl chain and these points fall on a smooth curve. In table 2, the transition temperatures and the enthalpies of transitions for three of the [1-(4-*n*-alkoxybiphenyl)-3-(4''-cyanobiphenyl)propane]-1,3-diones are summarized. The melting points of the corresponding non-mesogenic methoxy-

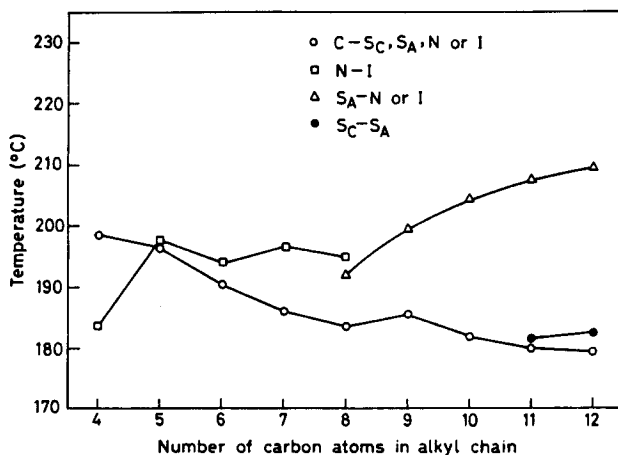
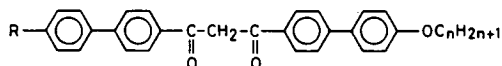


Figure 3. Plot of transition temperatures vs the number of carbon atoms in the chain for the  $\beta$ -diketones I,  $R = C_nH_{2n+1}$ ,  $R' = CN$ .

Table 2. Mesomorphic transition temperatures ( $^{\circ}C$ ) and enthalpies (kcal/mol) of



Compound number	<i>n</i>	R	C	S <sub>A</sub>	I
13	10	CN	215.5	217.0	
			11.95	0.5	
14	11	CN	212.5	220.0	
			8.59	0.78	
15	12	CN	210.0	223.0	
			12.51	1.18	
16	10	OCH <sub>3</sub>	234.0	—	
			11.30		
17	11	OCH <sub>3</sub>	233.5	—	
			11.57		
18	12	OCH <sub>3</sub>	234.0	—	
			12.28		

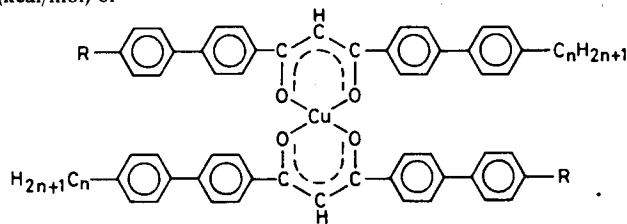


substituted derivatives are also given in this table. It is seen that on substituting an *n*-alkyl chain by an *n*-alkoxy chain, the  $C \rightarrow S_A$  and  $S_A \rightarrow I$  transition temperatures are raised by 30–34°C and 13–14°C respectively.

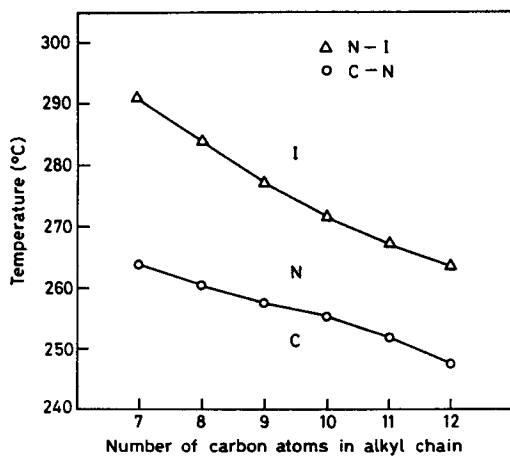
A comparison of the transition temperatures of compound 9 with those of [1-(4-*n*-dodecylbiphenyl)-3-(4''-cyanophenyl)propane]-1,3-dione (Sadashiva *et al* 1991) reveals certain interesting features. Although a terminal cyano group lies high in the nematic group efficiency order and low in the smectic group efficiency order, it promotes a smectic A phase in these  $\beta$ -diketones. Surprisingly, as a result of extension of the core by a phenyl group the clearing temperature increased by 64.5°C and the smectic A phase is retained in the extended compound. However, an opposite trend was observed when a compound containing a terminal methyl group (Thompson *et al* 1991) was extended by the addition of a phenyl group, viz. the mesophase thermal stability decreases in the resulting extended compound and sometimes renders the compound non-mesogenic. Normally, the introduction of a phenyl group into a linear compound would have caused a significant elevation of the clearing point due to increase in the molecular polarizability. Hence, it can be concluded from this that although the phenyl group increases the molecular polarizability, it also increases the molecular lateral dimensions as shown by molecular models resulting in bent structures. Such bent structures cannot be easily accommodated in a layered structure and hence smectogenicity will be suppressed.

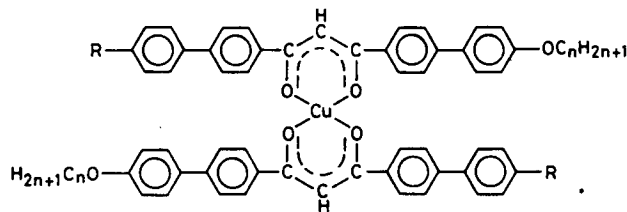
It is interesting to note that in compounds which are terminally substituted by polar groups such as a cyano, antiparallel correlations are commonly encountered (Cladis 1988). Such a possibility does exist in these  $\beta$ -diketones though none of them exhibit the reentrant phenomenon. It is also possible that antiparallel correlation leads to molecular pairing resulting in different smectic A modifications in the system. It is not clear whether such molecular pairing does occur in this system, as detailed X-ray diffraction studies are necessary to determine the same.

The transition temperatures and the corresponding enthalpies for *bis*[1-(4-*n*-alkylbiphenyl)-3-(4'''-cyanobiphenyl)propane-1,3-dionato]copper(II) complexes and for three methoxy-substituted derivatives are summarized in table 3. The compound with *n*-hexyl chain (no. 19) is non-mesomorphic and hence the lower homologues were not prepared. As can be seen complexes 26, 27 and 28 are nematogenic while the ligands from which they are derived are non-mesomorphic. Amongst the cyano-substituted complexes, except for the hexyl derivative (compound 19) all are nematogenic. The smectic phases observed in the higher homologues of the ligands are completely eliminated after complexation. As can be seen in the table, the temperature range of the nematic phase varies from 15.5 to 25.5°C. The melting points are raised by 70–78°C upon complexation, while the clearing points are raised by 56 to 89°C. The enthalpies of nematic to isotropic transitions are of the order of 0.03 to 0.08 kcal/mol. As reported earlier (Sadashiva *et al* 1991) for other metallonematogens this low value has been attributed to the persistence of nematic-like short-range order in the isotropic phase. It is also seen that the methoxy-substituted complexes (compounds 26, 27 and 28) are enantiotropic nematic while the ligands from which they are derived are non-mesomorphic. The nematic mesophase range is about 32°C for all the three derivatives. A plot of the transition temperatures against the number of carbon atoms in the alkyl chain for the above homologous series of cyano complexes is shown in figure 4. It is clearly seen that the N–I transition temperatures for this series decrease as the number of carbon atoms increase in the

**Table 3.** Mesomorphic transition temperatures ( $^{\circ}\text{C}$ ) and enthalpies (kcal/mol) of

Compound number	$n$	R	C	N	I
19	6	CN	286.0 5.55	—	·
20	7	CN	264.5 5.46	291.0*	·
21	8	CN	260.5 9.36	284.0 0.08	·
22	9	CN	257.5 4.99	277.0 0.10	·
23	10	CN	255.5 11.46	271.5 0.03	·
24	11	CN	252.0 13.66	267.5 0.07	·
25	12	CN	250.2 5.34	266.0 0.05	·
26	10	OCH <sub>3</sub>	215.5 10.03	247.0 0.07	·
27	11	OCH <sub>3</sub>	210.0 5.93	243.0 0.09	·
28	12	OCH <sub>3</sub>	202.0 5.6	235.0 0.08	·

**Figure 4.** Plot of transition temperatures vs. the number of carbon atoms in the chain for the chelates II, R = C<sub>n</sub>H<sub>2n+1</sub>, R' = CN, M = Cu.

**Table 4.** Mesomorphic transition temperatures ( $^{\circ}\text{C}$ ) and enthalpies (kcal/mol) of

Compound number	$n$	R	C	N	I
29	10	CN	239.0 12.78	270.5@	
30	11	CN	230.0 3.94	277.0@	
31	12	CN	238.0 11.81	273.0@	
32	10	OCH <sub>3</sub>	235.0 16.7	257.5 0.08	
33	11	OCH <sub>3</sub>	225.0 9.5	253.5 0.07	
34	12	OCH <sub>3</sub>	237.0 7.25	244.0 0.07	

@ Partial decomposition takes place before clearing.

alkyl chain. A similar trend has been observed in a homologous series of *bis*[1-(4-*n*-alkylbiphenyl)-3-(phenyl)propane-1,3-dionato]copper(II) complexes reported by Sadashiva *et al* (1991). The melting points for the entire series are quite high and in the range 250 to 264 $^{\circ}\text{C}$ .

The transition temperatures and enthalpies of transitions for *bis*[1-(4-*n*-alkoxybiphenyl)-3-(4''-cyanobiphenyl)propane-1,3-dionato]copper(II) complexes (compounds 29, 30 and 31) and the three corresponding methoxy derivatives (compounds 32, 33 and 34) are summarized in table 4. As can be seen all these six complexes exhibit an enantiotropic nematic phase with very low clearing enthalpies. A graphic representation of the transition temperatures of the cyano-substituted ligands (compounds 13, 14 and 15) and their copper(II) complexes are shown in figure 5. Complexation of the ligands has resulted in an increase of melting points by 18 to 24 $^{\circ}\text{C}$  and the clearing temperatures are raised by 50 to 47 $^{\circ}\text{C}$ . At very high clearing temperatures (> 270 $^{\circ}\text{C}$ ) thermal decomposition generally occurs.

A graphic representation of the mesomorphic behaviour of three *n*-alkyl-substituted complexes (compounds 26, 27 and 28) and three *n*-alkoxy-substituted chelates (compounds 32, 33 and 34) is shown in figures 6 and 7 respectively. All the six complexes exhibit enantiotropic nematic phases.

We have also investigated the properties of a few palladium(II) complexes of the above discussed  $\beta$ -diketones. The transition temperatures of these are summarized in table 5. It is seen that the cyano-substituted complexes (compounds 35, 36 and 37) do not exhibit any mesomorphism while the corresponding copper(II) chelates

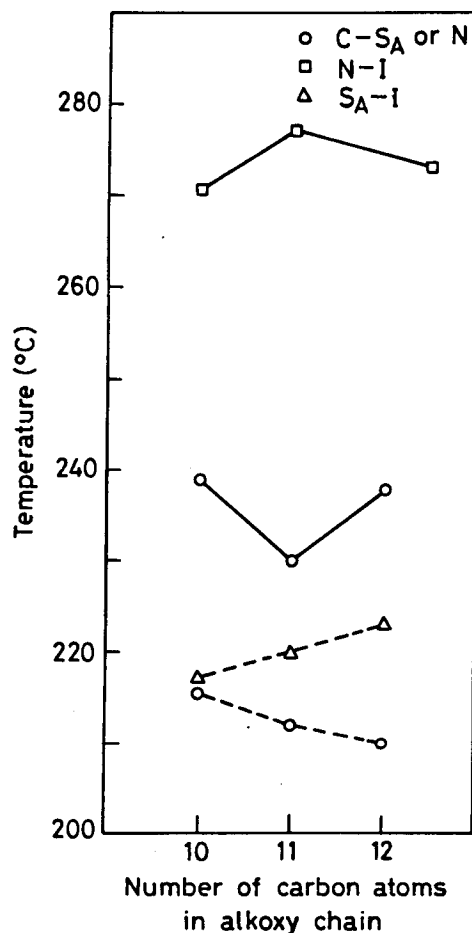


Figure 5. Plot of transition temperatures vs the number of carbon atoms in the chain for the ligands I (dotted lines) and chelates II (solid lines),  $R = OC_nH_{2n+1}$ ,  $n = 10, 11$  and  $12$ ;  $R' = CN$ ;  $M = Cu$ .

do. The atomic radius of palladium is  $137 \text{ \AA}$  which is more than that of copper ( $128 \text{ \AA}$ ). The polarizability of an atom increases with increase in atomic radius (Gray 1962). It is probable that the polarizability of the above palladium complexes increases the intermolecular attractions to such an extent that the melting point increases and no mesophase is observed.

To summarize, the above described  $\beta$ -diketones show interesting behaviour; terminal cyano substitution showed enhanced smectic character and promotes mesomorphism in the compounds. Extension of the core of these compounds results in higher melting and clearing temperatures. On substituting the terminal  $n$ -alkyl chain by  $n$ -alkoxy chain, the melting and clearing temperatures are raised and the smectic A phase of the alkoxy-substituted compounds became thermally more stable. The copper(II) complexes of the above described alkyl and alkoxy ligands exhibit enantiotropic nematic phase.

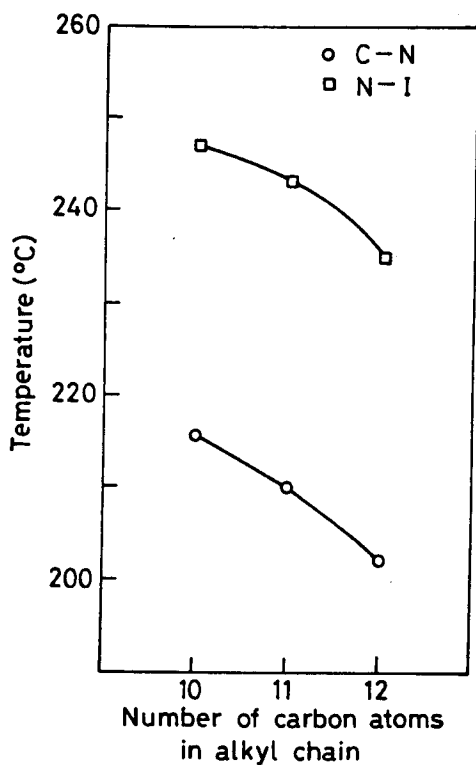


Figure 6. Plot of transition temperatures vs the number of carbon atoms in the chain for the chelates II,  $R = C_nH_{2n+1}$ ,  $n = 10, 11$  and  $12$ ;  $R' = OCH_3$ ;  $M = Cu$ .

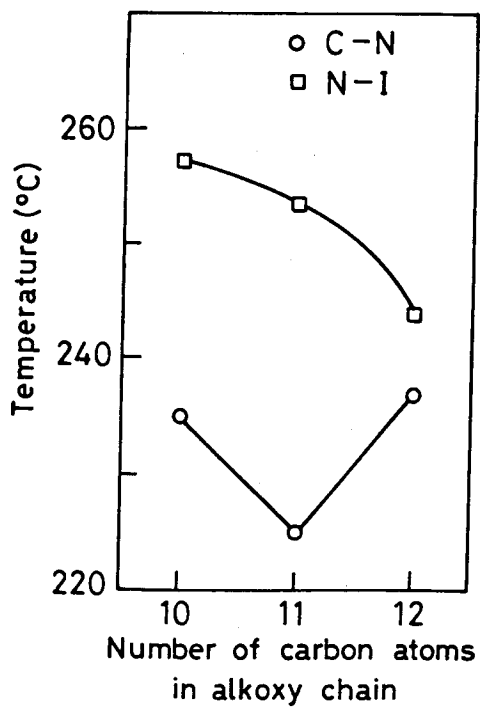
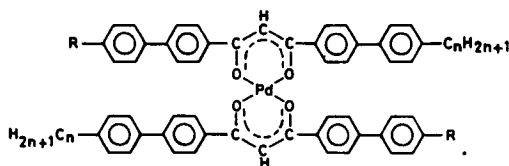


Figure 7. Plot of transition temperatures vs the number of carbon atoms in the chain for the chelates II,  $R = OC_nH_{2n+1}$ ,  $n = 10, 11$  and  $12$ ;  $R' = OCH_3$ ,  $M = Cu$ .

**Table 5.** Mesomorphic transition temperatures (°C) and enthalpies (kcal/mol) of

Compound	n	R	C	N	I
35	10	CN <sup>†</sup>	· 270.0 9.90	—	·
36	11	CN	· 269.5 10.35	—	·
37	12	CN	· 264.0 10.59	—	·
38	10	OCH <sub>3</sub>	· 236.8 5.46	· 237.2*	·
39	11	OCH <sub>3</sub>	· 227.6 5.59	· 227.8*	·
40	12	OCH <sub>3</sub>	· 227.2 5.46	· 227.6*	·

<sup>†</sup> C to C transition was observed at 268.5°C.

\*The enthalpy could not be determined because of partial sample decomposition.

Key: C:crystalline phase; S<sub>C</sub>:smectic C phase; S<sub>A</sub>:smectic A phase;  
N:nematic phase; I:isotropic phase.

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