

Chapter 2

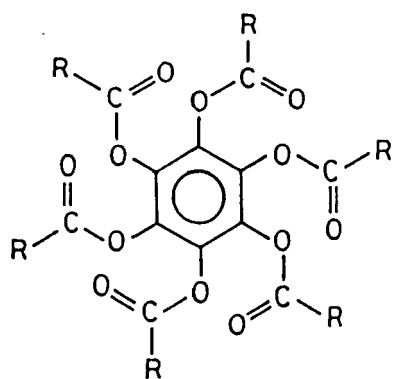
**Synthesis and mesomorphic properties of
1-(4-n-alkylphenyl)-3-(4'-n-alkyloxy-
phenyl)propane-1,3-diones and
their copper(II) complexes**

2.1 A survey of the discotic liquid crystals containing transition metal atoms

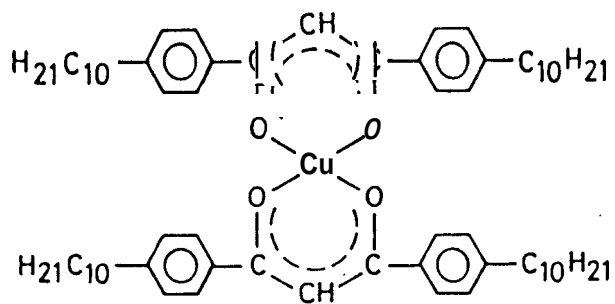
In 1977, it was discovered¹ that pure compounds composed of disc-shaped molecules also form stable thermotropic liquid crystals. The compounds investigated were the hexasubstituted esters of benzene, 2.a. A model for the mesophase formed by these compounds was also proposed² wherein the discs are stacked aperiodically atop one another to form liquid-like columns, the different columns forming a hexagonal array. Thus, the structure had translational order in two dimensions but not in the third. This is the first example to be discovered of a system "melted" in one dimension. This new type of liquid crystal was designated as discotic or columnar liquid crystal.^{3,4} Since then many other pure compounds showing discotic phases have been reported.⁵

The first organometallic disc-like mesogen synthesised was bis(p-n-decylbenzoyl)-methanato copper(II)⁶, the structure of which is shown in 2.b. It showed a single mesophase between 85.5' and 128.5°C. From X-ray diffraction experiments of the above complex, Levelut⁷ deduced that the mesophase is lamellar in nature having a thickness of 29 Å. However, the precise structure could not be determined. Billard⁸ suggested from microscopic observation of defects in the mesomorphic texture of the above complex, that this mesophase may have both columnar and lamellar characteristics.

Piechocki et al.⁹ have reported columnar mesophases obtained from substituted metallophthalocyanines. They have also studied the structural parameters of this mesophase at 80°C from X-ray diffraction experiments. In the small angle region they observed at least four sharp Bragg reflections. Their spacings were exactly in the ratio 1:1 / $\sqrt{3}$:1 / $\sqrt{4}$:1 / $\sqrt{7}$ which was in perfect agreement with a two-



2.a

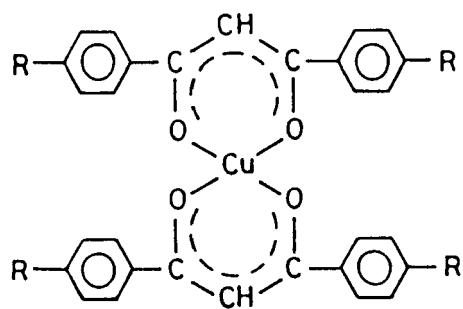


2.b

dimensional hexagonal lattice. Guillon *et al.*¹⁰ have synthesised and studied a series of octasubstituted phthalocyanine derivatives. These compounds contained various metal atoms such as copper, zinc or manganese at the centre of the molecules. All the compounds exhibited a hexagonal columnar mesophase which was stable over a wide range of temperature.

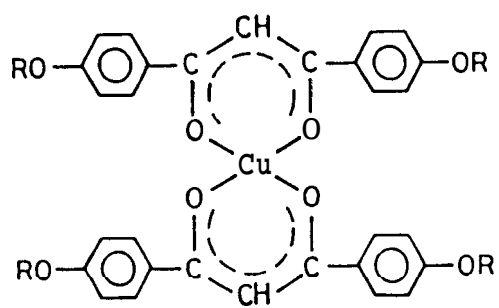
Ohta *et al.*¹¹ have investigated the mesomorphic properties of a series of disc-like complexes, bis[1,3-di(p-n-alkylphenyl)propane-1,3-dionato]copper(II), 2.c. They found that all the complexes from n=4 to n=12 were discogens and that complexes where n=7 and 8 had two discotic mesophases whereas the complex with n=9 had three discotic mesophases. In a later paper Olita *et al.*¹² have reported the synthesis and mesomorphic properties of a series of bis[1,3-di(p-n-alkyloxyphenyl)propane-1,3-dionato]copper(II) complexes, 2.d. They found that each of the complexes from n=3 to n=12 was a discogen exhibiting only one discotic mesophase. For complexes n=3 to n=5 they observed mosaic texture while for complexes n=6 to n=12 a broken fan like texture was observed. They have also established from X-ray diffraction measurements that each of these complexes from n=6 to n=12 exhibits a lamellar phase. They have designated this as discotic lamellar phase (D_L) which is different from the mesophase in 2.b and that the D_L phase has a structure in which the molecules tilt with respect to the layers. The tilt angle of the molecules with respect to the layer normal is about 5° . The detailed X-ray diffraction studies on these complexes were reported by Sakashita *et al.*¹³ and the structure of the discotic lamellar phase deduced from these is shown in figure 2.1.

Giroud *et al.*¹⁴ have examined a series of copper β -diketonates similar to 2.d, but substituted by eight alkyloxy chains. By miscibility studies they established the structure of the mesophase shown by these complexes as hexagonal columnar (D_h).



2.c

$R = C_nH_{2n+1}$



2.d

$R = C_nH_{2n+1}$

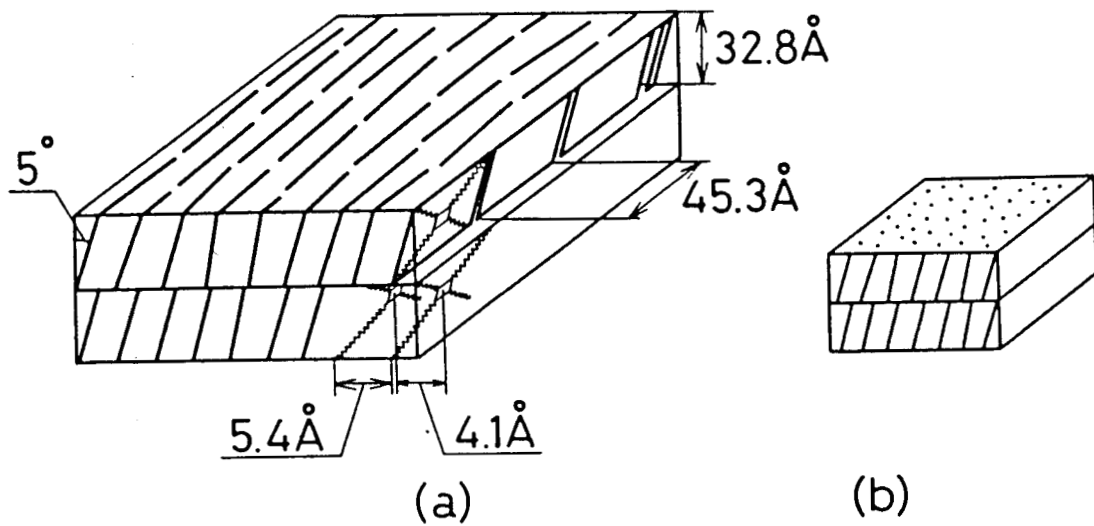


Figure 2.1: Schematic representations of the structures of (a) discotic lamellar phase (D_L) and (b) the classical smectic C phase of rod-like molecules. The layer structure in (a) resembles that in (b) (after Sakashita et al.¹³):

There is one more report by Giroud *et al.*¹⁵ on copper(II) laurate which exhibited a thermotropic columnar mesophase. This mesophase has the characteristics of a hexagonal columnar lattice with a repeat distance of about 20 Å. Each column consists of stacked units with a period of about 4.7 Å. The repeating unit in a column is the binuclear complex $\text{Cu}_2(\text{C}_{11}\text{H}_{23}\text{CO}_2)_4$ which is the first example of a discotic mesogen with only four peripheral chains.

Ohta *et al.*¹⁶ have reported another series of bis(p-n-alkyloxybiphenylbutane-1,3-dionato)copper(II) complexes. A detailed X-ray diffraction study on one of these homologues indicated that the mesophase is discotic rectangular ordered (D_{ro}). They have also concluded that these form dimers in a rectangular columnar array. Ohta *et al.*¹⁷ have also investigated some nickel complexes, viz, tetrakis(n-alkyldithiolato)dinickel(II) and bis(n-alkylxanthato)nickel(II) complexes which exhibited discotic lamellar mesomorphism. They established the structure of the mesophase exhibited by these complexes by X-ray diffraction experiments and further by infrared spectral studies which indicated that this mesophase resembles isotropic liquid more than that of the crystal.

2.2 Results and discussion

As mentioned earlier, two homologous series of copper(II) chelates viz, 2.c and 2.d have been synthesised by Ohta *et al.*^{11,12} from symmetrical ligands. In other words, these chelates have either four identical alkyl or alkyloxy chains as viewed from the central metal atom. So it seemed interesting to study the mesomorphic properties of copper chelates obtained from unsymmetrical ligands. From this point of view, the following series of β -diketones and their copper complexes were prepared.

(i) 1-(4-n-Alkylphenyl)-3-(4'-n-alkyloxyphenyl)propane-1,3-diones (2.e) and

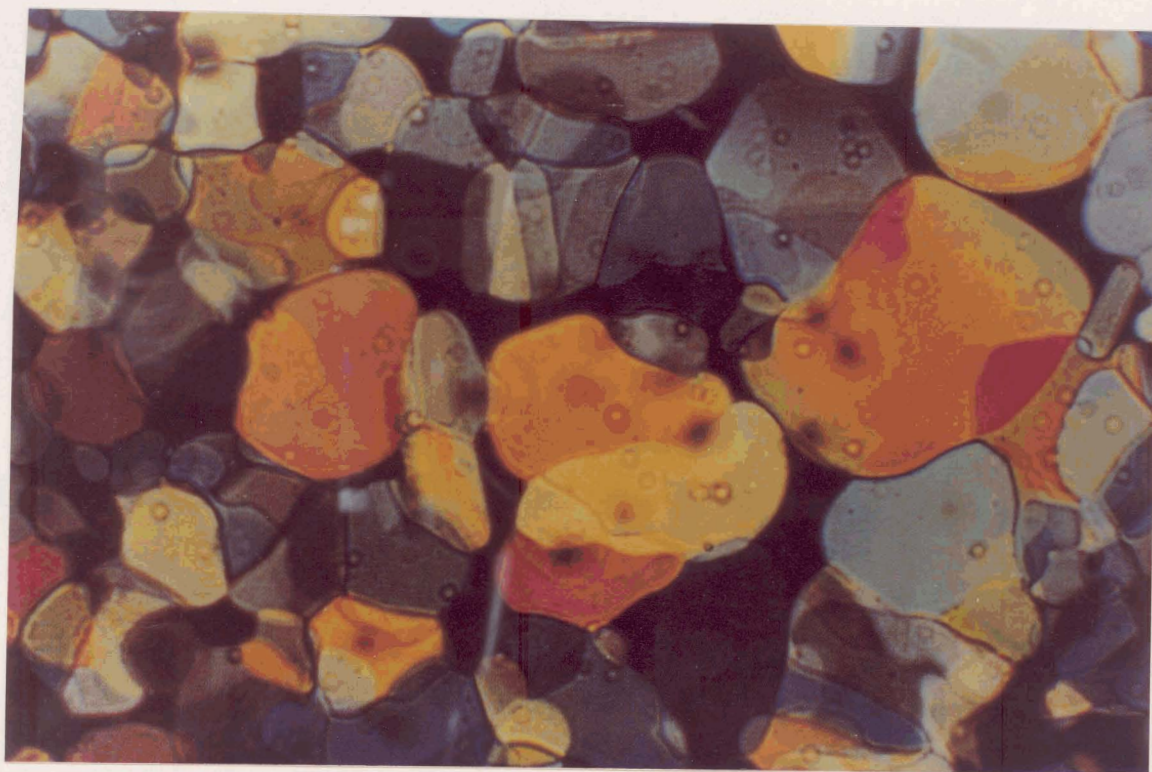


Plate 2.1: The mosaic texture of the mesophase of complex 2.f.7 at 129°C.

chapter 2

(ii) bis[1-(4-n-alkylphenyl)-3-(4'-n-alkyloxyphenyl)propane-1,3-dionato]copper(II) complexes (2.f).

To study the effect of other metal atoms on the mesophase, a few palladium complexes of these diketones were also prepared.

All the compounds were prepared following the schemes shown in figures 2.2 and 2.3. 4-n-Alkylacetophenones were prepared starting from benzene following the standard procedures.¹⁸ Ethyl-4-n-alkyloxybenzoates were prepared starting from ethyl-4-hydroxybenzoate. Alkylation was performed on ethyl-4-hydroxybenzoate using an appropriate n-alkylbromide in ethyl alcohol and sodium ethoxide as a base. The β -diketones were prepared by condensing 4-n-alkylacetophenones with ethyl-4-n-alkyloxybenzoates using sodium hydride as a base, in 1,2-dimethoxyethane. The corresponding copper and palladium complexes were synthesised by treating the ligands with cupric chloride dihydrate and palladium chloride respectively, in the presence of a base.

The transition temperatures and enthalpies associated with them for the ligands 1-(4-n-alkylphenyl)-3-(4'-n-alkyloxyphenyl)propane-1,3-diones are given in table 2.1. Compounds 2.e.1 to 2.e.5 are non-mesomorphic while the remaining exhibit a mesophase. The change from the crystal to the mesophase is accompanied by a small enthalpy as compared to the mesophase \rightarrow isotropic transition. The latter is of the order of 7 to 8 kcal/mol. As such, the isotropic liquid supercools considerably before the appearance of the mesophase. The enthalpy change during this transition is large when compared with the value for other known like transitions of layered mesophases. Also the optical texture observed for the mesophase exhibited by these ligands does not correspond to any of the textures seen for known smectic mesophases. The mesophase is also highly viscous, birefringent and optically biaxial.

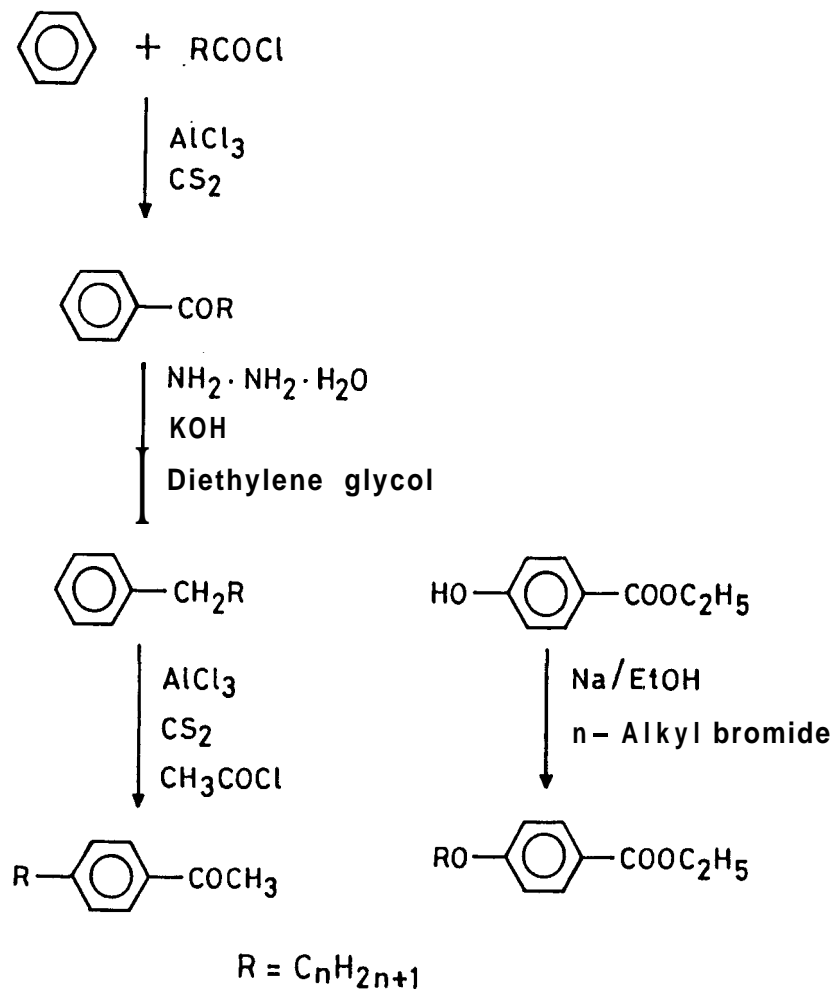


Figure 2.2

Table 2.1

**Transition temperatures (°C) and enthalpies (kcal/mol) for
1-(4-n-alkylphenyl)-3-(4'-n-alkyloxyphenyl)propane-1,3-diones,**

2.e

Compound number	n	C	S	I
2.e.1	4	. 67.5 5.89		
2.e.2	5	. 66.0 5.28		
2.e.3	6	. 68.5 6.60		
2.e.4	7	. 72.5 5.70		
2.e.5	8	. 74.5 6.18		
2.e.6	9	. 50.0 1.90	. 77.0 6.93	
2.e.7	10	. 53.0 2.58	. 78.0 7.85	
2.e.8	11	. 61.5 3.02	. 77.0 7.78	
2.e.9	12	. 62.5 4.17	. 76.5 8.40	

Giroud and Billard¹⁹ and Ohta et al.^{11,20} have prepared a number of β -diketones. They reported that some of these exhibited mesophases of the smectic type. However, except for the derivative 1,3-di(4-n-decylphenyl)propane-1,3-dione,²⁰ which has been tentatively identified as smectic E, the phase types of other compounds have not been established.

The transition temperatures and heats of transitions for bis[1-(4-n-alkylphenyl)-3-(4'-n-alkyloxyphenyl)propane-1,3-dionato]copper(II) complexes are given in table 2.2. Compound 2.f.1 is non-mesogenic while the compounds 2.f.2 to 2.f.4 showed a monotropic mesophase. The remaining homologues which have considerably lower melting points exhibit enantiotropic mesophases. As observed under a polarising microscope, the mesophases are highly ordered and birefringent. Sometimes, on slow cooling of the isotropic liquid they exhibited a mosaic texture which is characteristic of the conventional smectic E phase. A typical texture of this phase is shown in plate 2.1.

Ohta et al.¹² have carried out detailed X-ray measurements on the mesophase exhibited by bis[1,3-di(p-n-alkyloxyphenyl)propane-1,3-dionato]copper(II) complexes, 2.d. They identified the mesophase as a discotic lamellar phase in which the molecules tilt with respect to the layers. Preliminary X-ray studies on the mesophase of one of the copper(II) complexes synthesised by the author, also indicated a layered arrangement of the molecules.

The differential scanning calorimetric data [see table 2.2] indicate that the meso phase \rightarrow isotropic transition enthalpies are lower as compared to the corresponding crystal \rightarrow mesophase / isotropic transition enthalpies, though in a few cases they are about the same. The dsc thermogram for complex 2.f.8 is shown in figure 2.4. A plot of transition temperatures versus the number of carbon atoms in the alkyl

Table 2.2

Transition temperatures (°C) and enthalpies (kcal/mol) for bis[1-(4-n-alkylphenyl)-3-(4'-n-alkyloxyphenyl)propane-1,3-dionato]copper(II),

2.f

Compound number	n	C	D_L	I
2.f.1	4	. 172.5 7.67	-	
2.f.2	5 ⁺	. 158.0 9.66	(. 147.5) 4.59	.
2.f.3	6	. 153.5 9.86	(. 147.0) 9.23	.
2.f.4	7	. 150.3 9.97	(. 145.5) 6.32	.
2.f.5	8	. 80.0 9.47	. 143.0 9.30	.
2.f.6	9	. 96.5 12.75	. 136.5 7.03	.
2.f.7	10	. 94.0 14.94	. 130.5 7.35	.
2.f.8	11	. 82.0 20.38	. 127.0 9.30	.
2.f.9	12	. 81.5 25.05	. 121.0 9.16	.

+Compound 2.f.2 has a crystal → crystal transition at 133.0°C (5.71 kcal/mol).

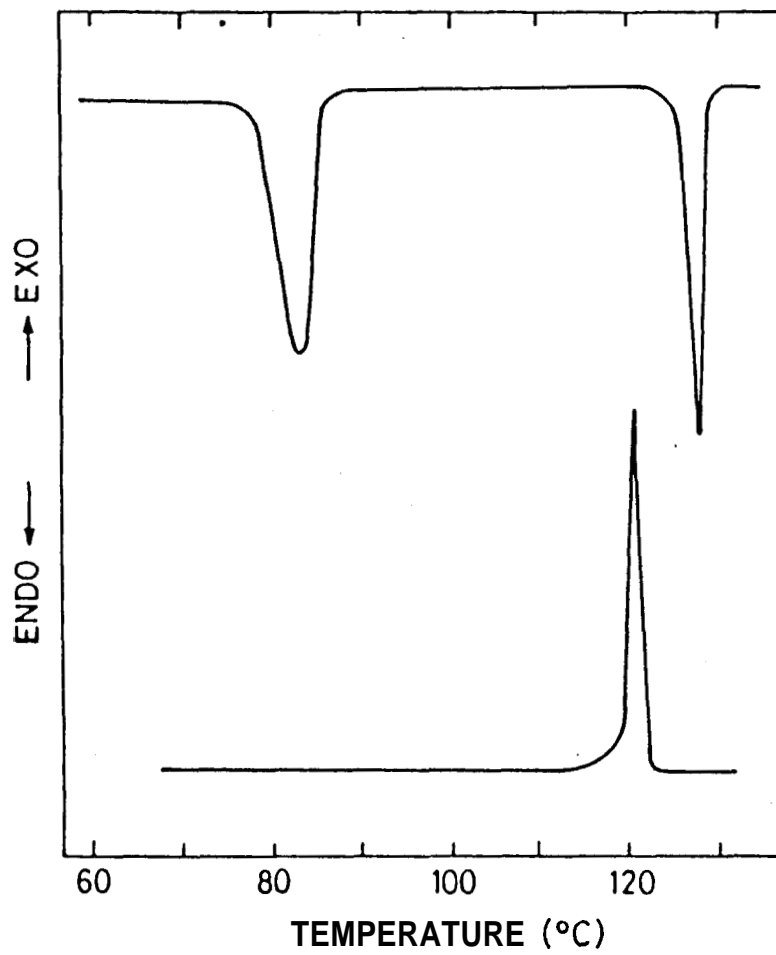


Figure 2.4: The dsc thermogram of compound 2.f.8.

chain is shown in figure 2.5. The mesophase \rightarrow isotropic transition points lie on a reasonably smooth falling curve. Apart from these copper(II) complexes, a few similar palladium(II) chelates have also been synthesised. But they were all found to be non-mesogenic and have melting points higher than those for the corresponding copper(II) chelates.

The chelates in the present study were prepared from unsymmetrical ligands and hence can exist as *cis* or *trans* isomers; *viz*, the two alkyl chains could either be on the same side or on opposite sides of the chelate ring. This can be exemplified by considering the tautomeric forms of the ligands as shown in figure 2.6. In this figure there is one keto and two *enol* forms. These tautomers will be in equilibrium with each other and with a suitable cation such as Cu^{++} can complex to give the chelate. Under slightly basic conditions the enolic forms are favoured and either of these gives the same product namely, the *trans*. However, if these '*enolic*' forms are in a 1:1 mixture then probably the product would be '*cis*'. The single crystal X-ray study of bis[1-(4-n-heptylphenyl)-3-(4'-n-heptyloxyphenyl)propane-1,3-dionato]copper(II) by Usha and Kalyani,²¹ confirmed a *cisoid* form as shown in figure 2.7. It was found that the copper atom is significantly displaced from the plane of the coordinating oxygen atoms, the displacement being 0.027(2) Å. The centrosymmetrically related molecules in the unit cell tend to pair as shown in figure 2.8. Their studies also indicated that the molecular arrangement in the crystal is layer like.

In conclusion, the following generalisations can be made regarding the above copper(II) chelates. The copper(II) complexes, whether substituted symmetrically as in the case of 2.c and 2.d or unsymmetrically as in the case of 2.f, exhibit highly ordered discotic lamellar phase. In the case of unsymmetrically substituted copper(II) complexes, the single crystal X-ray study has confirmed a *cisoid* form for

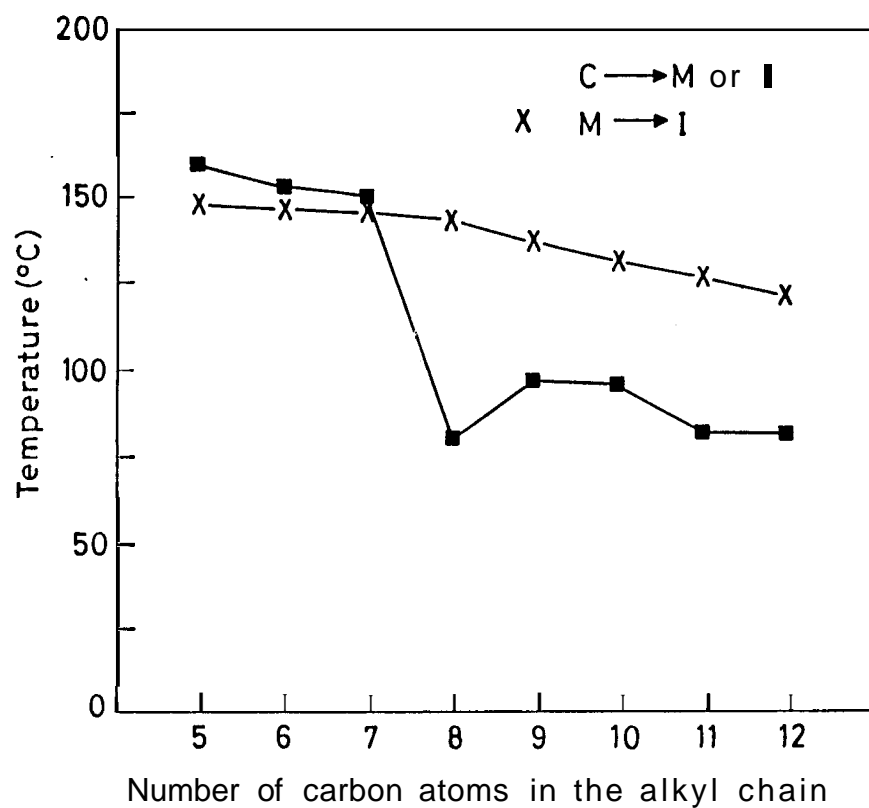


Figure 2.5: A plot of the transition temperatures *versus* the number of carbon atoms in the alkyl chain for series 2.f.

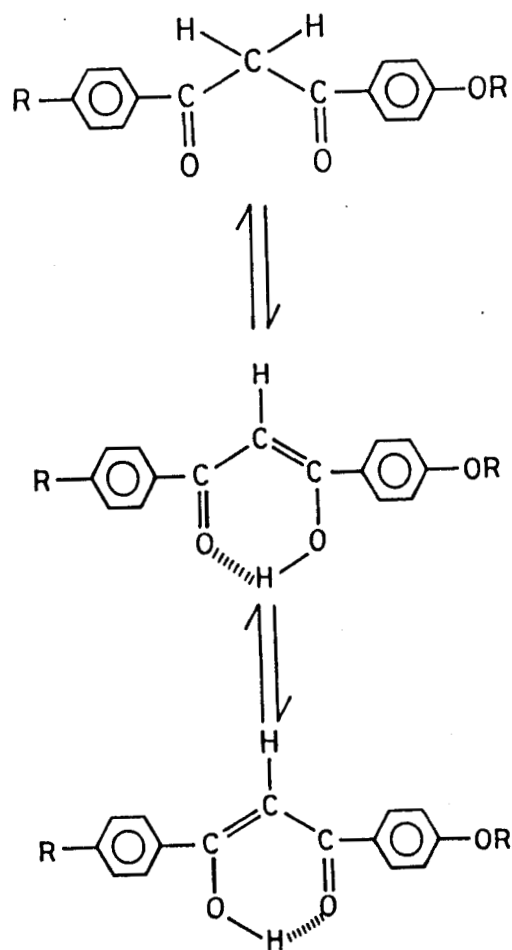


Figure 2.6: Keto-enol tautomerism in β -diketones.

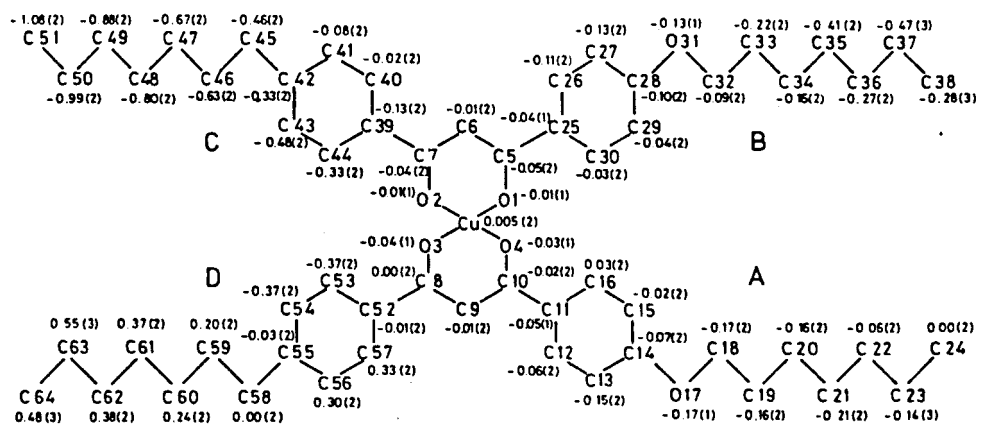


Figure 2.7: The displacement, $\delta/\text{\AA}$ of non-hydrogen atoms from the least squares plane through the eleven atom core of the molecule (after Usha and Kalyani²¹).

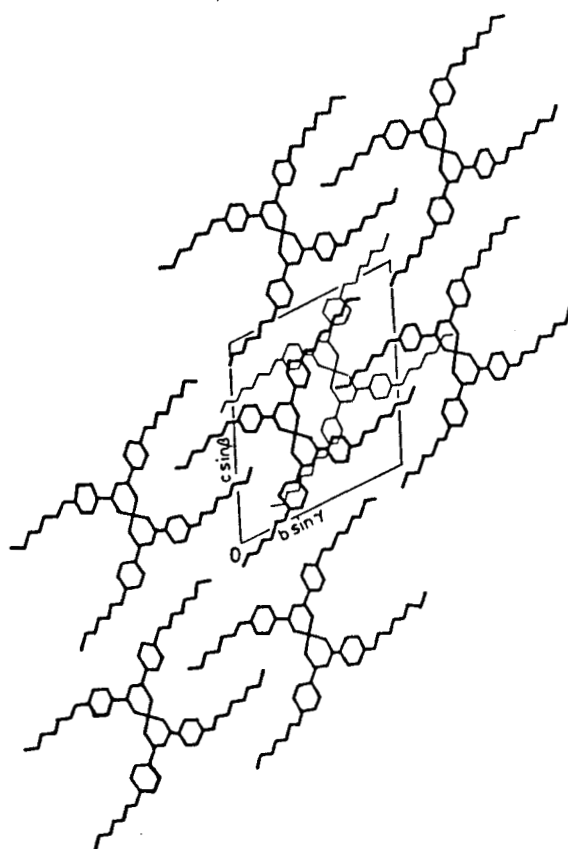


Figure 2.8: Molecular arrangement in the plane perpendicular to the a axis. The thin lines represent the centrosymmetrically related molecule in the unit cell. For the sake of clarity, the translation equivalents of this molecule have been omitted (after Usha and Kalyani²¹).

these chelates. Though, the complexes 2.f are mesogenic, the corresponding palladium(II) complexes are found to be non-mesomorphic. This may be due to the efficient packing of molecules in the crystal lattice of such compounds.

2.3 Experimental

General Methods Of Investigation

All starting materials were purified either by crystallisation or by fractional distillation before use. Anhydrous solvents used were prepared from commercial solvents following the standard procedures. Analytical tlc was carried out using silica gel supplied by BDH India Ltd. and the spots were rendered visible by brief exposure to iodine vapour. Readymade tlc aluminium plates coated with silica gel with a fluorescent indicator manufactured by Fluka AG, Switzerland, were also used. The spots on these plates were rendered visible by exposing them to a DESAGA HP-UVIS lamps at 254 and / or 366nm. Silica gel (60–120 mesh, ACME, India) was used for column chromatography. The solvents used for chromatography were petroleum ether (b.p.60–80°C), chloroform or a mixture of these two solvents unless otherwise stated.

The melting and boiling points reported herein are all corrected. Infrared absorption spectra were recorded on a Shimadzu IR - 435 spectrophotometer, as nujol mull. The proton magnetic resonance spectra were taken on a Bruker WP80 SY FT NMR spectrometer. CDCl_3 was used as a solvent for all the compounds unless otherwise stated. Tetramethylsilane was used as an internal reference standard and chemical shifts are quoted as "delta" (parts per million) downfield from the reference. The ultraviolet and visible absorption spectra were obtained on a Hitachi U - 3200 spectrophotometer. The solvent used for this was chloroform of HPLC grade. Elemental analyses were carried out on a CARLO - ERBA 1106 elemental analyser.

The transition temperatures were determined using a Leitz Laborlux 12 POL polarising microscope equipped with a Mettler FP52 heating stage and a FP5 con-

troller. Thin samples were prepared by sandwiching the compounds between a microscopic glass slide and a cover slip. The enthalpies of transitions were determined from thermograms obtained on a Perkin-Elmer, model DSC - 2 or DSC - 4 differential scanning calorimeter and are reported in kcal/mol. The calorimeters were calibrated using pure indium as a standard and heating and cooling rates of 2°, 5" and 10°C/min. were used.

All the required 4-n-alkylacetophenones and ethyl-4-n-alkyloxybenzoates were prepared following the standard procedures.¹⁸ These have been characterised by their physical constants as well as spectral data. The observed boiling points of these compounds have been given in tables 2.3 and 2.4 respectively.

1-(4-n-Decylphenyl)-3-(4'-n-decyloxyphenyl)propane-1,3-dione:

In a 100 ml two-necked round bottom flask fitted with a reflux condenser and a nitrogen inlet tube was placed a mixture of 4-n-decylacetophenone (2.6 g, 0.01 mol) and ethyl-4-n-decyloxybenzoate (3.06 g, 0.01 mol) in dry 1,2-dimethoxyethane (60 ml). This was stirred magnetically and sodium hydride (0.8 g, 0.02 mol, 60 % in paraffin oil) was added and the mixture refluxed for four hours and cooled. Ice cold dilute hydrochloric acid (20 ml) was added and the mixture extracted with chloroform (3×50 ml). The chloroform solution was washed with water (3×50 ml) and dried (Na₂SO₄). Removal of solvent and chromatography of the residue gave a pale yellow product. This was crystallised from acetonitrile, to constant melting point.

Yield, 2.02 g, (39%); m.p. 53.0°C; IR ν_{max} : 2900, 2800, 1610, 1588, 1470, 1260, 1180, 850 and 780 cm⁻¹; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 375 (19,800), 353 (33,600), 283 (8,700), 265 (9,200), 228 (12,800); NMR δ : 0.85 (t, 6H, 2×-CH₃), 1.0–2.0 (m, 32H, 16×-CH₂), 2.7 (t, 2H, arCH₂), 4.0 (t, 2H, arOCH₂), 6.75 (s, 1H, -C=C_H), 6.85–7.75 (m, 8H, arH), 17.0 (s, 1H, =C-OH).

Anal. calcd. for C₃₅H₅₂O₃,

C, 80.77 ; H, 10.0 %

Found: C, 80.90 ; H, 10.14 % .

The physical data of the other 1-(4-n-alkylphenyl)-3-(4'-n-alkyloxyphenyl)prop-

Table 2.3
Physical constants for 4-n-alkylacetophenones,
 $C_nH_{2n+1} \cdot C_6H_4 \cdot COCH_3$

n	Observed b.p.^{°C}/mm	Reported b.p.^{°C}/mm	Reference
4	110-112/1	101-102/1.5	22
5	120-123/1	106-109/1.1	23
6	125-127/1	120/1	22
7	140/2	165-175/10	24
8	170/2	149-150/1	22
9	147-150/1	159-162/2-3	22
11	195-197/2	180-185/3	25
12	205-207/2	47-48(m.p)	22

Table 2.4

Physical constants for ethyl-4-n-alkoxybenzoates,



n	Boiling point(°C)/mm
1	88-90/1
2	130-132/1
3	160-162/2
4	137-140/2
5	148-150/2
6	148-150/1
7	165-168/2
8	152-155/1
9	185-188/2
10	180/1
11	205-207/2
12	193/1

chapter 2

ane-1,3-diones are given below:

1-(4-n-Butylphenyl)-3-(4'-n-butyloxyphenyl)propane-1,3-dione:

Yield, 45%; m.p. 67.5°C; IR ν_{max} : 2900, 2850, 1608, 1590, 1470, 1260, 1180, 850 and 780 cm^{-1} ; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 375 (19,700), 353 (34,800), 283 (9,200), 265 (9,800), 228 (14,600); NMR δ : 0.85 (t, 6H, 2 \times -CH₃), 1.0–2.0 (m, 8H, 4 \times -CH₂), 2.65 (t, 2H, arCH₂), 3.95 (t, 2H, arOCH₂), 6.7 (s, 1H, -C=CH), 6.8–8.0 (m, 8H, arH), 17.15 (s, 1H, =C-OH).

Anal. calcd. for C₂₃H₂₈O₃,

C, 78.41 ; H, 7.95 %

Found: C, 78.98 ; H, 8.08 % .

1-(4-n-Pentylphenyl)-3-(4'-n-pentyloxyphenyl)propane-1,3-dione:

Yield 47%; m.p. 66.0°C; IR ν_{max} : 2900, 2850, 1610, 1590, 1475, 1260, 1180, 850 and 780 cm^{-1} ; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 375 (20,300), 353 (35,300), 283 (9,100), 264 (9,600), 228 (13,600); NMR δ : 0.9 (t, 6H, 2 \times -CH₃), 1.0–2.0 (m, 12H, 6 \times -CH₂), 2.7 (t, 2H, arCH₂), 4.0 (t, 2H, arOCH₂), 6.75 (s, 1H, -C=CH), 6.85–8.0 (m, 8H, arH), 17.1 (s, 1H, =C-OH).

Anal. calcd. for C₂₅H₃₂O₃,

C, 78.95 ; H, 8.4 %

Found: C, 79.33 ; H, 8.59 % .

1-(4-n-Hexylphenyl)-3-(4'-n-hexyloxyphenyl)propane-1,3-dione:

Yield, 46%; m.p. 68.5°C; IR ν_{max} : 2900, 2850, 1605, 1588, 1470, 1260, 1180, 860 and 780 cm^{-1} ; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 375 (20,900), 353 (35,600), 282 (9,600), 265 (10,300), 228 (14,400); NMR δ : 0.9 (t, 6H, 2 \times -CH₃), 1.0–2.0 (m, 16H, 8 \times -CH₂), 2.65

(t, 2H, arCH₂), 4.0 (t, 2H, arOCH₂), 6.75 (s, 1H, -C=CH), 6.8–8.0 (m, 8H, arH), 17.1 (s, 1H, =C-OH).

Anal. calcd. for C₂₇H₃₆O₃,

C, 79.41 ; H, 8.82 %

Found: C, 79.34 ; H, 9.01 % .

1-(4-n-Heptylphenyl)-3-(4'-n-heptyloxyphenyl)propane-1,3-dione:

Yield, 42%; m.p. 72.5°C; IR ν_{max} : 2900, 2850, 1606, 1588, 1470, 1260, 1180, 850 and 780 cm⁻¹; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 375 (22,800), 353 (38,400), 284 (10,800), 265 (11,600), 229 (16,500); NMR δ : 0.85 (t, 6H, 2×-CH₃), 1.0–2.0 (m, 20H, 10×-CH₂), 2.65 (t, 2H, arCH₂), 3.95 (t, 2H, arOCH₂), 6.8 (s, 1H, -C=CH), 6.8–8.0 (m, 8H, arH), 17.05 (s, 1H, =C-OH).

Anal. calcd. for C₂₉H₄₀O₃,

C, 79.81 ; H, 9.17 %

Found: C, 80.08 ; H, 9.29 % .

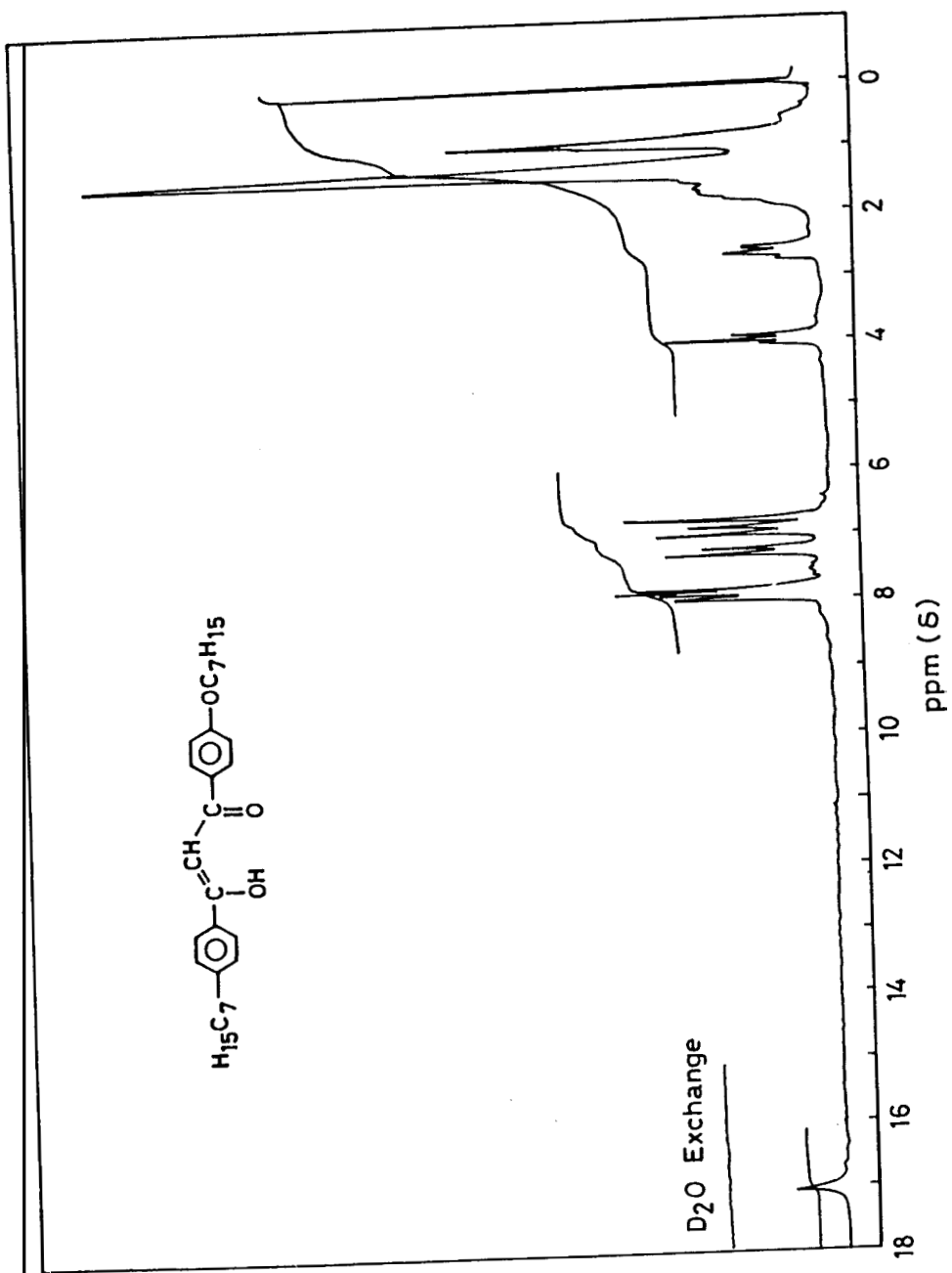
1-(4-n-Octylphenyl)-3-(4'-n-octyloxyphenyl)propane-1,3-dione:

Yield, 44%; m.p. 74.5°C; IR ν_{max} : 2900, 2800, 1608, 1588, 1480, 1260, 1180, 850 and 780 cm⁻¹; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 375 (20,300), 354 (34,100), 283 (8,700), 265 (9,200), 228 (13,100); NMR δ : 0.85 (t, 6H, 2×-CH₃), 1.0–2.0 (m, 24H, 12×-CH₂), 2.65 (t, 2H, arCH₂), 4.0 (t, 2H, arOCH₂), 6.8 (s, 1H, -C=CH), 6.85–8.0 (m, 8H, arH), 17.1 (s, 1H, =C-OH).

Anal. calcd. for C₃₁H₄₄O₃,

C, 80.17 ; H, 9.48 %

Found: C, 80.02 ; H, 9.57 % .



¹H NMR spectrum for compound 2.e.4.

1-(4-n-Nonylphenyl)-3-(4'-n-nonyloxyphenyl)propane-1,3-dione:

Yield, 46%; m.p. 50.0°C; IR ν_{max} : 2950, 2800, 1608, 1588, 1480, 1250, 1180, 850 and 780 cm^{-1} ; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 376 (20,500), 353 (35,700), 285 (10,400), 262 (11,200), 228 (15,700); NMR δ : 0.85 (t, 6H, 2 \times -CH₃), 1.0–2.0 (m, 28H, 14 \times -CH₂), 2.65 (t, 2H, arCH₂), 4.0 (t, 2H, arOCH₂), 6.75 (s, 1H, -C=CH₂), 6.8–8.0 (m, 8H, arH), 17.05 (s, 1H, =C-OH).

Anal. calcd. for C₃₃H₄₈O₃,

C, 80.48 ; H, 9.75 %

Found: C, 80.52 ; H, 9.90 % .

1-(4-n-Undecylphenyl)-3-(4'-n-undecyloxyphenyl)propane-1,3-dione:

Yield, 47%; m.p. 61.5°C; IR ν_{max} : 2950, 2800, 1608, 1588, 1480, 1250, 1180, 850 and 780 cm^{-1} ; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 376 (19,900), 354 (35,600), 285 (9,300), 264 (10,300), 227 (14,500); NMR δ : 0.9 (t, 6H, 2 \times -CH₃), 1.0–2.0 (m, 36H, 18 \times -CH₂), 2.7 (t, 2H, arCH₂), 4.0 (t, 2H, arOCH₂), 6.7 (s, 1H, -C=CH), 6.8–8.0 (m, 8H, arH), 17.1 (s, 1H, =C-OH).

Anal. calcd. for C₃₇H₅₆O₃,

C, 81.02 ; H, 10.22 %

Found: C, 81.02 ; H, 10.39 % .

1-(4-n-Dodecylphenyl)-3-(4'-n-dodecyloxyphenyl)propane-1,3-dione:

Yield, 41%; m.p. 62.5°C; IR ν_{max} : 2900, 2850, 1610, 1588, 1480, 1250, 1180, 850 and 780 cm^{-1} ; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 376 (20,800), 353 (36,100), 285 (9,900), 265 (10,600), 228 (15,000); NMR δ : 0.85 (t, 6H, 2 \times -CH₃), 1.0–2.0 (m, 40H, 20 \times -CH₂), 2.7 (t, 2H, arCH₂), 4.0 (t, 2H, arOCH₂), 6.75 (s, 1H, -C=CH), 6.85–8.0 (m, 8H, arH), 17.05 (s, 1H, =C-OH).

chapter 2

Anal. calcd. for $C_{39}H_{60}O_3$,

C, 81.25 ; H, 10.41 %

Found: C, 80.98 ; H, 10.62 % .

Bis[1-(4-n-decylphenyl)-3-(4'-n-decyloxyphenyl)propane-1,3-dionato]-copper(II):

A mixture of 1-(4-n-decylphenyl)-3-(4'-n-decyloxyphenyl)propane-1,3-dione (1.02 g, 2 mmol), powdered potassium hydroxide (0.112 g, 2 mmol) and ethyl alcohol (10 ml) were warmed until the solution became clear. To this was added a solution of cupric chloride dihydrate (0.17 g, 1 mmol) in ethyl alcohol (5 ml). The mixture became dark green and precipitation occurred immediately. This was stirred for four hours at room temperature and filtered. The green precipitate was collected, dissolved in chloroform (75 ml), washed with water (3x50 ml) and dried (Na_2SO_4). Removal of solvent and crystallisation of the residue from butan-2-one afforded green crystals of the complex.

Yield, 0.7 g, (64%); IR ν_{max} : 2950, 2800, 1608, 1590, 1485, 1385, 1175 and 780 cm^{-1} ; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 383 (38,000), 358 (65,500), 303 (38,200), 275 (32,500).

Anal. calcd. for $C_{70}H_{102}O_6Cu$,

C, 76.25 ; H, 9.26 %

Found: C, 76.05 ; H, 9.58% .

The physical data of the other bis[1-(4-n-alkylphenyl)-3-(4'-n-alkyloxyphenyl)propane-1,3-dionato]copper(II) complexes are given below:

Bis[1-(4-n-butylphenyl)-3-(4'-n-butyloxyphenyl)propane-1,3-dionato]-copper(II):

Yield, 65%; m.p. 172.5°C; IR ν_{max} : 2950, 2800, 1607, 1588, 1485, 1385, 1175 and 780 cm^{-1} ; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 383 (36,500), 357 (64,700) 303 (37,000), 275 (31,100).

Anal. calcd. for $\text{C}_{46}\text{H}_{57}\text{O}_6\text{Cu}$,

C, 72.10 ; H, 7.05 %

Found: C, 71.84 ; H, 7.09 % .

Bis[1-(4-n-pentylphenyl)-3-(4'-n-pentyloxyphenyl)propane-1,3-dionato]-copper(II):

Yield, 64%; m.p. 158.0°C; IR ν_{max} : 2950, 2800, 1608, 1588, 1485, 1385, 1175 and 780 cm^{-1} ; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 384 (33,900) 358 (61,500) 304 (36,300), 274 (29,900).

Anal. calcd. for $\text{C}_{50}\text{H}_{62}\text{O}_6\text{Cu}$,

C, 73.03 ; H, 7.54 %

Found: C, 73.15 ; H, 7.70 % .

Bis[1-(4-n-hexylphenyl)-3-(4'-n-hexyloxyphenyl)propane-1,3-dionato]-copper(II):

Yield, 67%; m.p. 153.5°C; IR ν_{max} : 2950, 2800, 1606, 1588, 1485, 1385, 1175 and 780 cm^{-1} ; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 384 (34,400) 358 (63,100), 304 (36,600), 274 (29,400).

chapter 2

Anal. calcd. for $C_{54}H_{70}O_6Cu$,

C, 73.84 ; H, 8.20 %

Found: C, 73.90 ; H, 8.19 % .

Bis[1-(4-n-heptylphenyl)-3-(4'-n-heptyloxyphenyl)propane-1,3-dionato]-copper(II):

Yield, 68%; m.p. 150.5°C; IR ν_{max} : 2950, 2800, 1608, 1588, 1485, 1380, 1175 and 780 cm^{-1} ; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 384 (35,700), 358 (65,000), 304 (38,000), 274 (31,100).

Anal. calcd. for $C_{58}H_{78}O_6Cu$,

C, 74.55 ; H, 8.35 %

Found: C, 74.17 ; H, 8.59 % .

Bis[1-(4-n-octylphenyl)-3-(4'-n-octyloxyphenyl)propane-1,3-dionato]-copper(II):

Yield, 66%; m.p. 80.0°C; IR ν_{max} : 2950, 2800, 1608, 1590, 1485, 1380, 1175 and 780 cm^{-1} ; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 386 (34,800), 358 (68,000), 304 (39,300), 275(32,500).

Anal. calcd. for $C_{62}H_{86}O_6Cu$,

C, 75.18 ; H, 8.69 %

Found: C, 75.05 ; H, 8.78 % .

Bis[1-(4-n-nonylphenyl)-3-(4'-n-nonyloxyphenyl)propane-1,3-dionato]-copper(II):

Yield, 68%; m.p. 96.5°C; IR ν_{max} : 2950, 2800, 1608, 1590, 1485, 1380, 1175 and 780 cm^{-1} ; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 383 (36,600), 359 (65,500), 304 (36,400), 277 (31,000).

chapter 2

Anal. calcd. for $C_{66}H_{94}O_6Cu$,

C, 75.75 ; H, 8.99 %

Found: C, 75.87 ; H, 9.15 % .

Bis [1-(4-n-undecylphenyl)-3-(4'-n-undecyloxyphenyl)propane-1,3-dionato]copper(II):

Yield, 65%; m.p.82.0°C; IR ν_{max} : 2950, 2800, 1607, 1588, 1480, 1380, 1175 and 780 cm^{-1} ; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 385 (34,600), 358 (63,800), 305 (36,700), 276 (30,000).

Anal. calcd. for $C_{74}H_{110}O_6Cu$,

C, 76.71 ; H, 9.50 %

Found: C, 77.04 ; H, 9.66 % .

Bis [1-(4-n-dodecylphenyl)-3-(4'-n-dodecyloxyphenyl)propane-1,3-dionato]copper(II):

Yield, 70%; m.p.81.5°C; IR ν_{max} : 2900, 2800, 1608, 1590, 1480, 1380, 1175 and 780 cm^{-1} ; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 384 (34,600), 358 (63,500), 304 (36,400), 276 (30,100).

Anal. calcd. for $C_{78}H_{118}O_6Cu$,

C, 77.13 ; H, 9.72 %

Found: C, 77.29 ; H, 10.03 % .

Bis[1-(4-n-decylphenyl)-3-(4'-n-decyloxyphenyl)propane-1,3-dionato]-palladium(II):

A mixture of 1-(4-n-decylphenyl)-3-(4'-n-decyloxyphenyl)propane-1,3-dione (1.04 g, 2 mmol), palladium chloride (0.195 g, 1.1 mol), anhydrous potassium carbonate (0.414 g, 3mmol) and dry acetonitrile (40 ml) was stirred and refluxed for eighteen hours, cooled, and filtered. The yellow precipitate was collected, dissolved in chloroform (150 ml), washed with water (3x100 ml) and dried (Na_2SO_4). Removal of solvent and crystallisation of the residue from 1,4-dioxane gave greenish yellow crystals of the complex.

Yield, 0.72 g, (63%); m.p. 149.5°C; IR ν_{max} : 2900, 2800, 1615, 1590, 1470, 1360, 1170 and 780 cm^{-1} ; UV-Vis: $\lambda_{\text{max}}^{\text{CHCl}_3}$ (ϵ): 402 (22,200), 377 (37,900), 312 (52,800), 272 (31,900), 240 (34,700); NMR δ : 0.9 (t, 12H, 4 \times -CH₃), 1.1–2.0 (m, 64H, 32 \times -CH₂), 2.7 (t, 4H, 2 \times arCH₂), 4.0 (t, 4H, 2 \times arOCH₂), 6.75 (s, 2H, 2 \times -C=CH), 6.85–8.1 (m, 16H, arH).

Anal. calcd. for $\text{C}_{70}\text{H}_{102}\text{O}_6\text{Pd}$,

C, 73.40 ; H, 8.91%

Found: C, 73.61 ; H, 9.07 % .

The physical data of the other bis[1-(4-n-alkylphenyl)-3-(4'-n-alkyloxyphenyl)propane-1,3-dionato]palladium(II) complexes are given below:

Bis[1-(4-n-undecylphenyl)-3-(4'-n-undecyloxyphenyl)propane-1,3-dionato]palladium(II):

Yield, 58% ; m.p. 148.0°C; IR ν_{max} : 2900, 2800, 1610, 1590, 1470, 1360, 1170 and 780 cm^{-1} ; UV-Vis: $\lambda_{\text{max}}^{\text{CHCl}_3}$ (ϵ): 402 (22,900), 377 (38,600), 313 (53,700), 272 (32,100), 241 (33,600); NMR δ : 0.9 (t, 12H, 4 \times -CH₃), 1.1–2.0 (m, 72H, 36 \times -CH₂),

2.7 (t, 4H, 2×arCH₂), 4.0 (t, 4H, 2×arOCH₂), 6.75 (s, 2H, 2×-C=CH), 6.85–8.1 (m, 16H, arH).

Anal. calcd. for C₇₄H₁₁₀O₆Pd,

C, 73.97 ; H, 9.16 %

Found: C, 73.75 ; H, 9.39 % .

Bis[1-(4-n-dodecylphenyl)-3-(4'-n-dodecyloxyphenyl)propane-1,3-dionato]palladium(II):

Yield, 49% ; m.p. 144.0°C; IR ν_{max} : 2900, 2800, 1608, 1590, 1475, 1365, 1170 and 780 cm⁻¹; UV-Vis: $\lambda_{max}^{CHCl_3}$ (ϵ): 403 (21,400), 377 (36,600) 313 (50,900), 271 (30,700), 241 (33,000) **NMR** δ : 0.9 (t, 12H, 4×-CH₃), 1.1–2.0 (m, 80H, 40×-CH₂), 2.7 (t, 4H, 2×arCH₂), 4.0 (t, 4H, 2×arOCH₂), 6.75 (s, 2H, 2×-C=CH), 6.85–8.1 (m, 16H, arH).

Anal. calcd. for C₇₈H₁₁₈O₆Pd,

C, 74.49 ; H, 9.39 %

Found: C, 74.91 ; H, 9.65 % .

References

- [1] S. Chandrasekhar, B.K. Sadashiva and K.A. Suresh, *Pramana*, **9**, 471 (1977).
- [2] S. Chandrasekhar, B.K. Sadashiva, K.A. Suresh, N.V. Madhusudana, S. Kumar, R. Shashidhar and G. Venkatesh, *J. Phys. (Paris)*, **40**, C3-120 (1979).
- [3] W. Helfrich, *J. Phys. (Paris)*, **40**, C3-105 (1979).
- [4] W. Helfrich, *Proc. Int. Liq. Cryst. Conf.*, Bangalore, Dec.1979, p.7.
- [5] S. Chandrasekhar, "Advances in Liquid crystals", Vol. 5, Ed. G.H. Brown (Academic press, 1982) p. 47.
- [6] A.M. Giroud-Godquin and J. Billard, *Mol. Cryst. Liq. Cryst.*, **66**, 147 (1981).
- [7] A.M. Levelut, *J. Chim. Phys.*, **80**, 149 (1983).
- [8] J. Billard, *C. R. Acad. Sc. Paris*, **299**, 905 (1984).
- [9] C. Piechocki, J. Simon, A. Skoulios, D. Guillon and P. Weber, *J. Am. Chem. Soc.*, **104**, 5245 (1982).
- [10] D. Guillon, P. Weber, A. Skoulios, C. Piechocki and J. Simon, *Mol. Cryst. Liq. Cryst.*, **130**, 223 (1985).
- [11] K. Ohta, H. Muroki, A. Takagi, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, **135**, 247 (1986).
- [12] K. Ohta, H. Muroki, A. Takagi, K. Ichihatada, H. Ema, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, **140**, 131 (1986).

- [13] H. Sakashita, A. Nishitani, Y. Sumiya, H. Terauchi, K. Ohta and I. Yamamoto, *Mol. Cryst. Liq. Cryst.*, 163, 211 (1988).
- [14] A.M. Godquin-Giroud, G. Sigaud, M.F. Achard and F. Hardouin, *J. Phys. Lett.*, 45, L-387 (1984); A.M. Giroud-Godquin, M.M. Gauthier, G. Sigaud, F. Hardouin and M.F. Achard, *Mol. Cryst. Liq. Cryst.*, 132, 35 (1986).
- [15] A.M. Godquin-Giroud, J.C. Marchon, D. Guillon and A. Skoulios, *J. Phys. Lett.*, 45, L-681 (1984).
- [16] K. Ohta, O. Takenaka, H. Hasebe, Y. Morizumi, T. Fujimoto and I. Yamamoto, *Mol. Cryst. Liq. Cryst.*, 195, 135 (1991).
- [17] K. Ohta, H. Ema, I. Yamamoto and K. Matsuzaki, *Liq. Cryst.*, 3, 1671 (1988).
- [18] Vogel's Textbook of Practical Organic *Chemistry*, Fourth Edition (Longman, 1978).
- [19] A.M. Giroud-Godquin and J. Billard, *Mol. Cryst. Liq. Cryst.*, 97, 287 (1983).
- [20] K. Ohta, H. Muroki, K. Hatada, A. Takagi, H. Ema, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, 140, 163 (1986).
- [21] K. Usha and K. Vijayan, *Liq. Cryst.*, 12, 137 (1992).
- [22] C.G. Overberger, C. Frazier, J. Mandelman and H. Smith, *J. Amer. Chem. Soc.*, 75, 3326 (1953).
- [23] J. Van der Veen, W.H. de Jeu, A.H. Grobben and J. Boven, *Mol. Cryst. Liq. Cryst.*, 17, 291 (1972).
- [24] M. Sulzbacher and E. Bergmann, *J. Org. Chem.*, 13, 303 (1948).

[25] **B.K. Sadashiva, Ph.D. Thesis, Bangalore University, Bangalore, 1979.**