CHAPTER II

Synthesis and mesomorphic properties of

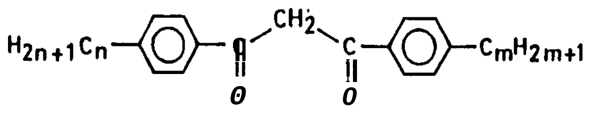
i) [1-(4-n-dodecylbiphenyl)-3-($4''$-substituted-phenyl)propane]-1,3-diones, their copper(II) and palladium(II) complexes, and

ii) a homologous series of [I-(4-n-alkylbipheny1)-3-(4"-chlorophenyl) propane]-1,3-diones

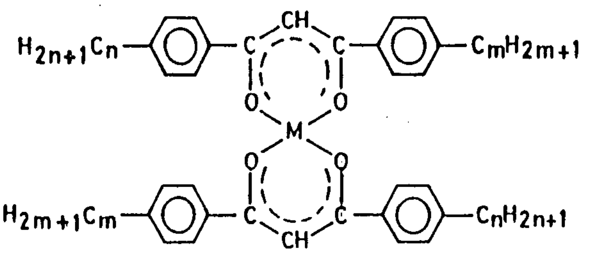
2.1 A brief survey of the mesogenic properties of aryl β-diketones and their metal chelates

As pointed out in the previous chapter, substituted β-diketones have been employed widely as ligands for obtaining mesomorphic derivatives because they are easy to synthesise and have a great ability to complex with various metal ions. However, only square planar and square pyramidal coordinate geometries have so far been found for the metals in mesogenic metallo β-diketonates. When appropriate substituents are present, in copper(II) β-diketonates, discotic, nematic and lamellar mesophases have been found. The metal atoms used in liquid crystalline β-diketonates reported so far are copper,^{1} palladium,^{2}, iron^3, nickel^1 and vanadium.'' Copper(II) and oxovanadium(IV) complexes have unpaired electrons (d orbitals) and exhibit paramagnetic properties. All these metal complexes are coloured materials.

The liquid crystalline properties of compounds containing a β-diketone group have been investigated only recently. The first report of such a compound was on 1,3-di(p-n-decylphenyl)propane-1,3-dione (2.1a) and its copper(II) and nickel(II) complexes compound (2.1b) prepared by Giroud and Billard,^{1,5} who concluded that for β-diketones only those compounds having more than 18 carbon atoms in the side chains exhibit a mesophase.



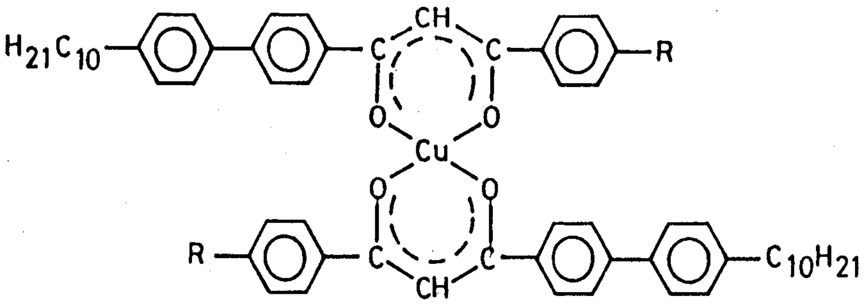
2.1a



2.1b

M = Cu or Ni
n = 7,8,9,10,12
m = 7,9,10,12,13

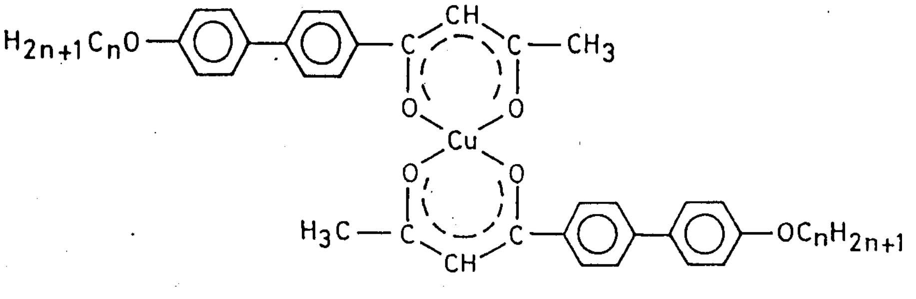
Based on the texture exhibited by these ligands, the phase was tentatively identified as smectic E (S_E) phase. The copper(II) complexes exhibited a very organised discotic phase and the clearing enthalpy was greater than the melting enthalpy. It has a two fold molecular symmetry. The corresponding nickel β-diketonate [2.1b, $n=m=10$] was found to be non-mesomorphic. Ohta *et al.*[6-11] prepared a number of β-diketones and their Cu complexes. They observed polymorphism and multiple melting behaviour on heating the complexes. Giroud *et al.*[12] have obtained a hexagonal columnar mesophase D_h in some transition metal complexes. This is believed to be the first observation of a columnar mesophase D_h in a compound consisting of a non-symmetrical surrounding of paraffin chains. Chandrasekhar *et al.*[13] reported a series of bis[1-(4-n-decylbiphenyl)-3-(4″-substitutedphenyl)propane -1,3-dionato]copper(II), compound (2.2), in order to investigate the type of mesophases by bridging a gap between disc-like and rod-like molecules.



$R = CH_3, C_2H_5, OCH_3,$
OC_2H_5 or OC_3H_7.

2.2

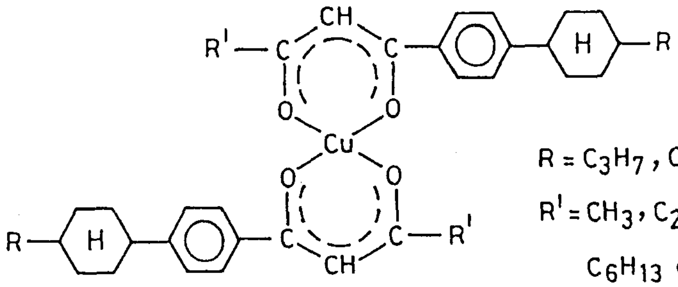
These complexes exhibited a monotropic nematic phase and constitute the first examples of paramagnetic nematic liquid crystals. In contrast to these compounds, the copper(II) β-diketonates which are substituted by two O-alkylated biphenyl moieties as in compound (2.3) exhibited discotic mesophases[15] with the melting point in the range of 127 to 193°C and the corresponding β-diketones showed smectic E phase



$n = 8-12, 16, 18$

2.3

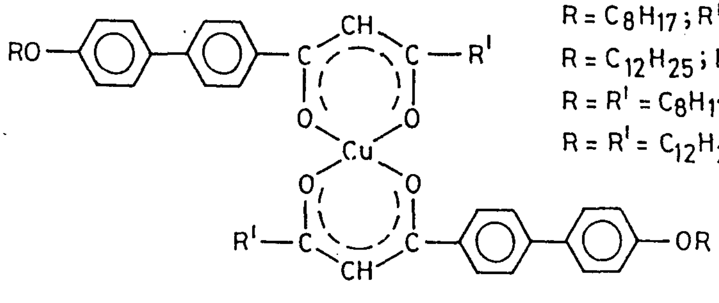
with multiple melting behavior.[16] Muhlberger and Haase[17] synthesised a series of bis{1-[*trans*-(4-n-alkylcyclohexyl)phenyl]-3-alkylpropane-1,3-dionato}copper(II) complexes [Compound (2.4)] in an attempt to obtain enantiotropic nematic phase but most of these complexes exhibited a monotropic nematic phase.



$R = C_3H_7, C_5H_{11}, C_7H_{15}$
$R' = CH_3, C_2H_5, C_3H_7, C_5H_{11}$
C_6H_{13} or C_8H_{17}

2.4

To investigate the effect of a slight change in the molecular structure on the mesophase, Ohta *et al.*[18] synthesised a series of bis[1-(p-n-alkoxybiphenyl)-3-alkyl propane-1,3-dionato]copper(II) complexes [compound (2.5)].



$R = R' = C_4H_9$
$R = C_8H_{17}; R' = C_4H_9$
$R = C_{12}H_{25}; R' = C_4H_9$
$R = R' = C_8H_{17}$
$R = R' = C_{12}H_{25}$

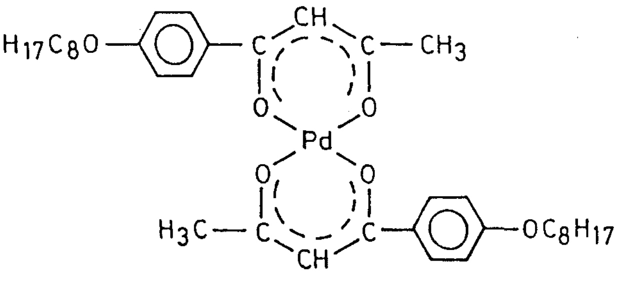
2.5

They observed that the shorter chain-substituted complexes show an enantiotropic nematic phase. On the other hand, the longer chain-substituted complexes exhibit a monotropic nematic phase. Furthermore, these showed helical formation on very slow cooling of the isotropic liquid, which is considered to be a property of molecular aggregation extremely close to discotic columnar mesomorphism.

Sadashiva *et al.*[19–21] synthesised several aryl β-diketones and their metal chelates in order to investigate the effect of terminal and lateral substituents on mesophases.

They found that on replacing a terminal hydrogen by another group in a series of [1-(p-n-alkylbiphenyl)-3-(phenyl) propane]-1,3-diones, melting point was raised and mesophases of the substituted compounds became more stable thermally. In order to examine the effect of lateral substituents on mesophase they synthesised two homologous series of [1-(4-n-dodecylbiphenyl)-3-(2-n-alkoxyphenyl) propane-1,3-diones and [1-(4-n-dodecylbiphenyl)-3-(3-n-alkoxyphenyl) propane] -1,3-diones respectively and observed that ortho-substitution favoured nematic mesophase while meta-substituted compounds were purely smectic in nature. **A** detailed comparison of the mesogenic behaviour of some β-diketones and their metal chelates have also been reported by Thompson et *al.*[22–24].

The first palladium(II) containing complex of a β-diketone examined for mesogenic behaviour was reported by Bulkin *et al.*[2] (compound 2.6]. Since then there was no report on mesogenic palladium β-diketonates. This prompted us to study the effect of substituents in palladium complexes of β-diketones. Palladium metal can take up square planar coordinate geometry which makes the molecular packing more efficient and this would favour high thermal stability of mesophases.



2.6

2.1 Results and Discussion

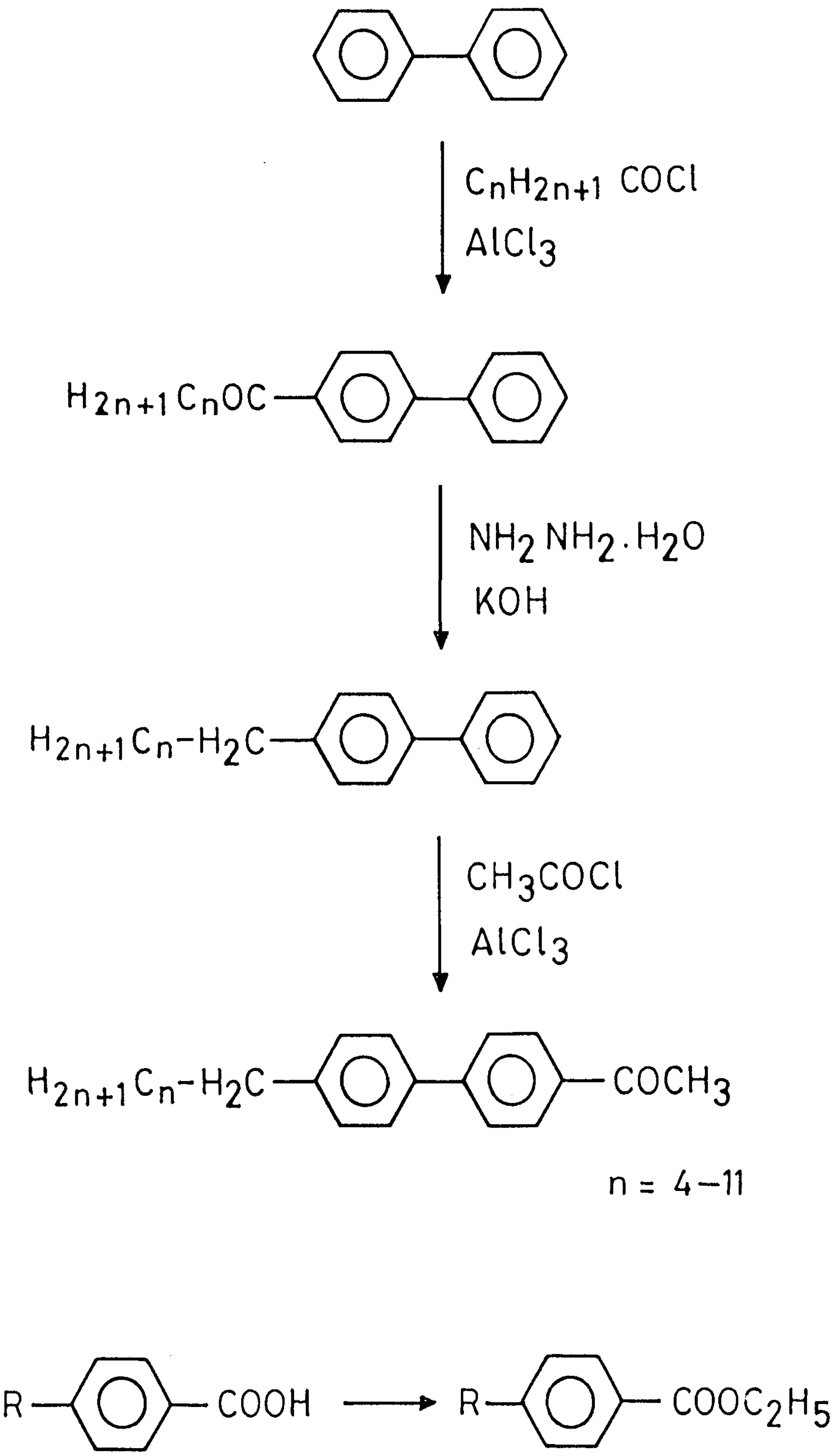
In the present investigations, the effect of terminal substituents on the mesophases exhibited by some metal β-diketonates have been undertaken. Hence, a number of copper(II) and palladium(II) complexes were synthesised. The ligands used to synthesise these complexes were [1-(4-n-dodecylbiphenyl)-3-(4"-substitutedphenyl) propane]-1,3-diones and all these were found to be mesogenic.

These ligands and their metal chelates were conveniently synthesised in good yields and their synthesis is shown schematically in figures 2.1 and 2.2 respectively.

4-n- Alkanoylbiphenyl was prepared from biphenyl and an appropriate n-acylhalide in carbon disulphide using Friedel-Crafts reaction. The ketone so obtained on Huang-Minlon modification of Wolff-Kishner reduction afforded 4-n-alkylbiphenyl which was again acylated with acetyl chloride to yield 4-n-alkyl-4′-acetylbiphenyl.

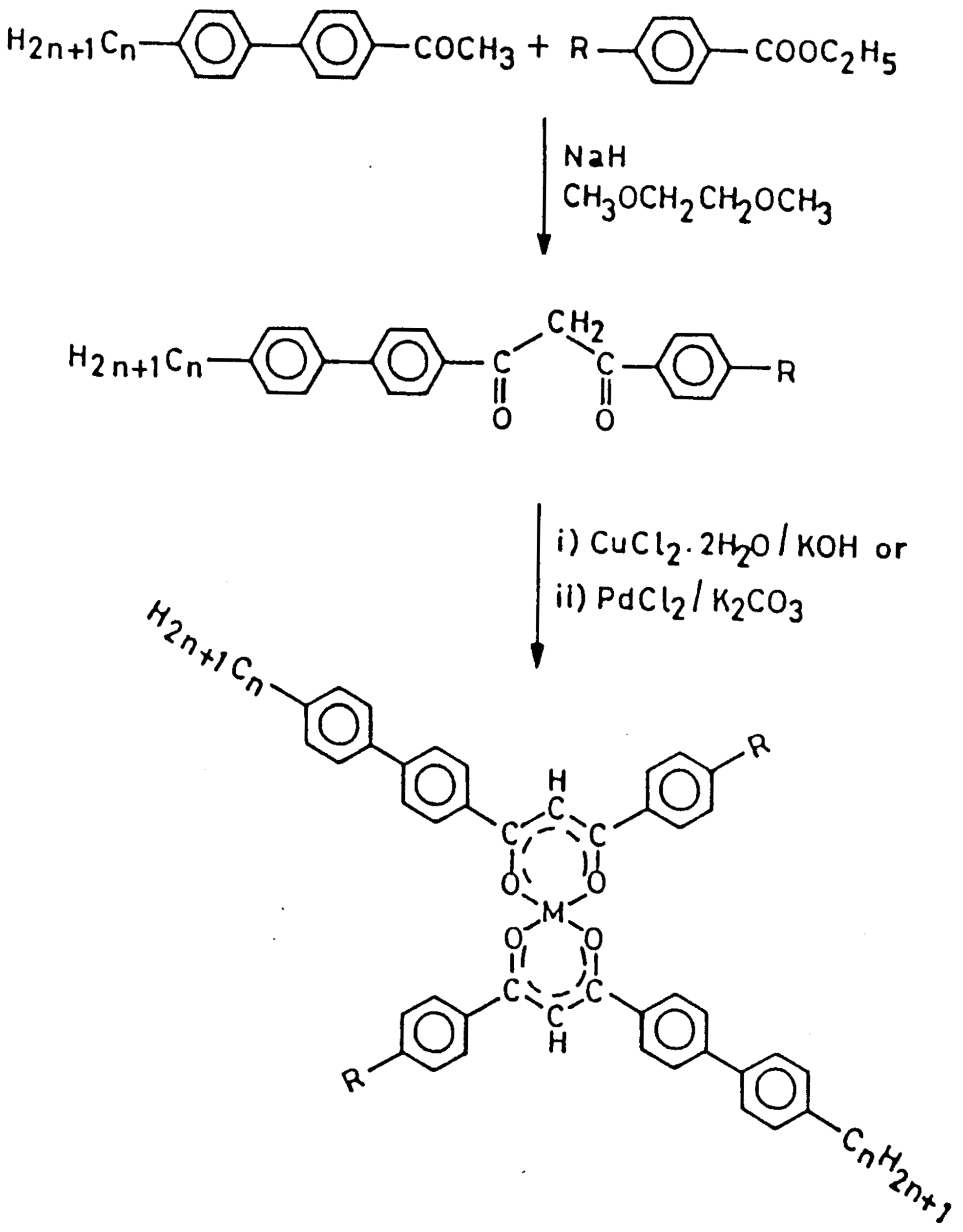
Synthesis of [1-(4-n-dodecylbiphenyl)-3-(4″-substitutedphenyl) propane]-1,3-dione was carried out by condensing ethyl 4-substituted benzoates with 4-n-dodecyl-4′-acetylbiphenyl in the presence of sodium hydride as a base, which resulted in the required β-diketones in 40-60% yield.

The PMR spectra of these ligands indicate that they exist in the enolic form. The enolic OH peak was observed at 16.8 ppm as shown in the PMR spectrum (fig.2.3) which is typical for all the other homologues. The infrared spectrum for the characteristic carbonyl stretching frequency shifted to lower wave number (1600-1605 cm^{-1}) than the normal C=O stretching frequency of carbonyl group. This is due to the intramolecular hydrogen bonding which exists in β-diketones. This can he clearly seen in the IR spectrum of [1-(4-n-dodecylbiphenyl)-3-(4″-methoxyphenyl) propane-1,3-dione as shown in figure 2.4. The copper(II) complexes were obtained in fairly good yield by adding an ethanolic solution of cupric chloride dihydrate to an ethanolic solution of the ligands in the presence of potassium hydroxide. They were crystallised from butan-2-one and were obtained as green needles or plates. Figure 2.5 shows the infrared spectrum of bis[1-(4-n-dodecylbiphenyl)-3-(4″-methoxyphenyl)propane -1,3-dionato]copper(II). In the infrared spectrum of these complexes, carbonyl stretching frequency shifted to higher wave number as compared to their corresponding ligands. Electronic absorption spectrum shows absorption around 366 nm and 315 nm. The golden yellow crystals of palladium complexes were synthesised by refluxing a mixture of an appropriate ligand, palladium chloride and anhydrous potassium carbonate in dry acetonitrile for twenty four hours. These were obtained in fairly good yields. The infrared spectroscopic behaviour of these compounds is similar to the copper complexes. The infrared spectrum of compound 2.c.3 is shown in figure 2.6. These complexes give absorption in visible region at 412 nm and 380 nm. Thus there is a bathochromic shift in the wavelength of absorption from copper to palladium complexes. Due to diamagnetic nature of



$C_nH_{2n+1}COCl$
$AlCl_3$
$H_{2n+1}C_nOC$
$NH_2NH_2 \cdot H_2O$
KOH
$H_{2n+1}C_n-H_2C$
CH_3COCl
$AlCl_3$
$H_{2n+1}C_n-H_2C$
$COCH_3$
n = 4–11
R
COOH
R
$COOC_2H_5$

Figure 2.1



M = Cu or Pd

R = **Cl**, n = 5, 6 12

R = Cl, Br, CN, CH_3, C_2H_5,
OCH_3 or OC_2H_5, n = 12

Figure *2.2*

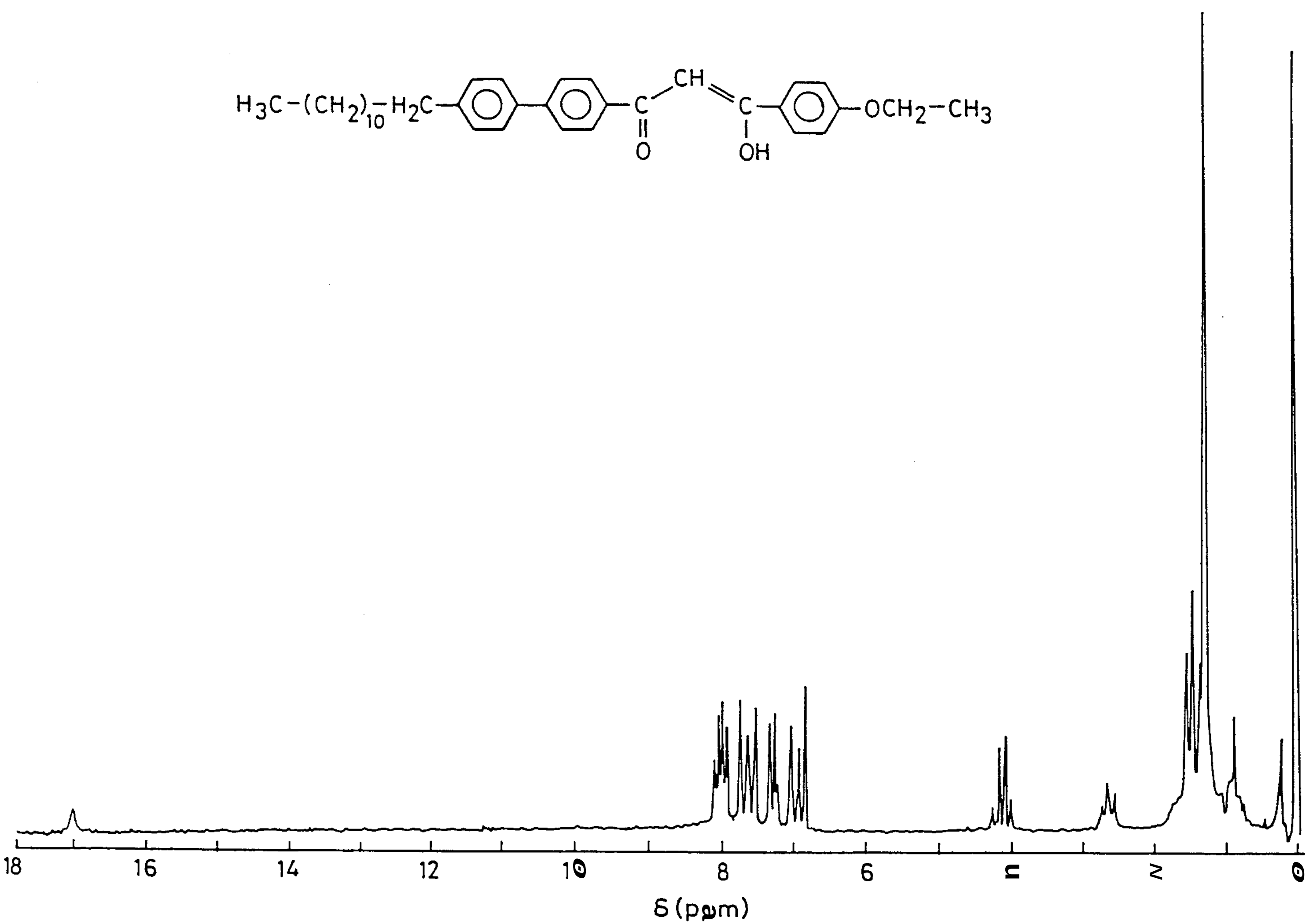


Fig.2.3. 80 MHz PMR spectrum of -(4′-n-dodecylbiphenyl)-3-(4-ethoxyphenyl)propane-1,3-dione, 2.a.4, in $CDCl_3$ containing 1% TMS.

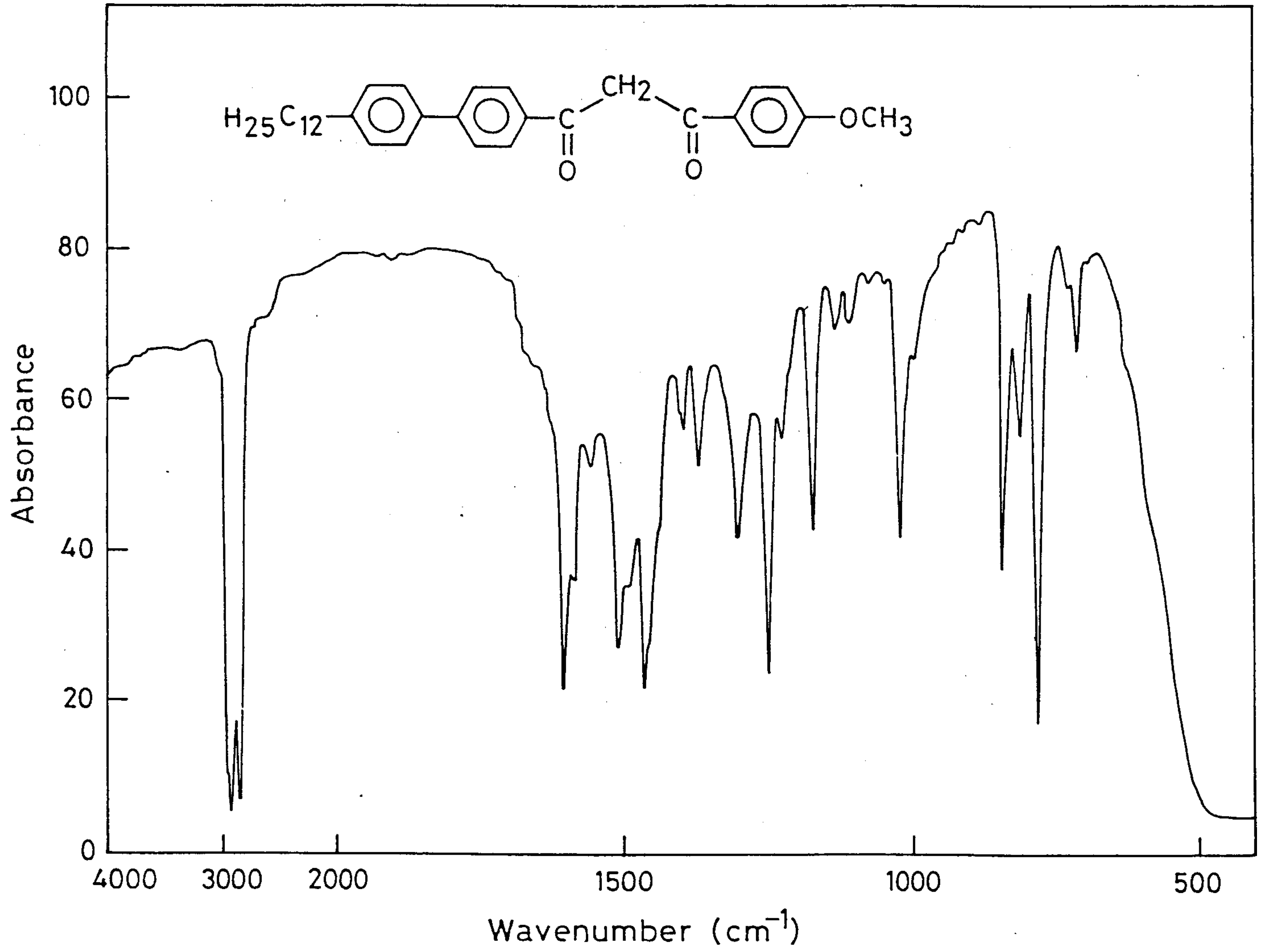


Fig.2.4. IR spectrum of 1-(4″-n-dodecylbiphenyl)-3-(4-methoxyphenyl)-propane-1,3-dione, 2.a.3.

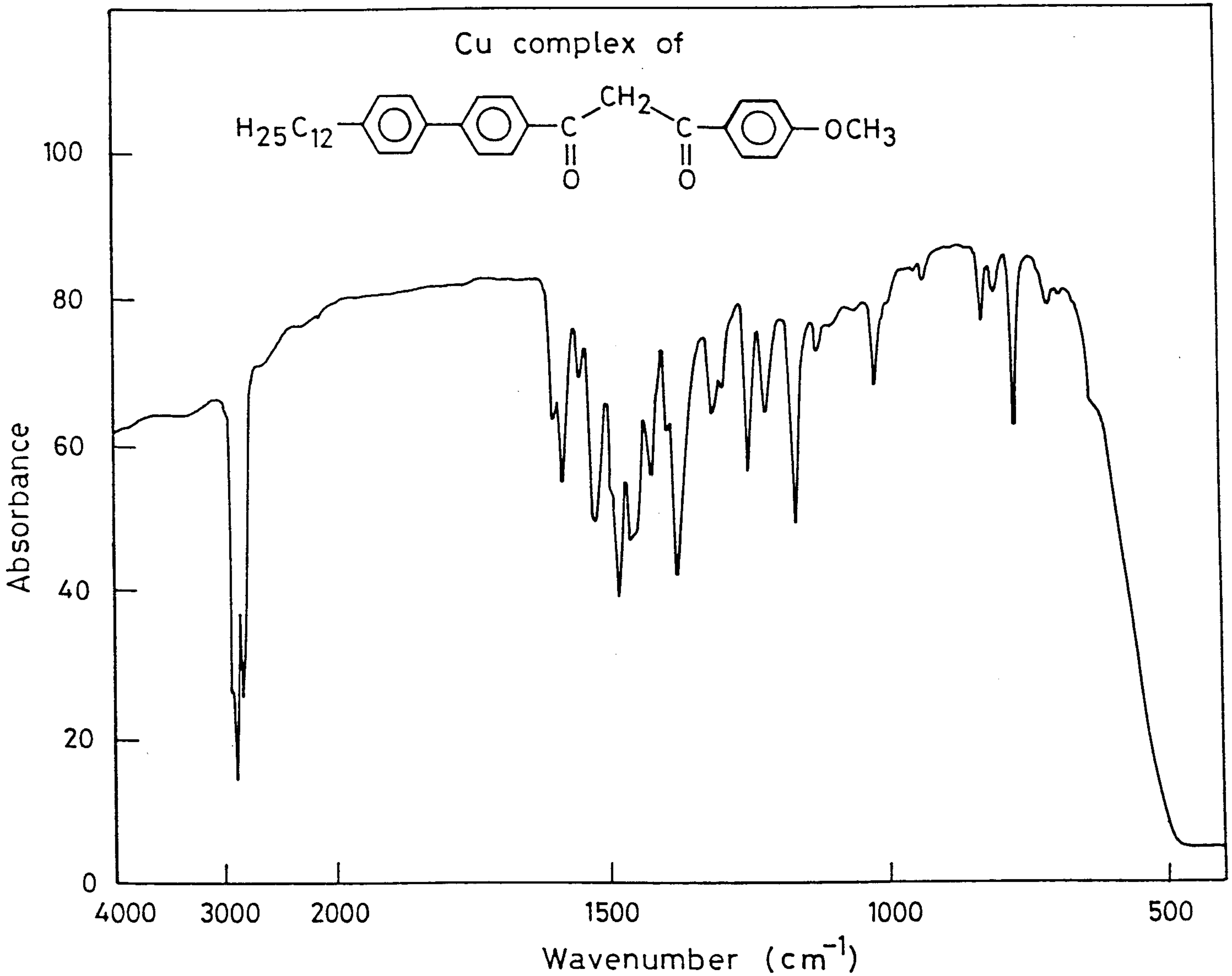


Fig.2.5. IR spectrum of bis[1-(4″-n-dodecylbiphenyl)-3-(4-methoxyphenyl)propane-1,3-dionato]copper(II), 2.b.3.

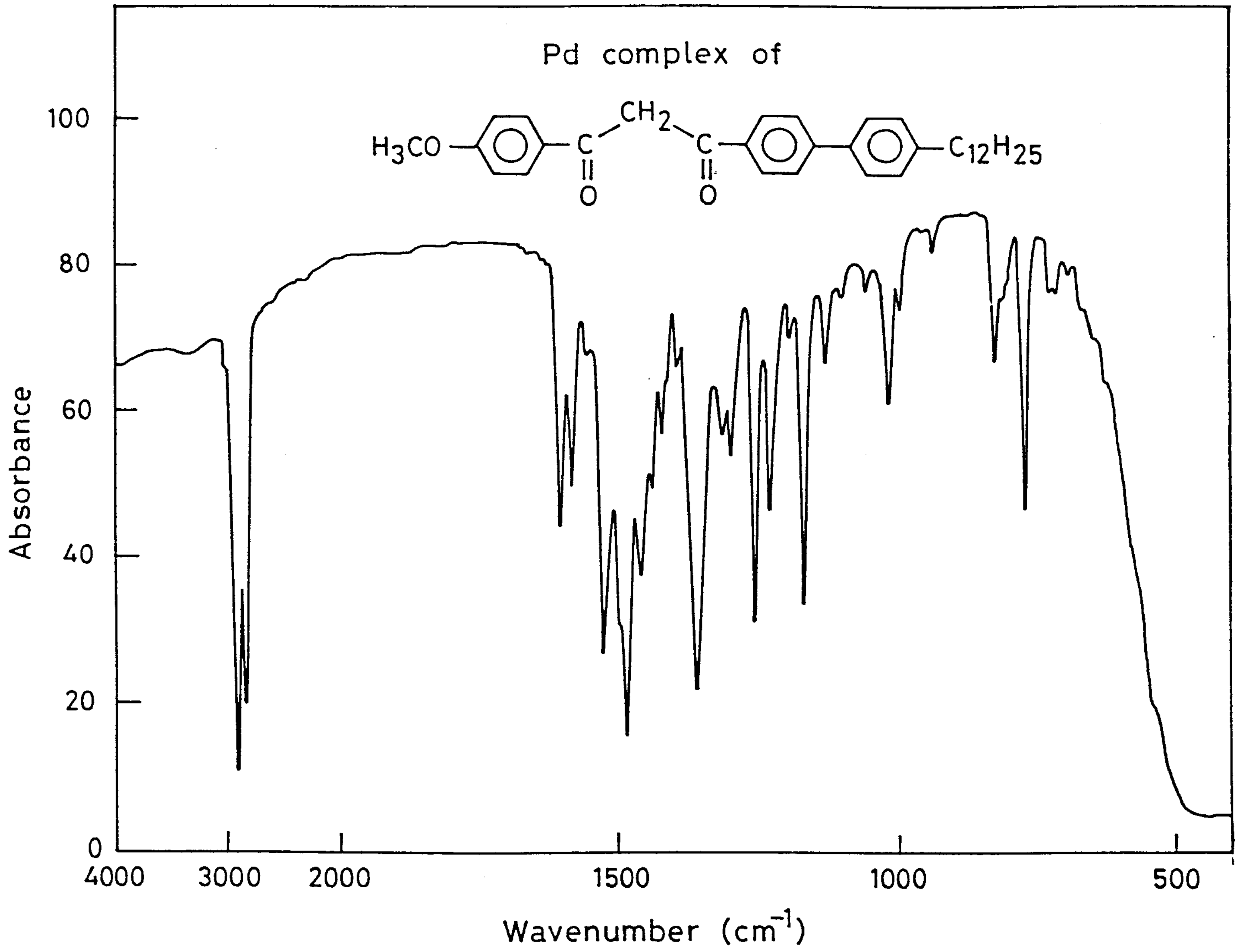
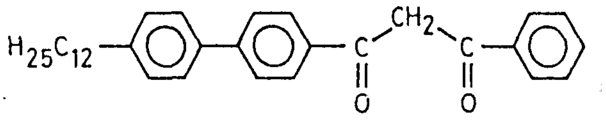


Fig.2.6. IR spectrum of bis[1-(4″-n-dodecylbiphenyl)-3-(4-methoxyphenyl)propane-1,3-dionato]palladium(II), 2.c.3.

these complexes, the PMR spectra could be conveniently recorded. A typical PMR spectrum is shown in figure 2.7.

The transition temperatures and the associated enthalpies for [1-(4-n-dodecylbiphenyl)-3-(4″-substitutedphenyl)propane-1,3-diones] are summarised in table 2.1. An examination of this table indicates that as the polarity of the terminal substituent increases, the melting and clearing points also increase. Except [1-(4-n-dodecylbiphenyl)-3-(4″-methoxyphenyl)propane] -1,3-dione (2.a.3) which is non-mesomorphic, the remaining compounds exhibit smectic phases. When the chloro group of [1-(4-n-dodecylbiphenyl)-3-(4″-chlorophenyl)propane]-1,3-dione (2.d.8) was replaced by a bromo group (2.a.6), the melting point increased by 11.5°C and the thermal stability of the monotropic S_E phase increased by 15.6°C. However, the clearing points of the two compounds are about the same. Some similar compounds have been reported recently,[23] which confirms this trend. Thus the reported compound [1-(4-n-decylbiphenyl)-3-(4″-bromophenyl)propane]-1,3-dione has higher melting point than its chloro analogue (2.d.6). They exhibit almost similar clearing temperatures. The bromo compound however showed a monotropic smectic E phase, which is only observed in the higher homologues of the chloro-substituted ligand (table 2.4, n=11,12) with somewhat lower smectic E to smectic **A** transition temperatures. The photomicrograph of the textures for smectic A and smectic E phases exhibited by these compounds are shown in plates 2.1 and 2.2 respectively.

Thus in all the above discussed mesogenic β-diketones there are always two terminal substituents. In order to compare the influence of the different terminal substituents on the mesomorphic properties, the unsubstituted parent β-diketone,[19] (compound 2.7) may be considered.



C 72 S_A 97 I

2.7

When this compound was terminally substituted with a methoxy group (2.a.3) the melting point increases and it becomes non-mesogenic. However, when cyano, chloro, bromo, methyl, ethyl or ethoxy groups were inserted terminally (table 2.1), the melting point was raised for each compound and the mesophase (smectic A) was

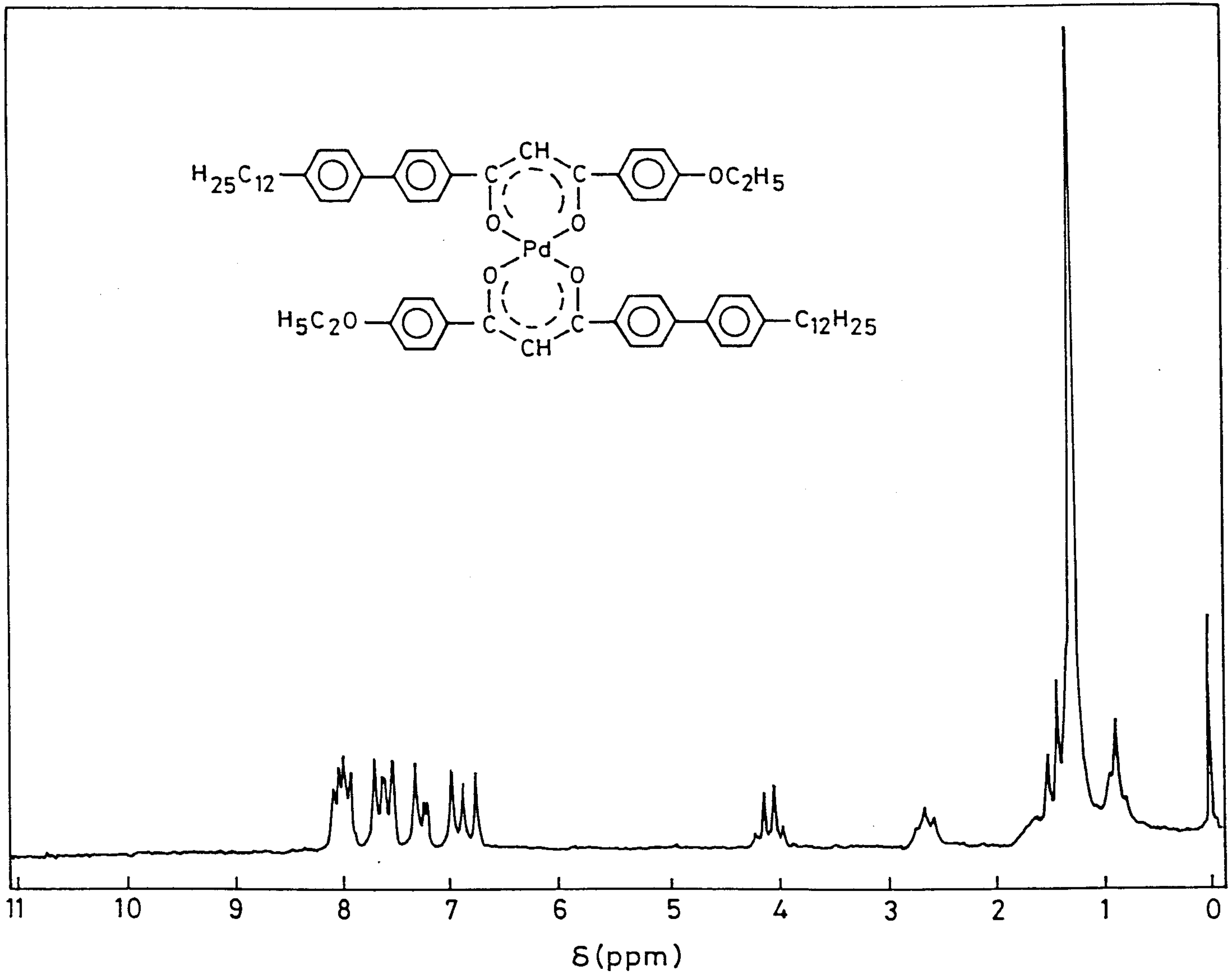
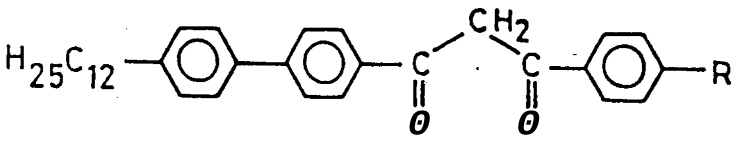


Fig.2.7. 80 MHz PMR spectrum of bis[1-(4″-n-dodecylbiphenyl)-3-(4-ethoxyphenyl)propane-1,3-dionato]palladium(II), 2.c.4, in $CDCl_3$ containing 1%TMS.

Table 2.1

Mesomorphic transition temperatures (°C) and enthalpies of transitions (kcal/mol) of



Series II(1)

Compound number	R	C		S_E		S_A		I
2.a.l	CH_3	.	101.5 5.25	-		.	111.0 0.95	.
2.a.2	C_2H_5	.	73.5 5.0	-		.	100.5 1.01	.
2.a.3	OCH_3	.	108.5 7.59	-				
2.a.4	OC_2H_5	.	112.5 5.6	-		(.	102.0) 0.73	.
2.a.5	Br	.	139.0 7.88	(.	131.4)*	.	143.5 0.59	.
2.a.6	CN	.	126.0 12.19	-		.	145.0 0.75	.

*The enthalpies could not be measured.

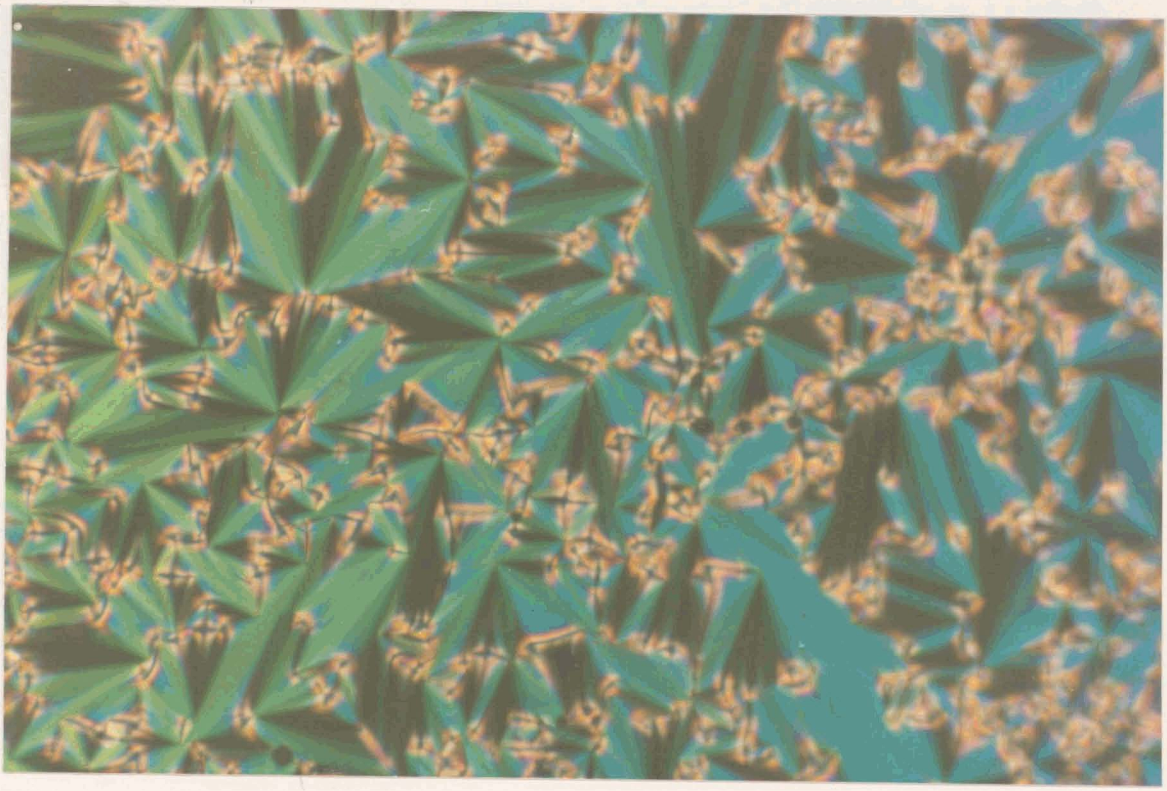


Plate 2.1. Photomicrograph of the texture of the smectic A phase of compound 2.d.7 at 142°*C*.

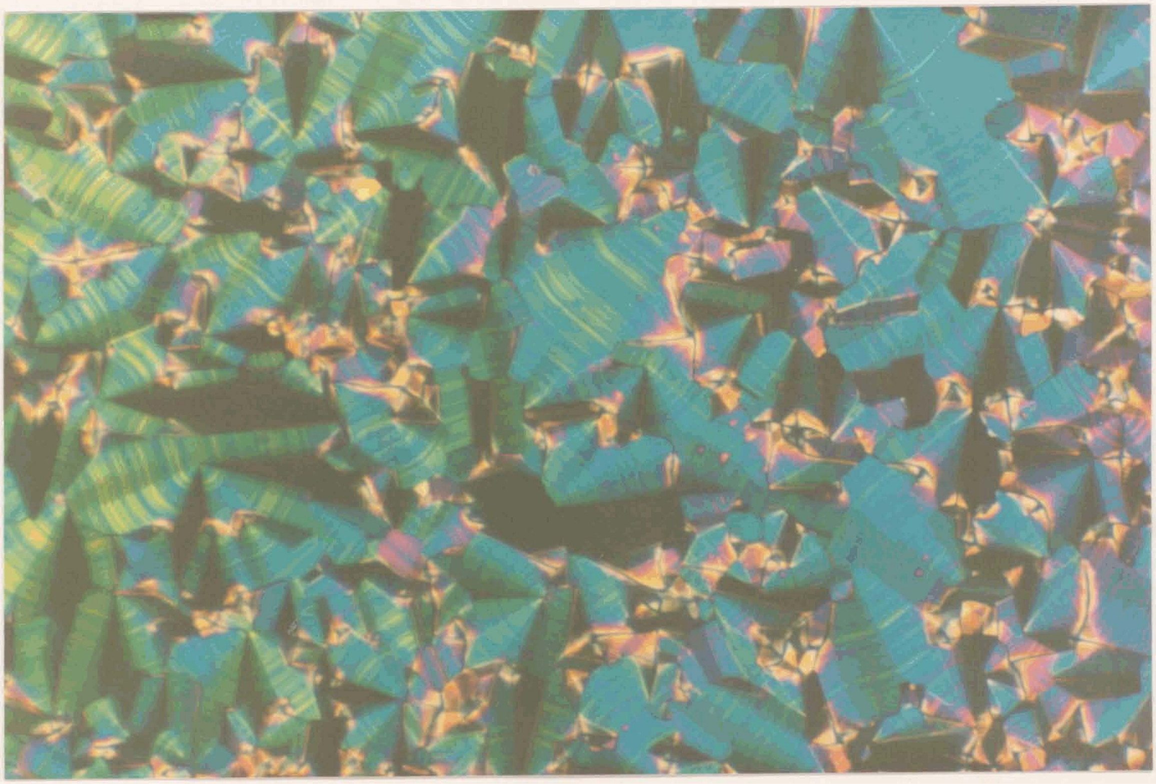
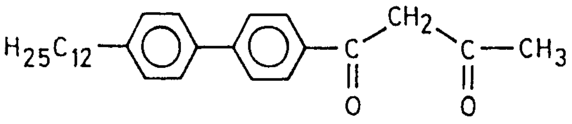


Plate 2.2. Photomicrograph of the texture of the smectic E phase of compound 2.d.7 at 117°*C*.

retained. This is not unusual since on substituting a terminal hydrogen in a mesogenic compound by another group usually, but not always the mesophases become thermally more stable.[26] Comparison of mesogenic behavior of [1-(4-n-dodecylbiphenyl)-3-(4″-methylphenyl) propane]-1,3-dione (2.a.1) and a compound (2.8) reported by Thompson *et al.*[22] indicates that when a phenyl unit was introduced into the parent *β*-diketone system, the clearing temperature of the smectic phase was markedly



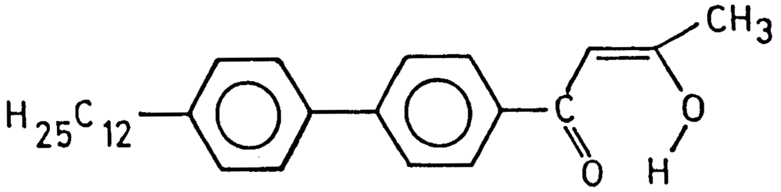
C 86 S_E 97 S_B 107 S_A 135 I

2.8

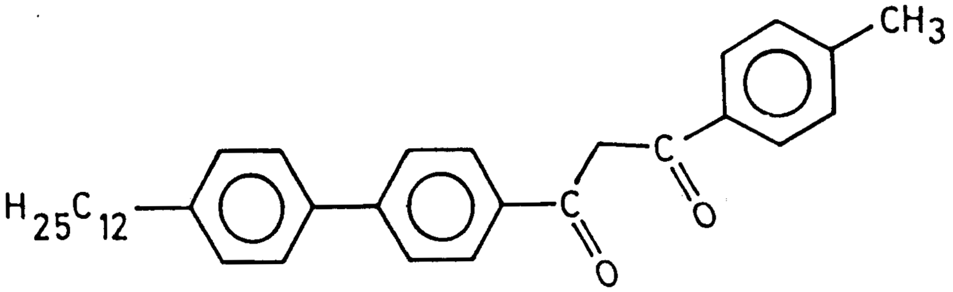
depressed. Normally the introduction of a phenyl unit into a linear molecule would have caused a significant elevation of the clearing point due to increase in the molecular polarisability. It can be concluded from this that although phenyl group increases the molecular polarisability, it also increases the molecular lateral dimensions, as shown in figure 2.8. Compound 2.8 is essentially a linear molecule, as can be seen in 2.8a. The addition of an extra phenyl ring in compound 2.8 results in a bent molecular structure as shown in 2.8b. This can be explained by considering the structures of keto and enol forms of [1-(4-n-dodecylbiphenyl)-3-(4″-methylphenyl)propane]-1,3-dione (2.a.1). Two different configurations of this keto form are possible as shown in 2.8b and 2.8c.

Figure 2.8b shows the broadened structure of the molecule but energetically this structure is less favourable due to the presence of two electronegative oxygen atoms in proximity. The other possible structure for keto form is shown in figure 2.8c, wherein the two oxygens of the diketone are opposing and which also gives almost a linear shape to the molecule. Since there is a decrease of thermal stability, after the addition of a phenyl ring this structure is not probably favourable.

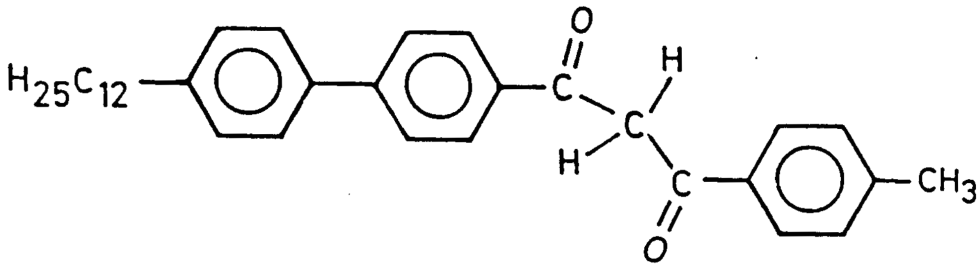
If we consider the molecule existing in the *enolic* form as shown in figure 2.8d, then a bent molecular structure with an increased breadth of the molecule is possible. This structure is favourable as evidenced by the PMR spectrum which shows enolic OH even in solution. Thus such molecules whose breadth has increased considerably cannot easily be accommodated in a layer structure and smectogenicity is suppressed. If we compare the mesogenic behavior of [1-(4-n-dodecylbiphenyl)-3-(4″-



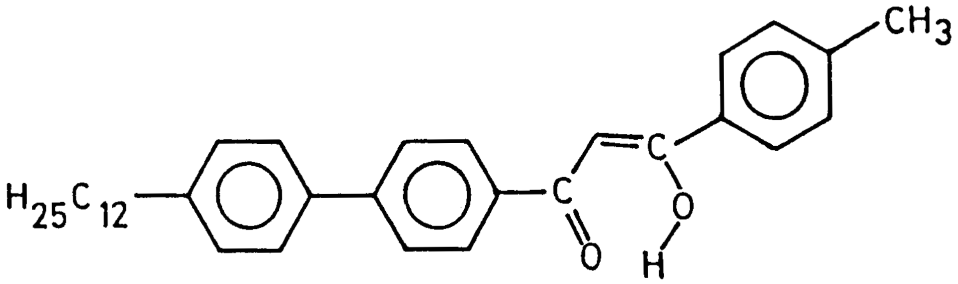
2.8a



2.8b



2.8c



2.8d

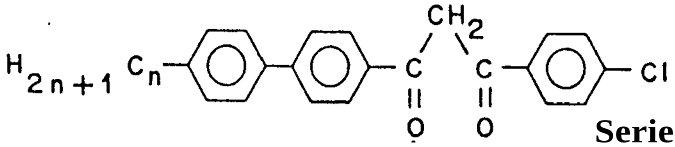
Figure 2.8: Different possible conformations of compounds 2.8 and 2.a.l.

methylphenyl)propane] -1,3-dione (2.a.1) with the methoxy substituted compound (2.a.3), the decreased stability of the smectic phase may be attributed to an increase in the size of the lateral group, which may be a dominant factor as compared to the increase in polarisability of the molecule. Thus compound 2.a.3 is non-mesogenic. In addition to this it was observed that the electron withdrawing chloro terminal group favours mesophase formation as compared to the electron donating methoxy group in the same 0-diketone parent system. Similarly if we compare the terminally substituted methyl compound (2.a.1) with the chloro compound (2.a.5) then the chloro substituted compound has higher melting and clearing points. In fact the change from the terminal methyl group to the terminal chloro group involves only a polarisability change, the size of chloro and methyl group being more or less the same.[31]

There are not many homologous series of compounds containing a terminal chloro substituent and also the β-diketone system had not been studied thoroughly. In view of this we synthesised a homologous series of [1-(4-n-alkylbiphenyl)-3-($4''$-chlorophenyl)propane]-1,3-diones. The transition temperatures and enthalpies of transitions for this series have been summarised in table 2.2. As can be seen all the homologues are mesogenic, the compound (2.d.1) with the n-pentyl chain shows a mesophase when its isotropic liquid was quenched. The hexyl homologue exhibits a monotropic smectic phase while the other higher homologues are enantiotropic smectic. The smectic phase of these homologues show a simple fan-shaped texture and in analogy with known textures, this has been characterised as smectic A. In addition, the undecyl and dodecyl homologues (2.d.7 and 2.d.8) exhibit a monotropic smectic phase on cooling the smectic A phase with concentric arcs and the homeotropic regions of smectic A phase show a mosaic texture. This behaviour is characteristic of smectic E phase. The photomicrograph of the textures for S_A and S_E phases shown by compound 2.d.8 are shown in plates 2.1 and 2.2 respectively. Figure 2.9 shows a DSC thermogram for the undecyl homologue (2.d.7). The enthalpy of smectic A-isotropic transition is typically of the order of 1 kcal/mol. A plot of the transition temperatures versus the number of carbon atoms in the alkyl chain for this homologous series is shown in figure 2.10. It is observed that as the alkyl chain is lengthened, the smectic A-isotropic temperature decreases gradually and these points lie on a smooth curve. Such a decrease has been observed in some homologous series of smectogens.[27] It is also seen that there is a general decrease of

Table 2.2

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



Series II(4)

Compound number	n	C		S_E		S_A		I
2.d.1	5	.	146.0 6.5	-				
2.d.2	6	.	142.5 6.84	-		(.	140.5) 0.75	.
2.d.3	7	.	138.5 6.6	-		.	144.5 1.03	.
2.d.4	8	.	137.5 4.6	-		.	146.0 1.1	.
2.d.5	9	.	136.5 6.6	-		.	146.0 1.1	.
2.d.6	10	.	133.0 10.56	-		.	145.0 1.23	.
2.d.7	11	.	124.5 8.48	(.	117.5)*	.	144.0 1.23	.
2.d.8	12	.	127.5 11.54	(.	116.0)'	.	143.0 1.05	.

Temperature in parenthesis indicates a monotropic transition.

'The enthalpy of transition could not be accurately determined.

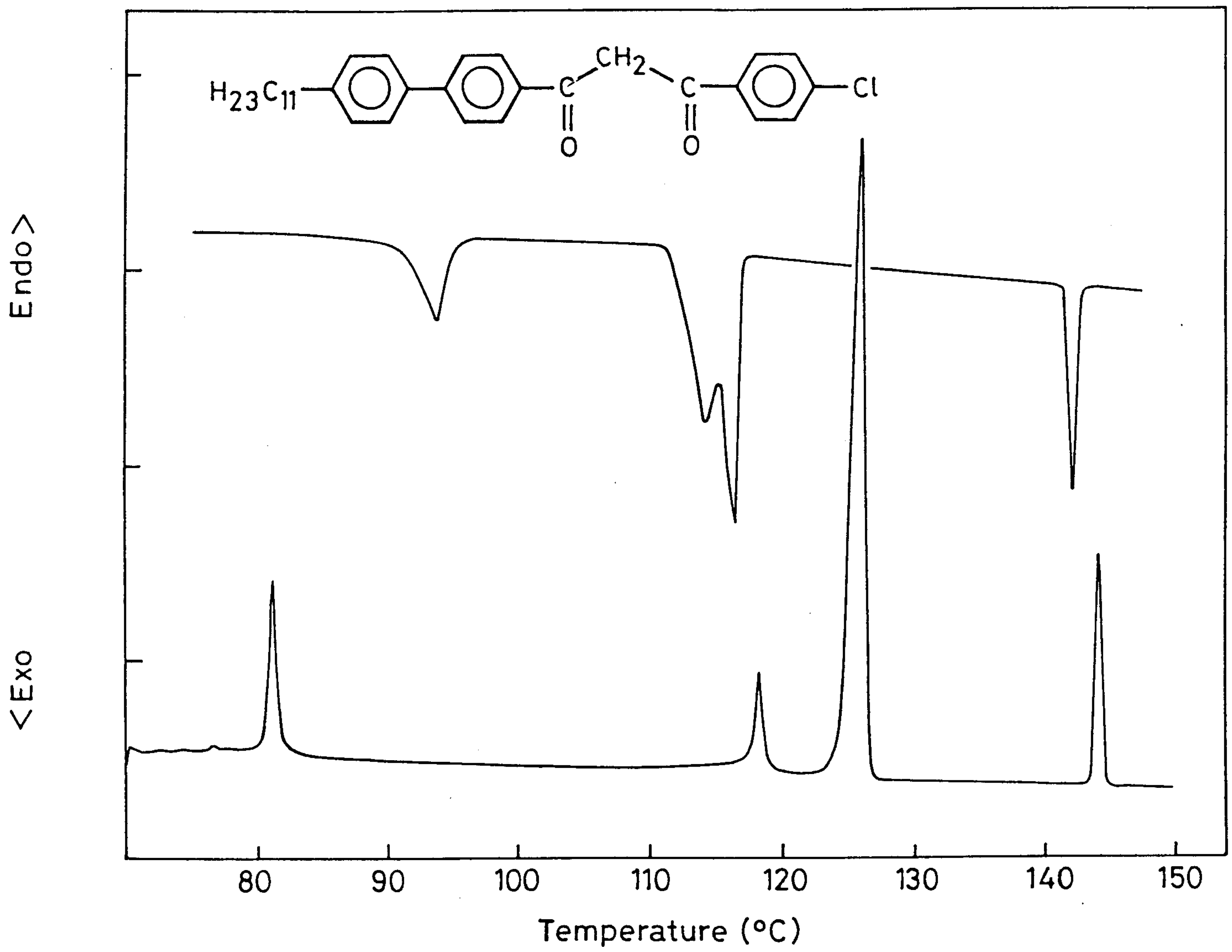


Fig.2.9. DSC thermogram of the compound 2.d.7.

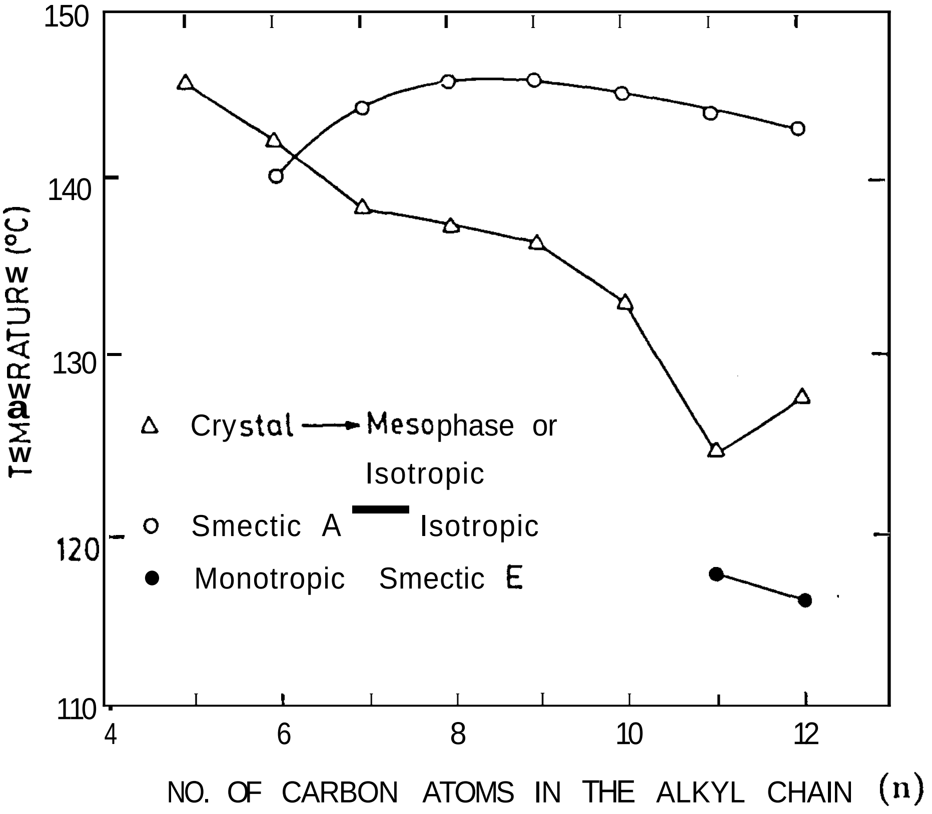


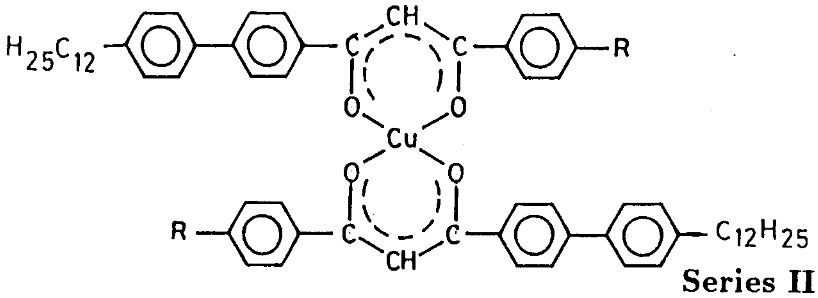
Fig.2.10. A plot of the transition temperatures versus the number of carbon atoms (n) in the alkyl chain for a series of 1-(4″-n-alkylbiphenyl)-3-(4-chlorophenyl)propane-1,3-diones.

melting points and the temperature range of the smectic A phase increases as the alkyl chain is lengthened.

Table 2.3 summarises the transition temperatures and enthalpies of transitions of bis[1-(4-n-dodecylbiphenyl)-3-(4″-substitutedphenyl)propane-1,3-dionato] copper(II) complexes. All the complexes exhibit a monotropic mesophase. As compared to the ligands the melting points are raised by 60-100°C, while the clearing points are raised by 28-67°C upon complexation. It is interesting to note that a chloro group in complex (2.b.5) induces a nematic phase while a bromo substituent induces a smectic phase. This is due to the fact that a chloro terminal group has a higher nematic group efficiency order while a bromo group has higher smectic group efficiency order in a series of calamitic mesogens. Surprisingly when the terminal substituent is a cyano group, for example, in bis[1-(4-n-dodecylbiphenyl)-3-(4″-cyanophenyl)propane -1,3-dionato] copper(II) (2.b.7) induces a smectic phase and actually a cyano group lies high in the nematic group efficiency order. This behaviour can be explained on the basis that the melting points and thermal stability of the smectic A phase has been increased to such an extent that the nematic phase is eliminated. It is important to note that bis[1-(4-n-dodecylbiphenyl)-3-(4″-methoxyphenyl)propane -1,3-dionato]copper(II) derived from non-mesogenic ligand, exhibits a monotropic nematic phase. Thus, it can be concluded that a ligand need not be mesogenic to obtain a mesogenic metal complex. The photomicrograph of the texture exhibited by bis[1-(4-n-dodecylbiphenyl)-3-(4″-methoxyphenyl)propane -1,3-dionato]copper(II) is shown in plate 2.3. We can assume that these metal complexes are elongated molecules with two lateral substituents, viz., the two biphenyl rings with the dodecyl chains form the long molecular axis, while the two phenyl rings with R form the lateral substituents. Consequently, the mesophase of these complexes may be expected to be the same as those exhibited by rod-like molecules. This was confirmed by miscibility studies[13] of a very similar complex with the well known nematogen 4"-n-pentyl-4-cyano-p-terphenyl. The nematic phases of the two were continuously miscible. The enthalpies of nematic-isotropic transition for these Cu(II) complexes are of the order of 0.03 to 0.04 kcal/mol which is extremely low when compared with those of the normal low molecular weight calamitic nematogens.[28] In fact very similar values were also obtained by Caruso *et al.*,[29] Marcos *et al.*,[30] Ovchinnikov *et al.*[14] and Sadashiva *et al.*,[31] for various metal complexes. This low enthalpy value is perhaps due to the persistence of a high degree of nematic-like

Table 2.3

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



Series II(2)

Compound number	R	C		S_A		N		I
2.b.1	CH_3	.	201.0 9.79	-		(.	162.0) 0.04	.
2.b.2	C_2H_5	.	160.0 4.5	-		(.	146.5) 0.04	.
2.b.3	OCH_3	.	179.0 10.4	-		(.	169.5) 0.03	.
2.b.4	OC_2H_5	.	179.0 8.1	-		(.	158.0) 0.04	.
2.b.5	Cl	.	196.0 11.41	-		(.	171.0)*	.
2.b.6	Br	.	201.0 8.03	(.	170.5)*	-		.
2.b.7	CN	.	218.0 6.76	(.	212.0) 0.93	-		.

'The enthalpies could not be determined because of immediate onset of crystallisation.

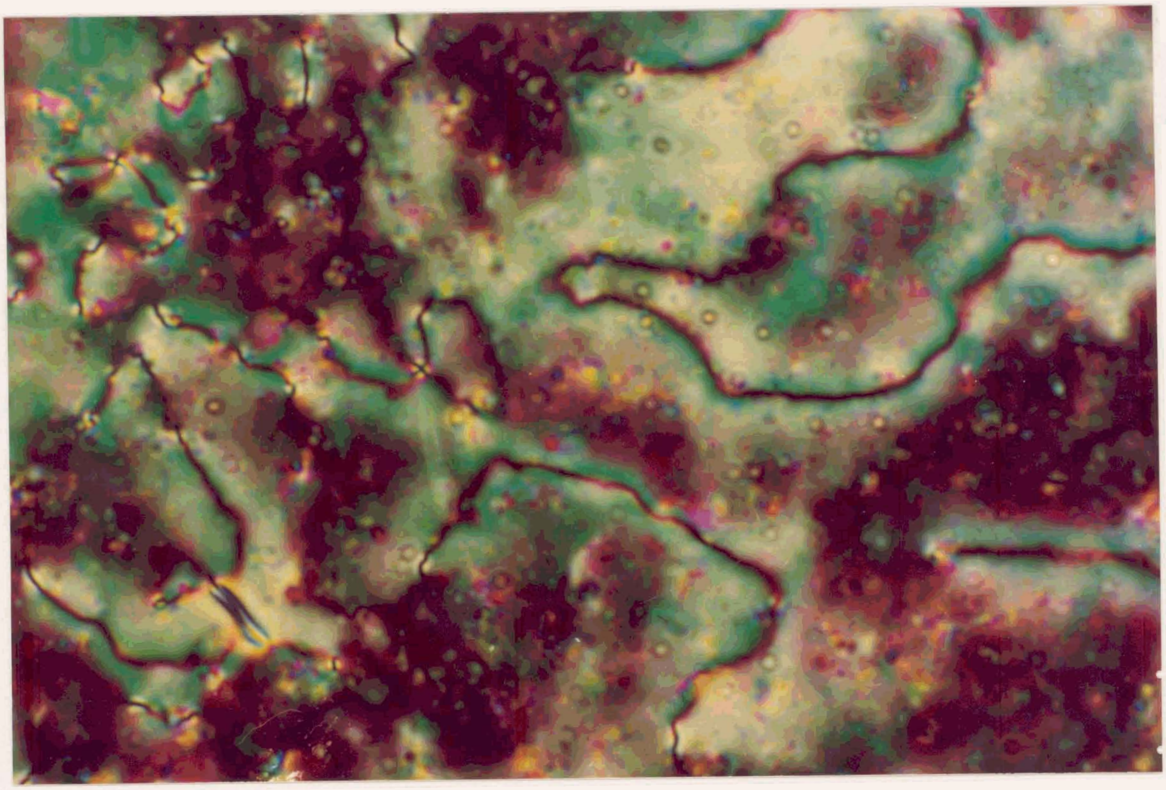


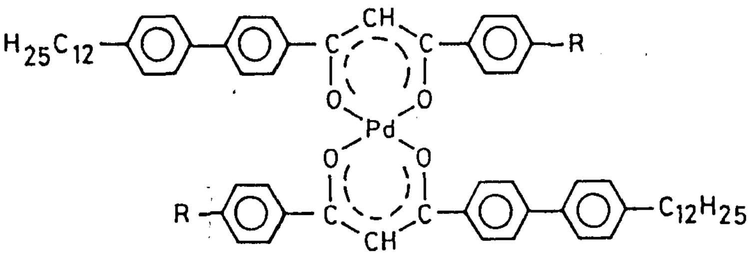
Plate 2.3. Photomicrograph of the texture of the nematic phase of compound 2.b.3 at 168°C.

short range order in the isotropic phase.

The transition temperatures of yellow coloured, crystalline bis[1-(4-n-dodecylbiphenyl)-3-(4″-substitutedphenyl)propane-1,3-dionato]palladium(II) complexes have been summarised in table 2.4. As can be seen, all of them exhibit metastable mesophases. Alkyl/Alkoxy substituted complexes show a nematic phase while the halogen as well as the cyano substituted analogues exhibit a smectic phase. Compound 2.c.5 arid the analogous cyano compound (2.c.7) exhibited a simple fan-shaped texture and is characterised as smectic A phase. It was observed that bis[1-(4-n-dodecylbiphenyl)-3-(4″-cyanophenyl)propane -1,3-dionato] palladium(II) has higher melting point and higher thermal stability of smectic A phase, as compared to all other palladium complexes reported here. The mesophase-isotropic transition temperatures of these compounds are about the same as their corresponding copper(II) congeners, except in the case of cyanophenyl derivative (2.c.7) where the difference is about $15°C$. The enthalpies of transitions could not be determined due to thermal decomposition of the samples.

Table 2.4

Mesomorphic transition temperatures (°C)
of



Series II(3)

Compound number	R	C		S_A		N		I
2.c.1	CH_3^*	.	195.0	-		(.	162.0)	.
2.c.2	$C_2H_5^*$	.	177.0	-		(.	149.0)	.
2.c.3	OCH_3	.	177.0	-		(.	164.5)	.
2.c.4	OC_2H_5	.	183.0	-		(.	151.0)	.
2.c.5	Cl*	.	201.0	(.	178)	-		.
2.c.6	Br*	.	196.0	(.	177.0)	-		
2.c.7	CN	.	212.0	(.	197.5)	-		

[†] Enthalpies of these chelates could not be determined because of their thermal decomposition

[*] Chelates 2.c.1, 2.c.2, 2.c.5 and 2.c.6 have crystal-crystal transitions at 134.0, 138.0, 167.5 and 169.0°C respectively

Temperatures in parentheses indicate monotropic transitions.

EXPERIMENTAL - GENERAL

All the commercial solvents were distilled prior to use. Anhydrous solvents were prepared by following the standard procedures. All the solid and liquid starting materials were purified by crystallisations and distillations respectively before use. Column chromatography was performed using silica gel from ACME synthetic chemicals (60-120 mesh) without any pretreatment. Unless otherwise mentioned petroleum ether used had a boiling point range between 60-80°C. Analytical thin layer chromatography was carried out by using silica gel supplied by BDH India Ltd. or TLC aluminium cards coated with silica gel with a fluorescent indicator manufactured by Fluka AG, Switzerland.

PMR spectra were obtained using either a Bruker WP80SY FT NMR or Bruker AG200F FT-NMR spectrometer. Chemical shifts quoted are in ppm and are relative to tetramethylsilane (TMS) (δ =0) which was used as an internal standard. Unless otherwise mentioned $CDCl_3$ was used as a solvent for all the compounds. Infrared spectra, were obtained using a Shimadzu IR-435 spectrophotometer. The ultraviolet and visible absorption spectra were recorded on a Hitachi U-3200 spectrophotometer. Elemental analyses were carried out on a CARLO-ERBA 1106 elemental analyses.

The transition temperatures and nature of the phases were determined using a Leitz Laborlux 12 POL polarising microscope equipped with a Mettler FP52 heating stage and a FP5 controller or with a Mettler FP90 central processor and a Mettler FP82 HT hot stage. The heat of transitions were measured on a Perkin-Elmer, Model DSC-2 or DSC-4 differential scanning calorimeter, calibrated with pure indium sample.

2.2 Experimental

Ethyl-4-chlorobenzoate

A mixture of 4-chlorobenzoic acid (15.0 g, 0.09 mol), ethanol (100 ml) and concentrated sulphuric acid (2 ml) was refluxed for twelve hours. The excess ethanol was removed on a rotary evaporator and the residue was poured into ice-water. This was extracted with diethyl ether (2 x 125 ml). The combined ethereal solution was washed with cold 10% sodium bicarbonate solution (2 x 75 ml), water (2 × 100 ml) and dried (Na_2SO_4). Removal of solvent afforded a colourless liquid which was purified by distillation under reduced pressure. Yield (10.0 g, 56.6%); b . ~82.2°C/0.4 mm (Reported[30] 122.0°C/15 mm.)

Ethyl-4-ethylbenzoate

A mixture of 4-ethylbenzoic acid (10.0 g, 0.07 mol), concentrated sulphuric acid (2 ml) and ethyl alcohol (100 ml) was refluxed for twelve hours. The excess ethyl alcohol was removed by distillation and the residue was poured into ice cold water. This was extracted with ether (2 x 100 ml). The combined ethereal extracts was washed with ice-cold 10% sodium bicarbonate solution (2 x 75 ml), water (2 × 100 ml) and dried (Na_2SO_4). Removal of solvent afforded a colourless liquid which was purified by distillation under reduced pressure. Yield (10.6 g, 83.5%); b.p. 80.0°C/0.1 mm (Reported[31] 129-30/15 mm)

The physical data of the cognate preparations of other ethyl-4-substituted benzoates are given in table 2.5.

4-n-Dodecanoylbiphenyl

This was prepared following the procedure of Long and Henz.[37] Thus, to a vigorously stirred suspension of anhydrous aluminium chloride (61.6 g, 0.46 mol) in dry carbon disulphide (200 ml), contained in a one litre three-necked flask, a mixture of biphenyl (52.0 g, 0.38 mol) and n-dodecanoyl chloride (84.03 g, 0.38 mol) in dry carbon disulphide (250 ml) was added through a dropping funnel during one

Table 2.5

Physical data of $RPhCOOC_nH_{2n+1}$

R	n	Observed		Reported	Ref.
		m.p.°C,b.p.°C/mm,	Yield, %	m.p.°C,b.p.°C/mm	
CN	1	66.5	76.5	62.0	32
Br	2	87.0/0.4	87.5	131.0113	33
CH_3	2	68-70/2.0	79.6	110.0/12	34
OCH_3	2	80-9011.0	92.5	263.0/760	35
OC_2H_5	2	130-132/1.00	94.0	148-149/14	36

hour. After completion of the addition, stirring was continued for two hours and the mixture was then refluxed for a further four hours. Carbon disulphide was removed by distillation and the syrupy residue was added slowly to ice-water (500 ml) and hydrochloric acid (10 ml). The pale yellow precipitate so obtained was filtered on a buchner funnel, washed with water until the washings were acid free and air dried. This was crystallised from ethyl alcohol using activated charcoal to give colourless crystals of 4-*n*-dodecanoylbiphenyl (113.0 gm, 87.5%) m.p. 100.0°C.

The physical constants of the cognate preparations of other 4-*n*-alkanoylbiphenyls are given in table 2.6.

4-*n*-Dodecylbiphenyl

This was prepared by a Huang-Minlon modification[38] of the Wolff-Kishner reaction. Thus, a mixture of 4-*n*-dodecanoylbiphenyl (65.0 g, 0.19 mol), potassium hydroxide (32.5 g, 0.58 mol) and hydrazine hydrate (80%, 35.6 ml, 0.58 mol) in diethylene glycol (520 ml) was refluxed for two hours. Then the temperature was gradually raised to 200°C distilling off the volatile matter and the reaction mixture was refluxed for a further four hours. This was allowed to cool and poured into cold water. The organic material was extracted into chloroform (3 × 200 ml) and the combined chloroform extracts was washed with water (3 × 100 ml), dilute hydrochloric acid (3 × 50 ml) and water (3 × 100 ml), and dried (Na_2SO_4). The solvent was removed and the crude product was recrystallised from petroleum ether to give colourless crystals. Yield (55.0 g, 88.0%); m.p. 59.0°C.

The physical constants of the cognate preparations of other 4-*n*-alkylbiphenyls are given in table 2.7.

4-n-Dodecyl-4′-acetylbiphenyl

This was prepared following the procedure of Byron, Gray and Wilson.[42] Thus, to a one litre three-necked flask, fitted with a reflux condenser carrying a calcium chloride guard tube, a mechanical stirrer and a pressure equalising dropping funnel, was introduced anhydrous aluminium chloride (23.8 g, 0.17 mol), dry carbon disulphide (400 ml) and 4-*n*-dodecylbiphenyl (48.0 g, 0.14 mol). The reaction flask was

Table 2.6

Physical data of $PhPhCOC_nH_{2n+1}$

n	Observed		Reported		Ref.
	m.p.°C	Yield, %	m.p.°C	Yield,%	
4	79.0	80.0	76-78	63.0	37
5	95.0	88.5	96.5	67.0	37
6	86.0	90.0	85.5-86.5	52.0	37
7	99.0	91.5	101-102	90.0	41
8	92.0	91.0	93-94	69.5	41
9	98.5	89.0			
10	97.5	91.0			

Table 2.7

Physical data of $PhPhC_nH_{2n+1}$

n	Observed		Reported		Ref
	b.p.°C/mm,m.p.°C	Yield,%	b.p.°C/mm,m.p.°C	Yield,%	
5	147-155/2	78.0	106-109/0.1	65.5	39
6	150-152/2	70.5	175-176/3.0	65.0	40,41
7	185-190/2	72.0	124-12711.0	65.0	39
8	42.5	69.5	187-188/2.0	72.5	39,40
9	40.5	63.5	42-43	73.5	41
10	53.5	68.0			
11	51.2	67.0			

cooled in an ice-bath. To this stirred mixture was added a solution of acetyl chloride (11.69 g, 0.14 mol) in dry carbon disulphide (50 ml) during thirty minutes. After the completion of addition it was stirred for thirty minutes and the ice-bath was removed and the stirring continued at room temperature for a further two hours. Finally this was refluxed for three hours on a steam-bath and left overnight at room temperature. Carbon disulphide was distilled off and the complex was decomposed by careful addition of ice-cold dilute hydrochloric acid. The pale yellow precipitate so obtained was filtered off, washed with water until the washings were acid free and dried. Crystallisation of this product from ethyl alcohol gave the 4-n-dodecyl-4'-acetylbiphenyl.
Yield (40.0 g, 73.7%); m.p. 94.5°C; IR ν_{max}^{nujol} 2900, 2850, 1680, 1605, 1470, 1370, 1270, 810 and 730 cm^{-1}; NMR δ 0.75(t,3H,C$\underline{H}_3$), 1.14-1.73(m,20H,10×C$\underline{H}_2$), 2.6(s,3H, COC$\underline{H}_3$), 2.6(t,2H,ArC$\underline{H}_2$),7.2-8.14(m,8H,Ar$\underline{H}$).

Following the above procedure, 4-n-undecyl-4'-acetylbiphenyl and 4-n-decyl-4'-acetylbiphenyl were prepared and their physical data are given below.

4-*n*-Undecyl-4′-acetylbiphenyl

Yield 65.5%; m.p. 90.0°C; IR ν_{max}^{nujol} 2900, 2850, 1680, 1600, 1465, 1380, 1265 and 800 cm^{-1}; NMR δ 0.79(t,3H,C$\underline{H}_3$), 1.14-1.73(m,18H,9×C$\underline{H}_2$), 2.6(s,3H, COC$\underline{H}_3$), 2.6(t, 2H, ArC$\underline{H}_2$), 7.17-8.1(m,8H,Ar$\underline{H}$).

4-*n*-Decyl-4′-acetylbiphenyl

Yield 58.0%: m.p. 90.0°C; ν_{max}^{nujol} 2900, 2850, 1680, 1600, 1460, 1375, 1265 and 805 cm^{-1}; NMR 6 0.73(t,3H,C$\underline{H}_3$), 1.14-1.5(m,16H,8×C$\underline{H}_2$), 2.6(s,3H, COC$\underline{H}_3$), 2.6(t, 2H, ArC$\underline{H}_2$), 7.14-8.14(m,8H,Ar$\underline{H}$).

The physical constants of the cognate preparations of other 4-n-alkyl-4'-acetyl biphenyls are given in table 2.8.

Table 2.8

Physical data of $H_{2n+1}C_nPhPhCOCH_3$

n	Observed		Reported	Ref.
	m.p.°C	Yield, %	m.p.°C	
5	82.5	58.0	77.0	43
6	84.0	45.3	79.0	43
7	74.5	40.0	76.5	43
8	85.1	69.0	86.5	43
9	85.4	55.0	85.0	43

1-(4″-*n*-Dodecylbiphenyl)-3-(4-ethylphenyl)propane-1,3-dione, (2.a.2)

This was prepared following the procedure of Holten and Webb.[44] Thus, a mixture of 4-n-dodecyl-4'-acetylbiphenyl (7.28 g, 0.02 mol) and ethyl-4-ethylbenzoate (3.56 g, 0.02 mol) were dissolved in dry 1,2-dimethoxyethane (175 ml) in a 250 ml two-necked flask, to which was attached a reflux condenser and a nitrogen inlet tube. This was stirred magnetically and sodium hydride (60% suspension in paraffin oil, 0.96 g, 0.04 mol) was added to it. The reaction mixture was refluxed for four hours and left at room temperature overnight. The reaction flask was cooled in ice and cold dilute hydrochloric acid (20 ml) was carefully added to it. A yellow stew was obtained and this was extracted into chloroform (3 x 60 ml). The combined chloroform solution was washed with water (3 x 50 ml) and dried (Na_2SO_4). Removal of solvent and chromatography of the residue gave a pale yellow material. This was crystallised from n-hexane several times until the transition temperatures were constant.

Yield (4.5 g, 45.0%); transition temperatures C73.5S_A100.5I; IR ν_{max}^{nujol} 2950, 2850, 1605, 1590, 1460, 1370, 1300, 840 and 780 cm^{-1}; NMR δ 0.9(t,3H,C$\underline{H}_3$), 1.1-2.0 (m,20H,10×-C$\underline{H}_2$), 2.65(t,4H, ArC$\underline{H}_2$), 6.9(s,1H,-C=C$\underline{H}$-), 7.2-8.25 (m,12H,Ar$\underline{H}$), 16.95(s,1H, enol-O$\underline{H}$); UV-Vis $\lambda_{max}^{CH_2Cl_2}$ (ϵ) 384(54,200), 363(86,200), 298.5(24,900), 263.5(21,000), 232 (35,400).

Elemental analysis: Found, C,84.89; H,8.95% $C_{35}H_{44}O_2$ requires C,84.67; H,8.87%.

Physical data of the cognate preparations of other 1-(4″-*n*-dodecylbiphenyl)-3-(4-substitutedphenyl)propane -1,3-diones are given below.

1-(4″-*n*-Dodecylbiphenyl)-3-(4-methylphenyl)propane-1,3-dione, (2.a.1)

Yield 42.0%; transition temperatures C101.5S_A111.0I; IR ν_{max}^{nujol} 2900, 2850, 1605, 1590, 1470, 1380, 1305, 840 and 780 cm^{-1}; NMR δ 0.85(t,3H,C$\underline{H}_3$), 1.0-1.8(m,20H, 10×-C$\underline{H}_2$), 2.5(t,3H,ArC$\underline{H}_3$), 2.65(t,2H,ArC$\underline{H}_2$), 6.9(s,1H,-C=C$\underline{H}$-), 7.2-8.2 (m,12H, Ar$\underline{H}$), 16.9(s,1H, enol-O$\underline{H}$); UV-Vis $\lambda_{max}^{CH_2Cl_2}$ (ϵ) 386(47,800), 364(81,300), 300(23,700), 264(19,700), 262(19,800), 233(33,700).

Elemental analysis: Found, C,84.54; H,8.85% $C_{34}H_{42}O_2$ requires C,84.64; H,8.71%.

1-(4″-*n*-Dodecylbiphenyl)-3-(4-methoxyphenyl)propane-1,3-dione, (2.a.3)

Yield 42.0%; m.p. 108.5°C; ν_{max}^{nujol} 2900, 2850, 1605, 1590, 1470, 1380, 1300, 840 and 760 cm^{-1}; NMR δ 0.9(t,3H,$C\underline{H}_3$), 1.2-1.9(m,20H,10×-$C\underline{H}_2$), 2.7(t,2H,Ar$C\underline{H}_2$), 3.9(s,3H,-O$C\underline{H}_3$), 6.9(s,1H,-C=C$\underline{H}$-), 6.95-8.2 (m,12H,Ar$\underline{H}$), 17.0(s,1H, enol-O$\underline{H}$); UV-Vis $\lambda_{max}^{CH_2Cl_2}$ (c) 386.5(29,500), 368(43,300), 306(15,500), 235(19,200).

Elemental analysis: Found, C,81.92; H,8.59% $C_{34}H_{42}O_3$ requires C,81.92; H,8.43%.

1-(4″-*n*-Dodecylbiphenyl)-3-(4-ethoxyphenyl)propane-1,3-dione, (2.a.4)

Yield 45.0%; transition temperatures C112.5S_A(102.0)I; IR ν_{max}^{nujol} 2950, 2850, 1605, 1590, 1470, 1380, 1305,840 and 785 cm^{-1}; NMR δ 0.85(t,3H,$C\underline{H}_3$), 1.04-1.57(m,20H, 10×-$C\underline{H}_2$), 2.66(t,2H,Ar$C\underline{H}_2$), 3.95-4.33(q,2H,-O-$C\underline{H}_2$-CH_3), 6.85 (s,1H,-C=C$\underline{H}$-), 6.9-8.1 (m,12H,Ar$\underline{H}$), 17.0(s,1H, enol-O$\underline{H}$); UV-Vis $\lambda_{max}^{CH_2Cl_2}$ (c) 389 (29,600), 368 (46,100), 302(14,000),234(20,400).

Elemental analysis: Found, C,82.01; H,8.69% $C_{35}H_{44}O_3$ requires C,82.03; H,8.59%.

1-(4″-*n*-Dodecylbiphenyl)-3-(4-bromophenyl)propane-1,3-dione, (2.a.5)

Yield 50.0%; transition temperatures C139.0S_E(131.4)S_A143.51; ν_{max}^{nujol} 2900, 2850, 1600, 1590, 1460, 1380, 1310, 840 and 780 cm^{-1}; NMR δ 0.9(t,3H,$C\underline{H}_3$), 1.15-1.85 (m,20H,10×-$C\underline{H}_2$), 2.65(t,2H,Ar$C\underline{H}_2$), 6.85(s,1H,-C=C$\underline{H}$-), 7.15-8.2 (m,12H,Ar$\underline{H}$), 16.8(s,1H,enol-O$\underline{H}$); UV-Vis $\lambda_{max}^{CH_2Cl_2}$ (c) 364.5(43,500), 265(14,300), 232.5(19,200).

Elemental analysis: Found, C,72.08; H,7.21% $C_{33}H_{39}O_2Br$ requires C,72.39; H,7.12%.

1-(4″-*n*-Dodecylbiphenyl)-3-(4-cyanophenyl)propane-1,3-dione, (2.a.6)

Yield 60%; transition temperatures C126.0S$_A$142.01; IR ν_{max}^{nujol} 2920, 2850, 2250, 1605, 1590, 1460, 1380, 1290, 860 and 790 cm^{-1}; NMR δ 0.9(t,3H,C$\underline{H}_3$), 1.1-1.9(m,20H, 10×-C$\underline{H}_2$), 2.7(t,2H,ArC$\underline{H}_2$), 6.9(s,1H,-C=C$\underline{H}$-), 7.2-8.2 (m,12H,Ar$\underline{H}$), 16.7(s,1H, enol-O$\underline{H}$); UV-Vis $\lambda_{max}^{CH_2Cl_2}$ (ϵ) 366.5(38,700), 304(13,000), 264(17,600), 247(19,600).

Elemental analysis: Found, C,82.79; H,7.88% $C_{34}H_{40}O_2N$ require C,82.75; H,7.91%.

Bis[1-(4″-*n*-dodecylbiphenyl)-3-(4-ethylphenyl)propane-1,3-dionato] copper(II), (2.b.2)

A solution of potassium hydroxide (0.03 g, 0.48 mmol) in ethanol (10 ml) was added to a rapidly stirred solution of 1-(4″-*n*-dodecylbiphenyl)-3-(4-ethylphenyl)propane-1,3-dione (0.24 g, 0.48 mmol) in ethanol (20 ml). To this was added an ethanolic solution (10 ml) of cupric chloride dihydrate (0.041 g, 0.24 mmol). The mixture was stirred at room temperature for four hours. The green precipitate so obtained was collected and dissolved in chloroform (50 ml), washed with water (2 × 25 ml) and dried (Na_2SO_4). Removal of solvent afforded a green residue which was crystallised several times from butan-2-one.

Yield (0.1 g, 20%); transition temperatures C160.0N(146.5)I; IR ν_{max}^{nujol} 2950, 2850, 1615, 1590, 1530, 1490, 1460, 1390, 1310, 1230 and 780 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 363(73,200), 312(47,000), 270(30,700), 234.5(39,000).

Elemental analysis: Found, C,79.80; H,8.30% $C_{70}H_{86}O_4Cu$ requires C,79.74; H,8.16%.

Bis[1-(4″-*n*-dodecylbiphenyl)-3-(4-methylphenyl)propane-1,3-dionato] copper(II), (2.b.1)

Yield 19.5%; transition temperatures C201.0N(162.0)I; IR ν_{max}^{nujol} 2950, 2850, 1610, 1590, 1530, 1490, 1460, 1390, 1310, 1180 and 770 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (c) 363(75,300), 312(47,700), 272(31,500), 233(41,000).

Elemental analysis: Found, C,79.52; H,8.14% $C_{68}H_{82}O_4Cu$ requires C,79.58; H,8.0%.

Bis[1-(4″-*n*-dodecylbiphenyl)-3-(4-methoxyphenyl)propane-1,3-dionato] copper(II), (2.b.3)

Yield 20%; transition temperatures C179.5N(169.5)I; IR ν_{max}^{nujol} 2950, 2850, 1615, 1590, 1530, 1490, 1460, 1390, 1330, 1170 and 780 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (t) 365.5(71,500), 315.5(56,500), 233(50,000).

Elemental analysis: Found, C,77.00; H,7.84% $C_{68}H_{82}O_6Cu$ requires C,77.17; H,7.75%.

Bis[1-(4″-*n*-dodecylbiphenyl)-3-(4-ethoxyphenyl)propane-1,3-dionato] copper(II), (2.b.4)

Yield 25%; transition temperatures C179.0N(158.0)I; IR ν_{max}^{nujol} 2950, 2850, 1610, 1590, 1540, 1490, 1470, 1390, 1310, 1180 and 780 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (t) 366(79,200), 317(53,500), 234(44,600).

Elemental analysis: Found, C,77.34; H,8.04% $C_{70}H_{86}O_6Cu$ requires C,77.39; H,7.92%.

Bis[1-(4″-*n*-dodecylbiphenyl)-3-(4-chlorophenyl)propane-1,3-dionato] copper(II), (2.b.5)

Yield 25%; transition temperatures C196.0N(171.0)I; IR ν_{max}^{nujol} 2950, 2850, 1618, 1590, 1530, 1480, 1380, 1320, 1220, 1090, 1010 and 780 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 365(75,000), 317(45,200), 271(37,300), 235(42,600).

Elemental analysis: Found, C,73.89; H,7.18% $C_{66}H_{76}O_4Cl_2Cu$ requires C,74.26; H,7.12%.

Bis[1-(4″-*n*-dodecylbiphenyl)-3-(4-bromophenyl)propane-1,3-dionato] copper(II), (2.b.6)

Yield 30%; transition temperatures C201.0S_A(170.5)I; ν_{max}^{nujol} 1610, 1590, 1530, 1470, 1380, 1310, 1220 and 780 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 365(73,500), 317(44,600), 275(38,300), 228(45,000).

Elemental analysis: Found, C,68.20; H,6.61% $C_{66}H_{76}O_4BrCu$ requires C,68.54; H,6.57%.

Bis[1-(4″-*n*-dodecylbiphenyl)-3-(4-cyanophenyl)propane-1,3-dionato] copper(II), (2.b.7)

Yield 20%; transition temperatures C218.0S_A(212.0)I; ν_{max}^{nujol} 2950, 2850, 1610, 1590, 1530, 1490, 1390, 1310, 1220 and 780 cm^{-1}; UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 371(67,000), 325(34,500), 259(44,400).

Elemental analysis: Found, C,77.88; H,7.33% $C_{68}H_{76}O_4N_2Cu$ requires C,77.90; H,7.25%.

Bis[1-(4″-*n*-dodecylbiphenyl)-3-(4-ethylphenyl)propane-1,3-dionato] palladium(II), (2.c.2)

A stirred mixture of 1-(4″-*n*-dodecylbiphenyl)-3-(4-ethylphenyl)propane-1,3-dione (0.28 g, 0.56 mmol), palladium chloride (0.055 g, 0.28 mmol), dry acetonitrile (60 ml) and anhydrous potassium carbonate (0.12 g, 1.2 mmol) was heated in an oil bath at 50°C for twenty hours. The cooled reaction mixture was filtered and the solid was taken up in chloroform (100 ml), washed with water (3x50 ml) and dried (Na_2SO_4). Removal of solvent afforded a bright yellow residue which was crystallised from butan-2-one several times.

Yield 34.0%; transition temperatures C177.0N(149.0)I; IR ν_{max}^{nujol} 2950, 2850, 1618, 1585, 1520, 1470, 1380, 1310, 1190 and 790 cm^{-1}; NMR δ 0.87[t,6H,(-C$\underline{H}_3$)$_2$], 1.1-1.6 [m,40H,(10×-C$\underline{H}_2$)$_2$], 2.66[t,4H(ArC$\underline{H}_2$)$_2$], 6.78 [s,2H,(-C=C$\underline{H}$)$_2$], 7.15-8.18 (m,24H,Ar$\underline{H}$); $\lambda_{max}^{CHCl_3}$ (ϵ) 411(24,200), 380(42,700), 322(66,400), 274(39,200).

Elemental analysis: Found, C,76.52; H,7.97% $C_{70}H_{86}O_4Pd$ requires C,76.61; H,7.84%.

Bis[1-(4″-*n*-dodecylbiphenyl)-3-(4-methylphenyl)propane-1,3-dionato] palladium(II), (2.c.1)

Yield 47.5%; transition temperatures C195.0N(162.0)I; IR ν_{max}^{nujol} 2950, 2850, 1610, 1580, 1540, 1490, 1380, 1310, 1180 and 760 cm^{-1}; NMR 6 0.8[t,6H,$(-C\underline{H}_3)_2$], 1.2-1.72 [m,40H,$(10\times-C\underline{H}_2)_2$], 2.66[t,4H($ArC\underline{H}_2)_2$], 6.78 [s,2H,$(-C{=}C\underline{H})_2$], 7.15-8.18(m, 24H, Ar$\underline{H}$); $\lambda_{max}^{CHCl_3}$ (ϵ) 411(24,200), 380(42,700), 322(66,400), 274(39,200).

Elemental analysis: Found, C,76.52; H,7.97% $C_{70}H_{86}O_4Pd$ requires C,76.61; H,7.84%.

Bis[1-(4″-*n*-dodecylbiphenyl)-3-(4-methoxyphenyl)propane-1,3-dionato] palladium(II), (2.c.3)

Yield 42.0%; transition temperatures C179.5N(169.5)I; IR ν_{max}^{nujol} 2950, 2850, 1618, 1590, 1530, 1490, 1460, 1360, 1260, 1230, 1020 and 780 cm^{-1}; NMR 6 0.87[t,6H,$(-C\underline{H}_3)_2$], 1.12-1.65 [m,40H,$(10\times -C\underline{H}_2)_2$], 2.72[t,4H$(ArC\underline{H}_2)_2$], 3.87[s,6H,$(OC\underline{H}_3)_2$], 6.75 [s,2H,$(-C{=}C\underline{H})_2$], 6.87-8.2(m,24H,Ar$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 410(25,800), 381 (46,300), 324(72,600).

Elemental analysis: Found, C,73.77; H,7.43% $C_{68}H_{82}O_6Pd$ requires C,74.15; H,7.45%.

Bis[1-(4″-*n*-dodecylbiphenyl)-3-(4-ethoxyphenyl)propane-1,3-dionato] palladium(II), (2.c.4)

Yield 45.0%; transition temperatures C179.0N(158.0)I; IR ν_{max}^{nujol} 2950, 2850, 1610, 1582, 1540, 1490, 1460, 1380, 1310, 1180 and 760 cm^{-1}; NMR 6 0.9[t,6H, $(-C\underline{H}_3)_2$], 1.09-1.63 [m,40H,$(10\times-C\underline{H}_2)_2$], 2.69[t,4H($ArC\underline{H}_2)_2$], 3.90-4.27[q,4H,($ArOC\underline{H}_2)_2$], 6.78 [s,2H,$(-C{=}C\underline{H})_2$], 6.87-8.15 (m,24H,Ar$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 412(26,500), 382 (46,900), 325(73,000).

Elemental analysis: Found, C,74.50; H,7.74% $C_{70}H_{86}O_6Pd$ requires C,74.44; H,7.62%.

Bis[1-(4″-*n*-dodecylbiphenyl)-3-(4-chlorophenyl)propane-1,3-dionato] palladium(II), (2.c.5)

Yield 40%; transition temperatures C201.0N(178.0)I; IR ν_{max}^{nujol} 2950, 2850, 1610, 1580, 1510, 1460, 1380, 1310, 1180, 1090, 1060, 1010, 840 and 780 cm^{-1}; NMR δ 0.85[t,6H,(-C$\underline{H}_3$)$_2$], 1.1-1.62 [m,40H,(10×-C$\underline{H}_2$)$_2$], 2.68[t,4H(ArC$\underline{H}_2$)$_2$], 6.77 [s,2H,(-C=C$\underline{H}$)$_2$], 7.2-8.14 (m,24H,Ar$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 415(21,300), 381(40,800), 324(59,400), 271(38,700), 242(53,600).

Elemental analysis: Found, C,71.19; H,6.90% $C_{66}H_{76}O_4Cl_2Pd$ requires C,71.38; H,6.85%.

Bis[1-(4″-*n*-dodecylbiphenyl)-3-(4-bromophenyl)propane-1,3-dionato] palladium(II), (2.c.6)

Yield 35%; transition temperatures C196.0N(177.5)I; IR ν_{max}^{nujol} 2950, 2850, 1610, 1580, 1510, 1460, 1380, 1310, 1180, 1080, 1010,940, 840, 780 and 720 cm^{-1}; NMR 6 0.84[t,6H,(-C$\underline{H}_3$)$_2$], 1.07-1.8 [m,40H,(10×-C$\underline{H}_2$)$_2$], 2.65[t,4H(ArC$\underline{H}_2$)$_2$], 6.7 [s,2H,(-C=C$\underline{H}$)$_2$], 7.1-8.07 (m,24H,Ar$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 415(23,500), 381(43,000), 325(63,000), 275(41,200), 236(60,100).

Elemental analysis: Found, C,65.80; H,6.41% $C_{66}H_{76}O_4Br_2Pd$ requires C,66.08; H,6.34%.

Bis[1-(4″-*n*-dodecylbiphenyl)-3-(4-cyanophenyl)propane-1,3-dionato] palladium(II), (2.c.7)

Yield 40%; transition temperatures C212.0N(197.5)I; IR ν_{max}^{nujol} 2950, 2850, 2250, 1618, 1580, 1530, 1490, 1470, 1380, 1310 and 780 cm^{-1}; NMR δ 0.9[t,6H,(-C$\underline{H}_3$)$_2$], 1.12-1.85 [m,40H,(10×-C$\underline{H}_2$)$_2$], 2.65[t,4H(ArC$\underline{H}_2$)$_2$], 6.75 [s,2H,(-C=C$\underline{H}$)$_2$], 7.17-8.2 (m,24H,Ar$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 423(20,800), 382(38,200), 337(48,700), 257(60,400).

Elemental analysis: Found, C,74.69; H,7.08, N,2.46% $C_{68}H_{76}O_4N_2Pd$ requires
C,74.83; H,6.9, N,2.56%.

1-(4″-*n*-Dodecylbiphenyl)-3-(4-chlorophenyl)propane-1,3-dione, (2.d.8)

This was prepared following a procedure described by Holten and Webb.[4] Thus, a mixture of 4-*n*-dodecyl-4′-acetylbiphenyl (3.43 g, 9.43 mmol) and ethyl-4-chloro benzoate (1.74 g, 9.43 mmol) was dissolved in dry 1,2-dimethoxyethane (100 ml) under nitrogen in a 250 ml round bottom flask. This was stirred magnetically and sodium hydride (60% suspension in paraffin oil, 0.45 g, 18.86 mmol) was added to it and the mixture refluxed for four hours and left overnight at room temperature. The reaction flask was cooled in ice and ice-cold dilute hydrochloric acid (20 ml) was added carefully to the reaction mixture and the yellow stew obtained was extracted with chloroform (3 x 60 ml). The combined chloroform solution was washed with water (3 x 50 ml) and dried (Na_2SO_4). Removal of solvent afforded a yellow material which was chromatographed on silica gel. The required compound so obtained was crystallised several times from benzene till the transition temperatures were constant.

Yield 2.1 g, 41.8%; transition temperatures, C127.5S_E(116.0)S_A143.0I; ν_{max}^{nujol} 2950, 2850, 1600, 1460, 1380, 1310, 1230, 1100, 1010,850 and 780 cm^{-1}; NMR δ 0.75(t,3H,$C\underline{H}_3$), 1-1.85 (m,20H,10×$C\underline{H}_2$), 2.69(t,2H,Ar$C\underline{H}_2$), 6.8(s,1H,-C=C$\underline{H}$-), 7.1-8.1 (m,12H,Ar$\underline{H}$), 16.85(s,1H, enol-O$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 363.0(42,760), 263(13,100), 234.0(17,000).

Elemental analysis: Found, C,78.72; H,7.84% $C_{33}H_{39}O_2Cl$ requires
C,78.80; H,7.76%.

The physical data of the cognate preparations of other 1-(4″-*n*-alkylbiphenyl)-3-(4-chlorophenyl)propane-1,3-diones are given below.

1-(4″-n-Pentylbiphenyl)-3-(4-chlorophenyl)propane-1,3-dione, (2.d.1)

Yield 51.0%; m.p. 146.0°C, ν_{max}^{nujol} 2950, 2850, 1600, 1460, 1380, 1090 and 780 cm^{-1}; NMR δ 0.8(t,3H,$C\underline{H}_3$), 1.05-1.95 (m, 6H, 3×$C\underline{H}_2$), 2.6(t,2H,Ar$C\underline{H}_2$), 6.8(s, 1H, -C=C$\underline{H}$-), 7.1-8.15 (m,12H, Ar$\underline{H}$), 16.9(s, 1H, enol-O$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 363.0 (43,125), 262(12,985), 234(17,080).

Elemental analysis: Found, C,77.15; H,6.18% $C_{26}H_{25}O_2Cl$ requires
C,77.13; H,6.18%.

1-(4″-n-Hexylbiphenyl)-3-(4-chlorophenyl)propane-1,3-dione, (2.d.2)

Yield 35.0%; transition temperatures C142.5S_A(140.5)I; IR ν_{max}^{nujol} 2950, 2850, 1600, 1465, 1370, 1090 and 760 cm^{-1}; NMR 6 0.9(t,3H,$C\underline{H}_3$), 1.15-1.95(m,8H,4×$C\underline{H}_2$), 2.65(t,2H,ArC$\underline{H}_2$-), 6.8(s,1H,-C=C$\underline{H}$-), 7.15-8.2(m,12H,Ar$\underline{H}$), 16.8(s,1H, enol-O$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 363(45,000), 262.5(14,500), 229(19,900).

Elemental analysis: Found, C,77.70; H,6.49% $C_{27}H_{27}O_2Cl$ requires
C,77.41; H,6.15%.

1-(4″-n-Heptylbiphenyl)-3-(4-chlorophenyl)propane-1,3-dione, (2.d.3)

Yield 35.5%; transition temperatures C138.5S_A144.51; IR ν_{max}^{nujol} 2950, 2850, 1600, 1460, 1380, 1090 and 780 cm^{-1}; NMH 6 0.7(t,3H,$C\underline{H}_3$), 1.1-2(m,10H,5×-$C\underline{H}_2$), 2.65(t,2H, ArC$\underline{H}_2$), 6.8(s,1H,-C=C$\underline{H}$-), 7.1-8.2 (m,12H,Ar$\underline{H}$), 16.8(s,1H, enol-O$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (E) 363(45,000), 262.5(14,500), 229(19,900).

Elemental analysis: Found, C,77.44; H,6.68% $C_{28}H_{29}O_2Cl$ requires
C,77.68; H,6.70%.

1-(4″-n-Octylbiphenyl)-3-(4-chlorophenyl)propane-1,3-dione, (2.d.4)

Yield 60%; transition temperatures C137.5S_A146.0I; IR ν_{max}^{nujol} 2950, 2850, 1595, 1465, 1380, 1090 and 780 cm^{-1}; NMR 6 0.92(t,3H,$C\underline{H}_3$), 1.08-1.84 (m,12H,6×-$C\underline{H}_2$), 2.65(t,2H,ArC$\underline{H}_2$), 6.8(s,1H,-C=C$\underline{H}$-), 7.08-8.32 (m,12H,Ar$\underline{H}$), 16.75(s,1H, enol-O$\underline{H}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (E) 363(44,000), 261.5(14,250), 230.5(19,200).

Elemental analysis: Found, C,78.05; H,7.05% $C_{29}H_{31}O_2Cl$ requires
C,77.90; H,6.90%.

1-(4″-n-Nonylbiphenyl)-3-(4-chlorophenyl)propane-1,3-dione, (2.d.5)

Yield 41.0%; transition temperatures C136.5S_A146.0I; IR ν_{max}^{nujol} 2950, 1600, 1465, 1380, 1090 and 780 cm^{-1}; NMR δ 0.9(t,3H,$\mathrm{C\underline{H}_3}$), 1.1-1.9(m,14H,7×-$\mathrm{C\underline{H}_2}$), 2.65 (t,2H,Ar-$\mathrm{C\underline{H}_2}$), 6.8(s,1H,-C=C$\underline{\mathrm{H}}$-), 7.15-8.15 (m,12H,Ar$\underline{\mathrm{H}}$), 16.9(s,1H, enol-O$\underline{\mathrm{H}}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 263(46,780), 262(15,000), 230.5(19,250).

Elemental analysis: Found, C,78.54; H,7.27% $C_{30}H_{33}O_2Cl$ requires
C,78.17; H,7.16%.

1-(4″-n-Decylbiphenyl)-3-(4-chlorophenyl)propane-1,3-dione, (2.d.6)

Yield 56%; transition temperatures C133.0S_A145.0I; IR ν_{max}^{nujol} 2950, 2850, 1595, 1460, 1370, 1090 and 780 cm^{-1}; NMR δ 0.8(t,3H,$\mathrm{C\underline{H}_3}$), 2.5-2.8(m,16H,8×-$\mathrm{C\underline{H}_2}$), 2.65(t,2H,Ar$\mathrm{C\underline{H}_2}$), 6.75(s,1H,-C=C$\underline{\mathrm{H}}$-), 7.15-8.2 (m,12H,Ar$\underline{\mathrm{H}}$), 16.8(s,1H, enol-O$\underline{\mathrm{H}}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 362(45,240), 263(13,850), 231.5(18,885).

Elemental analysis: Found, C,78.77; H,7.48% $C_{31}H_{35}O_2Cl$ requires
C,78.39; H,7.37%.

1-(4″-n-Undecylbiphenyl)-3-(4-chlorophenyl)propane-1,3-dione, (2.d.7)

Yield 33.0%; transition temperatures C124.5S_E(117.5)S_A144.0I; IR ν_{max}^{nujol} 2950, 2850, 1600, 1460, 1365, 1090 and 780 cm^{-1}; NMR 6 0.9(t,3H,$\mathrm{C\underline{H}_3}$), 1.1-1.85 (m,18H,9×-$\mathrm{C\underline{H}_2}$), 2.65(t,2H,Ar$\mathrm{C\underline{H}_2}$), 6.85(s,1H,-C=C$\underline{\mathrm{H}}$-), 7.2-8.15 (m,12H,Ar$\underline{\mathrm{H}}$), 16.85 (s,1H, enol-O$\underline{\mathrm{H}}$); UV-Vis $\lambda_{max}^{CHCl_3}$ (ϵ) 362.5(42,100), 262(13,350), 231.5(18,000).

Elemental analysis: Found, C,78.43; H,7.64% $C_{32}H_{37}O_2Cl$ requires
C,78.60; H,7.57%.

References

[1] A.M.Giroud-Godquin and J.Billard, Mol. *Cryst. Liquid Cryst.*, 66, 147 (1981).

[2] B.J.Bulkin, R.K.Rose and A.Santoro, Mol. *Cryst. Liquid Cryst.*, 43, 53 (1977).

[3] A.M.Giroud-Godquin and A.Rassat, C. *R.* Seances Acad. Sci. Ser.2, 294, 241 (1982).

[4] P.Styring, S.Tantrawong, D.R.Beattie and J.W.Goodby, *Liquid* Crystals, 10, 581 (1991).

[5] A.M.Giroud-Godquin and J.Billard, Mol. *Cryst. Liquid Cryst.*, 97, 287 (1983).

[6] K.Ohta, A.Ishii, J.Yamamoto and K.Matsuzaki, J. Chem. *Soc.* Chem. *Commun.*, 1099 (1984).

[7] K.Ohta, G.J.Jiang, M.Yokoyama, S.Kusabayashi and H.Mikawa, Mol. *Cryst. Liquid Cryst.*, 66, 283 (1981).

[8] K.Ohta, M.Yokoyama, S.Kusabayashi and H.Mikawa, Mol. *Cryst. Liquid .Cryst.*, 69, 131 (1981).

[9] K.Ohta, H.Muroki, A.Takagi, K.Hatada, H. Ema, I.Yamamoto and K.Matsuzaki, Mol. *Cryst. Liquid Cryst.*, 140, 131 (1986).

[10] K.Ohta, H.Muroki, A.Takagi, I.Yamamoto and K.Matsuzaki, Mol. *Cryst. Liquid Cryst.*, 135, 247 (1986).

[11] K.Ohta, I.Ishii, H.Muroki, I.Yamamoto and K.Matsuzaki, Mol. *Cryst. Liquid Cryst.*, 116, 299 (1985).

[12] A.M.Giroud-Godquin, M.M.Gauthier, G.Sigaud, F.Hardouin and M.F.Achard, Mol. *Cryst. Liquid Cryst.*, 132, 35 (1986).

[13] S.Chandrasekhar, B.K.Sadashiva, S.Ramesha and B.S.Srikanta, Pramana - *J.Phys.*, 27, L-713 (1986); S.Chandrasekhar, B.K.Sadashiva and B.S.Srikanta, *Mol. Cryst. Liquid Cryst.*, 151, 93 (1987).

[14] I.Y.Ovchinnikov, Yu.G.Galyametdinov, G.I.Ivanova arid L.M.Yagfarova, *Dokl.* Akad. Nauk. USSR, 276, 126 (1984); Yu.G.Galyametdinov, D.Z.Zakieva, I.V.Ovchinnikov, *Izv.* Akad. Nauk. SSSR, Ser. *Khim.(2)*, 491 (1986).

[15] K.Ohta, O.Takenaka, H.Hasebe, Y.Morizumi, T.Fujimoto and I.Yamamoto, Mol. *Cryst.* Liquid *Cryst.*, 195, 135 (1991).

[16] K.Ohta, O.Takenaka, H.Hasebe, Y.Morizumi, T.Fujimoto and I.Yamamoto, Mol. *Cryst.* Liquid *Cryst.*, 195, 103 (1991).

[17] B.Muhlberger and W.Haase, Liquid Crystals, 5, 251 (1989).

[18] K.Ohta, O.Takenaka, H.Hasebe, Y.Morizumi, T.Fujimoto arid I.Yamamoto, Mol. *Cryst.* Liquid *Cryst.*, 195, 123 (1991).

[19] B.K.Sadashiva, P.Rani Rao and B.S.Srikanta, Mol. *Cryst.* Liquid *Cryst.*, 168, 103 (1989).

[20] B.K.Sadashiva and S.Ramesha, Mol. *Cryst.* Liquid *Cryst.*, 141, 19 (1986); Veena Prasad, B.K.Sadashiva, Mol. *Cryst.* Liquid *Cryst.*, 195, 161 (1991).

[21] B.K.Sadashiva and Veena Prasad, Paper *presented* at the *Fourteenth International* Liquid Crystal Conference, Pisa, Italy, June 21-26, 1992, Abst. No. A-P 14.

[22] N.J.Thompson, G.W.Gray, J.W.Goodby and K.J.Toyne, Mol. *Cryst.* Liquid *Cryst.*, 213, 187 (1992).

[23] D.Demus and H.Demus, Flussige *Kristalle* in Tabellen, Vol.1 (VEB Deutscher, Verlag fur Grundstoffindustrie, Leipzig, 1974),p.188.

[24] G.W.Gray, in Liquid Crystals and Plastic Crystals, Eds. G.W.Gray and P.A.Winsor (Ellis Harwood Ltd., 1974), p.115.

[25] G.W.Gray, Molecular Structure and the Properties of Liquid Crystals, (Academic Press, London, New York, 1962), p.251; ibid 227.

[26] For a theoretical discussion, G.R.Luckhurst, C.Zannoni, P.L.Nordio and U.Sergre, Mol. Phys., **30,** 1345 (1975).

[27] U.Caruso, A.Roviello and A.Sirigu, Liquid Crystals, 7, 421 (1990); ibid, 7, 431 (1990).

[28] M.Marcos, M.B.Ros and J.L.Serrano, Mol. *Cryst.* Liquid *Cryst.*, 3, 1129 (1988); M.Marcos, P.Romero, J.L.Serrano, J.Barbera and A.M.Levelut, Liquid Crystals, 7, 251 (1990).

[29] B.K.Sadashiva, L.Umadevi and Archana Ghode, Paper presented at the Thirteenth International Liquid Crystal Conference, Vancouver, Canada, July 22-27, 1990, Abstr. No. SYN-42-p-TUE.

[30] F.Effenberger and R.Gleiter, Chem. *Ber.,* 97, 480 (1964).

[31] W.S.Emerson, J. Am. Chem. *Soc.*, 69, 1947 (1905).

[32] H.Rupe and Fr. Van Watraven, Helv. Chim. *Acta*, 13, 468 (1930)

[33] W.J.Hale and T.Lambert, J. Am. Chem. *Soc.*, 25, 262 (1913)

[34] E.N.Kaiser and R.A.Woodruff, J. *Org.* Chern., 36, 1198 (1970).

[35] H.Gilman, W.Langham and H.B.Willis, J. Am. Chem. *Soc.*, 62, 346 (1940).

[36] *Beilstein's Handbuch*, Vol. 10, p.98.

[37] L.M.Long and H.R.Henze, J. Am. Chem. *Soc.*, 63, 1939 (1941).

[38] Reduction, Techniques and Application in Organic Synthesis, Ed. by Robert L. Augustine, p.174.

[39] C.S.Oh, Liquid Crystals and Ordered *Fluids*, **Vol.** 3, Ed. J.F.Johnson and R.H.Porter (Plenum Press, New York, 1978), p.53.

[40] E.P.Kaplan, Z.I.Kazakova and A.D.Petrov, *Zur. Obsch. Khim.*, **30**, 369 (1960).

[41] B.K.Sadashiva, Ph.D. Thesis, Bangalore University (1979), pp.148-150.

[42] D.J.Byron, G.W.Gray and R.G.Wilson, J. *Chem. Soc.*, 840 (1966).

[43] D.Demus, H.Demus and H.Zaschke, *Flussige* Kristalle in *Tabellen*,Vol.1 (VEB Deutscher Verlag fur Grundstoffindustrie, Leipzig, 1974), pp. 186-187.

[44] J.G.Burr, W.F.Holten and G.N.Webb, *J.* Am. *Chem. Soc.,* 72, 4903 (1950)