Mesomorphic properties of 1-(4′-dodecylbiphenyl-4-yl)-3-(2 or 3-alkoxyphenyl)propane-1,3-diones: the influence of alkoxy-substituent position

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Two homologous series of β-diketones, *viz.* 1-(4′-dodecylbiphenyl-4-yl)-3-(2-alkoxyphenyl)propane-1,3-diones and 1-(4′-dodecylbiphenyl-4-yl)-3-(3-alkoxyphenyl)propane-1,3-diones have been synthesised. The mesomorphic behaviour of all the compounds has been investigated using optical polarising microscopy and differential scanning calorimetry. The enthalpies associated with the transitions of all the liquid crystalline materials have also been determined. The mesophases exhibited by these compounds are explained on the basis of the structural features associated with such compounds.

A large number of β-diketones have been synthesised in the last ten years or so for use as ligands in the preparation of metallomesogens.[1–3] Since many β-diketones themselves exhibit mesophases they have been investigated in great detail.[4–7] In the majority of the liquid crystalline materials, the alkyl/alkoxy chain is normally substituted in the *para*- (terminal) position and in all the mesogenic β-diketones reported so far the long chains are in the *para*-position. For a long time it was believed that on introduction of long chains/bulky substituents into positions other than the *para*, either the thermal stability of the mesophase would be greatly reduced or the system would be rendered non-mesomorphic. However, Demus *et al.*[8] examined a number of systems in which the long alkyl chain was not in the terminal *para* position but was located laterally. In other words, the chain was incorporated either in the *ortho*- or *meta*-position with respect to the bridging group or on the bridging group itself. In this paper we report the synthesis and mesomorphic properties of two homologous series of β-diketones in which the substituents are in the *ortho*- or *meta*-positions of a terminal phenyl ring and compare these properties with a few similar compounds.

Experimental

Synthesis

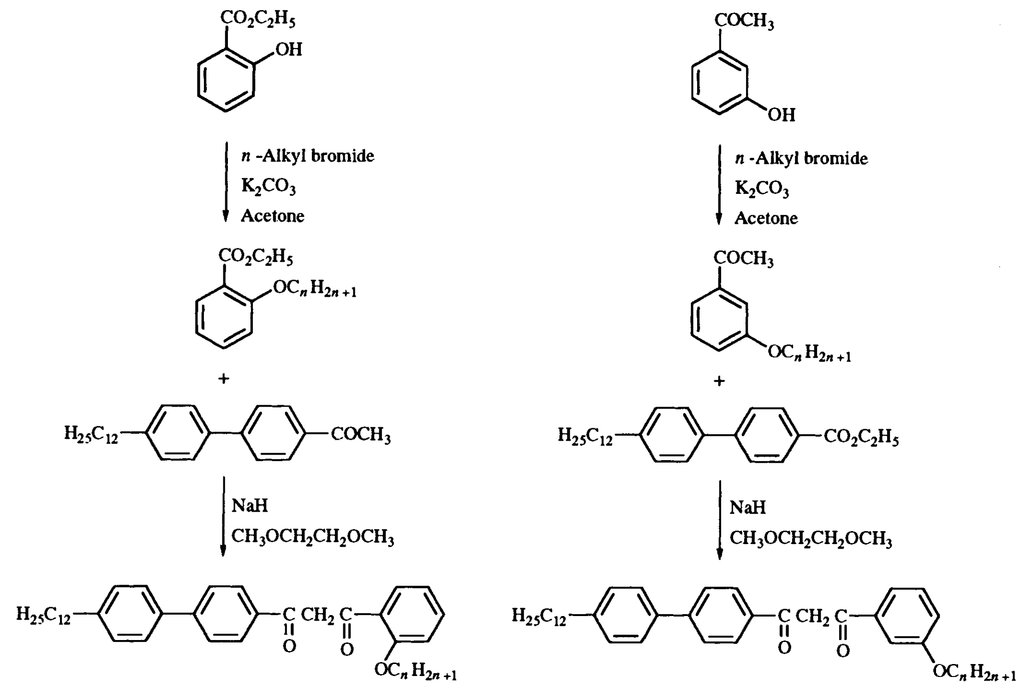
1-(4′-Dodecylbiphenyl-4-yl)-3-(2-alkoxyphenyl)propane-1,3-diones **I** and 1-(4′-dodecylbiphenyl-4-yl)-3-(3-alkoxyphenyl)-propane-1,3-diones **II** were prepared by following the general procedure described below, as shown schematically in Fig. 1. 4′-Dodecyl-4-acetylbiphenyl was prepared by following the literature procedure.[10] Ethyl 4′-dodecylbiphenyl-4-carboxylate was prepared in two steps from 4′-dodecyl-4-acetylbiphenyl, first by sodium hypobromite oxidation and then esterification of the resulting carboxylic acid using ethyl alcohol and sulfuric acid. 4′-Dodecyl-4-aminobiphenyl was also obtained in two steps from 4′-dodecyl-4-acetylbiphenyl by following a procedure similar to that described by van der Veen *et al.*[11] Ethyl 2-alkoxybenzoates and 3-alkoxyacetophenones were prepared by alkylating ethyl salicylate and 3-hydroxyacetophenone, respectively, with an appropriate alkyl bromide. 3-Decyloxybenzaldehyde was prepared by alkylating *m*-hydroxybenzaldehyde with decyl bromide. 4-Dodecyloxyphenol was obtained by alkylating 4-benzyloxyphenol with dodecyl bromide and then cleaving the benzyl group by hydrogenolysis. 4′-Dodecyloxy-4-hydroxybiphenyl was prepared by monoalkylation of 4,4′-dihydroxybiphenyl. Ethyl 3-methylbenzoate, ethyl 3-chlorobenzoate, ethyl 3-bromobenzoate and ethyl 3-cyanobenzoate were prepared by esterification of their corresponding carboxylic acids with ethanol. The chiral derivatives ethyl 3-(2-methylbutyloxy)benzoate and 4-(2-methylbutyloxy)-4′-acetylbiphenyl were synthesised *via* Mitsunobu reaction[12] using (−)-2-methylbutan-1-ol and ethyl 3-hydroxybenzoate and 4-acetyl-4′-hydroxybiphenyl, respectively.

Measurements and characterisation

All the compounds synthesised were purified by chromatography over silica gel (60–120 mesh) using a mixture of chloroform–petroleum ether (bp 60–80 °C) as eluent. They were recrystallised several times from the appropriate solvents until a constant melting point was obtained. The chemical structures as well as the purity of all the compounds investigated were checked by microanalytical and spectral data. The IR absorption spectra were recorded on a Shimadzu IR-435 spectrophotometer, as Nujol mulls. The ^1H NMR spectra were recorded on a Bruker WP 80 SY FT NMR spectrometer in deuteriochloroform using tetramethylsilane as an internal reference standard. The UV and visible absorption spectra were obtained in chloroform on a Hitachi U 3200 spectrophotometer in chloroform. 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 FP5 temperature controller. The enthalpies of transitions were determined from thermograms obtained on a Perkin-Elmer Model DSC-4 differential scanning calorimeter. The calorimeter was calibrated using pure indium as a standard and a heating/cooling rate of 5 °C min^{-1} was generally employed. X-ray diffraction experiments were conducted using a Huber 644 Guinier diffractometer employing Cu-Kα radiation.

1-(4′-Dodecylbiphenyl-4-yl)-3-(2-undecyloxyphenyl)propane-1,3-dione 11

In a 250 cm^3 two-necked round-bottom flask, fitted with a reflux condenser and an inlet tube for passing dry nitrogen, was placed a mixture of 4′-dodecyl-4-acetylbiphenyl (3.64 g, 0.01 mol) and ethyl 2-undecyloxybenzoate (3.2 g, 0.01 mol) in anhydrous 1,2-dimethoxyethane (80 cm^3). To this stirred mixture was added sodium hydride (0.8 g, 0.02 mol, 60% in paraffin oil) and the whole was refluxed for 4 h and cooled. Ice cold dilute hydrochloric acid (30 cm^3) was added and the mixture was extracted with chloroform (3 × 50 cm^3). The combined chloroform solution was washed with water (4 × 100 cm^3) and dried (Na_2SO_4). Removal of solvent and chromatography of the residue on silica gel gave a pale yellow



I **II**

Fig. 1 General scheme used for the synthesis of β-diketones; **I**, compounds **1**–**12**, n = 1–12 and **II**, compounds **13**–**24**, n = 1–12

product. This was crystallised from propan-2-ol several times until the transition temperatures were constant. Yield 1.1 g (17%); ν_{max} 1608 cm^{-1}; δ_H(solvent $CDCl_3$) 0.88 (t, 6 H, 2 × $-CH_3$), 1.0–2.0 (m, 38 H, 19 × $-CH_2$), 2.6 (t, 2 H, $ArCH_2$), 4.1 (t, 2 H, $ArOCH_2$), 7.0 (s, 1 H, =C–H), 7.2–8.2 (m, 12 H, ArH), 16.9 (s, 1 H, =C–OH) (Found: C, 83.04; H, 9.93. $C_{44}H_{62}O_3$ requires C, 82.75; H, 9.71%).

1-(4′-Dodecylbiphenyl-4-yl)-3-(3-octyloxyphenyl)propane-1,3-dione 20

This was prepared by the same procedure as described above using the following reagents. Ethyl 4′-dodecylbiphenyl-4-carboxylate (3.24 g, 0.01 mol), 3-octyloxyacetophenone (2.48 g, 0.01 mol) and sodium hydride (0.8 g, 0.02 mol, 60% in paraffin oil). Yield 1.8 g, 30%; ν_{max} 1610 cm^{-1}; δ_H(solvent $CDCl_3$) 0.8 (t, 6 H, 2 × $-CH_3$), 1.0–2.0 (m, 32 H, 16 × $-CH_2$), 2.7 (t, 2 H, $ArCH_2$), 4.05 (t, 2 H, $ArOCH_2$), 6.85 (s, 1 H, –C=CH), 7.2–8.2 (m, 12 H, ArH), 16.85 (s, 1 H, =C–OH) (Found: C, 82.75; H, 9.57. $C_{41}H_{56}O_3$ requires C, 82.55; H, 9.39%).

Transition temperatures

The transition temperatures and enthalpies for 1-(4′-dodecylbiphenyl-4-yl)-3-(2-alkoxyphenyl)propane-1,3-diones **I** are summarised in Table 1. As can be seen, all the compounds are enantiotropic nematic. Compound **12** exhibits a monotropic smectic A phase in addition to a nematic phase. The enthalpy for the N ——→ I transition is *ca.* 0.4 kJ mol^{-1} for most of the compounds, in agreement with that reported[13] for such a transition. All the compounds have fairly low melting points (< 80 °C) as well as low clearing points (below 94 °C).

A plot of the transition temperatures *versus* the number of carbon atoms in the alkoxy chain for compounds **1**–**12** is shown in Fig. 2. Though there is an alternation in the N ——→ I transition points, the transition temperatures tend to decrease initially and then increase gradually as the series is ascended.

Table 1 Transition temperatures (°C) and *enthalpies* (kJ mol^{-1}) for 1-(4′-dodecylbiphenyl-4-yl)-3-(2-alkyloxyphenyl)propane-1,3-diones **I**[a]

Compound number	n	C		S_A	N		I
1	1	·	79.5 *21.71*	—	·	89.0 *0.67*	·
2	2	·	70.5 *27.02*	—	·	93.5 *0.33*	·
3	3	·	60.0 *44.18*	—	·	66.0 *0.37*	·
4	4[b]	·	47.5 *27.78*	—	·	70.5 *0.50*	·
5	5	·	53.5 *40.58*	—	·	65.0 *0.42*	·
6	6	·	51.5 *43.01*	—	·	67.5 *0.42*	·
7	7	·	48.5 *50.42*	—	·	66.0 *0.33*	·
8	8	·	60.5 *35.77*	—	·	71.0 *0.42*	·
9	9	·	66.5 *38.78*	—	·	70.5 *0.37*	·
10	10	·	67.0 *36.73*	—	·	76.5 *0.37*	·
11	11	·	63.0 *37.2*	—	·	77.5 *0.46*	·
12	12	·	63.5 *32.55*	(· 49.5)[c]	·	81.5 *0.46*	·

[a] For key to column headings and Table entries, see footnote to Table 2. [b] Compound **4** has a crystal ——→ crystal transition at 42.0 °C (12.76 kJ mol^{-1}). [c] Enthalpy could not be measured.

The transition temperatures and enthalpies for 1-(4′-dodecylbiphenyl-4-yl)-3-(3-alkoxyphenyl)propane-1,3-diones **II** are given in Table 2. All the compounds are mesogenic. Except for compound **13**, which exhibits a monotropic nematic phase, all the remaining homologues exhibit a focal-conic texture and have been characterised as smectic A. Compounds **14** and **15** are monotropic whereas the other higher homologues are enantiotropic. As in the previous homologous series of compounds, these also have fairly low melting as well as clearing temperatures (< 101 °C). A graphic representation of these temperatures as a function of the number of carbon atoms in the alkyl chain is shown in Fig. 3. Clearly the S_A ——→ I transition points fall on a smooth curve.

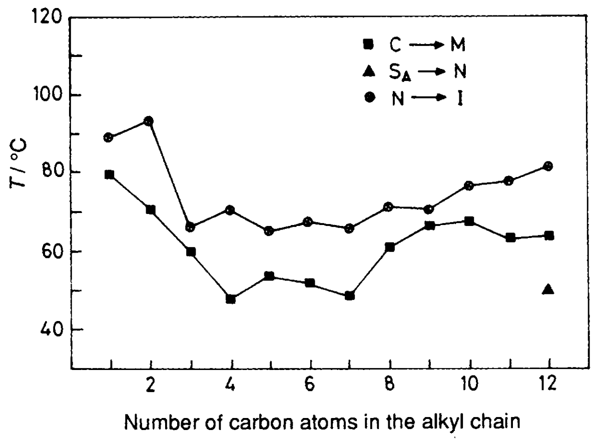


Fig. 2 Plot of transition temperatures *versus* the number of carbon atoms in the alkyl chain for the β-diketones **I**

Table 2 Transition temperatures (°C) and *enthalpies* (kJ mol^{-1}) for 1-(4′-dodecylbiphenyl-4-yl)-3-(3-alkyloxyphenyl)propane-1,3-diones **II**[a]

Compound number	*n*	C_1	C	S_A	N	I
13	1	—	• 100.0 *56.90*	—	(• 97.5) *0.54*	•
14	2	—	• 100.0 *50.62*	(• 96.0) *4.39*	—	•
15	3	• 84.0 *16.94*	• 95.5 *38.99*	(• 95.0) *5.82*	—	•
16	4	• 79.5 *19.30*	• 93.0 *29.70*	• 98.5 *6.94*	—	•
17	5	• 78.0 *20.29*	• 90.0 *30.37*	• 99.0 *7.49*	—	•
18	6	• 79.0 *19.70*	• 85.5 *24.52*	• 99.5 *8.16*	—	•
19	7	—	• 78.0 *49.29*	• 99.0 *8.20*	—	•
20	8	—	• 76.5 *48.07*	• 99.5 *8.70*	—	•
21	9	• 60.5 *8.95*	• 74.5 *46.77*	• 98.5 *8.37*	—	•
22	10	• 54.5 *10.42*	• 73.5 *46.98*	• 98.0 *9.04*	—	•
23	11	—	• 75.0 *64.68*	• 97.5 *9.54*	—	•
24	12	—	• 73.5 *62.30*	• 97.5 *9.12*	—	•

[a] Key: • phase exists; — phase does not exist; C_1 and C: crystalline phases; S_A: smectic A phase; N: nematic phase; I: isotropic phase.

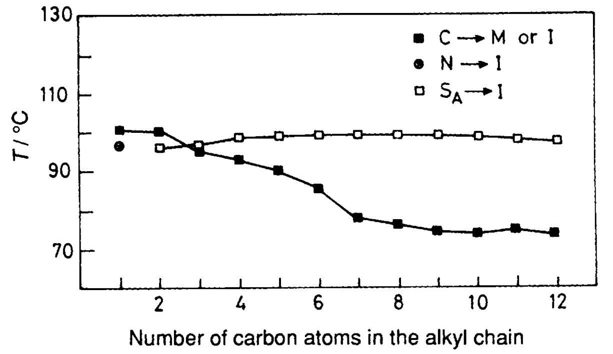
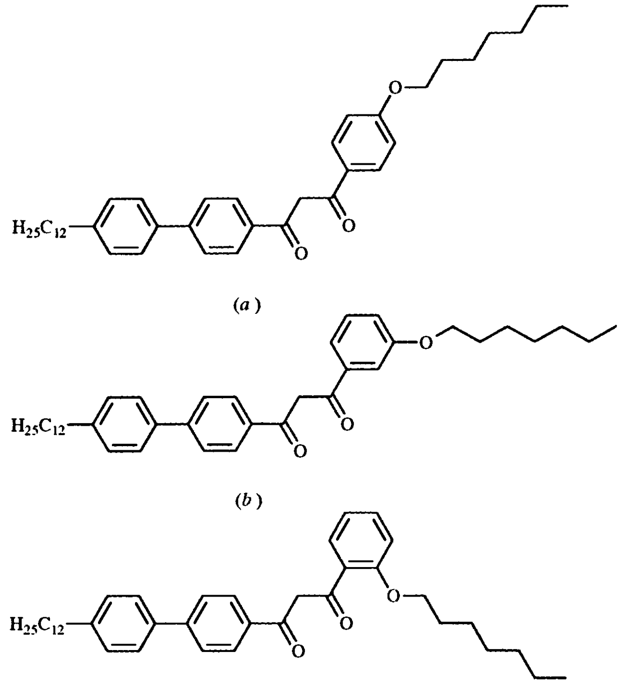


Fig. 3 Plot of transition temperatures *versus* the number of carbon atoms in the alkyl chain for the β-diketones **II**



(*a*)

(*b*)

(*c*)

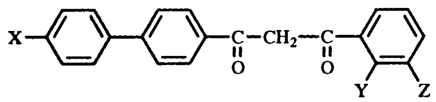
Fig. 4 Different possible conformations of *para*-, *meta*- and *ortho*-substituted β-diketones

Results and discussion

The parent β-diketone [1-(4′-dodecylbiphenyl-4-yl)-3-(phenyl)-propane]-1,3-dione, a molecule with a bent structure, shows mesomorphic properties when there is no substituent on the phenyl ring.[6a] Any substituent in the *para* position of this phenyl ring would increase the lateral molecular dimensions and hence reduce the potential of the system to exhibit mesomorphism. Two such homologous series of compounds have been examined recently[14] and the trend in the mesomorphic behaviour is in accordance with this assumption. There are very few examples of liquid crystalline materials in which there is only one terminal chain and the other is in a lateral position attached to the core. In one case the lateral chain was incorporated on the >C=N bridging group which is considered to be part of the aromatic ring system. In both these systems, a nematic phase was obtained.[15]

In the present two series of compounds **I** and **II**, the alkoxy chain is not incorporated at the *para* position of the terminal phenyl ring. All the compounds in the two series exhibit mesophases including the long-chain derivatives in contrast to their *para* substituted analogues. While in series **I** all the homologues exhibit enantiotropic nematic phases, in series **II** smectic A phase is predominant. This mesomorphic behaviour may be explained on the basis of the conformations of the β-diketones of the three series as shown in Fig. 4. In the case of *para*-substituted derivatives (*a*), the shorter chain length compounds exhibit mesophases while for longer chain lengths, say $C_{12}H_{25}$, the mesophase disappears.[14] This seems to suggest that the bent molecular structure would adopt a conformation in which the breadth would increase. In the case of *meta*-substituted compounds (*b*), the chain takes a position such that the molecule is almost linear. In fact, X-ray studies of the mesophase of one of the homologues *viz.* compound **24** gave a value of 43.3 Å for the layer spacing at 76 °C. This value is in reasonable agreement with the measured molecular length (45 Å, CPK molecular model) of the compound in its fully extended conformation. In the case of the *ortho*-substituted derivatives (*c*), the chain orients to a position such that a rod-like structure is obtained with the phenyl ring protruding slightly. Such a structure is conducive to the formation of a nematic phase as observed in these homologues. As reported previously by Thompson *et al.*,[7a] the probable reason for such behaviour is that in the *meta*-substituted compounds the more linear molecules can be accommodated much better in a layered arrangement thus giving rise to a smectic phase. However,

Table 3 Transition temperatures (°C) and *enthalpies* (kJ mol^{-1}) for[a]



Compound number	X	Y	Z	C	S_A	N*	I
25	$C_{12}H_{25}$	H	CH_3	• 89.5 *34.14*	• 94.5 *4.02*	— —	•
26	$C_{12}H_{25}$	H	CN	• 131.5 *35.60*	—	— —	•
27	$C_{12}H_{25}$	H	Cl	• 98.5 *34.98*	• 110.5 *4.18*	—	•
28	$C_{12}H_{25}$	H	Br	• 100.5 *45.06*	• 109.5 *4.22*	—	•
29	$C_{12}H_{25}$	H	$\mathrm{OCH_2\underset{*}{\overset{\overset{CH_3}{\vert}}{C}}HC_2H_5}$	• 91.0 *34.81*	(• 84.0) *6.69*	—	•
30	$\mathrm{OCH_2\underset{*}{\overset{\overset{CH_3}{\vert}}{C}}HC_2H_5}$	$OC_{10}H_{21}$	H	• 97.0 *41.59*	—	(• 80.0) *0.88*	•

[a] Key: • Phase exists; — phase does not exist; C_1 and C: crystalline phases; S_A: smectic A phase; N: nematic phase; N*: chiral nematic phase; I: isotropic phase.

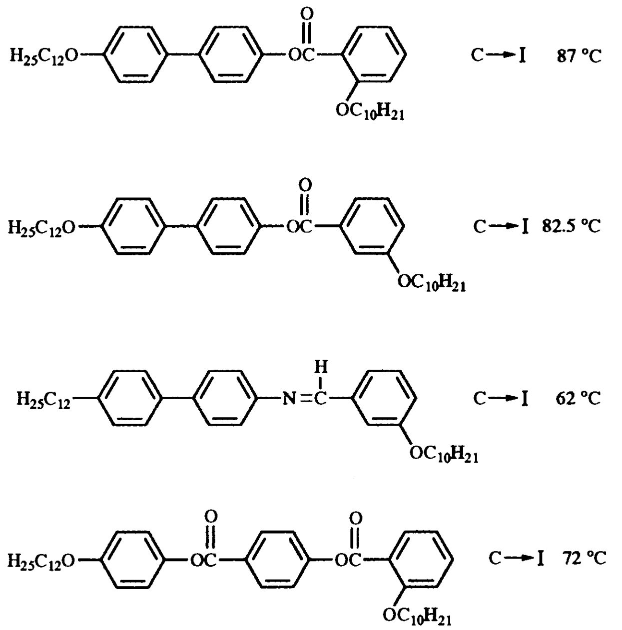


Fig. 5 Structure and melting points of some esters and a Schiff's base

the more 'branched' like structure of the *ortho*-substituted derivatives can be more easily accommodated in the less ordered imbricated structure thus allowing the formation of a nematic phase. The above conformations have been considered as they would greatly reduce lateral intermolecular steric repulsions.

With a view to understanding whether this behaviour is true exclusively for β-diketones, a few esters and a Schiff base having a chain in the *ortho* or *meta* position of a terminal phenyl ring were synthesised, and these are shown in Fig. 5. From Fig. 5, all the compounds are non-mesogenic. Hence it can be inferred that even though a β-diketone has a bent structure, by suitable substitution a stable mesophase can be generated. In order to examine the influence of polar and chiral substituents on the mesophase in these β-diketones, a few representative derivatives were prepared and the transition temperatures as well as the associated enthalpies of these are summarised in Table 3. It is seen that with a small substituent such as methyl (compound **25**) in the *meta* position exhibits an enantiotropic smectic A phase. Similarly, chloro- and bromo-substituents which lie high in the smectic group efficiency order do show enantiotropic smectic A phases. However, surprisingly, the cyano-substituted derviative (compound **26**) is non-mesomorphic. This is probably due to the high melting point of 131 °C as compared to the remaining compounds in Table 3. The chiral substituent in the *meta* position does exhibit a metastable smectic A phase. However, the chiral substituent in the *para* position of the biphenyl moiety (compound **30**) exhibits a monotropic chiral nematic phase. Perhaps by introducing a longer chiral chain in this position it may be possible to obtain an enantiotropic chiral nematic phase.

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