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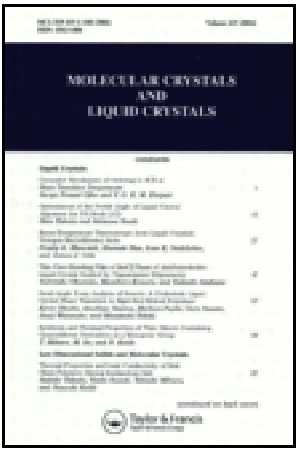

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# Liquid Crystalline Behaviour in Some Homologous Series of β-diketones and a Few of Their Copper(II) and Palladium(II) Complexes

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The synthesis and mesomorphic properties of three homologous series of β-diketones as well as one series each of copper(II) and palladium(II) complexes are reported. The β-diketones exhibit a smectic A phase while both the copper(II) and palladium(II) complexes show only a metastable nematic phase. Optical microscopy and differential scanning calorimetry have been used to characterize the mesophases.

*Keywords: β-diketone, ligands, chelates, nematic, smectic A*

## 1. INTRODUCTION

Metal containing liquid crystalline materials or metallo-mesogens are being investigated with renewed interest during the past fifteen years or so.[1,2] One of the widely used ligands is a β-diketone system to obtain mesogenic metal β-diketonates.[3–8] Since many of the β-diketones themselves are mesognetic a systematic study of the mesomorphic properties of a number of these have been undertaken by different groups.[9–13] For example, we have examined[14] the influence of polar terminal substituents such as chloro, bromo and cyano groups on the mesophases of both ligands and the copper(II) complexes, in addition to a few other small substituents. Thompson *et al.*[13] have investigated the effect of polar terminal substituents, in the lateral phenyl and biphenyl units and found that many complexes showed enhanced smectic character as compared to their nonpolar analogues. They have also examined the effect of a fluoro substituent on the mesophase when it is in different positions ($o^-, m^-$ and $p^-$) of the lateral biphenyl moiety of a β-diketone as well as their copper(II) complexes. It is now well established that β-diketones containing two rings exhibit highly ordered phases while those with three or four rings exhibit nematic and smectic A phases.

In continuation of our work,[14] on the mesomorphic behavior of β-diketones and their metal complexes, we have synthesized three homologous series of β-diketones containing three rings (a biphenyl moiety and a phenyl ring) and a series each of copper(II) and palladium(II) complexes and report here their mesogenic properties. All

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the β-diketones which are mesomorphic exhibit the smectic A phase while all the mesogenic metal complexes exhibit a metastable nematic phase.

## 2. EXPERIMENTAL

The synthetic route for the preparation of the β-diketones was similar to the one already described by us previously.[10,14] 4-*n*-Alkyl-4′-acetylbiphenyls were synthesized following literature procedure.[15] Similarly 4-*n*-alkoxy-4′-acetylbiphenyls were prepared according to the procedure described by Gray *et al.*[16] The ethyl *p*-substituted benzoates were prepared from the corresponding benzoic acids and ethanol using sulphuric acid. The copper(II) and palladium(II) chelates were synthesized as described earlier.[14]

The purity of all the compounds synthesized was checked by microanalytical and spectral data. The infrared absorption spectra were recorded on a Shimadzu IR-435 spectrophotometer, as Nujol mull. The proton magnetic resonance spectra were taken on a Bruker WP 80SY FT NMR spectrometer in deuterochloroform using tetramethylsilane as an internal standard. The ultraviolet and visible absorption spectra were obtained 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 polarizing microscope equipped with a Mettler FP52 heating stage and a FP5 controller. The enthalpies of transitions were determined from thermograms obtained on a Perkin-Elmer Model DSC-4 differential scanning carlorimeter. The calorimeter was calibrated using pure indium as a standard and a heating and cooling rate of 5°C/min was used.

In Figure 1, various β-diketones and the metal complexes that have been synthesized and whose properties are discussed here are given.

## 3. RESULTS AND DISCUSSION

The transition temperatures and enthalpies of transitions for 1-(4″-*n*-alkoxybiphenyl)-3-(phenyl)propane-1,3-diones are summarized in Table 1. As can be seen all these β-diketones except for compound 1 are mesogenic. Compounds 2 and 3 exhibit monotropic and the remaining enantiotropic mesophases. The mesophases exhibit a focal-conic texture characteristic of a smectic A phase with a mesophase range of about 20° for the higher homologues. Some of the homologues also undergo a crystal → crystal transition. The enthalpies of the $S_A \rightarrow I$ transition as determined from thermograms obtained on a differential scanning calorimeter for the various homologues range between 1 and 1.4 kcal/mol. A graphic representation of the transition temperatures as a function of alkyl chain length for the above β-diketones is shown in Figure 2. It is seen that there is an initial increase followed by alternation of the $S_A \rightarrow I$ transition temperatures as the series is ascended before leveling off at the undecyloxy derivative. Also, the alternation is not pronounced and is rather small from the butoxy derivative onwards.

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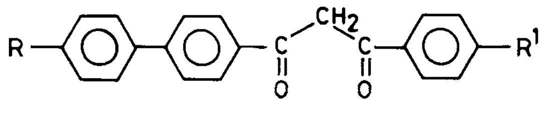
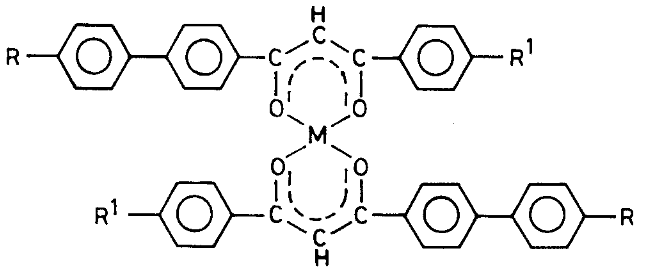


$R = C_nH_{2n+1}$ ; $R^1 = H$ I

$R = OC_nH_{2n+1}$ ; $R^1 = H$ II

$R = n\text{-}C_{12}H_{25}$ ; $R^1 = C_nH_{2n+1}$ III

$R = n\text{-}C_{12}H_{25}$ ; $R^1 = OC_nH_{2n+1}$ IV



$R = OC_nH_{2n+1}$ ; $R^1 = H$ ; $M = Cu$ V

$R = C_nH_{2n+1}$ ; $R^1 = H$ ; $M = Pd$ VI

$R = n\text{-}C_{12}H_{25}$ ; $R^1 = CH_3$ ; $M = Cu$ VIIa

FIGURE 1 Various β-diketones and the metal complexes synthesized.

The mesomorphic behavior of the corresponding 1-(4-*n*-alkylbiphenyl)-3-(phenyl)propane-1,3-diones, I, has already been reported.[10] In that series, the *n*-butyl, *n*-pentyl and *n*-hexyl derivatives exhibited monotropic nematic as well as smectic A phases while the *n*-heptyl derivatives exhibited an enantiotropic nematic phase though over a narrow range. The remaining higher homologues exhibited a smectic A phase. A comparison of these two series indicates that alkoxy substitution has destablized the nematic phase, as is to be expected, besides increasing the thermal stability of the smectic A phase.

The transition temperatures and enthalpies of transitions for bis[1-(4″-*n*-alkoxybiphenyl)-3-(phenyl)propane-1,3-dionato]copper(II) complexes, V, are summarized in Table 2. Except for the butoxy derivative (compound 12, which is non-mesomorphic, the remaining show a monotropic nematic phase. As can be seen from the table, the thermal stability of the mesophase goes on decreasing as the series is ascended. Many of the complexes exhibit crystal → crystal transitions and have fairly high melting points. Since the enthalpy associated with N → I transition is negligibly small, the same could

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TABLE 1

Transition temperatures (°C) and enthalpies of transitions (kcal/mol) for 1-(4″-n-alkyloxybiphenyl)-3-(phenyl)propane-1,3-dione, II

| Compound number | n | C | $S_A$ | I |
|---|---|---|---|---|
| 1 | 2 | . 125.5<br>7.99 | — | . |
| 2 | 3 | . 139.0<br>8.94 | (. 124.5)[†] | . |
| 3 | 4 | . 135.5<br>8.91 | (. 135.0)<br>1.03 | . |
| 4 | 5 | . 128.0<br>7.74 | . 133.5<br>1.04 | . |
| 5 | 6 | . 124.0<br>8.05 | . 135.0<br>1.10 | . |
| 6 | 7* | . 121.5<br>7.93 | . 134.5<br>1.13 | . |
| 7 | 8* | . 120.0<br>8.05 | . 136.0<br>1.21 | . |
| 8 | 9 | . 115.5<br>10.98 | . 135.5<br>1.30 | . |
| 9 | 10* | . 116.5<br>8.25 | . 136.5<br>1.30 | . |
| 10 | 11 | . 118.5<br>12.61 | . 136.5<br>1.40 | . |
| 11 | 12 | . 116.5<br>13.05 | . 136.0<br>1.33 | . |

* Compounds 6, 7 and 9 have crystal → crystal transitions at 90.0°C (1.61 kcal/mol), 87.0°C (1.31 kcal/mol) and 107.0°C (2.53 kcal/mol) respectively.

[†] Enthalpy could not be measured due to onset of crystallization.

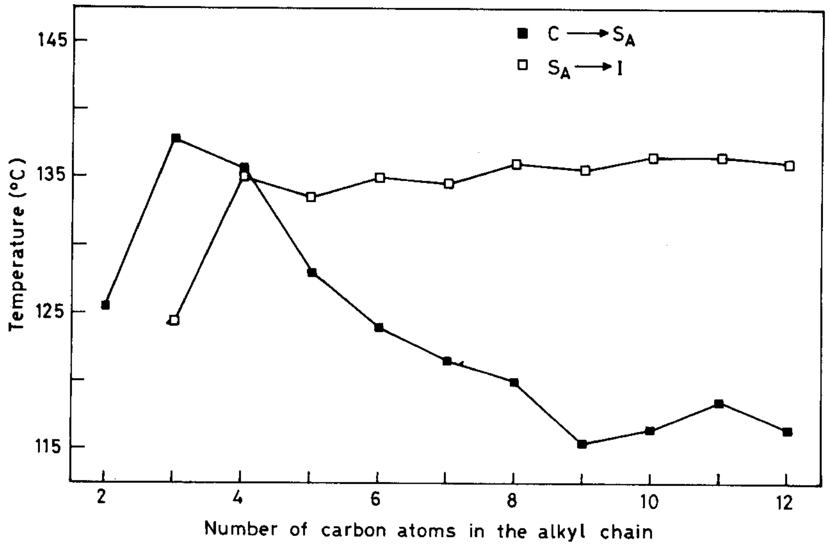

FIGURE 2 Plot of transition temperatures vs. the number of carbon atoms in the alkyl chain for the β-diketones, II.

TABLE 2

Transition temperatures (°C) and enthalpies of transitions (kcal/mol) for bis[1-(4″-n-alkyloxybiphenyl)-3-(phenyl)propane-1,3-dionato]copper(II), V

| Compound number | n | $C_1$ | C | N | I |
|---|---|---|---|---|---|
| 12 | 4 | . 238.0<br>1.39 | . 263.0<br>8.66 | — | . |
| 13 | 5 | . 229.0<br>2.32 | . 260.5<br>11.82 | (. 225.5) | . |
| 14 | 6 | — | . 255.5<br>15.79 | (. 217.5) | . |
| 15 | 7 | — | . 247.0<br>15.51 | (. 208.0) | . |
| 16 | 8 | . 132.5<br>2.0 | . 235.0<br>15.67 | (. 202.5) | . |
| 17 | 9 | — | . 222.0<br>15.97 | (. 195.5) | . |
| 18 | 10* | . 144.5<br>1.41 | . 207.0<br>11.43 | (. 189.0)† | . |
| 19 | 11* | . 187.0<br>1.93 | . 197.0<br>9.12 | (. 183.0)† | . |
| 20 | 12* | . 172.0<br>1.36 | . 195.0<br>7.77 | (. 177.0)† | . |

*Compounds 18, 19 and 20 have crystal → crystal transitions at 120.5°C (1.0 kcal/mol), 133.0°C (2.69 kcal/mol) and 144.5°C (2.36 kcal/mol) respectively.

† Mesophase is highly unstable due to onset of crystallization.

N → I transition enthalpies could not be determined.

not be determined. In fact, as reported previously,[14] the N → I transition enthalpies of many metal β-diketonates are very small.

A plot of the transition temperatures vs. the number of carbon atoms in the alkyl chain for the above copper complexes is shown in Figure 3. It is seen that the N → I transition points decrease almost linearly. The melting points also decrease on ascending the series and surprisingly these points lie on a smooth curve.

Replacement of copper with palladium in the above complexes (complexes of ligand I) also yields mesomorphic chelates (VI). The transition temperatures and their associated enthalpies for these bis[1-(4″-*n*-alkylbiphenyl)-3-(phenyl)propane-1,3-dionato]palladium(II) complexes are given in Table 3. As in the case of the copper complexes, the butoxy derivative (compound 21) was found to be non-mesognetic while the remaining exhibited a monotropic nematic phase. The melting temperatures are slightly higher as compared to their copper(II) congeners. These chelates seem to decompose partially at their melting points and hence the enthalpies of transitions have not been determined.

In the above discussed β-diketones (series I and II), the terminal phenyl ring is unsubstituted. These β-diketones have a bent structure[13] and any substituent in the *para* position of the phenyl ring would increase the breadth of the molecule. The effect of a few of such substituents on the nature of the mesophase had been studied earlier.[14]

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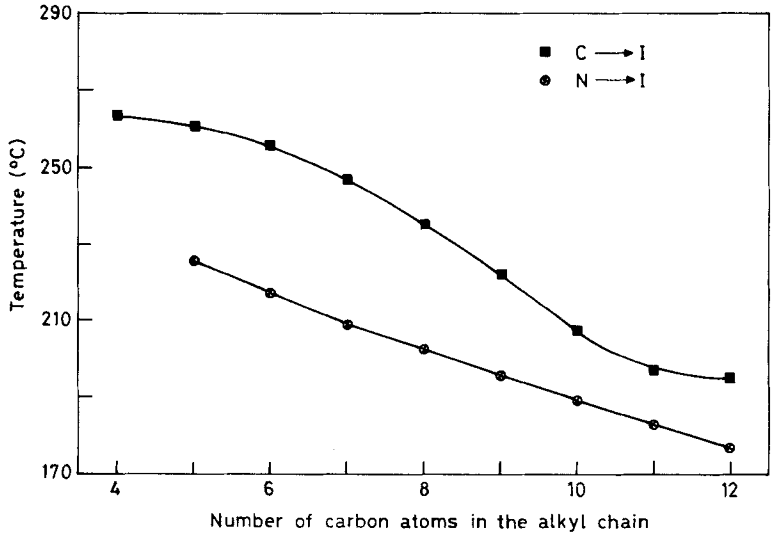

FIGURE 3 Plot of transition temperatures vs. the number of carbon atoms in the alkyl chain for the chelates, V.

TABLE 3

Transition temperatures (°C) and enthalpies of transitions (kcal/mol) for bis[1-(4″-n-alkylbiphenyl)-3-(phenyl)propane-1,3-dionato]palladium(II), VI

| Compound number | n | C | | N | | I |
|---|---|---|---|---|---|---|
| 21 | 4 | . | 244.0 | — | | . |
| 22 | 5 | . | 254.0 | (. | 147.0) | . |
| 23 | 6 | . | 230.0 | (. | 157.5) | . |
| 24 | 7 | . | 230.5 | (. | 172.0) | . |
| 25 | 8 | . | 214.0 | (. | 167.0) | . |
| 26 | 9 | . | 209.0 | (. | 167.5) | . |
| 27 | 10 | . | 203.5 | (. | 156.5) | . |
| 28 | 11 | . | 194.0 | (. | 159.5) | . |
| 29 | 12 | . | 194.5 | (. | 153.0) | . |

Enthalpies of transitions could not be determined due to partial decomposition of the compounds.

In an effort to study the effect of increasing the length of an alkyl chain in the *para* position of the phenyl ring on the mesophase, the following two homologous series of compounds were synthesized.

(i) 1-(4″-*n*-dodecylbiphenyl)-3-(4-*n*-alkylphenyl)propane-1,3-diones, III, and
(ii) 1-(4″-*n*-dodecylbiphenyl)-3-(4-*n*-alkoxyphenyl)propane-1,3-diones, IV.

TABLE 4

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

| Compound number | n | C | $S_A$ | I |
|---|---|---|---|---|
| 30 | 1 | . 100.5<br>4.95 | . 108.0<br>0.99 | . |
| 31 | 2 | . 79.0<br>7.43 | . 99.0<br>1.02 | . |
| 32 | 3 | . 83.5<br>5.40 | . 101.5<br>1.06 | . |
| 33 | 4 | . 82.0<br>5.21 | . 99.5<br>1.20 | . |
| 34 | 5 | . 81.5<br>4.92 | . 101.5<br>1.23 | . |
| 35 | 6 | . 83.5<br>5.06 | . 100.0<br>1.25 | . |
| 36 | 7 | . 85.0<br>5.12 | . 103.5<br>1.30 | . |
| 37 | 8 | . 86.0<br>4.20 | . 101.0<br>1.11 | . |
| 38 | 9 | . 91.5<br>7.71 | . 103.5<br>1.40 | . |
| 39 | 10 | . 103.5<br>9.97 | (. 102.5)<br>1.41 | . |
| 40 | 11 | . 104.0<br>8.29 | (. 101.5)<br>1.51 | . |
| 41 | 12 | . 108.5<br>10.28 | — | . |

The transition temperatures and their corresponding enthalpies for series III are summarized in Table 4. All the homologues except compound 41 are mesogenic. They exhibit a focal-conic texture and have been characterized as smectic A phase. As can be seen, the first nine members of the series are enantiotropic in nature, the next two are monotropic and the dodecyl derivative is non-mesogenic. As has been discussed earlier, these β-diketones assume a slightly bent structure and as the length of the para substituent on the phenyl ring is increased, the lateral dimensions of the molecule also gets increased. This will have a destabilizing effect on mesophase as the intermolecular separation becomes greater. Hence the lower members are mesomorphic and as soon as the limiting value is reached (compound 41 in this case) the compound becomes non-mesomorphic.

A plot of the transition temperatures vs. the number of carbon atoms in the alkyl chain for series III is shown in Figure 4. It is seen that there is alternation in the $S_A \rightarrow I$ transition temperatures for successive homologues. As the series is ascended the melting points also increase and when $n = 10$, the melting point is so high that only a metastable mesophase is observed and the mesophase completely disappears for the dodecyloxy derivative (compound 41).

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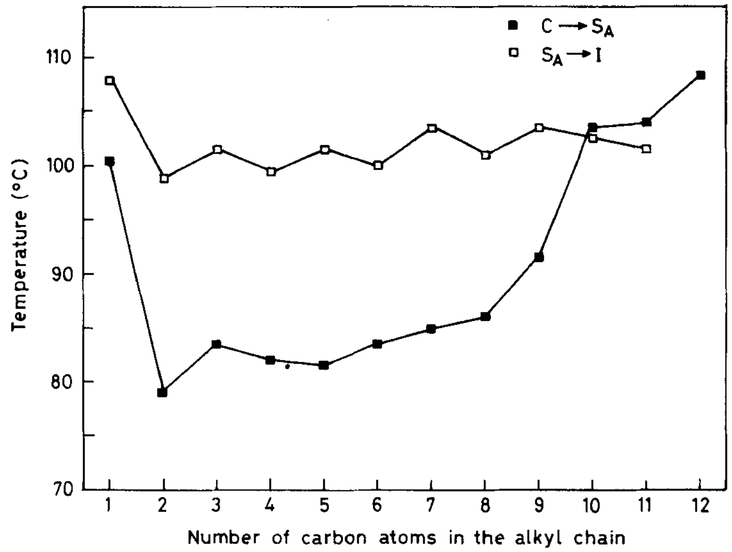

FIGURE 4 Plot of transition temperatures vs. the number of carbon atoms in the alkoxy chain for the β-diketones, III.

The transition temperatures and the associated enthalpies for 1-(4″-*n*-dodecylbiphenyl)-3-(4-alkoxyphenyl)propane-1,3-diones, IV, are given in Table 5. The trend in the mesomorphic behaviour is rather unusual. The first member of the series is non-mesogenic while the next three show monotropic smectic phases. The next four homologues (compounds 46 to 49) are enantiotropic smectic and becomes metastable for the nonyloxy and decyloxy derivatives (compounds 50 and 51). The series becomes non-mesogenic from the undecyloxy derivative (compound 52) as compared to the dodecyl derivative of the previous series, III, the oxygen atom being considered as equivalent to a $—CH_2—$ unit. The smectic phase of these homologues also exhibits a focal-conic texture and these have been characterized as smectic A phase.

A graphical representation of the transition temperatures vs. the number of carbon atoms in the alkoxy chain for the series IV is depicted in Figure 5. Here again there is alternation for the smectic-isotropic transition points and there is an overall increase of clearing temperature as the series is ascended. There is also a decrease in the melting point and reaches a minimum at the hexyloxy derivative (compound 47), from which there is a sharp increase until the nonyloxy derivative after which there is only a gradual increase.

From the available data, the mesmorphic behaviour of the β-diketones may be summarized as follows. Generally, the β-diketones exhibit the smectic A phase. The predominance of the smectic A phase is probably due to the dipole associated with such a molecule as also the bent structure discussed earlier. Further, replacing a terminal *n*-alkyl chain by an *n*-alkoxy chain stablizes the smectic A phase. As reported earlier,[12,14] replacing a terminal hydrogen with a chloro or bromo substituent, smectic E phase is obtained. Ohta *et al.*[11] have observed smectic E phase in a series of

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TABLE 5

Transition temperatures (°C) and enthalpies (kcal/mol) for 1-(4″-n-Dodecylbiphenyl)-3-(4-n-alkoxyphenyl)propane-1.3-diones, IV

| Compound number | n | $C_1$ | C | $S_A$ | I |
|---|---|---|---|---|---|
| 42 | 1 | . 105.5<br>2.70 | . 109.5<br>3.24 | — | . |
| 43 | 2 | . 99.5<br>8.58 | . 105.0<br>0.95 | (. 100.0)* | . |
| 44 | 3 | . 96.5<br>9.73 | . 107.5<br>2.24 | (. 95.0)* | . |
| 45 | 4 | . 90.0<br>3.10 | . 100.5<br>5.98 | (. 99.5)* | . |
| 46 | 5 | — | . 88.0<br>4.43 | 97.0<br>0.86 | . |
| 47 | 6 | — | . 82.0<br>6.63 | . 98.5<br>0.82 | . |
| 48 | 7 | . 81.5<br>6.30 | . 90.0<br>0.51 | . 98.0<br>0.52 | . |
| 49 | 8 | . 77.0<br>6.20 | . 104.0<br>1.37 | . 108.0<br>1.19 | . |
| 50 | 9 | . 79.5<br>8.99 | . 109.0<br>3.85 | (. 108.5)* | . |
| 51 | 10 | . 76.5<br>8.67 | . 110.5<br>3.87 | (. 109.5)* | . |
| 52 | 11 | . 79.5<br>1.16 | . 112.5<br>3.46 | — | . |
| 53 | 12 | . 74.0<br>7.10 | . 113.0<br>4.52 | — | . |

* Enthalpies could not be measured due to onset of crystallization.

Key: $C_1$ & C: crystalline phases; $S_A$: smectic A phase; N: nematic phase; I: isotropic phase.

*p*-n-alkoxybiphenylbutane-1,3-diones. The nematic phase has been observed only in a few series of $\beta$-diketones. The first nematogenic $\beta$-diketones reported by Eidenschink and Pohl[17] contain a cyclohexyl moiety. We observed nematic phases in four homologues of a series of [1-(*p*-*n*-alkylbiphenyl)-3-(phenyl)propane.-1,3-diones.[10] Thompson *et al.*[18] have also reported some nematogenic $\beta$-diketones containing a cyclohexyl moiety or a lateral fluoro substituted biphenyl unit.

A few representative copper(II) complexes from the above two homologous series have been synthesized, (VII a,b,c,d)

VII a $R = n\text{-}C_{12}H_{25}$, $R' = CH_3$, M = Cu, m.p. 208°C
b $R = n\text{-}C_{12}H_{25}$, $R' = n\text{-}C_{10}H_{21}$, M = Cu, m.p. 160°C
c $R = n\text{-}C_{12}H_{25}$, $R' = OCH_3$, M = Cu, C 180N(168.0)I
d $R = n\text{-}C_{12}H_{25}$, $R' = OC_8H_{17}$, M = Cu, m.p. 194°C

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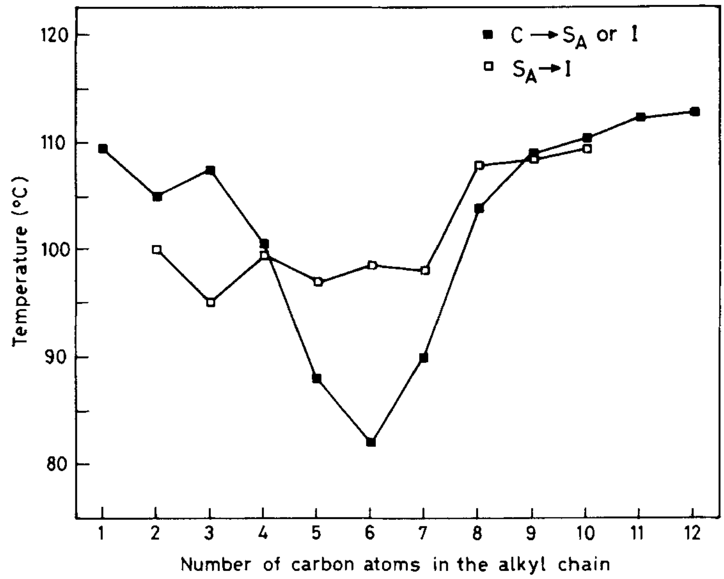

FIGURE 5 Plot of transition temperatures vs. the number of carbon atoms in the alkoxy chain for the β-diketones, IV.

It was found that except for complex VIIc which exhibited a monotropic nematic phase, all others were non-mesogenic.

However, these complexes have virtual transition points. These points have been determined experimentally by constructing binary phase diagrams with a known nematogenic copper(II) complex (X).[19] The phase diagrams for the complexes VIIa, VIIb and VIId are shown in Figure 6. It is clear from these phase diagrams that the N→I transition points are too much below the melting points and on cooling the isotropic liquids at different rates these complexes crystallize before the appearance of the mesophase.

A comparison of the influence of different substituents ($R^1$) on the mesomorphic behavior of complexes having general structure similar to V and VI reveals certain interesting features. As reported[14] earlier small substituents such as methyl, ethyl, methoxy and ethoxy do not affect the nature of the mesophase observed in the parent system; in otherwords the monotropic nematic phase is still retained. However, a cyano substituent in such a system has a significant effect. In both the copper(II) and palladium(II) complexes,[14] a smectic A phase is obtained at the expense of the nematic phase. A similar effect was also observed by Thompson *et al.*[13] In addition, they have examined the influence of polar substituents such as fluoro and trifluoromethyl groups on the mesophase of similar copper(II) complexes; while the former exhibits a monotropic nematic phase the latter shows both monotropic nematic as well as smectic A phases.[13]

Ohta *et al.*[11] have reported a series of bis[1-(*p*-*n*-alkoxybiphenyl)-3-alkylpropane-1,3-dionato.copper(II) complexes in which the phenyl ring (having the $R^1$ substituent) is completely removed thus retaining only the *n*-alkyl chain. When this substituent is a small methyl group, they exhibit discotic rectangular ordered phases. But when this

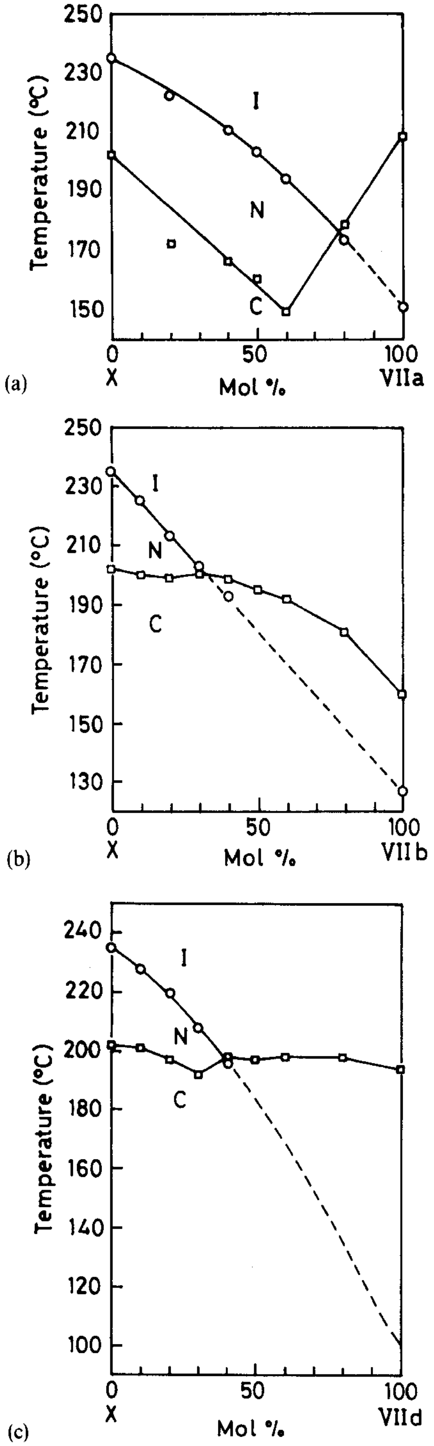

FIGURE 6 Binary phase diagram of (a) Complex VIIa with bis[1-4‴-*n*-dodecylbiphenyl)-3-(4-methoxybiphenyl)propane-1,3-dionato]copper(II), X, (b) Complex VIIb with X and (c) Complex VIId with X.

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substituent is changed to *n*-butyl group, the complexes show enatiotropic nematic phases. However, for longer *n*-octyl or *n*-dodecyl groups the complexes exhibit monotropic nematic phases.

The above results clearly indicate that in complexes such as V and VI there has to be a balance between the elongated parts of the molecule (biphenyl moities) and the "lateral substituents" (phenyl ring with $R^1$ substituent or just an *n*-alkyl chain) for the complexes to exhibit a mesophase.

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