This article was downloaded by:
On: *26 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Structural characteristics of some metallo-organic discogens

K. Usha[a]; Kalyani Vijayan[b]; S. Chandrasekhar[c]
[a] Raman Research Institute, Bangalore, India [b] Materials Science Division, National Aeronautical Laboratory, Bangalore, India [c] Centre for Liquid Crystal Research, Bangalore, India

To cite this Article Usha, K. , Vijayan, Kalyani and Chandrasekhar, S.(1993) 'Structural characteristics of some metallo-organic discogens', Liquid Crystals, 15: 5, 575 — 589
To link to this Article: DOI: 10.1080/02678299308036479
URL: http://dx.doi.org/10.1080/02678299308036479

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Liquid Crystals, 1993, Vol. 15, No. 5, 575–589

Structural characteristics of some metallo-organic discogens†

by K. USHA, KALYANI VIJAYAN‡ and S. CHANDRASEKHAR*§
Raman Research Institute, Bangalore 560080, India
‡ Materials Science Division, National Aeronautical Laboratory,
Bangalore 560017, India
§ Centre for Liquid Crystal Research, P.O. Box 1329,
Jalahalli, Bangalore 560013, India

(*Received 22 December 1992; accepted 21 May 1993*)

We have recently analysed the crystal and molecular structures of six metallo-organic discogens with substituted β-diketone ligands. The molecules consist of a rigid 11 atom core and a fringe made up of four phenyl rings substituted with alkyl/alkoxy chains. In complex (i), with four octyloxy chains, there are four oxygen atoms around the core. Complex (ii) is asymmetrically substituted with two heptyloxy and two heptyl chains and therefore has two oxygen atoms and complexes (iii) to (vi) have only alkyl chains and hence no oxygen atoms around the core. The metal atom used for coordination has been chosen as Cu/Pd/Ni. Determination of the crystal and molecular structures of these discogens has led to the identification of the following similarities: (1) All the six discogens crystallize in the triclinic space group $P\bar{1}$. The recurrence of the space group may be correlated with the structural requirements for efficient packing of the molecules in the crystal lattice. (2) The coordination around the metal atom is square planar. (3) The 11 atom core is only nearly planar. (4) The phenyl rings and the chains are tilted with respect to the core. (5) The molecular conformation in the crystal confers a nearly rectangular shape to these discogens. (6) The chains are fully extended in an all *trans* conformation. (7) The molecular arrangement is tilted columnar except for the crystal structure of complex (ii).

In addition to the similarities, distinct differences in the crystal structural characteristics have also been observed. For example, when oxygen atoms are present in the fringe, the molecules have no crystallographic symmetry and they tend to pair. In the crystal structure of (i) where the repeat unit along the column is a molecular pair, the metal atoms are distributed in a zig-zag fashion. In the other crystals with columnar arrangement, the metal atoms are stacked one over another. Complex (ii) has a layer-like molecular arrangement in the crystalline phase.

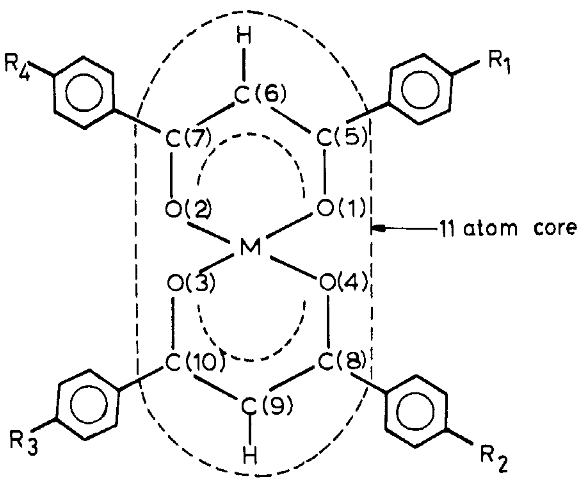
1. Introduction

Close correlations between the structural characteristics of the crystalline phase and the mesophase have often been found to exist [1–4]. X-ray determination of the crystal and molecular structures is therefore an important aspect of any programme of structural studies on liquid crystals. Recently, we have analysed the crystal and molecular structures of six metallo-organic discogens with a substituted β-diketone ligand, the structural formula of which is shown in figure 1. The molecules consist of a rigid 11 atom core (shown encased in figure 1) and a fringe made up of four phenyl rings

---

* Author for correspondence.

† Presented at the Fourteenth International Liquid Crystal Conference, 21–26 June 1992, University of Pisa, Italy.



(i) M = Cu, $R_1 = R_2 = R_3 = R_4 = OC_8H_{17}$
(ii) M = Cu, $R_1 = R_2 = OC_7H_{15}$; $R_3 = R_4 = C_7H_{15}$
(iii) M = Cu, $R_1 = R_2 = R_3 = R_4 = C_8H_{17}$
(iv) M = Pd, $R_1 = R_2 = R_3 = R_4 = C_{10}H_{21}$
(v) M = Pd, $R_1 = R_2 = R_3 = R_4 = C_8H_{17}$
(vi) M = Ni, $R_1 = R_2 = R_3 = R_4 = C_8H_{17}$

Figure 1. Structural formula.

substituted with alkyl or alkoxy chains at the respective *para* positions. In (i) with four alkoxy chains, there are four oxygen atoms around the core; in (ii), with two alkoxy and two alkyl chains, there are only two oxygen atoms and in (iii) to (vi) there are no oxygen atoms around the core. The lengths of the substitutes have also been varied as heptyl, octyl and decyl chains. The transition metal atom used for coordination has been chosen as Cu/Pd/Ni. These distinguishing molecular features provide useful handles to identify structural changes, if any, associated with (*a*) the oxygen content in the fringe, (*b*) the length of the hydrocarbon chain and (*c*) the type of metal atom.

Crystallization experiments have shown that the copper complex (iii) has two polymorphic crystalline modifications, viz. crystal with prismatic (P) and needlelike (N) forms, characterized by distinctly different crystal structures. Hence, although the series listed in figure 1 includes only six complexes, seven crystal structures have been analysed. The structure determinations also showed that the crystal structures of the Pd and the Ni complexes (v) and (vi) are isomorphous with that of the P form of the Cu complex (iii).

Complexes (i) to (v) are reported [5–9] to be mesogenic. Table 1 presents the details of the transitions from the crystalline phase (C) to the mesophase (D) and the isotropic phase (I). Quite intriguingly, the Ni complex (vi) despite its unambiguous structural isomorphism with the mesogens (iii) and (v), is reported to be non-mesogenic [4, 9]. Thermal studies on the Ni complex (vi) are being carried out and the results will be reported elsewhere.

Details of the crystal structure determinations and descriptions of the individual crystal structures of the complexes (i) to (iv) have already been published [10–13]. Comparison of the seven crystal structures has shown that some of the structural

Table 1. Transition temperatures (°C) and the molecular arrangement in the mesophase. Quantities below the arrow represent the enthalpy values (K mol^{-1}).

Complex	Transition temperatures/°C	Molecular arrangement in mesophase
(i) Cu–OC_8H_{17}	$C \xrightarrow[50\cdot0]{94\cdot5} D \xrightarrow[47\cdot2]{176} I$	Lamellar [5]
(ii) Cu–OC_7H_{15}–C_7H_{15}	$\begin{array}{ccc} C & \xrightarrow[41\cdot7]{150\cdot5} & I \\ & \overset{145\cdot5}{\underset{26\cdot4}{\swarrow}} & \\ & D & \end{array}$	Not known
(iii) Cu–C_8H_{17}	$C \xrightarrow[70\cdot5]{76\cdot5} D \xrightarrow[2\cdot0]{117} D \xrightarrow[28\cdot4]{142\cdot5} I$	Lamellar [9]
(iv) Pd—$C_{10}H_{21}$	$C \xrightarrow[48\cdot0]{101\cdot5} D \xrightarrow[0\cdot7]{106} D \xrightarrow[23\cdot8]{119} I$	Not known
(v) Pd–C_8H_{17}	$C \xrightarrow[15\cdot5]{99} D \xrightarrow[19\cdot0]{121\cdot5} D \xrightarrow[23\cdot5]{138\cdot5} I$	Not known

features are characteristic of this entire group of complexes. Details of these similarities, along with a few conspicuous differences which have also been observed, are described in this paper.

Very few X-ray studies have been carried out on the crystalline phase of metallo-organic discogens. Muhlburger and Haase have determined the crystal structures of two mesogenic copper complexes with β-diketone ligands [14], one of which is more rod-like. Crystal structures of many complexes with β-diketone ligands have in fact been determined in the past [15–25], but none of them is mentioned to be discogenic.

2. Results and discussion

2.1. *Space group and molecular symmetry*

Table 2 compares some of the relevant crystal data. The most striking feature is the propensity for the entire series to crystallize in the triclinic space group $P\bar{1}$. As is well-known [26], $P\bar{1}$ is one of the space groups which permits a closest packed arrangement of molecules. The values of the packing coefficient [27] k defined as

$$k=\frac{\text{volume of molecules in the unit cell}}{\text{unit cell volume}},$$

and listed in table 2, show that in the crystal structure, the molecules are close packed. Thus it appears that the repeated occurrence of the space group $P\bar{1}$ is primarily due to packing considerations.

The structural formula (see figure 1) shows that the molecule could possess a crystallographic centre of symmetry. The data in table 2, however, show that only five out of the seven molecules possess a crystallographic centre of symmetry. Interestingly, the molecules (i) and (ii) which do not have crystallographic symmetry are those in which oxygen atoms are present around the core. This feature suggests the possibility of a correlation between the absence of molecular symmetry in the crystal and the presence of oxygen atoms in the hydrocarbon chain. The statistical significance of a

Table 2. Crystal data.

Complex	Space group	Z	Unit cell constants	Molecular symmetry	k
$Cu–OC_8H_{17}$	$P\bar{1}$	2	$a=11·300(9)$Å $b=16·101(1)$Å $c=17·089(2)$Å $\alpha=82·23(1)°$ $\beta=74·88(4)°$ $\gamma=77·43(3)°$	1	0·70
$Cu–OC_7H_{15}–C_7H_{15}$	$P\bar{1}$	2	$a=10·228(7)$Å $b=16·607(5)$Å $c=18·273(6)$Å $\alpha=64·40(2)°$ $\beta=78·53(6)°$ $\gamma=72·66(5)°$	1	0·70
$Cu–C_8H_{17}$(N)	$P\bar{1}$	1	$a=5·821(3)$Å $b=14·332(1)$Å $c=17·630(2)$Å $\alpha=107·35(1)°$ $\beta=98·86(2)°$ $\gamma=93·58(3)°$	$\bar{1}$	0·72
$Cu–C_8H_{17}$(P)	$P\bar{1}$	1	$a=10·341(3)$Å $b=11·621(2)$Å $c=12·817(2)$Å $\alpha=103·99(1)°$ $\beta=92·73(2)°$ $\gamma=109·55(2)°$	$\bar{1}$	0·70
$Pd–C_{10}H_{21}$	$P\bar{1}$	1	$a=10·260(2)$Å $b=12·961(2)$Å $c=13·403(2)$Å $\alpha=110·54(1)°$ $\beta=101·75(1)°$ $\gamma=98·44(1)°$	$\bar{1}$	0·70
$Pd–C_8H_{17}$	$P\bar{1}$	1	$a=10·318(2)$Å $b=11·537(1)$Å $c=13·089(2)$Å $\alpha=104·119(9)°$ $\beta=94·73(1)°$ $\gamma=108·88(1)°$	$\bar{1}$	0·70
$Ni–C_8H_{17}$	$P\bar{1}$	1	$a=10·139(1)$Å $b=11·3201(8)$Å $c=13·242(2)$Å $\alpha=101·919(8)°$ $\beta=92·796(9)°$ $\gamma=108·520(7)°$	$\bar{1}$	0·70

correlation which is based on only two observations is admittedly low. Further conclusive evidence can be obtained only when more data on compounds with oxygen atoms in the chains are generated.

It is also observed from table 2 that factors such as the length of the substituents R_1 to R_4 or the type of metal atom at the centre, do not affect the molecular symmetry.

2.2. *Metal coordination*

In all the seven crystal structures, the disposition of oxygen atoms around the metal atom resembles a square planar arrangement. As the oxygen atoms are part of the diketone ring systems, the coordination polyhedron has a rectangular characteristic, the distance O(1)... O(2) being larger than the distance O(1)... O(4). It is also observed that in the crystal structure of (ii), the geometry of the rectangle is further distorted, i.e. O(1)... O(4) = 2·57(1) Å whereas O(2)... O(3) = 2·67(1) Å. This difference is primarily due to the *cis* arrangement of the similar chains in this molecule and possible interactions between the oxygen atoms, details of which are to be described in the subsequent section of this paper. Average values of the M–O distance, the O–M–O valence angles and the O... O distances are presented in table 3. As could be expected, an increase in the size of the metal ion is accompanied by an increase in the M–O distance.

It must be pointed out that in the case of salicylaldimine complexes of nickel and cobalt [4], absence of mesomorphism has been associated with tetrahedral coordination around the metal atom. In the case of the Ni complex (vi) which is reported to be non-mesogenic [4, 9], there is clearly no evidence for such tetrahedral coordination.

Robertson and Truter [22] have mentioned the occurrence of weak interactions between the metal atom and the core atoms of neighbouring molecules of some diketone complexes. Koyama *et al.* [25] also report the occurrence of such a coordination by the CH groups of molecules above and below. Such interactions which correspond to the fifth and the sixth coordinating positions to the metal atom are found to be present only in the crystal structure of complex (i). Here, two phenyl ring atoms from the neighbouring molecules are found to be situated at 3·17 and 3·24 Å, respectively, from the copper atom, close to the fifth and the sixth coordinating positions. Both the carbon atoms are shifted from the normal to the copper–oxygen plane by 0·17 Å.

2.3. *Dimensions of the core*

The average values of the bond lengths and valence angles characterizing the core are listed in table 3. The dimensions are found to be normal.

2.4. *Planarity*

The structural formula (see figure 1) shows that with the β-diketone ligand and the square planar coordination around the metal atom, the 11 atom core could be expected to form a flat planar moiety. However, the present crystal structure investigations have shown that the cores exhibit significant deviations from strict planarity. In the crystal structures of complexes (i) and (ii) where the chemically identical halves of the molecules are not related by crystallographic symmetry, a slight buckling is found to exist between the two halves of the core. Presence of such buckling is evidenced by the non-zero value of the angle between the normals to the least squares planes through the two halves of the core, viz., through O(1), O(2), C(5) to C(7) and O(3), O(4), C(8) to C(10), respectively. In the case of (i) and (ii), the angles are ~3 and 1°, respectively. Similar

Table 3. Average dimensions of the core.

Complex	M–O/Å	O–C/Å	C–C/Å	O...O/Å	O–M–O/°	M–O–C/°	O–C–C/°	C–C–C/°
Cu–OC_8H_{17}	1·895(9)	1·25(1)	1·405(5)	2·74(2)	92·6(2)	127·8(8)	124·3(4)	123(1)
Cu–OC_7H_{15}–C_7H_{15}	1·90(2)	1·28(3)	1·40(6)	2·74(1)	92·6(3)	127(1)	126(2)	122(1)
Cu–C_8H_{17}(N)	1·908(6)	1·27(1)	1·389(2)	2·764(6)	92·8(2)	126·3(4)	125·0(2)	124·2(6)
Cu–C_8H_{17}(P)	1·90(1)	1·27(2)	1·38(3)	2·744(5)	92·3(2)	127·2(2)	124·2(4)	124·7(7)
Pd–$C_{10}H_{21}$	1·9665(5)	1·278(1)	1·405(3)	2·874(6)	93·9(2)	124·6(4)	125·6(2)	125·7(6)
Pd–C_8H_{17}	1·9695(5)	1·274(2)	1·400(8)	2·871(4)	93·6(1)	124·8(3)	125·2(5)	126·4(5)
Ni–C_8H_{17}	1·837(8)	1·275(5)	1·38(2)	2·710(6)	95·1(2)	126·1(8)	124(1)	123·8(9)

Table 4. Values of η, δ and end-to-end molecular dimensions.

Complex	η°	δ of terminal atoms/Å	Molecular dimensions/Å
Cu–OC_8H_{17}	3, 1·5	0·88(9), 0·96(3), −0·66(6), −0·95(2)	31·6, 31·1, 10·8, 10·9
Cu–OC_7H_{15}–C_7H_{15}	0·9, 2·5	0·00(2), −0·28(3), −1·08(2), 0·48(3)	28·8, 28·5, 10·6, 9·9
Cu–C_8H_{17}(N)	4·8	2·016(8), −1·42(1)	30·4, 9·7
Cu–C_8H_{17}(P)	1·1	0·29(1), 0·10(1)	30·3, 9·6
Pd–$C_{10}H_{21}$	3·2	−0·35(1), 0·26(1)	35·3, 9·5
Pd–C_8H_{17}	2·8	0·05(1), 0·17(1)	30·2, 9·7
Ni–C_8H_{17}	3·1	0·27(1), 0·18(1)	30·3, 9·5

buckling has been observed in the crystal structures of two other diketone complexes [14, 23] wherein the corresponding angles are ~3 and 6°, respectively. In the case of the complexes (iii) to (vi), buckling between the two halves is inhibited by the presence of crystallographic symmetry in the molecule. Thus, it appears that when not constrained by crystallographic symmetry, the 11 atom core tends to buckle slightly. In addition to the buckling between the two halves of the core, another type of distortion is also observed in each half of the core. Table 4 lists the angle η between the planes through the group M–O–C–C in each half. The non-zero value of the dihedral angle shows that each half of the core is itself slightly bent.

It is also noticed that in these crystal structures, the displacement from the plane through the light atoms of the crystallographically independent part of the core, is consistently the highest for the metal atom. Such displacements can indeed contribute to the non-planar characteristics of the core. Non-planarity of a different type arising from the approach of the metal atom with the apex carbon atom of a neighbouring core has also been described by Hall *et al.* [28].

As could be expected, the presence of lengthy aliphatic chains confers a considerable non-planar character to the molecule as a whole. To provide an indication of the extent of non-planarity, the displacements, δ, of the terminal atoms of the aliphatic chains from the plane through the crystallographically independent part of the core have been included in table 4. The atomic displacements are the highest for the N form of (iii).

2.5. *Molecular conformation*

The conformations of the molecules (i) to (vi) in their respective crystal structures are very similar. In all the cases, the phenyl rings are tilted with respect to the core, the tilt being controlled primarily by steric effects. The alkyl/alkoxy chains are in an all *trans* conformation (see figure 2). The molecules are lath-like. The end-to-end dimensions of the molecules (see table 4) indicate that in all the cases, the length to width ratio is ~3. The observed conformations and the molecular dimensions closely resemble the model B proposed by Ohta *et al.* [5] for the mesophase of Cu–OC_8H_{17}. The repeated occurrence of model B suggests that this model is perhaps energetically more stable than their model A in which the conformation of the molecule corresponds to a length to width ratio of ~1. Table 4 shows that the increase in the length of the molecule Pd–$C_{10}H_{21}$ over that of Pd–C_8H_{17} is commensurate with the increase in the chain length. There is, however, no significant change in the molecular dimensions due to the replacement of copper by either palladium or nickel.

The conformation of the asymmetrically substituted molecule (ii) merits special mention. Here, two types of conformations are possible, viz., those corresponding to

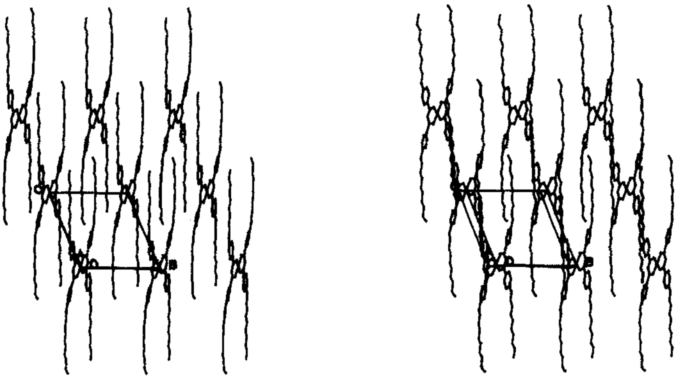


Figure 2. Stereo view of the molecular arrangement viewed along the *a* axis of Pd-$C_{10}H_{21}$ (iv).

the *trans* and the *cis* arrangements of the similar substitutions with respect to the core. From simple geometric considerations of molecular stability, it would appear that the chemically identical chains assume a *trans* arrangement with respect to the core. Interestingly, in the crystal structure, they are found to be *cis* with respect to the core. This result though unexpected is conclusive. The slight asymmetry in the widths of this molecule (see table 4) is also a consequence of the *cis* conformation and the difference in the lengths of the heptyl and the heptyloxy chains.

In the crystal structure of bis[1-thia-4-7-diazocyclononane] cobalt(III), which is not mesogenic, molecular calculations have shown [29] that the *cis* isomer is more stable than the *trans* isomer. Therefore it appears that the occurrence of a stable *cis* form in crystals is not an uncommon feature. It must also be mentioned that in the case of a Pd–diketone complex with dissimilar substitutions, two crystalline modifications corresponding to both the *cis* and the *trans* arrangements have been reported [23]. It is therefore not unlikely that in the case of (ii) also, a second crystalline modification with a *trans* arrangement of the similar substitutions exists. Examination of the crystallization dish of (ii) has shown that there are in fact crystals with three different morphologies, the crystal structure of one of which has been determined by us. It is proposed to examine the other two forms of crystals also, to find out if either of them correspond to the *trans* conformation. It must be mentioned that in the crystal structures of few other diketones with dissimilar substitution, only a *trans* arrangement has been reported [14–16, 19].

2.6. *Molecular arrangement*

The available structural data on the mesophase of diketone complexes with four chains suggest that many of them are characterized by a lamellar structure (see table 1). Recognizing that there is a relationship between the molecular arrangements in the mesophase and the crystalline phase, it may be expected that a lamellar structure exists in the crystalline phase also. Our results on complexes (i) to (vi) indicate that in the crystalline phase, the molecular arrangement is explicitly lamellar for complex (ii). For the rest of the complexes, the molecular arrangement has both lamellar as well as columnar characteristics. For complexes (i) and (iii) to (vi), the molecules are arranged in layers but the periodic stacking of the layers leads to the formation of columns. Figure 3 depicts a typical layered arrangement and the corresponding columnar arrangement is shown in figure 4. The most likely route for a transition from a columnar crystal structure to a lamellar mesophase structure is by the weakening of the interactions along the column axis, i.e. between the layers. Examination of the non-bonded intermolecular interactions/contact distances $\leqslant 4$ Å in these crystal structures shows an interesting distribution which permits such a weakening of inter-layer interactions. It is found that with the exception of the crystal structure of the N form of (iii), in the rest of the columnar structures, the number of intermolecular contact distances $\leqslant 4$ Å is more within a layer than along the column. For example, in the case of the P form of (iii), there are 28 contacts within a layer and only 16 along the column, i.e. between adjacent layers, thereby suggesting that the stability arising from non-bonded intermolecular interactions is more within a layer than between layers. Consequently the stacking of layers is likely to be more easily disturbed than the molecular arrangement within the layer. If the thermal energy associated with the crystalline to mesophase transition is sufficient to disturb the periodic stacking of layers in the crystalline phase, the columnar structure could get modified to a lamellar structure. The validity of the proposed mechanism for the columnar to lamellar transformation can be checked if X-ray data from both the crystalline and the mesophase are available. At present, such data are available only for complex (i). The layer spacing of 25 Å observed in the crystalline phase of (i) compares well with the corresponding value of 23 Å in its mesophase [5]. The good agreement is in support of the proposed mechanism of transformation. A layer thickness of ~29 Å has been mentioned by Giroud-Godquin and Billard [9] for the discogen, Cu–$C_{10}H_{21}$. The series investigated here does not include this copper complex but only its palladium analogue viz. Pd-$C_{10}H_{21}$, i.e. (iv) (see figure 1). In this case, the layer thickness in the crystalline phase is found to be ~ 32 Å, which is in reasonable agreement with the value for the corresponding copper complex.

Only in the crystal structure of the N form of (iii), the cohesion due to non-bonded intermolecular interactions appears to be more along the column than within the layer. Here, there are only14 contact distances within the layer whereas along the column there are 33. This feature does not appear to be very conducive for the occurrence of a lamellar structure in the mesophase of this crystal.

Details of the structural characteristics of the lamellar and the columnar arrangements observed in the crystal structures of complexes (i) to (vi) are described below.

2.6.1 *Layer structure*

In this series, layer structure is observed for the asymmetrically substituted complex (ii) (see figure 5). It is noticed that although adjacent cores related by a centre of inversion are well-separated, the phenyl rings of a molecule overlap with those of the centrosymmetrically related molecule. Conspicuously, the overlapping phenyl rings are those substituted with heptyloxy chains. The possible role of oxygen atoms in favouring such an overlap cannot therefore be ignored. It is also observed that intermolecular contact distances $\leqslant 4$ Å are concentrated between the centrosymmetrically related molecules. These features suggest that the centrosymmetrically related molecules tend to pair in the crystal structure. In the layer, each of the centrosymmetrically related pairs is surrounded by four other similar pairs.

2.6.2. *Columnar structure*

For complexes (iii) to (vi), the repeat unit along the column is a single molecule. For complex (i), which has oxygen atoms around the core, the repeat unit is a centrosymmetrically related molecular pair. It may be pointed out that the two crystal

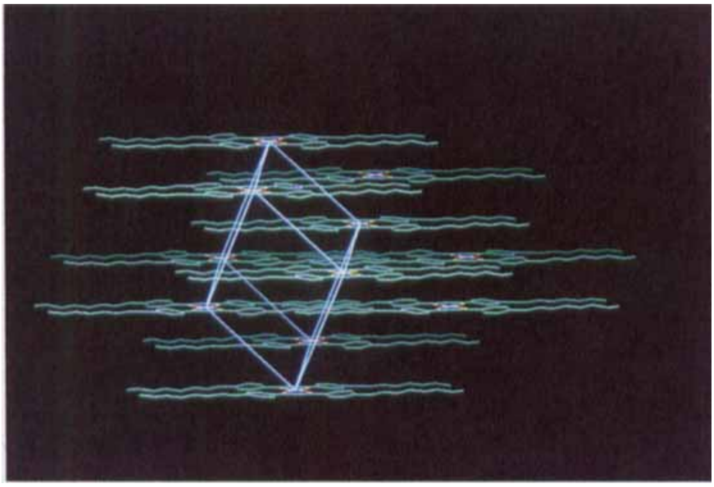


Figure 3. Layered arrangement of the molecules in complex (V).

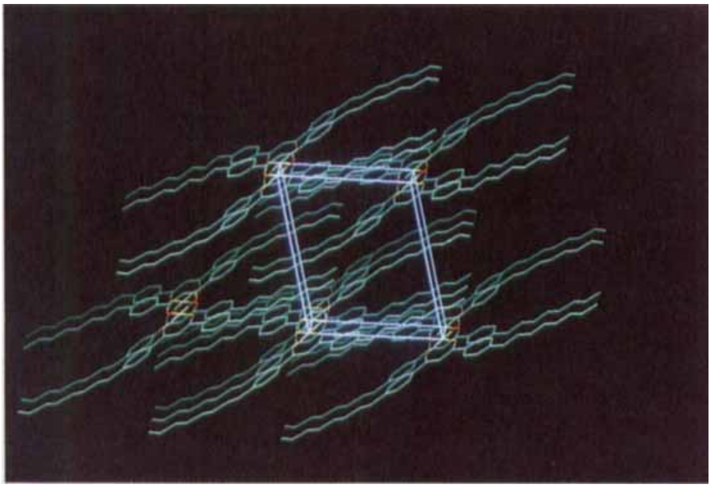


Figure 4. Columnar arrangement of the molecules in comples (v).

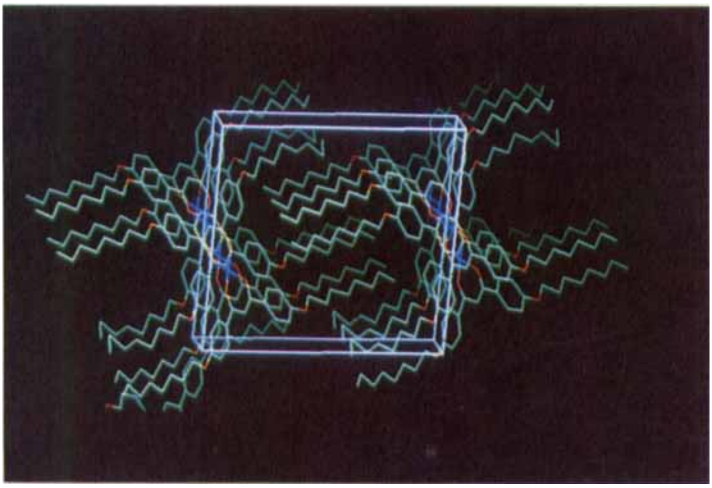


Figure 6. Columnar stacking of the molecular pairs.

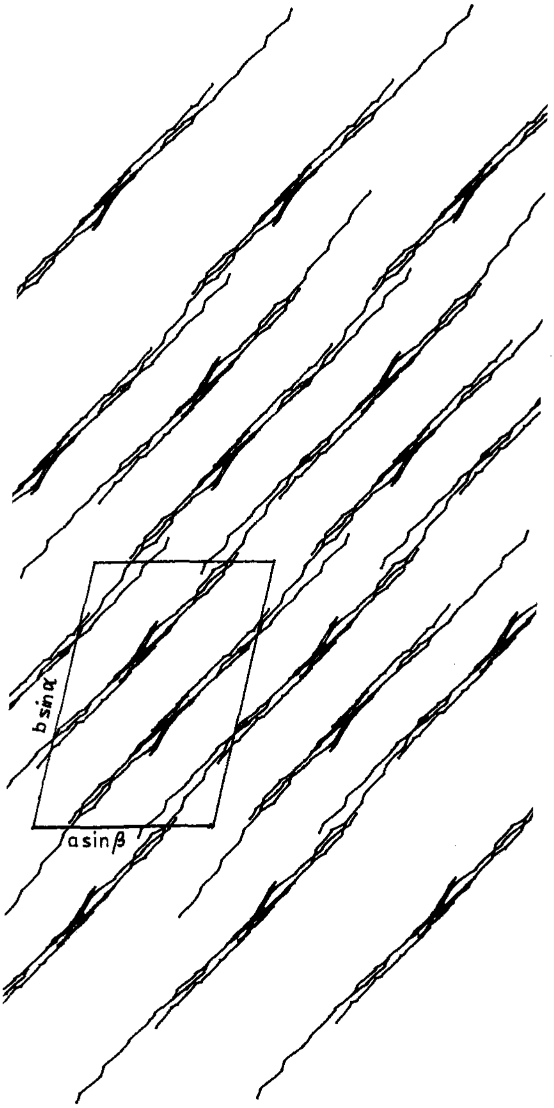


Figure 5. View of the layer structure in the plane perpendicular to the crystallographic *c* axis in the asymmetrically substituted complex (ii).

structures in which pairing is observed are those of molecules with oxygen atoms around the core, viz. (i) and (ii). It is likely that the presence of oxygen atoms favours such molecular pairing.

The columnar molecular arrangements in the crystal structures of (i) and (iii) to (vi) exhibit the following structural characteristics:

(1) The column axis coincides with the shortest axis of the unit cell which in these crystal structures is the crystallographic *a* axis. In the crystal structures of copper(II) ethyl acetoacetate [19] and bis-acetyl acetone copper(II) [25] which are also characterized by columnar stacking of the diketone cores, the shortest axis of the unit cell is found to be the column axis.

(2) In the crystal structures of compounds (iii) to (vi) the metal atoms are stacked atop. In the crystal structure of (i), the individual molecules of the pair which constitutes the repeat unit, are staggered with respect to each other. Consequently, the metal atoms are distributed about the column axis in a zig-zag fashion, the zig and the zag distances being 6·3 and 6·6 Å respectively. The angle at the zig-zag is 124°. Figure 6 shows the columnar stacking of the molecular pairs.

(3) In the crystal structures of the complexes (iv) to (vi), and the P form of (iii), the M ... M distance along the column is ~ 10 Å. In striking contrast, in the N form of (iii), the M ... M distance is ~ 6 Å. The distribution of intermolecular contact distances described earlier (§ 2.6) suggests a possible correlation existing between the M ... M distance along the column and the contact distances. It is found that the M ... M distance reduces with increase in the number of contact distances along the column axis or vice versa. It must be pointed out that Eastman *et al.* [30] also propose a columnar arrangement for (iii). The separation of 2 to3 nm between metal atoms of adjacent columns mentioned by them is observed by us in the crystal structure of the N form of (iii).

(4) Irrespective of the M ... M distance along the column axis, on account of the tilts of the molecules with respect to the column axis, the perpendicular distance between adjacent cores is conspicuously less than 4 Å and ranges from 3·2 to 3·7 Å. If the perpendicular distance between adjacent cores is assumed to be 3·6 Å, i.e. the sum of the van der Waals radii of two carbon atoms, the tilt θ of the column, defined as the angle between the column axis and the normal to the core, can be expressed as

$$\theta = \cos^{-1}\left(\frac{3{\cdot}6}{a}\right), \tag{1}$$

where a is the a axial length (columnar axis) of the unit cell (see figure 7). Equation (1) suggests that for columnar structures in which the molecules are stacked atop, approximate values of the tilt θ can be obtained from a knowledge of the shortest unit cell constant even without resorting to a complete structure determination. Table 5 compares the observed tilts with those calculated using equation (1). The agreement appears to be good.

(5) The interior of each column is made up of the aromatic groups, viz. the diketone core and the phenyl rings. Flexible alkyl/alkoxy chains extending outwards constitute the periphery of the column (see figure 2). A conspicuous feature concerns the orientation of the aliphatic chains. In each molecule, all the four chains are nearly parallel to each other and the parallelism is retained in all parts of the unit cell. Such an arrangement of the aliphatic chains can be expected to optimize the non-bonded interactions between the hydrogen atoms of the chains. The importance of such interactions in stabilizing the crystal structure has been emphasized by Desiraju [31]. Giroud-Godquin and Maitlis [4] also mention that the non-bonded interactions present in the flexible chains are associated with the stabilities of both the crystal and the mesophase structures.

(6) The stacking of molecules along the column is stabilized by non-bonded interactions of the type core ... phenyl, phenyl ... phenyl, phenyl ... chain and chain ... chain. The crystal structure in which the respective metal atom enters into interactions within the column are those of (i) and the N form of (iii).

(7) Each column in the crystal structure is surrounded by six others which do not form an ideal hexagon. Figure 8 is a schematic representation of the hexagonal arrangement in the two polymorphs of (iii). The interactions between adjacent columns is primarily of the van der Waals type. Also, the orientation of the molecules is the same in all the columns (see figure 8). This last feature is in contrast to the herringbone type of molecular arrangement observed in the columnar phases of certain discogens [32].

Table 5. Comparison of the observed and calculated tilts of the molecules with respect to the column axis.

Complex	$\theta_{obs}/°$	$\theta_{calc}/°$
Cu–OC_8H_{17}	128	124
Cu–C_8H_{17}(N)	122	128
Cu–C_8H_{17}(P)	111	110
Pd–$C_{10}H_{21}$	112	110
Pd–C_8H_{17}	112	110
Ni–C_8H_{17}	111	111

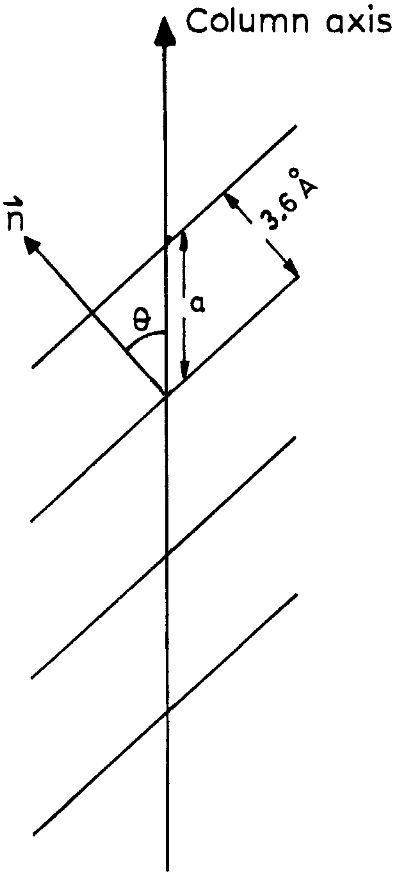


Figure 7. Schematic diagram of the columnar stacking.

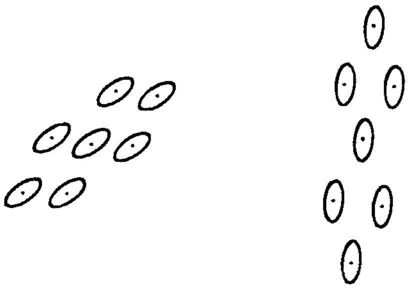


Figure 8. Two dimensional representation of the hexagonal arrangement of columns in the two polymorphs of complex (iii).

The authors wish to thank Dr B. K. Sadashiva for providing the samples. The transition temperatures and the enthalpy values listed in table 1 were also provided by him. One of the authors, (K. U.), thanks Professor K. Venkatesan of the Organic Chemistry Department, IISc, for allowing her to work in his laboratory as a short term worker during which period access to the Cambridge Structural Database was possible. Dr S. Ramakumar of the Physics Department, IISc, is also thanked in this context.

References

[1] Bernal, J. D., and Crowfoot, D., 1933, *Trans. Faraday Soc.*, **29,** 1032.

[2] Krigbaum, W. L., Chatani, Y., and Barber, P. G., 1970, *Acta crystallogr.* B, **26,** 97.

[3] Vani, G. V., and Vijayan, K., 1977, *Molec. Crystals liq. Crystals*, **42,** 249; 1977, *Acta crystallogr.* B, **33,** 2236.

[4] Giroud-Godquin, A. M., and Maitlis, P. M., 1991, *Angew. Chem.*, **30,** 375.

[5] Ohta, K., Muroki, H., Takagi, A., Hatada, K., Ema, H., Yamamoto, Y., and Matsuzaki, K., 1986, *Molec. Crystals liq. Crystals*, **140,** 131.

[6] Prasad, V., and Sadashiva, B. K., 1991, *Molec. Crystals liq. Crystals*, **201,** 13.

[7] Ohta, K., Muroki, H., Takagi, A., Yamamoto, I., and Matsuzaki, K., 1986, *Molec. Crystals liq. Crystals*, **135,** 247.

[8] Rao, P. R., and Sadashiva, B. K. (to be published).

[9] Giroud-Godquin, A. M., and Billard, J., 1983, *Molec. Crystals liq. Crystals*, **97,** 287.

[10] Usha, K., and Vijayan, K., 1989, *Molec. Crystals liq. Crystals*, **174,** 39. Usha, K., Vijayan, K., and Sadashiva, B. K., 1987, *Molec. Crystals liq. Crystals Lett.*, **5,** 67.

[11] Usha, K., and Vijayan, K., 1992, *Liq. Crystals*, **12,** 137.

[12] Usha, K., Vijayan, K., and Sadashiva, B. K., 1991, *Molec. Crystals liq. Crystals*, **201,** 13. Usha, K., and Vijayan, K., 1992, *Molec. Crystals liq. Crystals*, **220,** 77.

[13] Usha, K., Vijayan, K., Sadashiva, B. K., and Rao, P. R., 1990, *Molec. Crystals liq. Crystals*, **185,** 1.

[14] Muhlberger, B., and Haase, W., 1989, *Liq. Crystals*, **5,** 251.

[15] Hon, P., Pfluger, C. E., and Belford, R. L., 1967, *Inorg. Chem.*, **6,** 730.

[16] Hon, P., Pfluger, C. E., and Belford, R. L., 1966, *Inorg. Chem.*, **5,** 516.

[17] Baker, G. J., and Raynor, J. B., 1986, *J. chem. Soc. Dalton Trans.* B, p. 2655.

[18] Cotton, F. A., Rice, C. E., and Rice, G. W., 1977, *Inorg. Chim. Acta*, **24,** 231.

[19] Barclay, G. A., and Cooper, A., 1965, *J. chem. Soc.*, 3746.

[20] Watson, W. H., and Holley, W. W., 1984, *Croat. chem. Acta*, **57,** 467.

[21] Cotton, F. A., and Wood, J. S., 1964, *Inorg. Chem.*, **3,** 245.

[22] Robertson, I., and Truter, M. R., 1967, *J. chem. Soc.* A, p. 309.

[23] Okeya, S., Ooi, S., Matsumoto, K., Nakamura, Y., and Kawaguchi, S., 1981, *Bull. chem. Soc. Japan*, **54,** 1085.

[24] Cotton, F. A., and Wise, J. J., 1966, *Inorg. Chem.*, **5,** 1200.

[25] Koyama, H., Saito, Y., and Kuroya, H., 1953, *J. Inst. Polytech. Osaka Cy. Univ.* C, **4,** 43.

[26] Kitaigorodskii, A. I., 1973, *Molecular Crystals and Molecules* (Academic Press), p. 34.

[27] Kitaigorodskii, A. I., 1955, *Organic Chemical Crystallography* (Consultants Bureau Enterprises Inc.), p. 13.

[28] Hall, D., McKinnon, A. J., and Waters, T. N., 1966, *J. chem. Soc.* A, p. 615.

[29] Hambley, T. W., Gahan, L. R., and Searle, G. H., 1989, *Acta crystallogr.* C, **45,** 864.

[30] Eastman, M. P., Horng, M., and Sheu, K. W., 1987, *Liq. Crystals*, **2,** 223.

[31] Desiraju, G. R., 1989, *Crystal Engineering, The Design of Organic Solids* (Elsevier Science Publishing Co. Inc.), Chap. 4.

[32] Levelut, A. M., 1983, *J. Chim. phys.*, **80,** 149.