

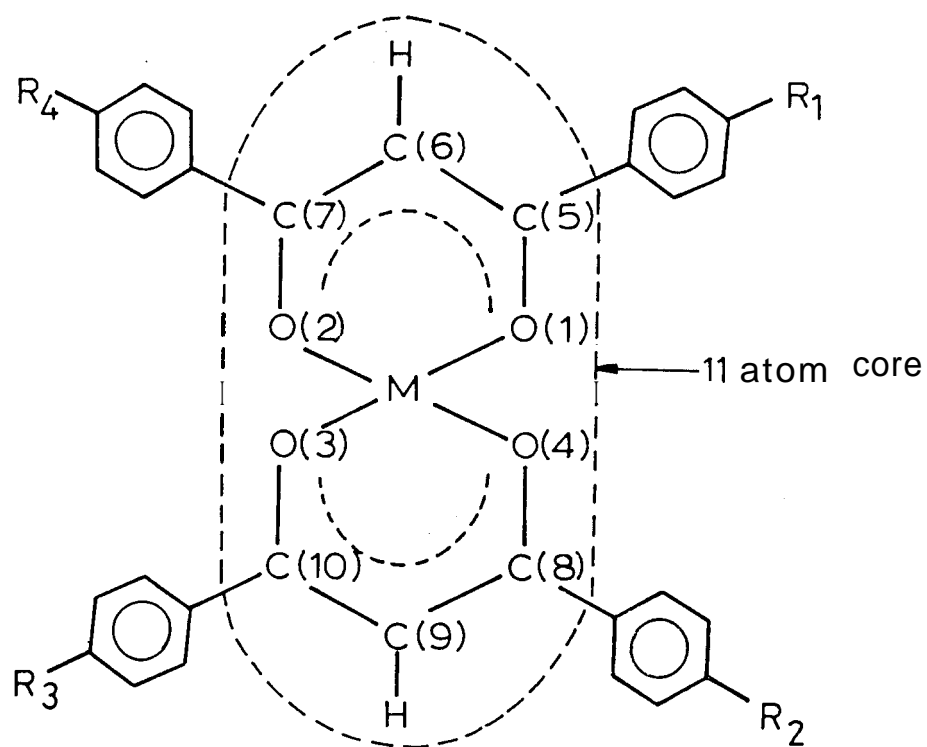
Chapter 7

Structural characteristics of discotic, metallo-organic β -diketonates

7.1 Introduction

In the preceding five chapters, details of the crystal and molecular structures of six metallo-organic discogens (Figure 1.6) were described. (For the sake of easy reading, Figure 1.6 has been re-included in this chapter). The molecules consist of a rigid 11-at0111core (shown encased in Figure 1.G) and a fringe made up of four phenyl rings substituted with alkyl or alkoxy chains at the respective para positions. In Cu-OC₈H₁₇ with four alkoxy chains, there are four oxygen atoms around the core; in Cu-OC₇H₁₅-C₇H₁₅, with two alkoxy and two alkyl chains, there are only two oxygen atoms and in Cu-C₈H₁₇, Pd-C₁₀H₂₁, Pd-C₈H₁₇ and Ni-C₈H₁₇ there are no oxygen atoms around the core. The length of the substitutions have also been varied i.e. 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.

Table 7.1 presents the details of the transitions from the crystalline phase (C) to the mesophase (D) and the isotropic phase (I). Comparison of the seven crystal structures has shown that some of the structural features are characteristic of this entire group of complexes. A resumé of these similarities, along with a few conspicuous differences which have also been observed, are described in this chapter.



- | | |
|--------------|---|
| (i) M = Cu | $R_1 = R_2 = R_3 = R_4 = \text{OC}_8\text{H}_{17}$ |
| (ii) M = Cu | $R_1 = R_2 = \text{OC}_7\text{H}_{15}; R_3 = R_4 = \text{C}_7\text{H}_{15}$ |
| (iii) M = Cu | $R_1 = R_2 = R_3 = R_4 = \text{C}_8\text{H}_{17}$ |
| (iv) M = Pd | $R_1 = R_2 = R_3 = R_4 = \text{C}_{10}\text{H}_{21}$ |
| (v) M = Pd | $R_1 = R_2 = R_3 = R_4 = \text{C}_8\text{H}_{17}$ |
| (vi) M = Ni | $R_1 = R_2 = R_3 = R_4 = \text{C}_8\text{H}_{17}$ |

Figure 1.B: Structural formula of the complexes studied in this thesis. The 11-atom core is shown encased.

Table 7.1: Transition temperatures (°C) and the molecular arrangement in the mesophase.

Complex	Transition temperatures (°C)	Molecular arrangement in the mesophase
(i) Cu-OC ₈ H ₁₇	$C \xrightarrow{83.5} D \xrightarrow{177} I$	lamellar [Ohta <i>et al</i> , 1986]
(ii) Cu-OC ₇ H ₁₅ -C ₇ H ₁₅	$ \begin{array}{c} C \xrightarrow{150.5} I \\ \swarrow \\ D \xrightarrow{145.5} I \end{array} $	not known
(iii) Cu-C ₈ H ₁₇	$C \xrightarrow{76} D \xrightarrow{117} D \xrightarrow{142.5} I$	lamellar [Giroud-Godquin and Billard, 1983]
(iv) Pd-C ₁₀ H ₂₁	$C \xrightarrow{101} D \xrightarrow{106} D \xrightarrow{119} I$	not known
(v) Pd-C ₈ H ₁₇	$C \xrightarrow{120.5} D \xrightarrow{138} I$	not known
(vi) Ni-C ₈ H ₁₇		reported non-mesogenic [Giroud-Godquin and Billard, 1983]

7.2 Space group and molecular symmetry

Table 7.2 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 [Kitaigorodskii, 1973], $P\bar{1}$ is one of the space groups which permits closest packed arrangement of molecules. Values of the packing coefficient [Kitaigorodskii, 1955] k defined as

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

and listed in Table 7.2 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 (Figure 1.6) shows that the molecule could possess a crystallographic centre of symmetry. The data in Table 7.2, however, show that only five out of the seven molecules possess a crystallographic centre of symmetry. Interestingly, the molecules $\text{Cu-OC}_8\text{H}_{17}$ and $\text{Cu-OC}_7\text{H}_{15}\text{-C}_7\text{H}_{15}$ 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 chains. The statistical significance of a 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.

Table 7.2: Crystal data.

Complex	Space group	Z	molecular symmetry	k
Cu-OC ₈ H ₁₇	P $\bar{1}$	2	1	0.70
Cu-OC ₇ H ₁₅ -C ₇ H ₁₅	P $\bar{1}$	2	1	0.70
Cu-C ₈ H ₁₇ (N)	P $\bar{1}$	1	$\bar{1}$	0.72
Cu-C ₈ H ₁₇ (P)	P $\bar{1}$	1	$\bar{1}$	0.70
Pd-C ₁₀ H ₂₁	P $\bar{1}$	1	$\bar{1}$	0.70
Pd-C ₈ H ₁₇	P $\bar{1}$	1	$\bar{1}$	0.70
Ni-C ₈ H ₁₇	P $\bar{1}$	1	$\bar{1}$	0.70

It is also observed from Table 7.2 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.

7.3 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 system, the coordination polyhedron has a rectangular characteristic, the distance $O(1)\dots O(2)$ being larger than the distance $O(1)\dots O(4)$. It is also observed that in the crystal structure of $Cu-OC_7H_{15}-C_7H_{15}$, the geometry of the rectangle is further distorted, i.e., $O(1)\dots O(4) = 2.57(1)\text{\AA}$ whereas $O(2)\dots O(3) = 2.67(1)\text{\AA}$. 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 chapter. Average values of the M-O distance, the O-M-O valence angles and the O...O distances are presented in Table 7.3. As could be expected, an increase in the size of the metal atom 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, absence of mesomorphism has been associated with tetrahedral coordination around the metal atom [Galyametdinov *et al*, 1988]. In the case of the Ni-complex, $Ni-C_8H_{17}$ which is reported to be non-mesogenic [Giroud-Godquin and Billard, 1983; Giroud-Godquin and Maitlis, 1991], there is clearly no evidence for such tetrahedral coordination.

Table 7.3: 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 ₈ H 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 ₇ H ₁₅ -C ₇ H ₁₅	1.90(2)	1.28(3)	1.40(6)	2.74(1)	92.6(3)	127(2)	126(2)	122(1)
Cu-C ₈ H 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 ₈ H 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	93.9(2)	124.6(4)	125.6(2)	125.7(6)
Pd-C ₈ H ₁₇	1.9695(5)	1.274(2)	1.4(1)	2.871(4)	93.6(1)	124.8(3)	125.2(5)	126.4(5)
Ni-C ₈ H ₁₇	1.837(8)	1.275(5)	1.38(2)	2.710(6)	95.1(2)	126(1)	124(1)	123.8(9)

Robertson and Truter [1967] have mentioned about the occurrence of weak interactions between the metal atom and the core atoms of neighbouring molecules of some diketone complexes. Koyama *et al* [1953] also report the occurrence of such a coordination by the C-H 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 Cu-OC₈H₁₇. Here, two phenyl ring atoms from the neighbouring molecules are found to be situated at 3.17 and 3.24Å 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 $\sim 0.17\text{\AA}$.

7.4 Dimensions of the core

The average values of the bond lengths and valence angles characterizing the core are listed in Table 7.3. The dimensions are found to be normal.

7.5 Planarity

The structural formula (Figure 1.6) 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 Cu-OC₈H₁₇ and Cu-OC₇H₁₅-C₇H₁₅ 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 evinced 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 Cu-OC₈H₁₇ and Cu-OC₇H₁₅-C₇H₁₅, the angles are ~ 3 and 1° respectively. Similar buckling has been observed in the crystal structures of other diketone complexes [Mühlburger and Haase, 1989; Okeya *et al.*, 1981; Fallon and Gatehouse, 1982] wherein the corresponding angles are ~ 3 , 6 and 2° respectively. In the case of the dimorphs Cu-C₈H₁₇, Pd-C₁₀H₂₁, Pd-C₈H₁₇ and Ni-C₈H₁₇ 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 7.4 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.* [1966].

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

Table 7.4: Values of η , δ and end to end molecular dimensions.

Complex	$\eta(^{\circ})$	δ of terminal atoms (\AA)	molecular dimensions (\AA)
Cu-OC ₈ H 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 ₇ H ₁₅ -C ₇ H 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 ₈ H ₁₇ (N)	4.8	2.016(8), -1.42(1)	30.4, 9.7
Cu-C ₈ H 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 ₈ H ₁₇	2.8	0.05(1), 0.17(1)	30.2, 9.7
Ni-C ₈ H ₁₇	3.1	0.27(1), 0.18(1)	30.3, 9.5

atoms of the aliphatic chains from the plane though the crystallographically independent part of the core have been included in Table 7.4. The atomic displacements are the highest for the N form of Cu-C₈H₁₇.

7.6 Molecular conformation

The conformations of the molecules studied in this thesis are very similar in their respective crystal structures. In all the cases, the phenyl rings are tilted with respect to the core, the tilt being controlled primarily by steric effects. Also, the tilts of the alkyl/alkoxy chains are comparable with those of the respective phenyl rings. Thus, despite the conformational flexibility available for the aliphatic chains, the contribution to the overall tilt of the molecule from the chains is not more than that from the phenyl rings. The alkyl/alkoxy chains are in an all-*trans* conformation (Figure 3.7). The end-to-end dimensions of the molecules (Table 7.4) indicate that in all the cases, the length to width ratio is ~ 3 . Thus, the overall molecular shape is close to a rectangular disc. The observed conformations and the molecular dimensions closely resemble the model B (Figure 2.6) proposed by Ohta et al [1986] for the mesophase of Cu-OC₈H₁₇. 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 7.4 shows that the increase in the length of the molecule Pd-C₁₀H₂₁ over that of Pd-C₈H₁₇ 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 Cu-OC₇H₁₅-C₇H₁₅ merits special mention. Here, two types of conformations are possible, *viz.*, those corresponding to 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 (Table 7.4) 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-(4-7-diazocyclononane)cobalt(III)], which is not mesogenic, molecular mechanics calculations have shown [Hambley *et al.*, 1989] 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 [Okeya *et al.*, 1981]. It is therefore not unlikely that in the case of Cu-OC₇H₁₅-C₇H₁₅ also, a second crystalline modification with *trans* arrangement of the similar substitutions exists. Examination of the crystallization dish of Cu-OC₇H₁₅-C₇H₁₅ 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 must be mentioned that in the crystal structures of few other diketones with dissimilar substitution, only a *trans* arrangement has been reported [Mühlberger and Haase, 1989; Hon

et al, 1966, Hon *et al*, 1966 and Barclay and Cooper, 1965].

7.7 Molecular arrangement

The available structural data on the mesophase of diketone complexes with four chains suggest that some of them are characterized by a lamellar structure (Table 7.1). 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 these complexes indicate that in the crystalline phase, the molecular arrangement is explicitly lamellar for the complex Cu-OC₇H₁₅-C₇H₁₅. For the rest of the complexes, the molecular arrangement has both lamellar as well as columnar characteristics. For the complexes Cu-OC₈H₁₇ Cu-C₈H₁₇, Pd-C₁₀H₂₁, Pd-C₈H₁₇ and Ni-C₈H₁₇, the molecules are arranged in layers but the periodic stacking of the layers leads to the formation of columns. 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 nonbonded intermolecular interactions/contact distances $\leq 4\text{\AA}$ 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 Cu-C₈H₁₇, in the rest of the columnar structures, the number of intermolecular contact distances $\leq 4\text{\AA}$ is more within a layer than along the column. For example, in the case of the P form of Cu-C₈H₁₇, 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 the complex $\text{Cu-OC}_8\text{H}_{17}$. The layer spacing of 25\AA observed in the crystalline phase of $\text{Cu-OC}_8\text{H}_{17}$ compares well with the corresponding value of 23\AA in its mesophase [Ohta *et al*, 1986]. The good agreement is in support of the proposed mechanism of transformation. A layer thickness of $\sim 29\text{\AA}$ has been mentioned by Giroud-Godquin and Billard [1983] for the discogen, $\text{Cu-C}_{10}\text{H}_{21}$. The series investigated in this thesis does not include this copper complex but only its palladium analogue *viz.*, $\text{Pd-C}_{10}\text{H}_{21}$. In this case, the layer thickness in the crystalline phase is found to be $\sim 32\text{\AA}$, which is in reasonable agreement with the value for the corresponding copper complex.

Only in the crystal structure of the N-form of $\text{Cu-C}_8\text{H}_{17}$, the cohesion due to non-bonded intermolecular interactions appears to be more along the column than within the layer. Here, there are only 14 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 the six complexes are described below.

7.7.1 Layer structure

In this series, layer structure is observed for the asymmetrically substituted complex $\text{Cu-OC}_7\text{H}_{15}\text{-C}_7\text{H}_{15}$ (Figure 3.9). 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 $\leq 4\text{\AA}$ 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.

7.7.2 Columnar structure

For the complexes $\text{Cu-C}_8\text{H}_{17}$, $\text{Pd-C}_{10}\text{H}_{21}$, $\text{Pd-C}_8\text{H}_{17}$ and $\text{Ni-C}_8\text{H}_{17}$, the repeat unit along the column is a single molecule. For the complex $\text{Cu-OC}_8\text{H}_{17}$, 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 structures in which pairing is observed are those of molecules with oxygen atoms around the core *viz.*, $\text{Cu-OC}_8\text{H}_{17}$ and $\text{Cu-OC}_7\text{H}_{15}\text{-C}_7\text{H}_{15}$. It is likely that the presence

of oxygen atoms favours such molecular pairing.

The columnar molecular arrangements in the crystal structures of $\text{Cu-OC}_8\text{H}_{17}$, the N and P-forms of $\text{Cu-C}_8\text{H}_{17}$, $\text{Pd-C}_{10}\text{H}_{21}$, $\text{Pd-C}_8\text{H}_{17}$ and $\text{Ni-C}_8\text{H}_{17}$ 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 [Barclay and Cooper, 1965] and bis-acetyl acetone copper(II) [Koyama *et al*, 1953] which are also characterized by columnar stacking of the diketonato cores, the shortest axis of the unit cell is found to be the column axis.
2. In the crystal structures of the complexes $\text{Cu-C}_8\text{H}_{17}$, $\text{Pd-C}_{10}\text{H}_{21}$, $\text{Pd-C}_8\text{H}_{17}$ and $\text{Ni-C}_8\text{H}_{17}$ the metal atoms are stacked atop. In the crystal structure of $\text{Cu-OC}_8\text{H}_{17}$, 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° .
3. In the crystal structures of the complexes, P-form of $\text{Cu-C}_8\text{H}_{17}$, $\text{Pd-C}_{10}\text{H}_{21}$, $\text{Pd-C}_8\text{H}_{17}$ and $\text{Ni-C}_8\text{H}_{17}$, and the P-form of $\text{Cu-C}_8\text{H}_{17}$, the M...M distance along the column is ~ 10 Å. In striking contrast, in the N-form of $\text{Cu-C}_8\text{H}_{17}$, the M...M distance is ~ 6 Å. The distribution of intermolecular contact distances described earlier (section 7.7) suggests a possible correlation existing between the M...M distance along the column and the con-

tact 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. As mentioned in Chapter 4, Eastman *et al* [1987] propose a columnar arrangement for Cu-C₈H₁₇. The separation of 2 to 3nm between metal atoms of adjacent columns mentioned by them is observed by us in the crystal structure of the N-form of Cu-C₈H₁₇.

4. Irrespective of the value 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 4Å and ranges from 3.2 to 3.7 Å. If the perpendicular distance between adjacent cores is assumed to be 3.6Å, *i.e.*, the sum of the van der Waal's 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

$$\theta = \cos^{-1}\left(\frac{3.6}{a}\right) \quad (7.1)$$

where a is the a -axial length (column axis) of the unit cell (Figure 7.1). Equation (7.1) 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 7.5 compares the observed tilts with those calculated using equation (7.1). The agreement appears to be good.

5. The interior of each column is made up of the aromatic groups, viz., the diketonato core and the phenyl rings. Flexible alkyl/alkoxy chains ex-

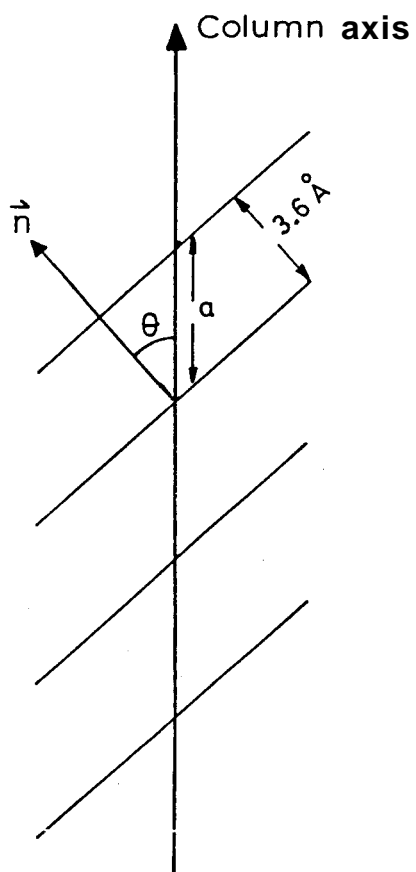


Figure 7.1: Schematic diagram of the columnar stacking.

Table 7.5: Comparison of the observed and calculated tilts of the molecules with respect to the column axis.

Complex	$\theta_{obs}(\text{°})$	$\theta_{calc}(\text{°})$
Cu-OC ₈ H ₁₇	128	124
Cu-C ₈ H ₁₇ (N)	122	128
Cu-C ₈ H ₁₇ (P)	111	110
Pd-C ₁₀ H ₂₁	112	110
Pd-C ₈ H ₁₇	112	110
Ni-C ₈ H ₁₇	111	111

tending outwards constitute the periphery of the column (Figure 4.13). 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 [1989]. Giroud-Godquin and Maitlis [1991] also mention that the non-bonded interactions present in the flexible chains are associated with the stability 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 Cu-OC₈H₁₇ and the N form of Cu-C₈H₁₇.
7. Each column in the crystal structure is surrounded by six others which do not form an ideal hexagon. Figure 4.12 is a schematic representation of the hexagonal arrangement in the two polymorphs of Cu-C₈H₁₇. The interactions between adjacent columns is primarily of the van der Waal's type. Also, the orientation of the molecules is the same in all the columns (Figure 4.11). This last feature is in contrast to the herringbone type of molecular arrangement (Figure 1.3) observed in the columnar phases of certain discogens [Levelut, 1983].

References

- Allen, F.H., Kennard, O., Watson, D.G., Brammer, L. and Orpen, A.G., *J. Chem. Soc. Perkin trans.*, S1, (1987).
- Barclay, G.A. and Cooper, A., *J. Chem. Soc.*, 3746, (1965).
- Bernal, J.D., and Crowfoot, D., *Trans. Faraday Soc.*, 29, 1032 (1933).
- Chandrasekhar, S., *Liquid* crystals; Cambridge University Press, Cambridge (1977); second edition (1992).
- Chandrasekhar, S., Sadashiva, B.K., and Suresh, K.A., *Pramana*, 9, 471 (1977).
- Cotrait, M., Marsau, P., Destrade, C. and Malthete, J., *J. Phys. Lett.*, 40, 519, (1979).
- Cromer, D.T. and Waber, J.T, *Acta cryst.*, 18, 104, (1965).
- Cromer, D.T. and Mann, J.B., *Acta cryst.*, A24, 321, (1968).
- Cromer, D.T. and Liberman, D., *J. Chem. Phys.*, 53, 1891, (1970)
- de Jeu, W.H., *Phil. Trans. R. Soc. Lond.*, A309, 102, (1983).

Desiraju, G.R., *Crystal Engineering, The Design of Organic Solids*, Elsevier Science Publishing Co. Inc., New York, (1989).

Destrade, C., Bernaud, M.C., Gasparoux, H., Levelut, A.M. and Tinli, N.H., *Proc. Int. Liq. Cryst. Conf., Bangalore*, p. 29, (1979).

Eastman, M.P., Horng, M. and Sheu, K.W., *Liq. Cryst.*, 2, 223, (1987).

Fallon, G.D. and Gatehouse, B.M., *Cryst. Struct. Comm.*, 11, 1317, (1982).

Frank, F.C. and Chandrasekhar, S., *J. Phys. (Paris)*, 41, 1285, (1980).

Galyametdinov, Yu. G., Bikchantaev, I.G. and Ovchinnikov, I.V., *Zh. Obshch. Khim.*, 58, 1326, (1988).

Fontes, E., Heiney, P.A., and de Jeu, W.H., *Phys. Rev. Lett.*, 61, 1202, (1988).

Gavezzotti, A., *Acta Cryst.*, B46, 275, (1990).

Germain, G., Main, P., and Woolfson, M.M., *Acta Cryst.*, A27, 368, (1971).

Giroud-Godquin, A.M. and Billard, J., *Mol. Cryst. Liq. Cryst.*, 66, 147 (1981).

Giroud-Godquin, A.M. and Billard, J., *Mol. Cryst. Liq. Cryst.*, 97, 287, (1983).

Giroucl-Godquin, A.M. and Maitlis, P.M., *Angew. Chem.*, 30, 375, (1991).

Hall, D., McKinnon, A.J. and Waters, T.N., *J. Chem. Soc. (A)*, 615, (1966).

Hambley, T.W., Gahan, L.R. and Searle, G.H., *Acta Cryst.*, C45, 864, (1989).

Hon, P., Pflugel, C.E. and Belford, R.L., *Inorg. Chem.*, 5, 516, (1966).

Hon, P., Pflugel, C.E. and Belford, R.L., *Inorg. Chem.*, 6, 730, (1967).

Hoshino, N., Murakami, H., Matsunaga, Y., Inabe, T. and Maruyama, Y., *Inorg. Chem.*, 29, 1177, (1990).

Iannelli, P., Immirzi, A., Caruso, U., Roviello, A. and Sirigu, A., *Acta Cryst.*, C45, 879, (1989).

International Tables for X-ray Crystallography, 3, Kynoch Press, Birmingham, p276, (1968).

INSIGHT II, A Program for Molecular Modelling, BIOSYM, Australia.

Johnson, C.K., ORTEP-II, A Fortran Thermal Ellipsoid Plotting Program for Crystal Structure Illustration, ORNL-5138, Oak Ridge National Lab., Oak Ridge, Tenn., (1976).

Kitaigorodskii, A.I., *Molecular Crystals and Molecules*, (Academic Press, New York and London), p34, (1973).

Kitaigorodskii, A.I., *Organic Chemical Crystallography*, (Consultants Bureau Enterprises Inc., New York), p13, (1955)

Koyama, H., Saito, Y. and Kuroya, H., *J. Inst. Polytech. Osaka City Univ. Ser. C*, 4, 43, (1953).

Krigbaum, W.L., Chatani, Y. and Barber, P.G., *Acta Cryst.*, B26, 97, (1970).

Leadbetter, A.J., *Thermotropic Liquid Crystals*, Critical Reports in Appl. Chem., Ed. Gray, G. W., Wiley Chichester, 22, p1, (1987).

Leadbetter, a.J. and Mazid, M.A., *Mol. Cryst. Liq. Cryst.*, **65**, 265, (1981).

Levelut, A.M., *J. Phys. Lett.*, 40, L-81, (1979).

Levelut, A.M., *J. de chim. Phys.*, **80**, 149, (1983).

Mühlberger, B. and Haase, W., *Liquid Cryst.*, 5 251, (1989).

North, A.C.T, Phillips, D.C. and Mathews, F.S., *Acta Cryst.*, **A24**, 351, (1968).

Ohta, K., Muroki, H., Takagi, A., Hatada, K., Ema, H., Yamamoto, Y. and Matsuzaki, K., *Mol. Cryst. Liq. Cryst.*, 140, 131, (1986).

Okeya, S., Ooi, S., Matsumoto, K., Nakamura, Y. and Kawaguchi, S., *Bull. Chem. Soc. Jpn.*, 54, 1085, (1981).

Pattabli, V. and Craven, B.M., *J. Lip. Res.*, 20, 753, (1979).

Pauling, L., *The nature of the chemical bond*, Third Edition, Oxford and IBH Publishing Co., p.256, (1967).

Pershan, P.S., *Structure of liquid crystal phases*, World Scientific Publishing Co. Pte. Ltd., (1988).

Piccliocci, C., Simon, J., Skoulios, A., Guillon, D., and weber, P., *J. Am. Chem. Soc.*, 104, 5245, (1982).

Polishchuk, A.P., Antipin, M.Yu., Timofeeva, T.V., Struchkov, Yu.T., Galyametdinov, Yu. G. and Ovchinnikov, I.V., *Sov. Phys. Cryst.*, 31, 274, (1986).

Prasad, V. and Sadashiva, B.K., *Mol. Cryst. Liq. Cryst.*, 201, 13, (1991).

Queguiner, A., Zann, A., Dubois, J.C., and Billard, J., *Proc. Int. Liq. Cryst. Conf., Bangalore*, p. 35, (1979)

Robertson, I. and Truter, M.R., *J. Chem. Soc. (A)*, 309, (1967)

Roviello, A., Sirigu, A., Iannelli, P. and Immirzi, A., *Liq. Cryst.*, 3, 115, (1988).

Sadashiva, B.K. and Rao, P.R., (To be published).

Safinya, C.R., Liang, K.S., Varady, W.A., Clark, N.A. and Andersson, G., *Phys. Rev. Lett.*, 53, 1172, (1984).

Sakashita, H., Nishitani, A., Sumiya, Y., Terauchi, H., Ohta, K. and Yamamoto, I., *Mol. Cryst. Liq. Cryst.*, 163, 211, (1988).

Sheldrick, G.M., Program for Crystal Structure Determination, Univ. of Cambridge, England, (1976).

Shiono, R., SFLS Program, private circulation.

Stewart, R.F., Davidson, E.R. and Simpson, W.T., *J. Chem. Phys.*, 42, 3175, (1965).

Vani, G.V. and Vijayan, K., *Mol. Cryst. Liq. Cryst.*, 42, 249, (1977a); *Acta Cryst.*, B33, 2236, (1977b).

Watson, W.H. and Holley, W.W., *Croat. Chem. Acta*, 57, 467, (1984).

Zachariasen, W.H., *Acta Cryst.*, 16, 1139, (1963)