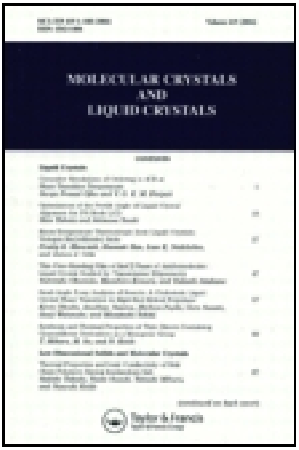

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Crystal and Molecular Structure of the Discogen bis[1,3-di(p-n-octylphenyl)-propane-1,3-dionato]copper(II)-A Second Crystalline Modification

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Crystal and Molecular Structure of the Discogen bis[1,3-di(*p*-*n*-octylphenyl)-propane-1,3-dionato]copper(II)—A Second Crystalline Modification

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The discogen bis[1,3-di(*p*-*n*-octylphenyl)propane-1,3-dionato]copper(II) crystallizes in two distinct morphologies, the more abundant needle-like form and the less abundant prismatic form. The crystal structure analysis of the first modification was reported in an earlier paper. Here we describe the structural details of the second modification. It belongs to the triclinic space group $P\bar{1}$ with the copper atom lying on an inversion centre. The coordination around the metal atom is square planar and the octyl chains have an all-*trans* conformation. The molecules stacked atop form a tilted columnar arrangement along the crystallographic *a*-axis. The shortest metal-metal distance is 10.3Å which is very much larger than the value of 5.8Å observed in the needle-like form, and the molecules are more planar. The crystal and molecular structure of the prismatic form closely resemble that of the palladium complex, analyzed by us earlier.

Keywords: discotic, crystal structure, tilted columnar

INTRODUCTION

In our earlier paper[1] on the copper complex bis[1,3-di(*p*-*n*-octylphenyl)propane-1,3-dionato]copper(II), i.e., Cu-C_8 H_{17} (Figure 1), we had mentioned that using acetone as the solvent, crystals with two distinct morphologies were obtained, *viz.*, the more abundant needle-like and the less abundant prismatic crystals, hereafter referred to as the N and P forms respectively (Figure 2). It was of interest to know whether the difference in the morphology was also accompanied by differences in crystal structural characteristics. Details concerning the X-ray analysis of the N form has already been published by us. In this paper, we report the crystal structure analysis of the P form and also compare the structural characteristics of the two

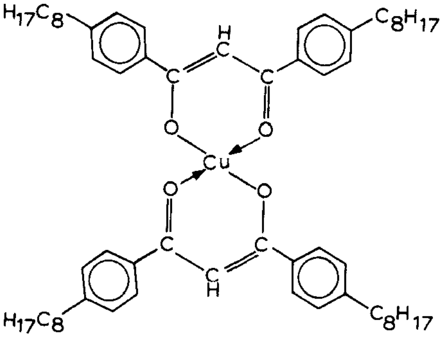

FIGURE 1 Structural formula of bis[1,3-di(*p*-*n*-octylphenyl)propane-1,3-dionato]copper(II).

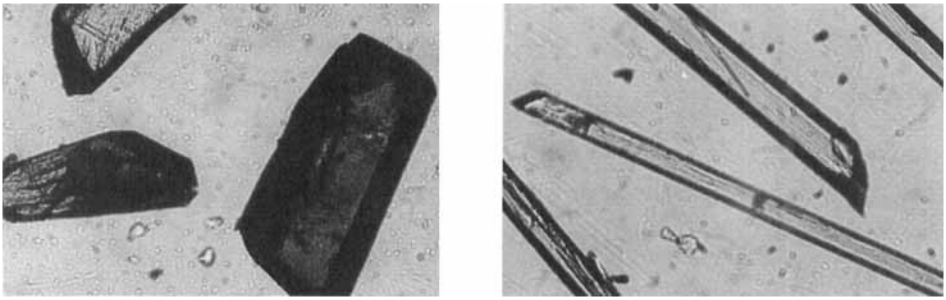

FIGURE 2 Photographs of the prismatic and the needle-like crystals. (Magnification 125 ×).

crystalline modifications. It must be mentioned that the morphologically distinct crystals correspond to separate crystallization experiments carried out during different periods of a year with, however, the same solvent. It is therefore likely that the occurrence of morphologically distinct crystals is related to factors such as the ambient temperature and humidity, which were not controlled in our experiments. Despite repeated attempts, only very few single crystals of the P form could be obtained. These crystals were not sufficient in quantity for carrying out thermal studies. Hence, at the moment, it is not clear whether the two forms are characterized by identical transition temperatures or not.

EXPERIMENTAL

The unit cell constants of the greenish, prismatic crystal (obtained by slow evaporation from a solution in acetone) were determined and refined by least squares procedure using 25 reflections on a CAD4 single crystal diffractometer. The crystal data are presented in Table I. For collection of intensity data the prescan speed was chosen as 5.5°/min. However, the final scan speed was varied to satisfy the relation, $[\sigma(I)/(I)] \leq 0.03$.

TABLE I

Molecular formula	$C_{62}H_{86}O_4Cu$
Crystal size	0.35 x 0.18 x 0.10 mm^3
a	10.341(3) Å
b	11.621(2)
c	12.817(2)
α	103.99(1)°
β	92.73(2)
γ	109.55(2)
V	1394 $Å^3$
Z	1
Space group	$P\bar{1}$
ρ_{calc}	1.134 gm/cc
μ_{MoK_α}	4.51 cm^{-1}
λ_{MoK_α}	0.7107 Å
Data collection	CAD4 diffractometer
Scan mode	$\omega/2\theta$
Independent reflections	4784
Reflections with $I \geq 3\sigma(I)$	2262
Corrections applied	Lp, absorption,[5] anomalous scattering[6] for Cu
Scattering factors	Cu (ref. 6)
	C, O (ref. 7)
	H (ref. 8)
R	0.0692
R_w	0.0721
Weighting scheme	$K/[\sigma^2(F) + g(F)^2]$
	K = 3.5101; g = 0.000163

STRUCTURE DETERMINATION

As in the case of the N type crystal, the statistical distribution of the normalized structure factors indicated[2] the space group to be centric, which in this case is $P\bar{1}$. With $Z = 1$, the copper atom lies on an inversion centre. Placing the copper atom at the origin, a difference electron density map was computed and the positions

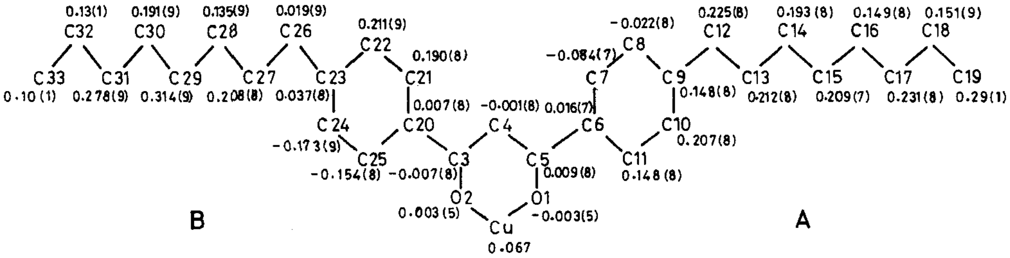

FIGURE 3 The displacement, δ, in Å of the non-hydrogen atoms from the least squares plane through the crystallographically independent half of the core.

of the rest of the non-hydrogen atoms in the molecule were identified. Using the program SHELX-76,[3] the positional and the anisotropic thermal parameters of all the non-hydrogen atoms were refined by full-matrix least-squares procedure. Hydrogen atoms were placed at their calculated positions corresponding to a C—H distance of 1.08Å.[4] The parameters of the hydrogen atoms were not refined but their contributions to the structure factors were included during the refinement procedure. The hydrogen atoms were assigned isotropic temperature factors, same as the equivalent isotropic temperature factor, U_{eq}, of the respective atom to which they are covalently bonded. Table I lists further details of the structure analysis.

RESULTS AND DISCUSSION

Comparison of the crystal structures of the P and the N forms shows that there are many similarities in the overall structural characteristics such as the copper atom lying on an inversion centre in a triclinic unit cell, square planar coordination, conformation of the octyl chains, columnar arrangement, etc. However, further examination clearly shows that there are distinct differences. The details are described in this section.

The atomic numbering scheme is shown in Figure 3. Table II lists the positional and the U_{eq} values of the non-hydrogen atoms. The unit cell volume of the P crystal is ~1% larger than that of the N crystal.[1] With $Z = 1$ in both cases, the molecule appears to have slightly more room in the unit cell of the P form. Consequently, it may be expected that the thermal parameters of the atoms/molecule in the P form are higher than for the N form. The average U_{eq} values of various atomic groups of the molecule, compared in Table III, indicate that is indeed the case. However, there is no evidence for any structural disorder.

Within the limits of experimental error, the bond lengths and bond angles listed in Table IV are normal. The average copper-oxygen distance is 1.903(4)Å and the coordination around the copper atom is square planar. In Figure 3, the displacements, δ, of the atoms from the least squares plane through the crystallographically independent half of the core, viz., Cu, O(1), O(2), C(3) to C(5) have been marked. As in the N form of Cu-C_8H_{17} and also in the Pd-complex,[9] bis[1,3-di(*p*-*n*-decylphenyl)propane-1,3-dionato]palladium(II), *i.e.*, Pd-$C_{10}H_{21}$, the δ value among the atoms of the core is highest for the metal atom, and the core is only nearly planar.

TABLE II

Final fractional atomic coordinates and U_{eq} (Å^2) values

ATOM	X	Y	Z	U_{eq}
Cu	0.0000	0.0000	0.0000	0.0616(6)
O(1)	0.1909(5)	0.1050(4)	0.0124(4)	0.065(2)
O(2)	0.0263(5)	-0.1400(4)	-0.0947(4)	0.070(2)
C(3)	0.1390(7)	-0.1426(7)	-0.1328(6)	0.056(3)
C(4)	0.2609(7)	-0.0433(7)	-0.1083(6)	0.057(3)
C(5)	0.2826(7)	0.0773(7)	-0.0371(6)	0.054(3)
C(6)	0.4197(7)	0.1821(6)	-0.0142(6)	0.052(3)
C(7)	0.5377(8)	0.1638(6)	-0.0561(6)	0.065(3)
C(8)	0.6625(7)	0.2659(7)	-0.0358(7)	0.072(4)
C(9)	0.6738(7)	0.3877(7)	0.0251(6)	0.055(3)
C(10)	0.5596(8)	0.4033(6)	0.0677(7)	0.067(4)
C(11)	0.4339(7)	0.3006(7)	0.0471(6)	0.063(3)
C(12)	0.8129(8)	0.4935(7)	0.0418(6)	0.076(4)
C(13)	0.8320(7)	0.6204(7)	0.1199(6)	0.068(3)
C(14)	0.9803(7)	0.7118(7)	0.1328(6)	0.066(4)
C(15)	0.0085(7)	0.8432(6)	0.2083(6)	0.060(3)
C(16)	0.1592(7)	0.9314(7)	0.2220(6)	0.065(3)
C(17)	0.1901(8)	0.0650(7)	0.2922(7)	0.076(4)
C(18)	0.3425(9)	0.1495(7)	0.3046(7)	0.094(4)
C(19)	0.372(1)	0.2822(9)	0.370(1)	0.134(6)
C(20)	0.1224(7)	0.7318(7)	0.7890(6)	0.059(3)
C(21)	-0.0084(8)	0.6419(7)	0.7566(7)	0.076(4)
C(22)	-0.0302(8)	0.5270(8)	0.6865(7)	0.078(4)
C(23)	0.0773(8)	0.4929(7)	0.6443(6)	0.062(4)
C(24)	0.2098(8)	0.5859(8)	0.6806(7)	0.070(4)
C(25)	0.2326(8)	0.7037(7)	0.7488(7)	0.066(4)
C(26)	0.0576(9)	0.3624(7)	0.5667(7)	0.079(4)
C(27)	-0.0939(9)	-0.7247(6)	-0.4575(6)	0.075(4)
C(28)	-0.1089(9)	-0.8571(8)	-0.5330(7)	0.080(4)
C(29)	-0.2602(9)	-0.9462(8)	-0.5577(7)	0.082(4)
C(30)	-0.2836(9)	-0.0778(7)	-0.6252(7)	0.079(4)
C(31)	-0.4351(9)	-0.1666(8)	-0.6415(7)	0.083(4)
C(32)	-0.458(1)	-0.3003(8)	-0.7084(8)	0.099(5)
C(33)	-0.602(1)	-0.3909(9)	-0.7180(9)	0.132(6)

The δ values of 0.29(1) and 0.10(1)Å of the terminal atoms C(19) and C(33) of the chains are conspicuously less than the corresponding values of 2.016(8) and 1.42(1)Å observed for the N form. Similarly, the tilts 6 and 9° respectively of the phenyl rings A and B, 3 and 7° respectively of the chains A and B, with respect

TABLE III

Comparison of the average U_{eq} values (Å^2) of similar groups of atoms in the prismatic and the needle-like forms. The quantities in parentheses represent the e.s.d. values

		Prismatic	Needle-like
Core [Cu, O(1), O(2) C(3) to C(5)]		0.061(2)	0.042(2)
Phenyl rings	A	0.062(3)	0.047(3)
	B	0.069(4)	0.042(3)
Chains	A	0.080(4)	0.056(3)
	B	0.089(4)	0.059(3)

to the core are strikingly less than the corresponding values 17, 11, 16 and 12° for the N form. Thus, in this crystal structure, the overall tilts as well as the displacements of the phenyl rings and the octyl chains with respect to the core are less than in the N form.

The octyl chains in the molecule are fully extended in an all-*trans* conformation (Figure 4). The molecular dimensions of 30.3 and 9.6Å calculated from the respective distances C(19) . . . C(33), C(33) . . . C(19)′ compare well with those observed for the N crystal and also resemble the model B proposed by Ohta *et al.*[10] Here, the symbol ′ denotes the atom related by centre of inversion. The arrangement of molecules in the plane perpendicular to the crystallographic *a*-axis is shown in Figure 5. In this plane, the molecular arrangement is essentially layer-like, with the molecules tilted with respect to the plane. Figure 5 also shows the interleaving of molecules related by the translation $\overrightarrow{(2b + c)}$. Examination of intermolecular contact distances ≤4Å shows that each molecule in the layer (Figure 5) is surrounded by six others situated at $\pm\overrightarrow{b}$, $\pm\overrightarrow{(b + c)}$ and $\pm\overrightarrow{(2b + c)}$, i.e., at ±11.6, ±15.1 and ±23.7Å respectively. For the N crystal, the corresponding distances are ±17.6, ±19.1 and ±33.9Å respectively. The geometry of the molecular coordination is thus different in the two structures. Figure 6 provides a schematic representation of this feature. The layer structure is stabilized by intermolecular non-bonded interactions, most of which are of the phenyl ring . . . chain and the core . . . chain type. As in the cases of Pd-$C_{10}H_{21}$ and the N form of Cu-C_8H_{17}, the layers in the crystal are stacked periodically along the crystallographic *a*-axis to give rise to a tilted columnar arrangement; however the tilt angle in the P form (111°) is less than the value (122°) in the N form. Figure 7 provides a comparison of the tilts in the two crystal forms. It is observed that the reduction in the metal. . . metal distance along the column axis is accompanied by an increase in the angle of tilt. Within a column the arrangement of the molecules is stabilized by interactions of the type core . . . phenyl ring, phenyl ring . . . phenyl ring, phenyl ring . . . chain and chain . . . chain, which exist between adjacent molecules

TABLE IV

Final bond lengths (Å) and bond angles (°). Values of the e.s.d.'s are in parentheses

BOND LENGTHS

Cu -O(2)	1.888(5)	C(15)-C(16)	1.526(9)
Cu -O(1)	1.917(4)	C(16)-C(17)	1.51(1)
O(1)-C(5)	1.25(1)	C(17)-C(18)	1.53(1)
O(2)-C(3)	1.292(9)	C(18)-C(19)	1.49(1)
C(3)-C(4)	1.354(9)	C(20)-C(21)	1.372(9)
C(3)-C(20)	1.51(1)	C(20)-C(25)	1.38(1)
C(5)-C(4)	1.41(1)	C(21)-C(22)	1.36(1)
C(5)-C(6)	1.487(8)	C(22)-C(23)	1.39(1)
C(6)-C(11)	1.37(1)	C(23)-C(24)	1.403(9)
C(6)-C(7)	1.41(1)	C(23)-C(26)	1.54(1)
C(7)-C(8)	1.391(9)	C(24)-C(25)	1.37(1)
C(8)-C(9)	1.41(1)	C(26)-C(27)	1.52(1)
C(9)-C(10)	1.37(1)	C(27)-C(28)	1.56(1)
C(9)-C(12)	1.512(9)	C(28)-C(29)	1.53(1)
C(10)-C(11)	1.400(9)	C(29)-C(30)	1.50(1)
C(12)-C(13)	1.51(1)	C(30)-C(31)	1.53(1)
C(13)-C(14)	1.520(9)	C(31)-C(32)	1.52(1)
C(14)-C(15)	1.52(1)	C(32)-C(33)	1.49(1)

BOND ANGLES

O(2)-Cu-O(1)	92.3(2)	C(13)-C(14)-C(15)	114.5(6)
O(2)-Cu-O(2)	180.0(2)	C(14)-C(15)-C(16)	113.2(6)
C(5)-O(1)-Cu	127.4(5)	C(17)-C(16)-C(15)	114.8(6)
C(3)-O(2)-Cu	127.0(5)	C(16)-C(17)-C(18)	113.0(7)
O(2)-C(3)-C(4)	124.6(7)	C(19)-C(18)-C(17)	113.0(8)
O(2)-C(3)-C(20)	113.4(6)	C(21)-C(20)-C(25)	118.8(7)
C(4)-C(3)-C(20)	122.0(7)	C(21)-C(20)-C(3)	118.4(7)
C(3)-C(4)-C(5)	124.7(7)	C(25)-C(20)-C(3)	122.8(7)
O(1)-C(5)-C(4)	123.8(7)	C(22)-C(21)-C(20)	121.3(8)
O(1)-C(5)-C(6)	114.5(7)	C(21)-C(22)-C(23)	122.5(8)
C(4)-C(5)-C(6)	121.7(7)	C(22)-C(23)-C(24)	114.8(8)
C(11)-C(6)-C(7)	118.1(7)	C(22)-C(23)-C(26)	124.2(7)
C(11)-C(6)-C(5)	120.1(7)	C(24)-C(23)-C(26)	121.0(7)
C(7)-C(6)-C(5)	121.8(7)	C(25)-C(24)-C(23)	123.2(8)
C(8)-C(7)-C(6)	119.8(7)	C(24)-C(25)-C(20)	119.4(8)
C(7)-C(8)-C(9)	121.2(7)	C(27)-C(26)-C(23)	111.6(7)
C(10)-C(9)-C(8)	118.4(7)	C(26)-C(27)-C(28)	110.1(7)
C(10)-C(9)-C(12)	124.0(7)	C(29)-C(28)-C(27)	110.9(7)
C(8)-C(9)-C(12)	117.6(7)	C(30)-C(29)-C(28)	114.6(8)
C(9)-C(10)-C(11)	120.3(7)	C(29)-C(30)-C(31)	112.9(7)
C(6)-C(11)-C(10)	122.2(7)	C(32)-C(31)-C(30)	112.8(8)
C(9)-C(12)-C(13)	118.0(7)	C(33)-C(32)-C(31)	113.8(9)
C(12)-C(13)-C(14)	110.8(6)		

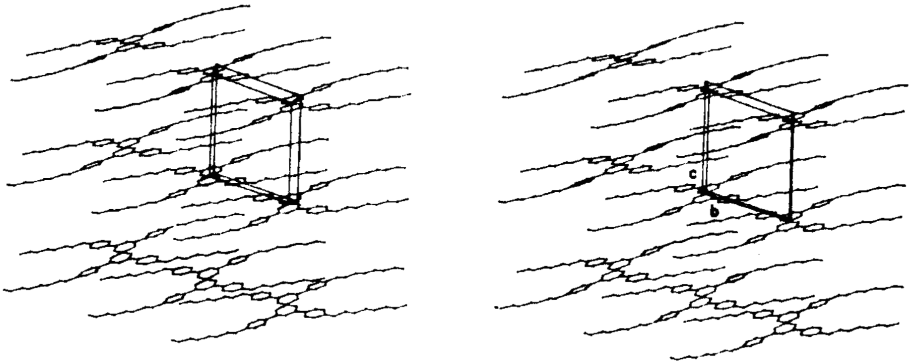

FIGURE 4 Stereo view of the crystal structure.

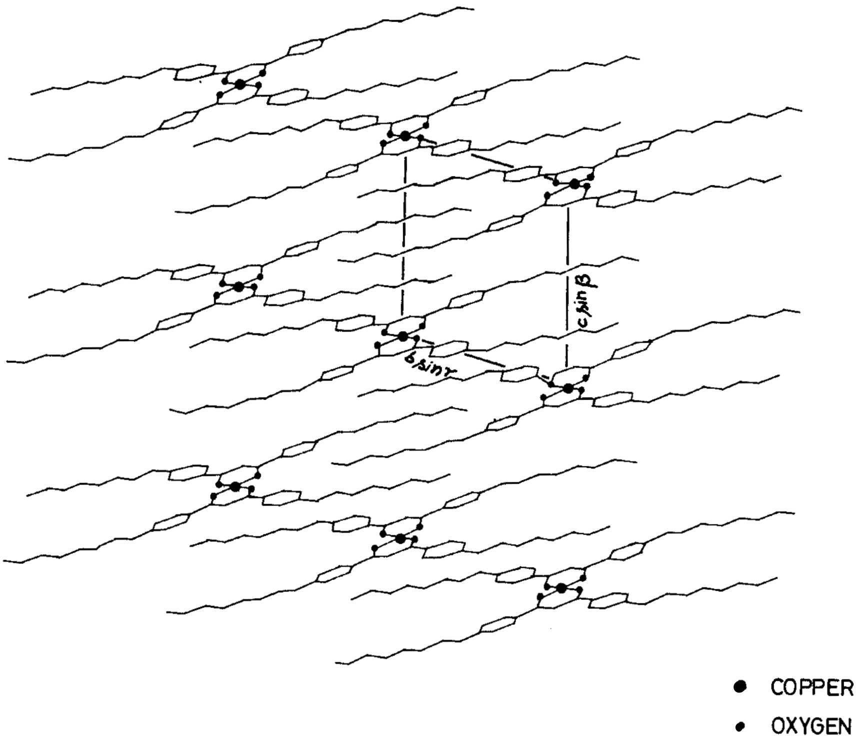

FIGURE 5 Molecular arrangement in the plane perpendicular to the crystallographic *a*-axis.

of the column. As in the case of the N form, each column in the crystal of P form is surrounded by six others. Interestingly, in the crystal lattices of the P and the N forms, the volume which is a product of the area of the hexagon formed by the six coordinating columns (Figure 6) and the distance between adjacent molecules along the column, is nearly the same, *viz.*, $414 \times 10.3 = 4.3 \times 10^3 \text{Å}^3$ for the P form and $814 \times 5.8 = 4.7 \times 10^3 \text{Å}^3$ for the N form. Figure 6 shows that the arrangement of the columns in the two forms is strikingly different, although the

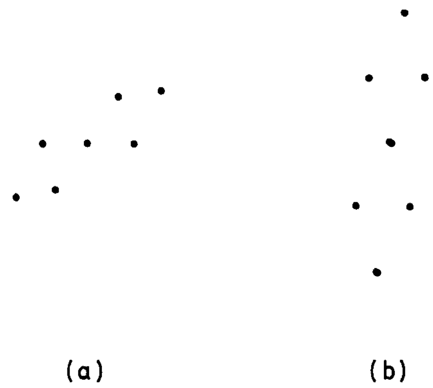

FIGURE 6 Schematic representation of the molecular coordination in the crystal structures of (a) prismatic and (b) needle-like forms.

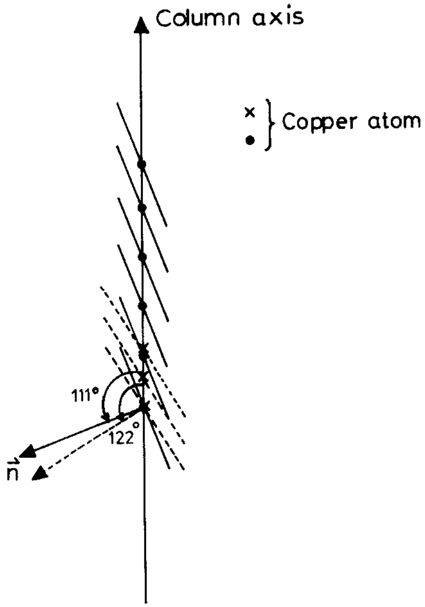

FIGURE 7 Schematic representation of the tilted columnar arrangement. $\vec{n}$ represents the normal to least squares plane through the core. The dashed lines represent the arrangement in the needle-like crystals.

volumes are nearly equal. Such a difference is perhaps connected with the molecular arrangement in the respective mesophases of these crystals. However, as structural data concerning the mesophases of these crystals are not available, the presence of such a correlation cannot be ascertained at the moment.

The most striking difference between the columnar arrangements in the N and P forms concerns the metal . . . metal distance along the column axis. In the former, it is 5.8Å whereas in the latter, it is enhanced to 10.3Å. It is also observed that in the N form, the number of intermolecular contact distances ≤4Å, present along the column is nearly 2.5 times that in the layer. In contrast, in the P form, the number of contact distances ≤4Å along the column is only about half of that in the layer. The conspicuous concentration of contact distances along the column axis is therefore likely to be a factor closely connected with the proximity of the metal atoms along the column axis of the N form. It may be pointed out that metal . . . metal distance of the order of 10Å along the column axis was earlier observed by us in the crystal structure[9] of Pd-$C_{10}H_{21}$ which also manifests a greater concentration of intermolecular contact distances ≤4Å in the layer than along the column. It may also be noted that in both the cases where the metal . . . metal distance is ~10Å, the crystals are prismatic in shape. This observation suggests the possibility of a correlation between the enhanced metal . . . metal distance and prismatic morphology. Such a correlation can, however, be confirmed only with the availability of more data. It is also observed that despite the Cu . . . Cu distance along the column being 10.3Å, on account of the tilt of the molecule with respect to the column axis (Figure 7), the perpendicular distance between adjacent molecules along the column is ~4Å.

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