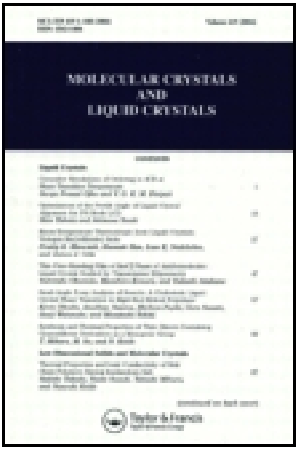

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Crystal and Molecular Structure of the Discogen bis[1,3-di(p-n-Decylphenyl)propane-1,3-dionato]palladium(II)

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Crystal and Molecular Structure of the Discogen bis[1,3-di(*p*-*n*-Decylphenyl)propane-1,3-dionato]palladium(II)

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The transition metal containing discogen, bis[1,3-di(*p*-*n*-decylphenyl)propane-1,3-dionato]palladium(II) crystallizes in the triclinic space group $P\bar{1}$ with one molecule in a unit cell of dimensions a = 10.260(2), b = 12.961(2), c = 13.403(2)Å, α = 110.54(1), β = 101.75(1) and γ = 98.44(1)°. The crystal structure was solved by direct methods and refined using full matrix least squares procedure. The palladium atom is lying on an inversion center. The decyl chains are fully extended in an all trans conformation. In the crystal structure, the molecules form a tilted columnar arrangement. The angle between the normal to the core and the column axis is 68°. Each column is surrounded by six others. Along the column axis, adjacent palladium atoms are separated by 10.26Å.

INTRODUCTION

The discotic mesophase was first discovered in 1977.[1] Since then, a wide variety of compounds which exhibit discotic mesomorphism have been identified.[2] Of these, the transition metal complexes with organic ligands form an important class of discogens with interesting properties. The first, thermotropic transition metal containing discogen bis(*p*-*n*-decylbenzoyl)methanato copper(II) was synthesized by Giroud-Godquin and Billard.[3] Discotic transition metal complexes which have been synthesized and studied since then, include the metal atoms Cu[3–10], Ni[4,11], Rh[12] and Mo[12]. It is observed that the number of copper complexes which have been studied is conspicuously higher than the other transition metal containing discogens.

Knowledge of the structural characteristics of the crystalline phase is an essential pre-requisite for understanding the nature of the structural changes associated with the crystal to mesophase transitions. In particular, in the case of transition metal complexes, details such as the nature of the coordination around the metal atom, the relative disposition of the metal atoms in the crystal structure, the possible effects of changes in the ligands on molecular conformation etc., are factors likely

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to be closely related to the properties of the discogens. With the objective of analyzing the structural characteristics of discogens of transition metal complexes, a program of investigations on their crystal structures has been initiated in our laboratory. We have earlier reported the crystal and the molecular structure of bis[1,3-di(*p*-*n*-octyloxyphenyl)propane-1,3-dionato]copper(II),[10] referred to as Cu—OC_8H_{17}, hereafter. In this paper, details of the crystal and the molecular structure of discotic bis[1,3-di(*p*-*n*-decylphenyl)propane-1,3-dionato]palladium(II) are being reported.

EXPERIMENTAL

The palladium complex (I) was synthesized following a scheme shown in Figure 1. It was purified by several crystallizations from butan-2-one. The purity was checked

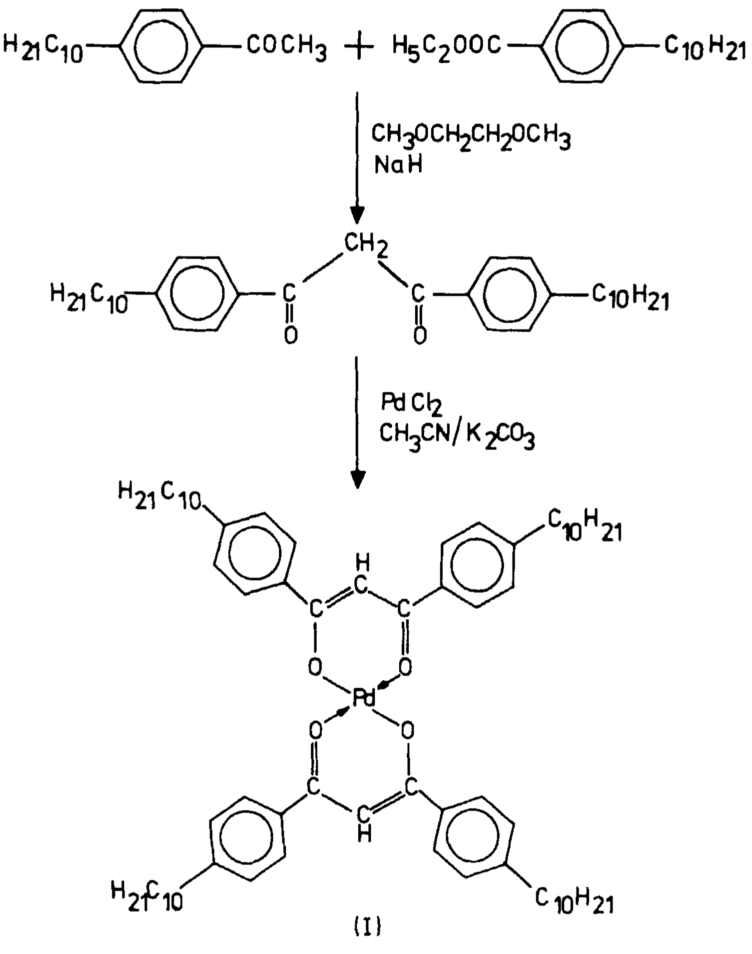

FIGURE 1 Synthetic route for the preparation of complex (I).

by standard analytical techniques. The complex exhibited the following transitions on heating,

$$K \xrightarrow{101} M_2 \xrightleftharpoons{106} M_1 \xrightleftharpoons{119°C} I$$

where K is crystal, M_2 and M_1 are mesophases and I is isotropic liquid. The mesogenic properties of other similar palladium complexes will be reported elsewhere.[13]

Transparent, golden-yellow, prismatic single crystals of (I) were obtained by slow evaporation from a solution in butan-2-one. The unit cell dimensions were determined and refined by least-squares procedure, using 25 reflections on a CAD-4 single crystal diffractometer. The crystal data and details concerning intensity data are presented in Table I. On account of the hydrophobicity exhibited by the crystal and also due to its solubility in most of the commonly available organic solvents, the density of (I) could not be measured.

STRUCTURE DETERMINATION

The statistical distribution of the normalized structure factors indicated the space group to be centric, in this case, $P\bar{1}$. Presence of one molecule in the unit cell necessitates that the palladium atom which is at the center of the symmetric mol-

TABLE I

Crystal data of (I), relevant details of the analysis

Molecular Formula	$C_{70}H_{102}O_4Pd$
a	10.260(2)Å
b	12.961(2)
c	13.403(2)
α	110.54(1)°
β	101.75(1)
γ	98.44(1)
V	1587 Å^3
Z	1
Space group	$P\bar{1}$
$\lambda_{MoK\alpha}$	0.7107Å
ρ_{Calc}	1.158 gms/cc
$\mu_{MoK\alpha}$	3.3378 cm^{-1}
Scan mode	ω/2θ
Scan speed	5.5°/min
Corrections applied:	Lp, absorption,[14] anomalous scattering for Pd.[18]
Scattering factors:	Pd (Ref. 18) C, O (Ref. 19) H (Ref. 20)
R	0.0513
R_w	0.0547
Weighting scheme (w)	$K/(\sigma^2(F) + g(F)^2)$ $K = 0.4677, g = 0.01033$

ecule, lies on an inversion center. Positions of the rest of the non-hydrogen atoms were identified from the best solution obtained from MULTAN-80.[15] The positional and the anisotropic thermal parameters of all the non-hydrogen atoms were refined by full-matrix least-squares method, using the SHELX-76 package.[16] Although all the hydrogen atoms in the molecule could be identified from a difference electron density map, they were only placed at the positions calculated with a C–H distance of 1.08 Å. The parameters of the hydrogen atoms were assigned isotropic thermal parameters equal to those of the respective carbon atoms to which they were covalently bonded. Further details concerning the R-factor, the weighting function and the atomic scattering factors are included in Table I.

RESULTS AND DISCUSSION

Figure 2 shows the atomic numbering scheme. In Table II values of the positional and the equivalent, isotropic thermal parameters U_{eq}, are listed for all the non-hydrogen atoms. The average of the U_{eq} values of the atoms in the crystallographically independent half of the core viz., the atoms Pd, O(1) to C(5), is 0.048(2)Å^2. The terminal atoms of the decyl chains are characterized by U_{eq} values significantly higher than the average U_{eq} value of the core. However, unlike in the case of the copper complex Cu-OC_8H_{17}, where the high thermal parameters of the terminal atoms were accompanied by abnormal molecular dimensions, in the case of the Pd complex, the molecular dimensions were normal and there was no indication of any disorder.

Table III lists the bond lengths and the bond angles. In Figure 2, the displacements, δ, of all the non-hydrogen atoms from the least squares plane through the core atoms Pd, O(1) to C(5) are marked. This plane is hereafter referred to as plane C. Among the atoms of the core, the displacement is highest for palladium. The comparatively high δ values of the phenyl ring atoms are due to the tilt of the rings, to be described subsequently. In each of the decyl chains, the displacements 0.26(1) and −0.35(1)Å of the respective terminal atoms are the highest. These values are, however, significantly less than the values of 0.97(3), −0.73(6), −1.00(2) and 0.89(9)Å observed for the terminal atoms of the octyloxy chains of Cu—OC_8H_{17}. This feature indicates that despite the increase in chain length in (I), deviation from planarity is less for the Pd-complex than that of Cu—OC_8H_{17}.

The planar phenyl rings on sides A and B of the core (Figure 2) are tilted with respect to plane C by 14 and 8° respectively. The tilts seem to be controlled by the intramolecular, nonbonded steric interactions O(1) . . . C(11) = 2.654(7)Å and C(4) . . . C(7) = 3.013(9)Å on side A and O(2) . . . C(27) = 2.696(7)Å and C(4) . . . C(23) = 2.976(8)Å, on side B. The decyl chains on sides A and B are tilted with respect to plane C by 12 and 8° respectively. The comparable tilts of the chains and the respective aromatic rings to which they are attached suggest that 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.

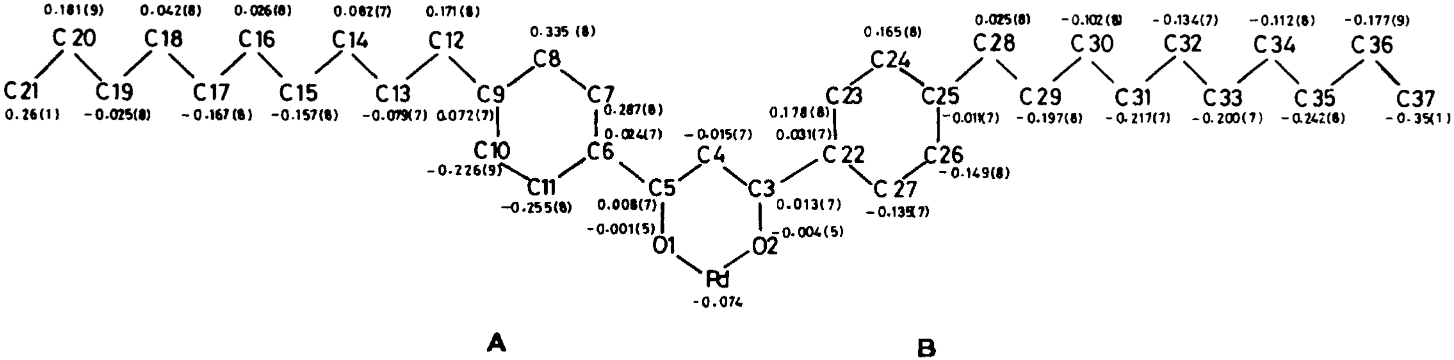

FIGURE 2 The displacements, δ, in Å of nonhydrogen atoms from plane C.

TABLE II

Final fractional atomic coordinates and U_{eq}(Å^2) U_{ij} values for Pd are also included

Atom	X	Y	Z	U_{eq}
Pd	0.000000	0.000000	0.000000	0.0468(3)
O(1)	0.0297(4)	−0.0986(4)	−0.1389(3)	0.056(2)
O(2)	0.1795(4)	0.0066(4)	0.0916(3)	0.053(2)
C(3)	0.2662(6)	−0.0470(5)	0.0550(4)	0.040(2)
C(4)	0.2479(6)	−0.1191(5)	−0.0560(5)	0.047(3)
C(5)	0.1354(6)	−0.1389(5)	−0.1453(4)	0.043(2)
C(6)	0.1296(6)	−0.2138(5)	−0.2600(5)	0.048(2)
C(7)	0.2397(7)	−0.2510(6)	−0.2933(5)	0.056(3)
C(8)	0.2253(7)	−0.3166(6)	−0.4029(5)	0.058(3)
C(9)	0.1003(7)	−0.3523(5)	−0.4837(5)	0.052(3)
C(10)	−0.0077(7)	−0.3185(7)	−0.4496(5)	0.074(3)
C(11)	0.0038(7)	−0.2501(6)	−0.3401(5)	0.068(3)
C(12)	0.0894(8)	−0.4218(6)	−0.6041(5)	0.061(3)
C(13)	−0.0529(7)	−0.4490(5)	−0.6831(5)	0.062(3)
C(14)	−0.0608(7)	−0.5140(5)	−0.8038(5)	0.058(3)
C(15)	−0.2060(7)	−0.5353(6)	−0.8769(5)	0.062(3)
C(16)	−0.2227(8)	−0.5972(6)	−0.0003(5)	0.062(3)
C(17)	−0.3668(7)	−0.6131(6)	−0.0711(5)	0.064(3)
C(18)	−0.3825(8)	−0.6726(6)	−0.1937(5)	0.066(3)
C(19)	−0.5203(8)	−0.6801(6)	−0.2660(6)	0.075(3)
C(20)	−0.5327(9)	−0.7418(7)	−0.3897(6)	0.082(4)
C(21)	−0.6626(11)	−0.7396(9)	−0.4628(8)	0.116(5)
C(22)	0.3928(6)	−0.0299(5)	0.1421(4)	0.045(2)
C(23)	0.5056(6)	−0.0715(6)	0.1190(5)	0.056(3)
C(24)	0.6191(6)	−0.0536(6)	0.2047(5)	0.057(3)
C(25)	0.6266(6)	0.0027(5)	0.3144(5)	0.051(3)
C(26)	0.5137(6)	0.0453(6)	0.3375(5)	0.057(3)
C(27)	0.3997(6)	0.0289(5)	0.2536(5)	0.050(3)
C(28)	0.7555(6)	0.0216(6)	0.4026(5)	0.053(3)
C(29)	0.7587(6)	0.0829(6)	0.5233(5)	0.056(3)
C(30)	0.8956(7)	0.0972(6)	0.6011(5)	0.058(3)
C(31)	0.9112(6)	0.1644(5)	0.7228(5)	0.053(3)
C(32)	0.0491(6)	0.1747(5)	0.7968(5)	0.055(3)
C(33)	0.0718(6)	0.2445(5)	0.9193(5)	0.054(3)
C(34)	0.2114(7)	0.2523(6)	0.9901(5)	0.059(3)
C(35)	0.2339(7)	0.3178(6)	0.1144(5)	0.064(3)
C(36)	0.3737(8)	0.3224(7)	0.1836(6)	0.085(4)
C(37)	0.3909(11)	0.3849(9)	0.3077(7)	0.115(5)
Pd	U_{11} = 0.0361(5), U_{23} = 0.0123(3),	U_{22} = 0.0589(5), U_{13} = −0.0052(3),	U_{33} = 0.0350(4) U_{12} = 0.0187(3)	

In the crystal structure, the palladium atom is surrounded by four oxygen atoms in a square planar arrangement. Figure 3 shows the molecular arrangement in the plane perpendicular to the crystallographic *a*-axis. In this plane, the molecule is fully extended and there is no overlap between adjacent molecules. The decyl chains oriented away from the core, assume an all-trans conformation. In this conformation, the linear dimensions of the molecule calculated as the intramolecular distances C(21) . . . C(37) and C(21) . . . (C37′) are 35.3 and 9.5Å respectively. (The symbol ′ denotes the atom related by a center of inversion.) As in the case of Cu—OC_8H_{17}, the molecular conformation resembles the model B proposed by

TABLE III

Final bond lengths (Å) and bond angles (°).
The quantities in parentheses represent the respective e.s.d.'s

Bond lengths

Pd - O(1)	1.966(4)	C(18) - C(19)	1.51(1)
Pd - O(2)	1.967(4)	C(19) - C(20)	1.54(1)
O(1) - C(5)	1.277(8)	C(20) - C(21)	1.50(1)
O(2) - C(3)	1.279(8)	C(22) - C(23)	1.39(1)
C(3) - C(4)	1.407(8)	C(23) - C(24)	1.384(8)
C(4) - C(5)	1.402(8)	C(24) - C(25)	1.373(9)
C(5) - C(6)	1.486(8)	C(25) - C(26)	1.40(1)
C(6) - C(7)	1.38(1)	C(26) - C(27)	1.379(8)
C(7) - C(8)	1.378(9)	C(27) - C(22)	1.400(8)
C(8) - C(9)	1.393(9)	C(25) - C(28)	1.507(8)
C(9) - C(10)	1.36(1)	C(28) - C(29)	1.523(9)
C(10) - C(11)	1.392(9)	C(29) - C(30)	1.512(9)
C(11) - C(6)	1.394(8)	C(30) - C(31)	1.518(9)
C(9) - C(12)	1.519(9)	C(31) - C(32)	1.512(8)
C(12) - C(13)	1.53(1)	C(32) - C(33)	1.520(8)
C(13) - C(14)	1.518(9)	C(33) - C(34)	1.517(9)
C(14) - C(15)	1.532(9)	C(34) - C(35)	1.529(9)
C(15) - C(16)	1.524(9)	C(35) - C(36)	1.52(1)
C(16) - C(17)	1.53(1)	C(36) - C(37)	1.53(1)
C(17) - C(18)	1.512(9)	C(3) - C(22)	1.488(8)

TABLE III (*continued*)

Bond angles

O(1)-Pd-O(2)	93.9(2)	C(17)-C(18)-C(19)	113.5(6)
Pd-O(1)-C(5)	124.6(4)	C(18)-C(19)-C(20)	111.9(7)
O(1)-C(5)-C(4)	125.7(6)	C(19)-C(20)-C(21)	112.6(8)
O(2)-C(3)-C(4)	125.4(6)	C(27)-C(22)-C(23)	117.4(6)
C(3)-C(4)-C(5)	125.7(6)	C(22)-C(23)-C(24)	120.1(6)
C(11)-C(6)-C(7)	117.5(6)	C(23)-C(24)-C(25)	123.1(6)
C(6)-C(7)-C(8)	120.6(7)	C(24)-C(25)-C(26)	116.8(6)
C(7)-C(8)-C(9)	122.3(7)	C(25)-C(26)-C(27)	121.2(6)
C(8)-C(9)-C(10)	116.6(7)	C(26)-C(27)-C(22)	121.4(6)
C(9)-C(10)-C(11)	122.6(7)	C(25)-C(28)-C(29)	118.2(6)
C(10)-C(11)-C(6)	120.4(7)	C(28)-C(29)-C(30)	111.6(6)
C(9)-C(12)-C(13)	114.2(6)	C(29)-C(30)-C(31)	115.1(6)
C(12)-C(13)-C(14)	113.7(6)	C(30)-C(31)-C(32)	112.9(5)
C(13)-C(14)-C(15)	110.0(6)	C(31)-C(32)-C(33)	115.1(6)
C(14)-C(15)-C(16)	113.8(6)	C(32)-C(33)-C(34)	113.2(5)
C(15)-C(16)-C(17)	112.6(6)	C(33)-C(34)-C(35)	114.0(6)
C(16)-C(17)-C(18)	112.5(6)	C(34)-C(35)-C(36)	112.9(6)
Pd-O(2)-C(3)	124.6(4)	C(35)-C(36)-C(37)	111.5(7)
O(2)-C(3)-C(22)	113.9(5)	C(4)-C(3)-C(22)	120.6(5)
O(1)-C(5)-C(6)	113.4(5)	C(4)-C(5)-C(6)	120.9(6)
C(5)-C(6)-C(7)	123.9(6)	C(5)-C(6)-C(11)	117.6(6)
C(8)-C(9)-C(12)	120.8(6)	C(10)-C(9)-C(12)	122.6(6)
C(3)-C(22)-C(23)	123.4(6)	C(3)-C(22)-C(27)	119.2(5)
C(24)-C(25)-C(28)	119.9(6)	C(26)-C(25)-C(28)	123.3(6)

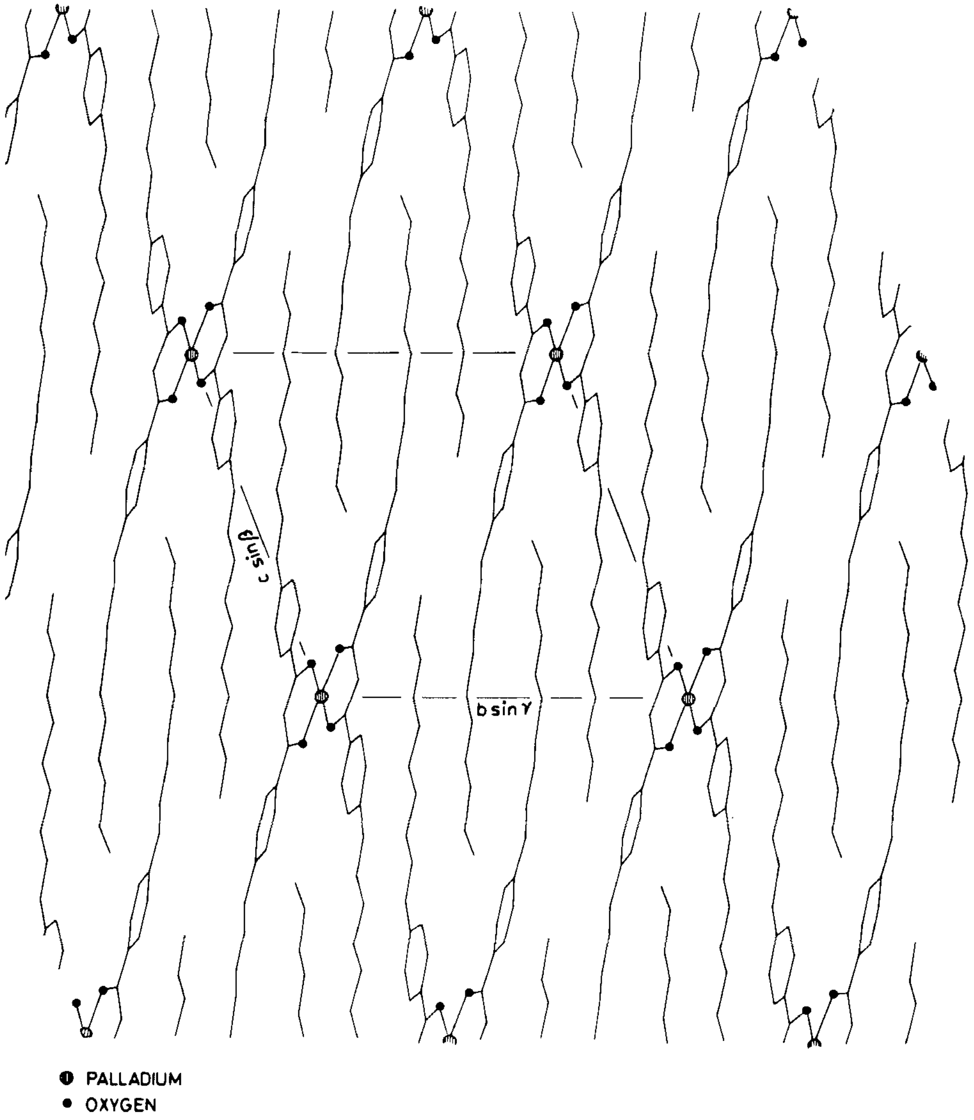

FIGURE 3 Molecular arrangement in the plane perpendicular to *a*-axis.

Ohta *et al.*[8] Figure 3 also shows the interleaving of the decyl chains of adjacent molecules. In this arrangement, the core of a molecule is surrounded by decyl chains. Thus, adjacent cores along the crystallographic *b*- and *c*-directions are separated by aliphatic chains belonging to different molecules.

The molecular arrangement shown in Figure 3 is essentially layer-like. The layer structure is stabilized by non-bonded interactions. Examination of the intermolecular contact distances ≤4Å shows that within a layer, each molecule is surrounded by six others situated at ±**c**, ±(**b** + **c**) and ±(**b** + 2**c**). In addition, each molecule in the layer is also involved in nonbonded interactions with two others situated above and below respectively, i.e., situated ±**a** with respect to the reference molecule. The intermolecular interactions within a layer involve atoms of the decyl chains, phenyl rings and the core. In contrast, along the *a*-direction, most of the interactions are confined to the atoms of the core and the phenyl rings only.

The layers shown in Figure 3 are stacked periodically along the crystallographic *a*-axis, atop one another and form an infinite columnar arrangement. In each molecule, the normal to plane C is tilted with respect to the crystallographic *a*-axis, (which is also the column axis) by 68°. In Figure 4, the tilted columnar arrangement of (I) in the crystal structure has been shown schematically. In the tilted columnar arrangement, adjacent Pd atoms are separated by 10.26Å. The Pd . . . Pd distance is conspicuously higher than the metal . . . metal distance observed in other mesogens.[10,21,22] The comparatively high value of the Pd . . . Pd distance is due to the angle of 68° between the core normal and the column axis and also due steric interactions between adjacent molecules within the columns. Although adjacent Pd atoms are separated by 10.26Å, the perpendicular distance between adjacent molecules in the column is ~4Å.

In the crystal structure, each column is surrounded by six others. In contrast with the regular, hexagonal arrangement of columns described for the mesophase of discogens,[7,23–25] in the crystal structure of (I), the arrangement of columns is not a regular hexagon. It is, however, likely that the basic columnar arrangement of the molecules and the six-fold coordination of each column are features closely

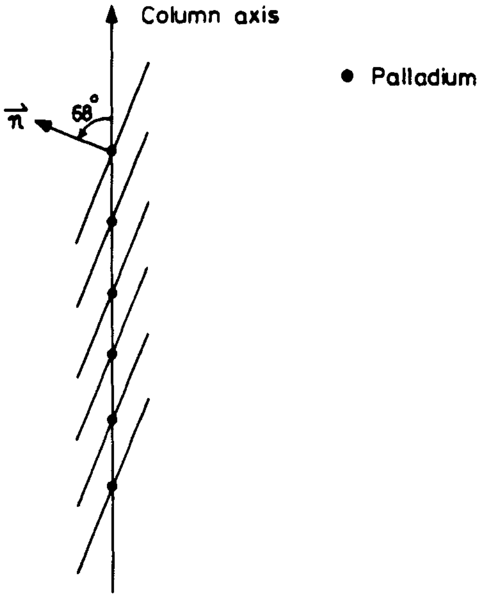

FIGURE 4 Schematic representation of the tilted columnar arrangement. **n** represents the normal to plane C.

related to the structural characteristics of the mesophase of (I). Further conclusive evidence for such a correlation can, however, be obtained when data on the mesophase of (I) are available.

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