

Chapter 5

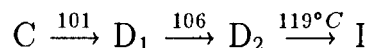
**Crystal and molecular structure of
bis[1,3-di(*p-n*-decylphenyl)
propane-1,3-dionato]palladium(II)**

5.1 Introduction

In the preceding three chapters, the crystal structures of three copper complexes were discussed. It was of interest to investigate the effect of replacing the copper atom by another transition metal atom. In this context, two palladium complexes with decyl and octyl substitutions were chosen. Details of the crystal structure analysis of bis[1,3-di(*p-n*-decylphenyl) propane-1,3-dionato]palladium(II) i.e., Pd-C₁₀H₂₁ (Figure 5.1) is presented in this chapter. The study on the second palladium complex of this series will be described in the next chapter. On account of the decyl chains, the fringe of the Pd-C₁₀H₂₁ molecule turns out to be longer than those of the copper complexes described in Chapters 2 to 4. Also, with the presence of only alkyl chains, the molecule of Pd-C₁₀H₂₁ does not include any oxygen atom in the fringe and in this respect, resembles the dimorphous copper complex Cu-C₈H₁₇ (Chapter 4).

5.2 Experimental details

Pd-C₁₀H₂₁ was supplied by Sadashiva and Rao. The complex exhibits the following transitions on heating:



where D₁ and D₂ correspond to two discotic mesophases. Prismatic, transparent single crystals of Pd-C₁₀H₂₁, golden yellow in colour were obtained by slow evaporation from a solution in butan-2-one. Preliminary characterization using

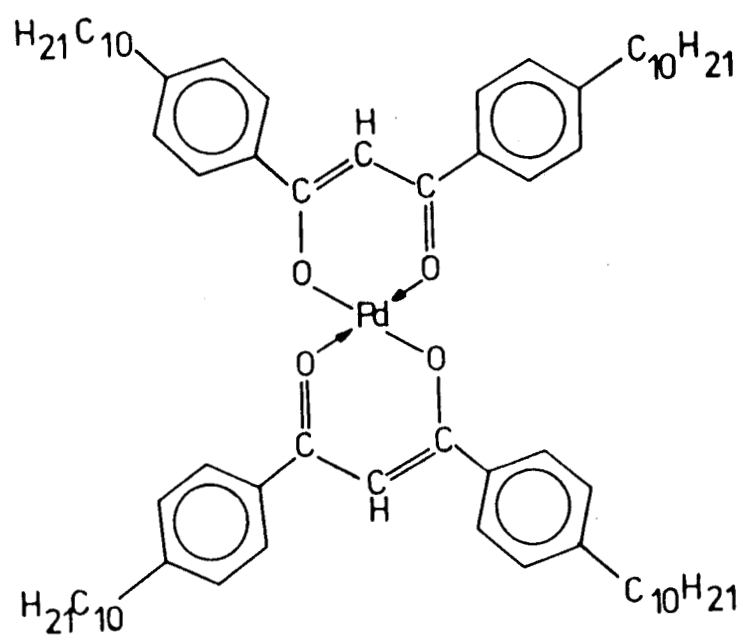


Figure 5.1: Structural formula of Pd-C₁₀H₁₇.

oscillation and Weissenberg photographs showed the crystal to belong to the triclinic crystal system. The unit cell parameters were determined and refined using 25 reflections in the θ range 8 to 14°, on a CAD4 single crystal diffractometer using graphite monochromated $\text{MoK}\alpha$ ($\lambda = 0.7107\text{\AA}$) radiation. Three dimensional intensity data were collected from a crystal of approximate dimensions $0.18 \times 0.08 \times 0.43 \text{ mm}^3$, in the $\omega/2\theta$ scan mode and in the theta range, 1 to 23°. The intensities of three reflections 408, $30\bar{6}$ and $\bar{4}08$ were measured once every hour and reflections $30\bar{6}$, 316 and $\bar{4}08$ were used as orientation controls. Of the 3586 independent reflections measured, 2680 had their intensity $I \geq 3\sigma(I)$. Crystal data and the details of the data collection are recorded in Tables 5.1 and 5.2 respectively. The intensities were corrected for Lorentz and polarization factors. The intensities were also corrected for absorption using a psi-plot [North *et al*, 1968].

5.3 Structure determination and refinement

Calculation of the density suggested that the unit cell contained one formula unit of $\text{Pd-C}_{10}\text{H}_{21}$. The statistical distribution of the normalized structure factors indicated the space group to be centric, *viz.*, $\text{P}\bar{1}$ (Table 5.3). With one molecule in the unit cell, the palladium atom has to lie on an inversion centre and the asymmetric part of the unit cell contains half the molecule *i.e.*, 37 other nonhydrogen atoms. Positions of all the 37 nonhydrogen atoms in the molecule could be identified from the best solution obtained from the program MULTAN-80. The package SHELX-76 was used to refine the structure by full

Table 5.1: Crystal data.

Molecular formula	$C_{70}H_{102}O_4Pd$
Molecular weight	1113.9
a	10.260(2) Å
b	12.961(2) Å
c	13.403(2) Å
α	110.54(1)°
β	101.75(1)°
γ	98.44(1)°
V	1587 Å ³
Space group	PI
Z	1
ρ_{calc}	1.158 gm/cc
$\mu_{MoK\alpha}$	3.3378 cm ⁻¹
F ₍₀₀₀₎	G00

Table 5.2: Details of data collection.

Radiation used	MoK α
Crystal size	0.18×0.08×0.43mm ³
Scan mode	$\omega/2\theta$
Maximum Bragg angle	23°
Number of unique reflections	3586
Number of reflections with $I \geq 3\sigma(I)$	2680
Ranges of h	0 to 11
k	-13 to 13
l	-14 to 13

Table 5.3: Distribution of the normalized structure factors.

Average	Experimental	Theoretical		
	all data	acentric	centric	hypercentric
$ E $	0.855	0.886	0.798	0.718
E^2	1.000	1.000	1.000	1.000
E^3	1.493	1.329	1.596	1.916
E^4	2.966	2.000	3.000	4.500
E^5	8.128	3.323	6.383	12.260
E^6	29.942	6.000	15.000	37.500
$ E^2-1 $	0.774	0.736	0.968	1.145
$(E^2 - 1)^2$	1.966	1.000	2.000	3.500
$(E^2 - 1)^3$	23.044	2.000	8.000	26.000

matrix least squares procedure. The initial R-factor was 0.301. Refining the positional and isotropic thermal parameters of all the nonhydrogen atoms led to R-value of 0.137. Weighted refinement of the positional and the anisotropic thermal parameters of the nonhydrogen atoms using only reflections with intensities $I \geq 3\sigma(I)$ reduced the R-factor to 0.066. The weighting function used is recorded in Table 5.4 along with other details of the refinement. Although all the hydrogen atoms could be located from a difference electron density map, only the geometrically fixed positions corresponding to C-H distance of 1.08\AA were used. The hydrogen atoms were assigned isotropic thermal parameters, same as the equivalent isotropic thermal parameters of the respective carbon atoms to which they are covalently bonded. The parameters of the hydrogen atoms were not refined but their contribution to the structure factors were included during the refinement. The refinement was terminated when the ratio, Δ/σ was less than one for all the parameters. The parameter U_{13} of the atom C(8) had the largest Δ/σ value of 0.302. The final R-factor was 0.051 and the weighted R-factor R_w was 0.055 for 2680 reflections.

5.4 Results and discussion

Figure 5.2 shows the atomic numbering scheme. Table 5.5 lists the fractional coordinates and the equivalent isotropic thermal parameters, U_{eq} , of all the nonhydrogen atoms. The thermal ellipsoids for all the nonhydrogen atoms (Figure 5.2) are plotted with 50% probability using the program ORTEP. The average of the U_{eq} values of the atoms in the crystallographically independent half of

Table 5.4: Some details of the refinement.

Weighting scheme	$K/\sigma^2(F)+g(F^2)$
K	0.4677
g	0.01033
R	0.0513
for 2680 reflections with $I \geq 3\sigma(I)$	
R_w	0.0547
Maximum shift/c.s.d (Δ/σ)	0.24
Residual electron density	
ρ_{min}	-0.779 el/ \AA^3
ρ_{max}	0.609 el/ \AA^3

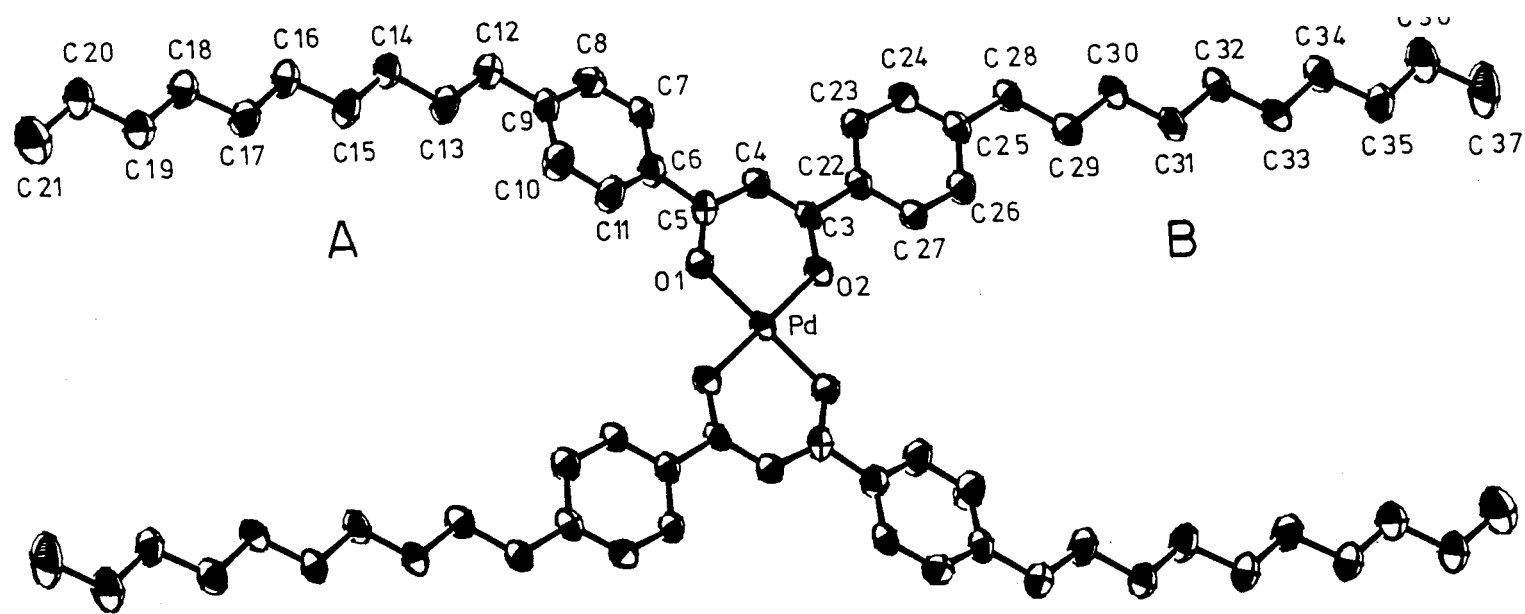


Figure 5.2: ORTEP diagram of the thermal ellipsoids drawn with 50% probability.

Table 5.5: Fractional coordinates and the values of $U_{eq}(\text{\AA}^2)$ of nonhydrogen atoms. The quantities in the parantheses are the respective e.s.d's.

Atom	x	y	z	U_{eq}
Pd	0.0000	0.0000	0.0000	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)	-0.663(1)	-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)	0.391(1)	0.3849(9)	0.3077(7)	0.115(5)

the core, *viz.*, the atoms Pd, O(1) to C(5) is $0.048(5)\text{\AA}^2$. The average U_{eq} values $0.059(9)$ and $0.053(4)\text{\AA}^2$ of the phenyl rings A and B (Figure 5.2) are only slightly higher than that of the core. The decyl chains are, however, characterized by significantly larger thermal parameters. The average of the U_{eq} values of atoms in chains A and B are $0.07(2)$ and $0.07(2)\text{\AA}^2$ respectively. As could be expected, the thermal parameters of the terminal atoms C(21) and C(37) are the highest *viz.*, $0.116(5)$ and $0.115(5)\text{\AA}^2$ respectively. The anisotropic thermal parameters, U_{ij} , for all the nonhydrogen atoms are listed in Table 5.6. The positional parameters and the isotropic thermal parameters, U_{iso} , of hydrogen atoms are given in Table 5.7.

5.4.1 Molecular geometry

The palladium atom lying on an inversion centre is surrounded by four oxygen atoms in a square planar arrangement. Figure 5.3 shows the dimensions of the coordination polyhedron around palladium.

The bond lengths, valence angles and the average dimensions of different groups are listed in Tables 5.8(a), (b) and (c) respectively. Within limits of experimental error, the dimensions could be considered normal. It is also observed that the chemically equivalent bonds of the core do not exhibit any significant difference in the lengths as such, there is no evidence for unequal contributions from the resonance hybrids (Figure 4.7(a) and (b)). In the core, the angle η between the least squares planes through the groups Pd, O(1), C(4), C(5) and Pd, O(2), C(3), C(4) is $\sim 3^\circ$ and is comparable with the values observed in the copper complexes described in Chapters 2 to 4.

Table 5.6: Anisotropic thermal parameters U_{ij} .

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Id	0.0361(5)	0.0589(5)	0.0350(4)	0.0123(3)	-0.0052(3)	0.0187(3)
O(1)	0.046(4)	0.075(3)	0.035(3)	0.010(2)	-0.001(2)	0.027(2)
O(2)	0.031(2)	0.074(3)	0.039(3)	0.013(2)	-0.004(2)	0.022(2)
C(3)	0.030(3)	0.049(3)	0.038(3)	0.018(3)	-0.002(3)	0.010(3)
C(4)	0.036(4)	0.058(4)	0.039(4)	0.015(3)	0.004(3)	0.012(3)
C(5)	0.044(4)	0.049(4)	0.032(3)	0.018(3)	0.005(3)	0.002(3)
C(6)	0.044(4)	0.057(4)	0.039(3)	0.018(3)	0.007(3)	0.009(3)
C(7)	0.045(4)	0.080(5)	0.037(3)	0.020(3)	-0.003(3)	0.023(4)
C(8)	0.051(4)	0.069(4)	0.052(4)	0.018(3)	0.012(3)	0.024(3)
C(9)	0.049(4)	0.065(4)	0.033(3)	0.014(3)	-0.000(3)	0.012(3)
C(10)	0.012(4)	0.111(6)	0.041(4)	0.008(4)	-0.004(3)	0.016(4)
C(11)	0.047(4)	0.101(5)	0.038(4)	0.010(4)	0.004(4)	0.022(4)
C(12)	0.067(5)	0.070(4)	0.040(3)	0.017(3)	0.012(3)	0.022(4)
C(13)	0.063(5)	0.066(4)	0.034(3)	0.003(3)	0.001(3)	0.008(4)
C(14)	0.066(5)	0.056(4)	0.039(3)	0.010(3)	0.003(3)	0.015(3)
C(15)	0.062(5)	0.070(4)	0.038(3)	0.011(3)	0.006(3)	0.007(4)
C(16)	0.069(5)	0.066(4)	0.036(3)	0.010(3)	0.005(3)	0.011(4)
C(17)	0.054(5)	0.075(5)	0.041(4)	0.006(3)	0.002(3)	0.013(4)
C(18)	0.072(5)	0.068(4)	0.039(4)	0.007(3)	0.002(3)	0.016(4)
C(19)	0.078(6)	0.086(5)	0.048(4)	0.016(4)	0.002(4)	0.030(4)
C(20)	0.089(6)	0.093(6)	0.042(4)	0.011(4)	-0.005(4)	0.029(5)
C(21)	0.115(8)	0.138(8)	0.081(6)	0.039(6)	-0.007(6)	0.046(7)
C(22)	0.039(4)	0.053(4)	0.035(3)	0.014(3)	0.002(3)	0.010(3)
C(23)	0.042(4)	0.086(5)	0.035(3)	0.016(3)	0.005(3)	0.026(4)
C(24)	0.040(4)	0.078(5)	0.047(4)	0.019(3)	0.005(3)	0.025(3)
C(25)	0.045(4)	0.063(4)	0.043(4)	0.021(3)	0.001(3)	0.016(3)
C(26)	0.041(4)	0.080(5)	0.041(4)	0.018(3)	0.001(3)	0.017(4)
C(27)	0.031(4)	0.069(4)	0.039(3)	0.014(3)	-0.002(3)	0.017(3)
C(28)	0.035(4)	0.076(4)	0.044(4)	0.022(3)	-0.001(3)	0.017(3)
C(29)	0.037(4)	0.073(4)	0.047(4)	0.019(3)	-0.001(3)	0.015(3)
C(30)	0.044(4)	0.075(4)	0.042(3)	0.017(3)	-0.008(3)	0.020(3)
C(31)	0.038(4)	0.072(4)	0.046(4)	0.027(3)	-0.003(3)	0.013(3)
C(32)	0.042(4)	0.072(4)	0.039(3)	0.018(3)	-0.006(3)	0.015(3)
C(33)	0.035(4)	0.068(4)	0.051(4)	0.021(3)	-0.003(3)	0.014(3)
C(34)	0.044(4)	0.071(4)	0.018(4)	0.020(3)	-0.004(3)	0.008(3)
C(35)	0.061(5)	0.079(5)	0.039(4)	0.016(3)	0.001(3)	0.015(4)
C(36)	0.073(6)	0.101(6)	0.057(5)	0.024(4)	-0.013(4)	0.014(5)
C(37)	0.106(8)	0.149(9)	0.01(5)	0.029(5)	-0.019(5)	0.010(7)

Table 5.7: Fractional coordinates and $U_{iso}(\text{\AA}^2)$ values of hydrogen atoms.

Atom	x	y	z	U_{iso}	Atom	x	y	z	U_{iso}
H(4)	0.3344	-0.1598	-0.0702	0.052	H(202)	-0.4467	-0.6983	-0.4095	0.091
H(7)	0.3397	-0.2268	-0.2314	0.057	H(281)	0.8436	0.0652	0.3866	0.062
H(8)	0.3172	-0.3409	-0.4264	0.061	H(282)	0.7806	-0.0607	0.3916	0.062
H(10)	-0.1066	-0.3477	-0.5118	0.078	H(291)	0.6763	0.0333	0.5417	0.061
H(11)	-0.0881	-0.2256	-0.3158	0.070	H(292)	0.7376	0.1663	0.5350	0.061
H(23)	0.5051	-0.1154	0.0324	0.060	H(301)	0.9778	0.1373	0.5757	0.068
H(24)	0.7062	-0.0884	0.1835	0.062	H(302)	0.9144	0.0123	0.5901	0.068
H(26)	0.5178	0.0914	0.4253	0.061	H(311)	0.8301	0.1221	0.7475	0.059
H(27)	0.3094	0.0612	0.2720	0.054	H(312)	0.8953	0.2483	0.7332	0.059
H(121)	0.1201	-0.5010	-0.6105	0.068	H(321)	0.1312	0.2126	0.7691	0.063
H(122)	0.1658	-0.3772	-0.6318	0.068	H(322)	0.0657	0.0901	0.7863	0.063
H(131)	-0.0838	-0.3692	-0.6738	0.067	H(331)	0.9920	0.2052	0.9472	0.058
H(132)	-0.1267	-0.4978	-0.6587	0.067	H(332)	0.0580	0.3292	0.9297	0.058
H(141)	-0.0330	-0.5942	-0.8143	0.064	H(341)	0.2930	0.2956	0.9651	0.064
H(142)	0.0115	-0.4629	-0.8296	0.064	H(342)	0.2293	0.1677	0.9760	0.064
H(151)	-0.2364	-0.4554	-0.8623	0.068	H(351)	0.1534	0.2745	0.1394	0.069
H(152)	-0.2781	-0.5866	-0.8522	0.068	H(352)	0.2201	0.4029	0.1289	0.069
H(161)	-0.1977	-0.6789	-0.0161	0.067	H(361)	0.4558	0.3674	0.1605	0.090
H(162)	-0.1484	-0.5469	-0.0249	0.067	H(362)	0.3896	0.2369	0.1685	0.090
H(171)	-0.3929	-0.5306	-0.0552	0.070	H(211)	-0.6716	-0.7833	-0.5499	0.119
H(172)	-0.4416	-0.6640	-0.0484	0.070	H(212)	-0.7512	-0.7840	-0.4452	0.119
H(181)	-0.3644	-0.7566	-0.2122	0.070	H(213)	-0.6736	-0.6541	-0.4469	0.119
H(182)	-0.3025	-0.6245	-0.2163	0.070	H(371)	0.4904	0.3898	0.3572	0.120
H(191)	-0.5389	-0.5953	-0.2507	0.080	H(372)	0.3779	0.4706	0.3234	0.120
H(192)	-0.6018	-0.7280	-0.2454	0.080	H(373)	0.3122	0.3410	0.3313	0.120
H(201)	-0.5243	-0.8281	-0.4078	0.091					

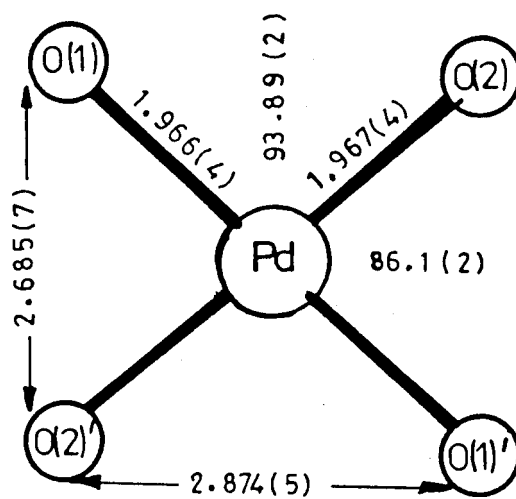


Figure 5.3: Coordination polyhedron around the palladium atom.

Table 5.8(a): Bond lengths (Å)

Pd-O(1)	1.966(4)	C(17)-C(18)	1.512(9)
Pd-O(2)	1.967(4)	C(18)-C(19)	1.51(1)
O(1)-C(5)	1.277(8)	C(19)-C(20)	1.54(1)
O(2)-C(3)	1.279(8)	C(20)-C(21)	1.50(1)
C(3)-C(4)	1.407(8)	C(22)-C(23)	1.39(1)
C(3)-C(22)	1.488(8)	C(22)-C(27)	1.400(8)
C(4)-C(5)	1.402(8)	C(23)-C(24)	1.384(8)
C(5)-C(6)	1.486(8)	C(24)-C(25)	1.373(9)
C(6)-C(7)	1.38(1)	C(25)-C(26)	1.40(1)
C(6)-C(11)	1.394(8)	C(25)-C(28)	1.507(8)
C(7)-C(8)	1.38(1)	C(26)-C(27)	1.379(8)
C(8)-C(9)	1.39(1)	C(28)-C(29)	1.523(9)
C(9)-C(10)	1.36(1)	C(29)-C(30)	1.512(9)
C(9)-C(12)	1.519(9)	C(30)-C(31)	1.518(9)
C(10)-C(11)	1.392(9)	C(31)-C(32)	1.512(8)
C(12)-C(13)	1.528(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)

Table 5.8(b): Bond angles(°)

O(1)-Pd)-O(2)	93.9(2)	C(15)-C(16)-C(17)	112.6(6)
O(1)-Pd)-O(2)	86.1(2)	C(18)-C(17)-C(16)	112.5(6)
C(5)-O(1)-Pd	124.6(4)	C(19)-C(18)-C(17)	113.5(6)
C(3)-O(2)-Pd	124.6(4)	C(18)-C(19)-C(20)	111.9(7)
O(2)-C(3)-C(4)	125.4(6)	C(21)-C(20)-C(19)	112.6(8)
O(2)-C(3)-C(22)	113.9(5)	C(23)-C(22)-C(27)	117.4(6)
C(4)-C(3)-C(22)	120.6(5)	C(23)-C(22)-C(3)	123.4(6)
C(5)-C(4)-C(3)	125.7(6)	C(27)-C(22)-C(3)	119.2(5)
O(1)-C(5)-C(4)	125.7(6)	C(24)-C(23)-C(22)	120.1(6)
O(1)-C(5)-C(6)	113.4(5)	C(25)-C(24)-C(23)	123.1(6)
C(4)-C(5)-C(6)	120.9(6)	C(24)-C(25)-C(26)	116.8(6)
C(7)-C(6)-C(11)	117.5(6)	C(24)-C(25)-C(28)	119.9(6)
C(7)-C(6)-C(5)	124.9(6)	C(26)-C(25)-C(28)	123.3(6)
C(11)-C(6)-C(5)	117.6(6)	C(27)-C(26)-C(25)	121.2(6)
C(8)-C(7)-C(6)	120.6(7)	C(26)-C(27)-C(22)	121.4(6)
C(7)-C(8)-C(9)	122.3(7)	C(25)-C(28)-C(29)	118.2(6)
C(10)-C(9)-C(8)	116.6(7)	C(30)-C(29)-C(28)	111.6(6)
C(10)-C(9)-C(12)	122.6(6)	C(29)-C(30)-C(31)	115.1(6)
C(8)-C(9)-C(12)	120.8(6)	C(32)-C(31)-C(30)	112.9(5)
C(9)-C(10)-C(11)	122.6(7)	C(31)-C(32)-C(33)	115.1(5)
C(10)-C(11)-C(6)	120.4(7)	C(34)-C(33)-C(32)	113.2(5)
C(9)-C(12)-C(13)	114.2(6)	C(33)-C(34)-C(35)	114.0(6)
C(14)-C(13)-C(12)	113.7(6)	C(36)-C(35)-C(34)	112.9(6)
C(13)-C(14)-C(15)	110.0(6)	C(35)-C(36)-C(37)	111.5(7)
C(16)-C(15)-C(14)	113.8(6)		

Table 5.8(c): Average values of bond lengths(Å) and valence angles(°) along with the values given by Allen *et al*, [1987]

	average bond lengths	values of Allen <i>et al</i>		average bond angles
Core: Pd-O O-C _{ar} (core) C _{ar} -C _{ar} (core)	1.9665(5) 1.278(1) 1.405(3)		O-Pd-O Pd-O-C _{ar} O-C _{ar} -C _{ar} Car-Car-Car	93.9(2) 124.6(4) 125.6(2) 125.7(6)
Phenyl ring: A B	1.38(1) 1.39(1)	1.380(13)		120(2) 120(2)
Chain: A B	1.52(1) 1.52(6)	1.530(15)		113(1) 113(1)
C _{core} -C _{phenyl} C _{sp³} -C _{phenyl}	1.487(1) 1.513(6)	1.513(14)	C _{phenyl} -C _{sp³} -C _{sp³}	116(2)

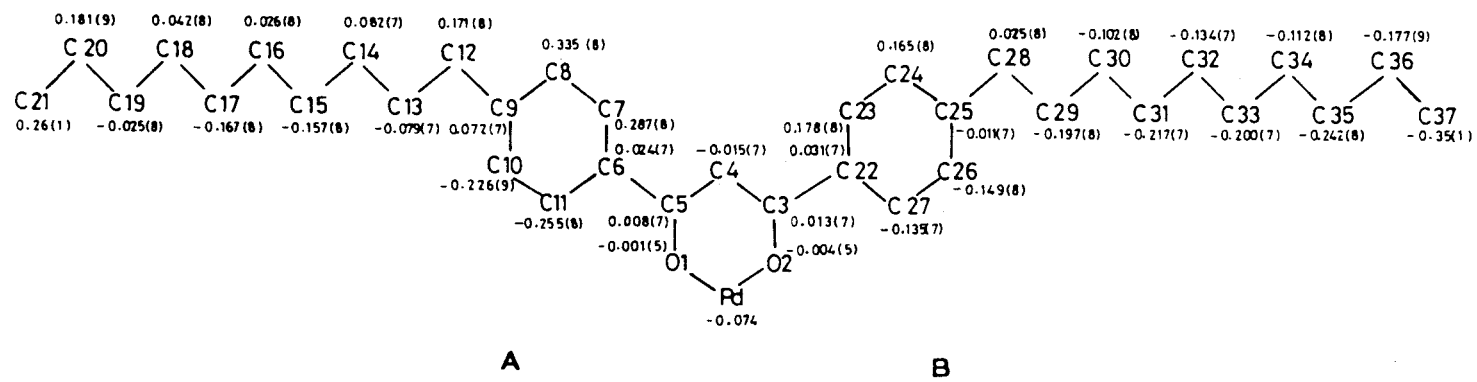


Figure 5.4: Displacements, δ 's, of all the nonhydrogen atoms of the molecule from the plane through the crystallographically independent half of the core.

In Figure 5.4, the displacements, δ 's, of the nonhydrogen atoms from the least squares plane through the crystallographically independent half of the core *viz.*, through the atoms Pd, O(1), O(2), C(3) to C(5) are given. Among the atoms of the core, the displacement is highest for the metal atom. 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. The magnitudes of these displacements are comparable with those found for the terminal atoms in the crystal structure of the P-form of Cu-C₈H₁₇ and are strikingly less than the corresponding displacements in the N-form of Cu-C₈H₁₇ (Chapter 4, section 4.4.2).

The planar phenyl rings A and B are tilted with respect to the core by 14 and 8° respectively. These tilts are controlled primarily by intramolecular non-bonded interactions indicated by the distances O(1)...C(11) = 2.654(7)Å and C(4)...C(7) = 3.013Å 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 A and B are tilted with respect to the core by 12 and 8° respectively. The molecular dimensions calculated as the distances C(21)...C(37) and C(21)...C(37)' are 35.3 and 9.5Å respectively. The length of the Pd-C₁₀H₂₁ molecule is significantly more than the corresponding dimensions of the copper complex Cu-OC₈H₁₇, Cu-OC₇H₁₅-C₇H₁₅ and Cu-C₈H₁₇. The observed increment could be attributed to the presence of longer, decyl chains in Pd-C₁₀H₂₁. As in the case of the copper complexes, the rectangular shape of the Pd-C₁₀H₂₁ molecule resembles the model B of Ohta et al [1986].

5.4.2 Molecular conformation

Figure 5.5 shows the conformation of the molecule. The decyl chains are fully extended and are oriented away from the core in an all *trans* conformation (Table 5.9).

5.4.3 Molecular packing

Figure 5.6 represents the arrangement of molecules in the plane perpendicular to the crystallographic a-axis. The core of each molecule is surrounded, strikingly by the decyl chains. Thus, adjacent cores along the crystallographic b and c-directions are separated by aliphatic chains belonging to different molecules. Figure 5.7 gives the stereo view of the packing as seen down the crystallographic c-axis.

Figure 5.8 shows that the molecular arrangement is essentially layer-like. The intermolecular van der Waal's interactions which stabilize the layer structure are of the type core...chain, phenyl ring...chain, phenyl...phenyl and chain...chain. Thus within a layer, all parts of the molecule, viz., core, phenyl rings and the chains, are involved in nonbonded interactions. Based on the criterion of contact distances being $\leq 4\text{\AA}$, it is found that within a layer each molecule is surrounded by six others situated at $\pm\vec{c}$, $\pm(\vec{b} + \vec{c})$ and $\pm(\vec{b} + 2\vec{c})$. In addition, each molecule in a layer is also involved in nonbonded interactions with two others situated above and below at $\pm\vec{a}$ with respect to the reference molecule.

The layers are stacked periodically along the crystallographic a-axis, atop one another and form an infinite columnar arrangement as shown in Figure 5.9. The

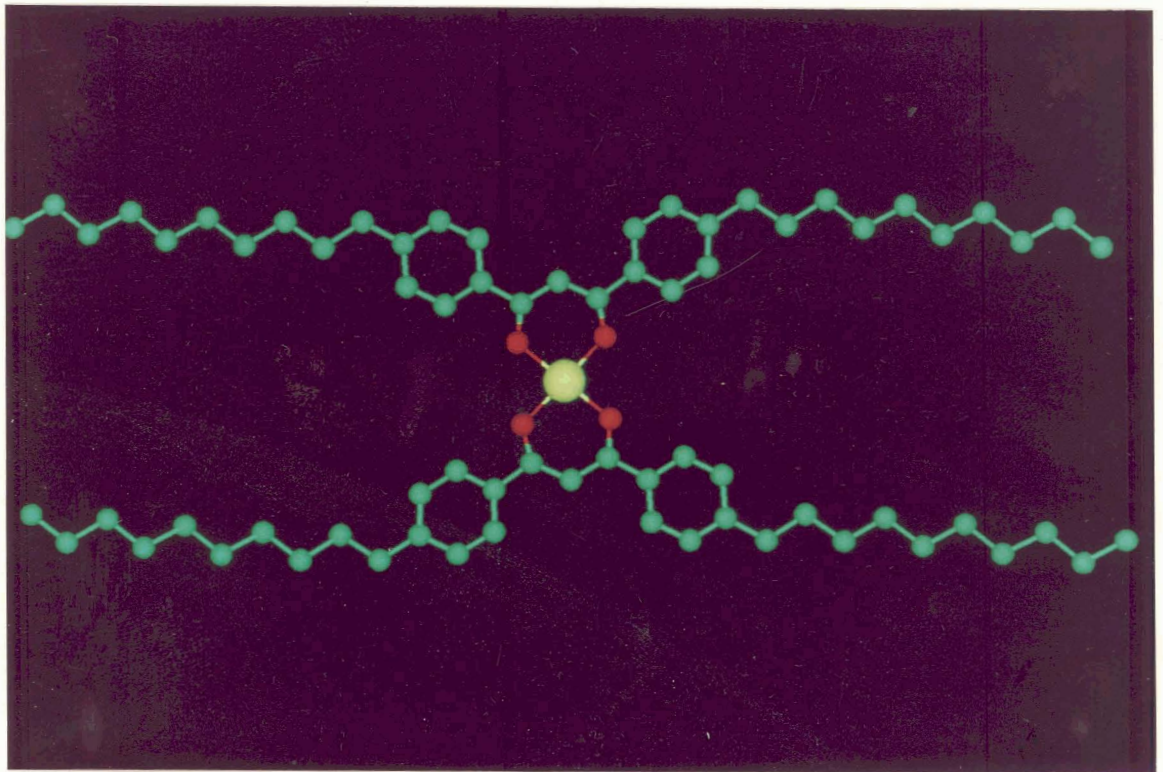


Figure 5.5: Conformation of the molecule.

Table 5.9: Observed torsional angles(°) in the chains.

C(9)-C(12)-C(13)-C(14)	177.5(6)
C(12)-C(13)-C(14)-C(15)	-178.8(6)
C(13)-C(14)-C(15)-C(16)	178.2(6)
C(14)-C(15)-C(16)-C(17)	-177.8(6)
C(15)-C(16)-C(17)-C(18)	178.9(6)
C(16)-C(17)-C(18)-C(19)	-175.0(6)
C(17)-C(18)-C(19)-C(20)	-179.6(6)
C(18)-C(19)-C(20)-C(21)	-174.2(7)
C(25)-C(28)-C(29)-C(30)	-178.9(6)
C(28)-C(29)-C(30)-C(31)	176.0(6)
C(29)-C(30)-C(31)-C(32)	179.2(6)
C(30)-C(31)-C(32)-C(33)	178.2(5)
C(31)-C(32)-C(33)-C(34)	-180.0(6)
C(32)-C(33)-C(34)-C(35)	-177.3(6)
C(33)-C(34)-C(35)-C(36)	178.9(6)
C(34)-C(35)-C(36)-C(37)	-178.2(7)

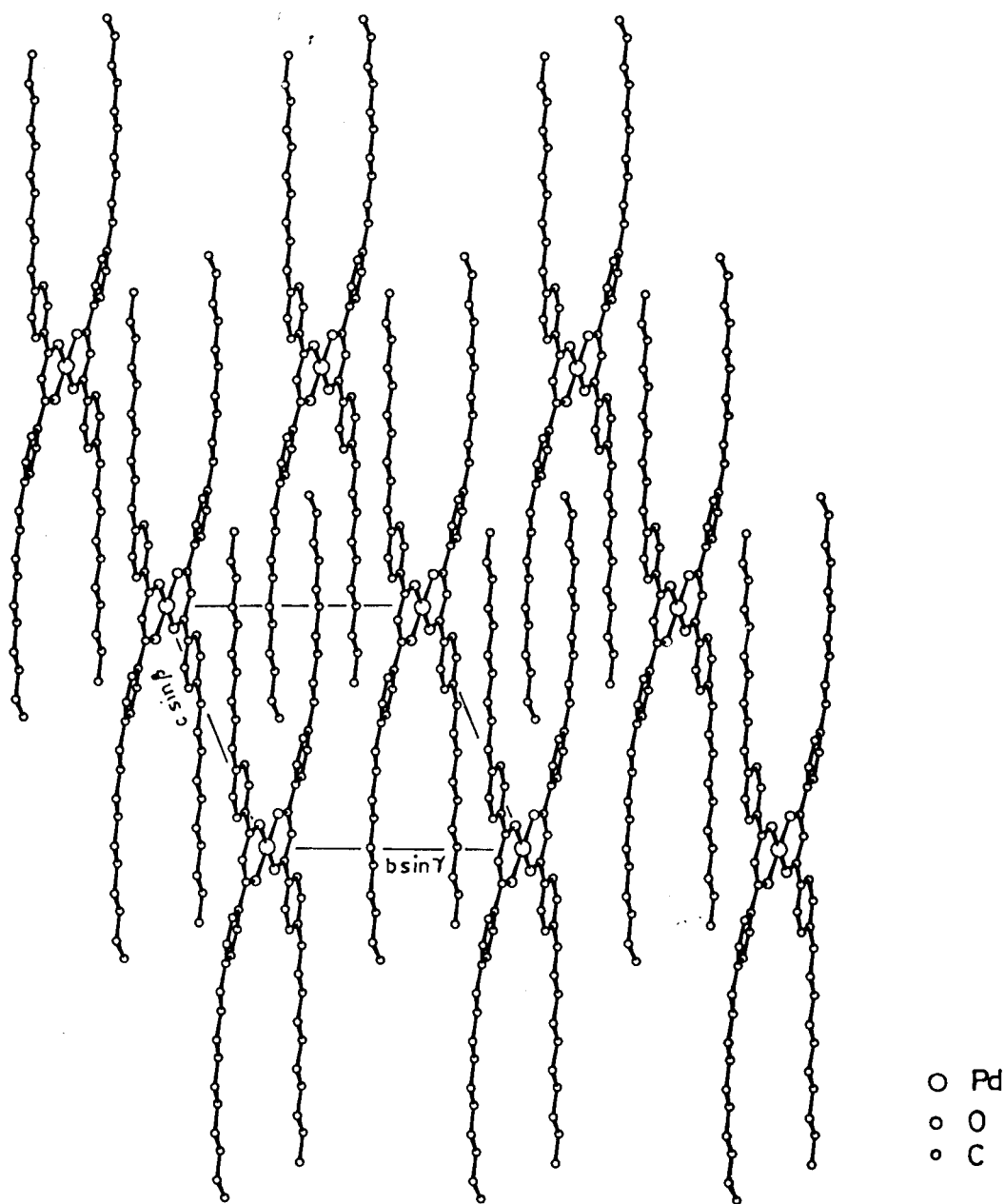


Figure 5.6: Arrangement of molecules in the plane perpendicular to the crystallographic a -axis.

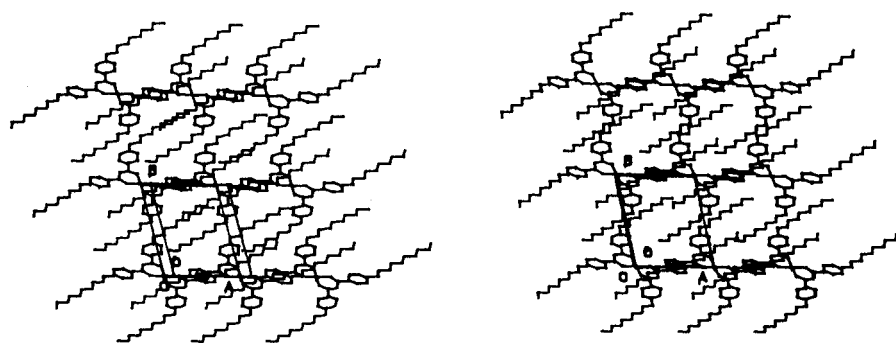


Figure 5.7: Stereo view of the molecular packing as seen down the crystallographic c-axis.

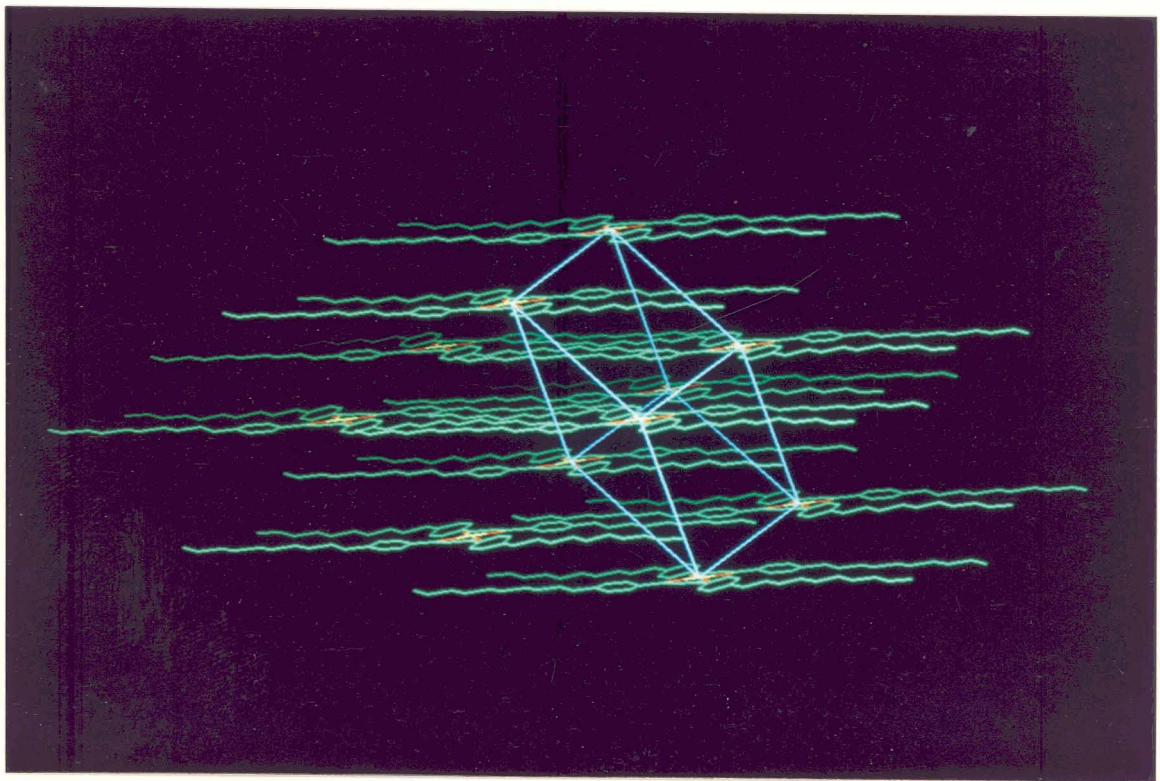


Figure 5.8: Layer-like arrangement of molecules.

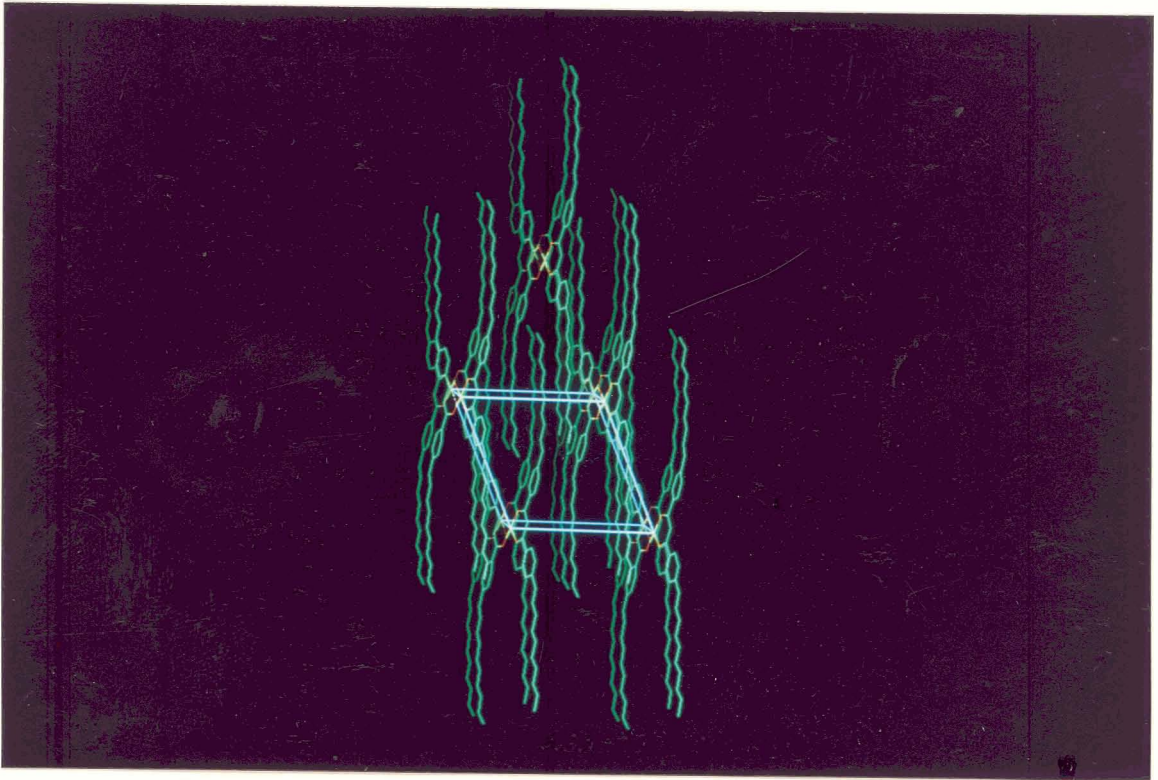


Figure 5.9: Columnar arrangement of molecules.

core of the molecule is tilted with respect to the column axis *i.e.*, crystallographic *a*-axis by 68° (Figure 5.10). The columnar structure is stabilized by nonbonded interactions of the type core...phenyl, phenyl...phenyl and phenyl...chain. It is also found that the majority of these interactions involve atoms of the aromatic groups. Thus, the columnar structure appears to be stabilized primarily by aromatic...aromatic type of interactions. It is also observed that as in the case of the P-form of Cu-C₈H₁₇ (Chapter 4), the number of nonbonded interactions along a column is only half of that in a layer.

In the direction of the column axis, the distance between adjacent palladium atoms is 10.26\AA and is comparable to the value of 10.34\AA observed in the columnar structure of the P-form of Cu-C₈H₁₇. It must, however, be mentioned that on account of the tilt of the molecule with respect to the column axis, the perpendicular distance between adjacent cores is less than 4\AA . Each column in the crystal is surrounded by six others which do not form a regular hexagon. It must be pointed out that the crystal structure of Pd-C₁₀H₂₁ has close resemblance to that of the P-form of Cu-C₈H₁₇. Table 5.10 presents some of the similarities which seem to occur despite the replacement of the copper atom and the octyl chains in the latter by the palladium atom and the decyl chains respectively. These observations suggest that the type of metal atom as well as the length of the alkyl chain have perhaps very little influence on the overall structural characteristics of these prismatic crystals.

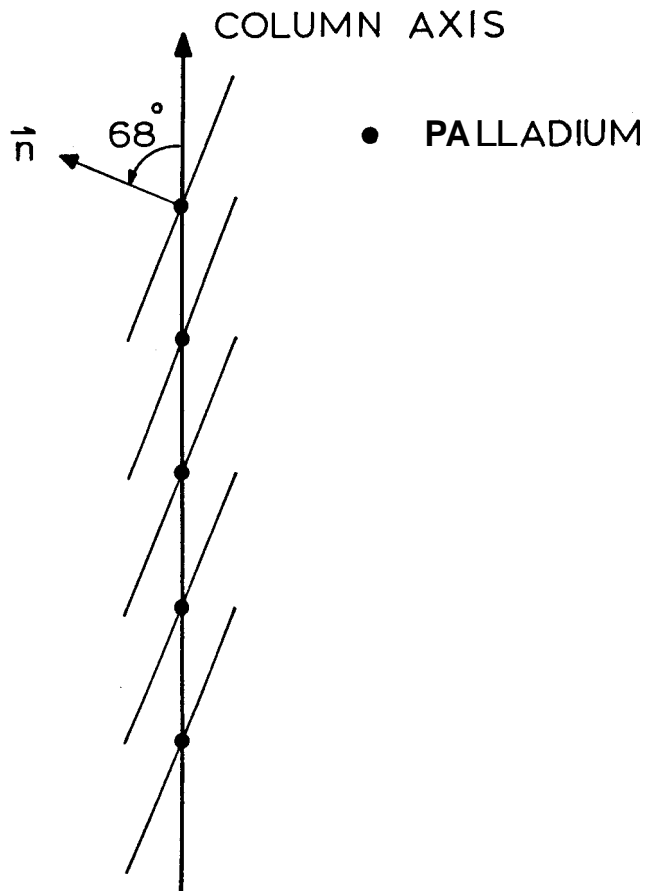


Figure 5.10: Schematic representation of the tilted columnar arrangement.

Table 5.10: Similarities between Pd-C₁₀H₂₁ and the P-form of Cu-C₈H₁₇.

	Pd-C ₁₀ H ₂₁	P-form
6 of terminal atoms (Å)	0.26, 0.35	0.29, 0.10
6 of metal atom (Å)	0.074	0.067
Tilt w.r.t column axis (°)	68	69
Shortest metal...metal distance (Å)	10.260(2)	10.341(3)