Chapter 4

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

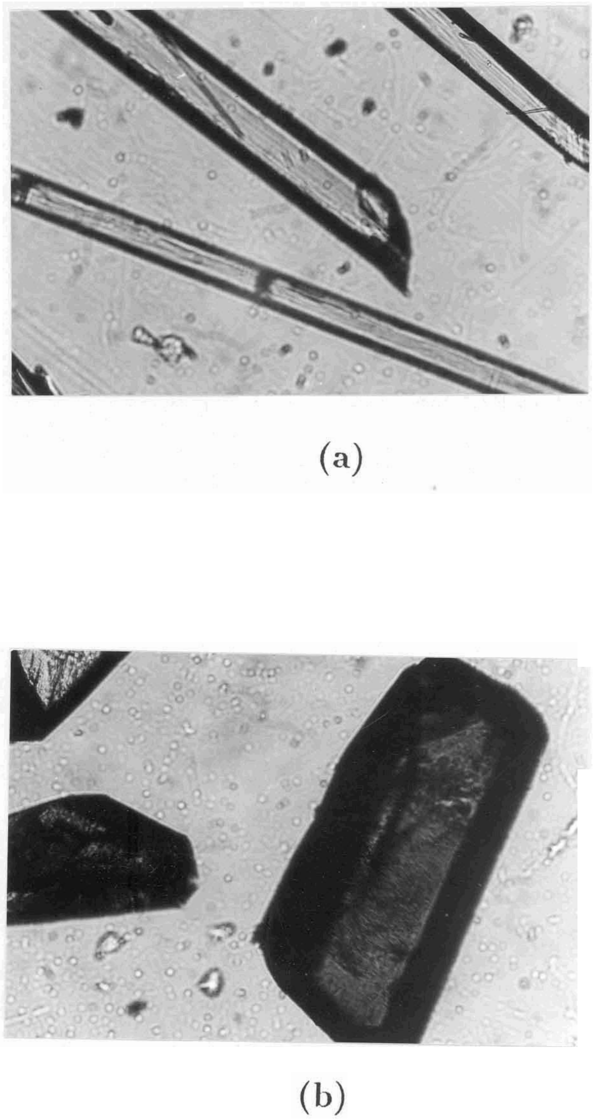


Figure 4.2: Photographs of **(a)** needle-like (N) and (b) prismatic (P) crystals.

4.1 Introduction

In the last two chapters, details of the crystal structure analysis of two copper complexes with oxygen atoms in the molecular fringe were presented. This chapter describes the crystal structure analysis of a copper complex bis[1,3-di(*p*-*n*-octylphenyl)propane -1,3-dionato]copper(II) or Cu-C_8H_{17}, which does not include oxygen atoms in the fringe. Figure 4.1 shows the structural formula of Cu-C_8H_{17}. As in the case of Cu-OC_8H_{17} (Chapter 2 of this thesis), Cu-C_8H_{17} also includes four similar chains in the molecular fringe. Whereas in Cu-OC_8H_{17}, the chains are of the octyloxy type, Cu-C_8H_{17} includes only octyl chains. Thus the only difference in between the chemical structures of Cu-OC_8H_{17} and Cu-C_8H_{17} is the absence of oxygen atoms in the chains of the latter complex. The crystal structure analysis of Cu-C_8H_{17} may hence be expected to throw some light on understanding the role of oxygen atoms in the chain, on the crystal structural characteristics.

4.2 Experimental details

Single crystals of Cu-C_8H_{17} were grown by slow evaporation of a solution in acetone. Interestingly, crystals with two distinct morphologies were obtained from the same solvent *viz.*, the more abundant needle-like crystals and the less abundant prismatic crystals. These two forms are hereafter referred to as N and P forms respectively. Photographs of both the forms of crystals viewed with the same magnification are given in Figure 4.2. It must be mentioned that crystals of the N and P forms were obtained from separate crystallization experiments

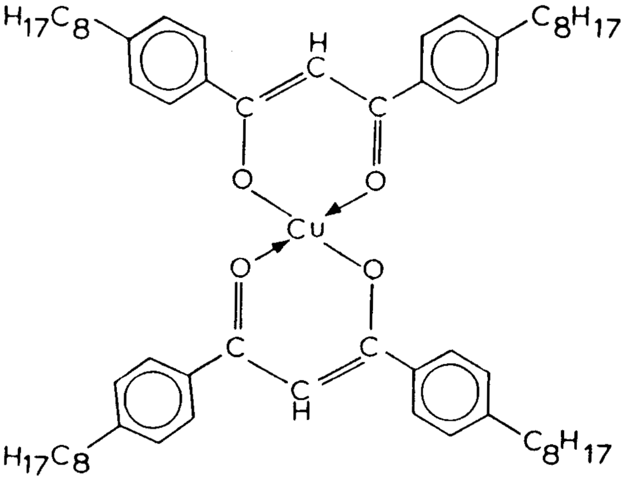


Figure 4.1: Structural formula of Cu-C_8H_{17}.

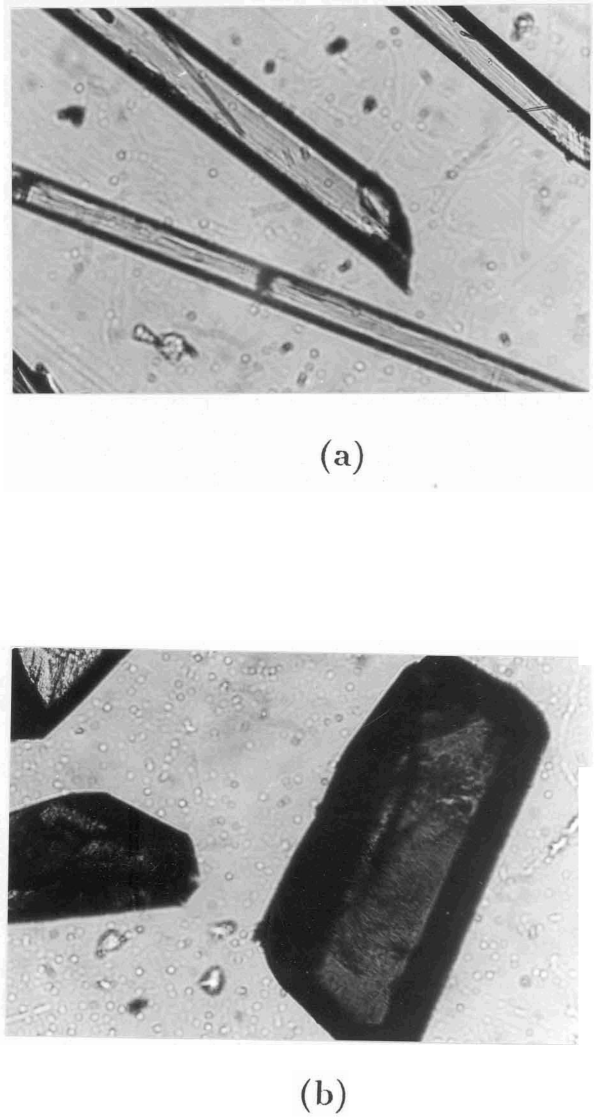


Figure 4.2: Photographs of **(a)** needle-like (N) and (b) prismatic (P) crystals.

conducted during different periods of the year. Whereas the crystals of the N-form could be obtained easily, despite repeated attempts, only very few crystals of the P-form could be obtained. It is likely that the occurrence of two morphologically distinct crystals is related to factors such as ambient temperature and humidity which were not controlled in our experiments. Crystals of the N-form exhibit the following transitions:

$$\mathrm{C} \xrightarrow{76.0} \mathrm{D} \xrightarrow{141.5^{\circ}C} \mathrm{I}$$

Due to the nonavailability of sufficient amount of crystals of the P-form, it was not possible to identify its transition temperatures. Hence, at the moment, it is not clear whether both the N and the P forms are characterized by identical transition temperatures or not. The crystal structure analyses were, however, carried out for both the forms and it was found that the crystal structures of the P and the N forms were in fact different. Details of these investigations are presented in the ensuing sections of this chapter.

Preliminary examination of the crystals using oscillation and Weissenberg photographs showed that the crystals of the P as well as the N form belonged to the triclinic crystal system. The unit cell dimensions, however, appeared to be different. The unit cell constants were subsequently determined and refined on a CAD4 single crystal diffractometer. In Table 4.1, the unit cell constants and other relevant crystal data are presented.

Three dimensional intensity data were collected in the $\omega/2\theta$ mode using graphite monochromated MoK_{α} radiation and a prescan speed of 5.5°/min. For the final data collection, the scan speed was appropriately varied to satisfy the

Table 4.1: Crystal data.

	N-form	P-form
Molecular formula	$C_{62}H_{86}O_4Cu$	$C_{62}H_{86}O_4Cu$
Molecular weight	958.8	958.8
a (Å)	5.821(3)	10.341(3)
b (Å)	14.332(1)	11.621.(2)
c (Å)	17.630(2)	12.817(2)
α (°)	107.35(1)	103.99(1)
β (°)	98.86(2)	92.73(2)
γ (°)	93.58(3)	109.55(2)
V($Å^3$)	1378	1394
Z	1	1
Space group	$P\bar{1}$	$I\ \bar{1}$
ρ_{calc} (gm/cc)	1.148	1.134
μ_{MoK_α} (cm^{-1})	4.57	4.51
$F_{(000)}$	519	519

relation, $\sigma(I)/I \leq 0.03$. Table 4.2 includes the orientation and intensity control reflections. Intensities of these reflections were checked once every hour of data collection. For the N form, intensities of 4890 reflections were measured of which 1980 reflections satisfied the relation $I \geq 3\sigma(I)$. The corresponding numbers are 4784 and 2262 respectively for the P-form. Both the sets of intensity data were corrected for Lorentz and polarization factors. Absorption correction was also applied using the method of North et *al* [1968].

4.3 Structure determination and refinement

The procedures adopted for the determination and refinement of the two crystal structures are very similar. The statistical distribution of the normalized structure factors (Table 4.3) indicated the space group to be centric, *i.e.*,, $P\bar{1}$ for both P and N forms. In both the cases, the calculated value of density indicated that the unit cell contains a single molecule. Thus, symmetry constraint necessitates the molecule to be centrosymmetric. Consequently, the copper atom which is at the centre of the molecule has to lie on an inversion centre. Placing the copper atom at (0,0,0) a difference electron density map was computed and in both the crystal structures, the remaining 33 nonhydrogen atoms could be readily identified. Full matrix least squares refinement of the positional and thermal parameters of all the nonhydrogen atoms was carried out using the program SHELX-76. Figure 4.3 describes the details of the refinement procedure. The hydrogen atoms were fixed geometrically using a C-H distance of 1.08Å. The parameters of the hydrogen atoms were not refined but their contribution was

Table 4.2: Details of data collection.

	N-form	P-form
Crystal size (mm^3)	$0.58\times0.07\times0.05$	$0.35\times0.18\times0.10$
Radiation used	MoK$_\alpha$	MoK$_\alpha$
Scan mode	$\omega/2\theta$	$\omega/2\theta$
Number of unique reflections	4890	4784
Number of reflections with $I \geq 3\sigma(I)$	1980	2262
Intensity control reflections	361 $0\bar{8}2$ $\bar{3}\bar{6}3$	026 330 $\bar{2}\bar{3}0$
Orientation control reflections	036 2012	026 343 330
Maximum Bragg angle	25°	25°
Ranges of h	0 to 6	0 to 12
k	-16 to 16	-13 to 13
l	-20 to 20	-15 to 15

Table 4.3: Distribution of the normalized structure factors.

Average	All data		Theoretical		
	N-form	P-form	acentric	centric	hypercentric
$\|E\|$	0.788	0.778	0.886	0.798	0.718
E^2	1.000	1.000	1.000	1.000	1.000
E^3	1.612	1.689	1.329	1.596	1.916
E^4	3.290	3.802	2.000	3.000	4.500
E^5	8.517	11.816	3.323	6.383	12.260
E^6	27.418	50.626	6.000	15.000	37.500
$\|E^2-1\|$	0.907	0.941	0.736	0.968	1.145
$(E^2-1)^2$	2.290	2.802	1.000	2.000	3.500
$(E^2-1)^3$	19.547	41.219	2.000	8.000	26.000

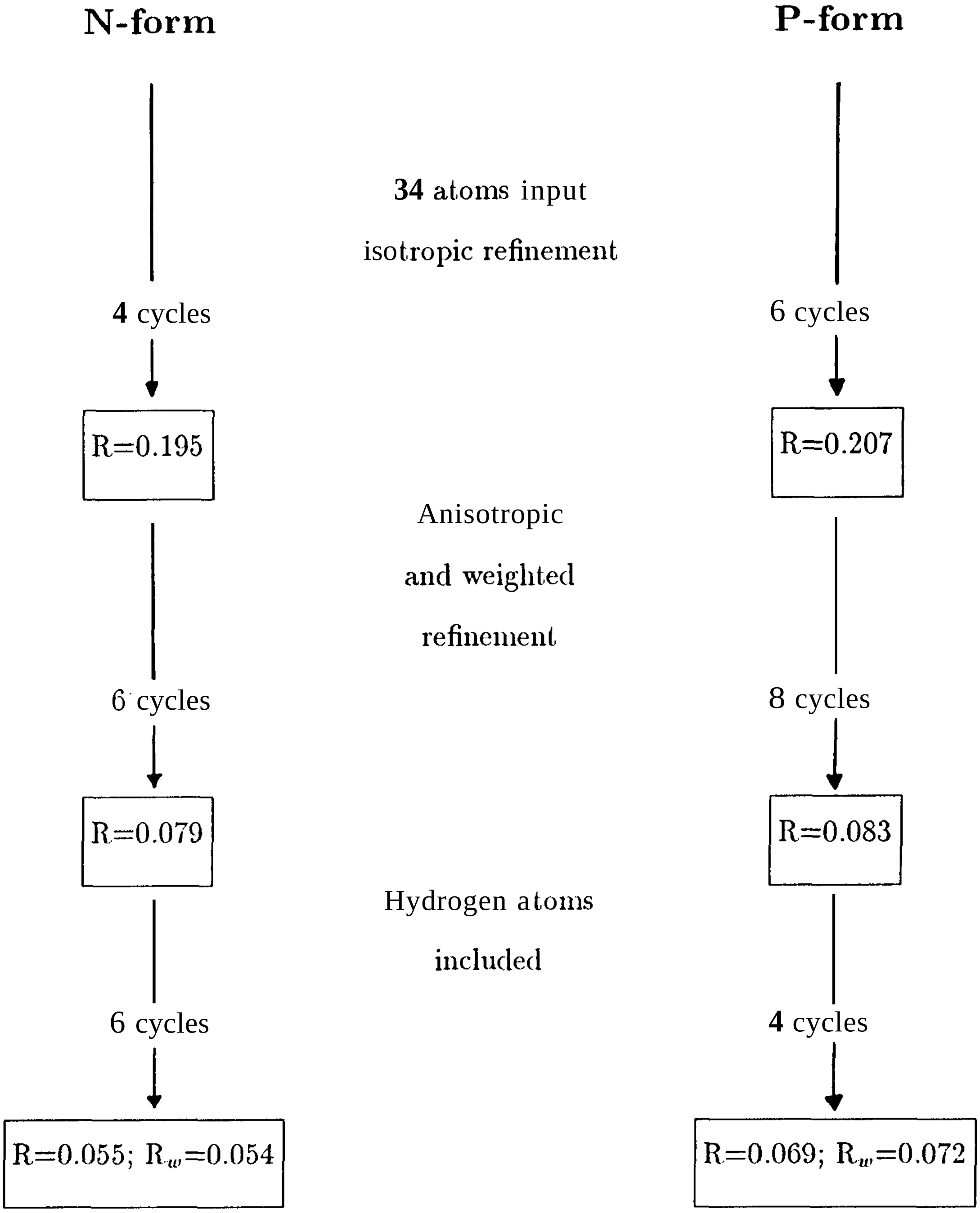


Figure 4.3: Details of the refinement procedure.

included in the structure factor calculation. Refinements were terminated when Δ was less than a for all the parameters. The final difference electron density map was featureless. The minimum and maximum values in the residual electron density are also included in Table 4.4.

4.4 Results and discussion

Comparison of the crystal structures the N and P forms shows that there are many similarities in their overall structural characteristics. However, examination of the details indicates distinct differences also to be present. In this section, both the similarities and the differences observed between the two crystal structures are described.

Figure 4.4 shows the atomic numbering scheme common to both the forms. Table 4.5 lists the positional and the equivalent isotropic thermal parameter, U_{eq}, of all the nonhydrogen atoms. Tables 4.6(a) and (b) present the anisotropic thermal parameters of the N and P-forms respectively. The positional and isotropic thermal parameters, U_{iso}, of the hydrogen atoms are listed in Table 4.7.

4.4.1 Thermal parameters

Figure 4.4 shows the thermal ellipsoids drawn with 50% probability using the program ORTEP. Comparison of the average U_{eq} values of the core, phenyl rings and the chains is given in Table 4.S. In the P-form, the average U_{eq} value of the different groups are significantly larger than the corresponding values characterizing the N-form. The enhanced thermal parameters of the P-form

Table 4.4: Details of refinement.

	N-form	P-form
Weighting scheme	$K/[\sigma^2(F) + g(F)^2]$	$K/[\sigma^2(F) + g(F)^2]$
K	2.3062	3.5101
g	0.00011	0.00016
R	0.055	0.0692
R_w	0.054	0.0721
Maximum shift/e.s.d	0.488	0.306
Residual electron density (el/Å^3)		
ρ_{max}	0.27	0.425
ρ_{min}	-0.24	-0.48

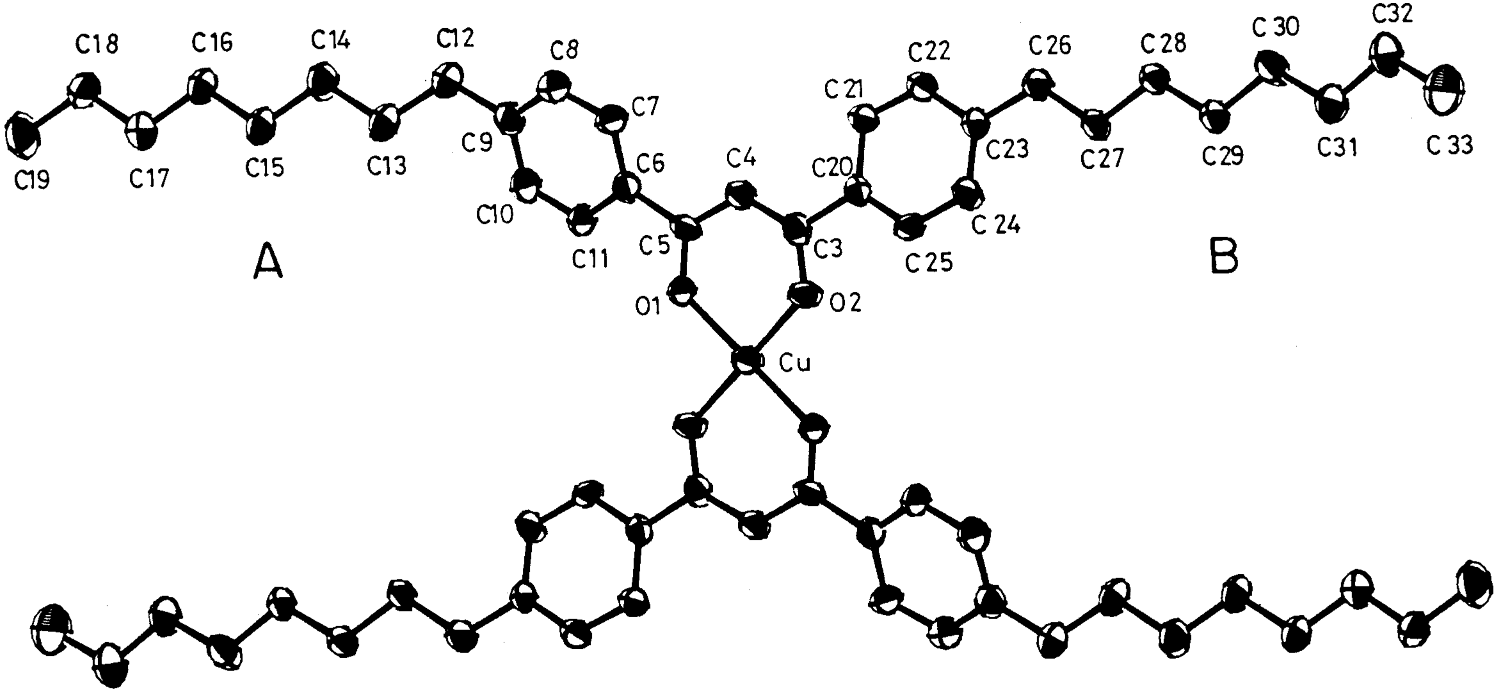


Figure 4.4(a): ORTEP diagram of the thermal ellipsoids drawn with 50% probability for the N-form.

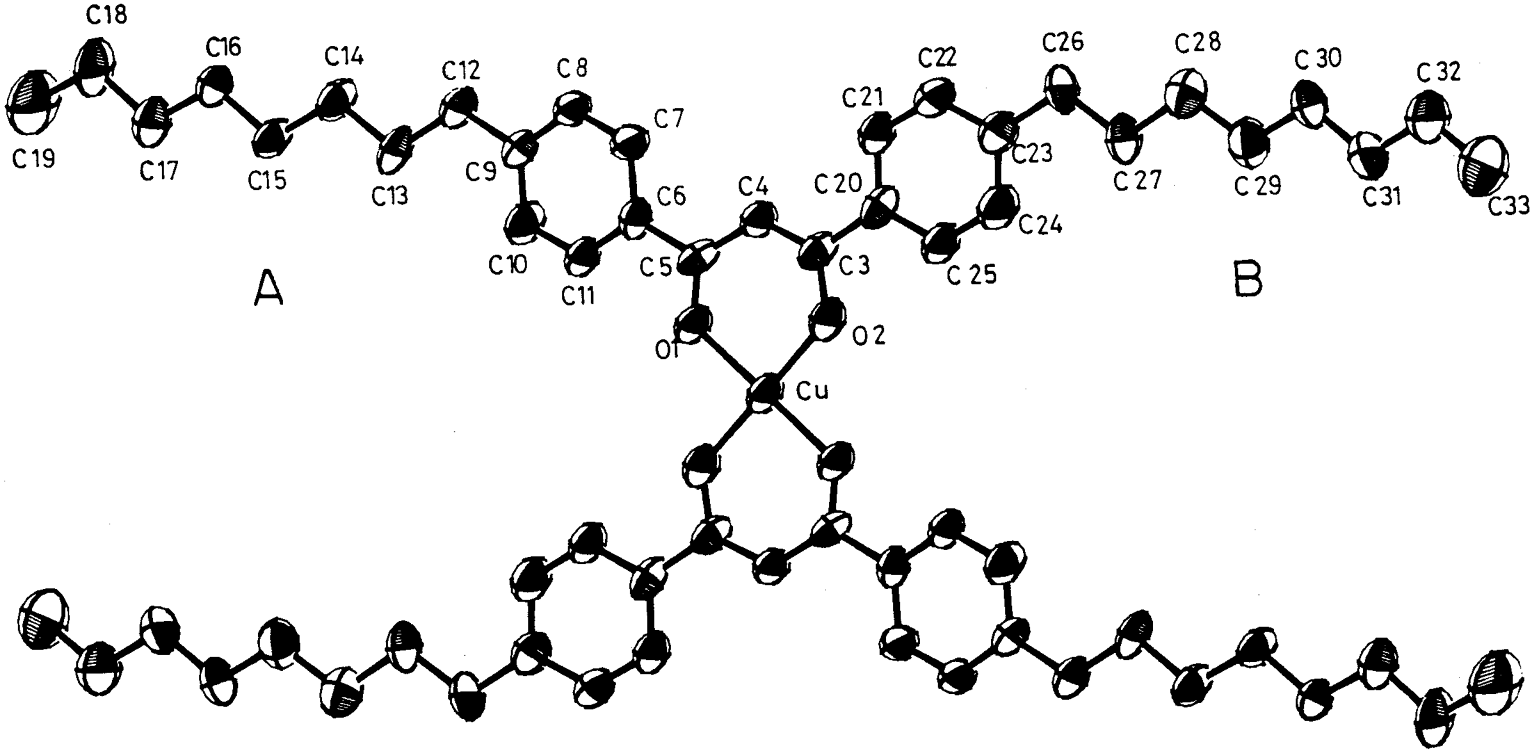


Figure 4.4(b): ORTEP diagram of the thermal ellipsoids drawn with 50% probability for the P-form.

Table 4.5(a): Final fractional atomic coordinates and the values of U_{eq}($\AA^2$) of the N-form.

Atom	x	y	z	U_{eq}
Cu	0.0000	0.0000	0.0000	0.0439(5)
O(1)	0.2644(8)	0.0546(3)	-0.0316(2)	0.046(2)
O(2)	0.0429(8)	0.1022(3)	0.1005(2)	0.046(2)
C(3)	0.216(1)	0.1695(4)	0.1291(3)	0.036(3)
C(4)	0.391(1)	0.1856(4)	0.0879(4)	0.041(3)
C(5)	0.402(1)	0.1298(4)	0.0097(3)	0.038(3)
C(6)	0.592(1)	0.1548(5)	-0.0328(3)	0.040(3)
C(7)	0.725(1)	0.2462(5)	-0.0078(4)	0.052(3)
C(8)	0.887(1)	0.2661(5)	-0.0519(4)	0.054(3)
C(9)	0.924(1)	0.1974(5)	-0.1214(4)	0.043(3)
C(10)	0.795(1)	0.1054(5)	-0.1446(4)	0.051(3)
C(11)	0.626(1)	0.0847(4)	-0.1022(4)	0.044(3)
C(12)	0.107(1)	0.2209(5)	-0.1667(4)	0.055(3)
C(13)	0.061(1)	0.1709(5)	-0.2564(4)	0.058(3)
C(14)	0.251(1)	0.1963(5)	-0.2995(4)	0.051(3)
C(15)	0.201(1)	0.1449(5)	-0.3903(4)	0.050(3)
C(16)	0.399(1)	0.1635(5)	-0.4331(4)	0.049(3)
C(17)	0.350(1)	0.1120(5)	-0.5238(4)	0.053(3)
C(18)	0.555(1)	0.1274(5)	-0.5648(4)	0.057(3)
C(19)	0.505(2)	0.0744(5)	-0.6553(4)	0.072(4)
C(20)	0.220(1)	0.2304(4)	0.2160(3)	0.033(3)
C(21)	0.411(1)	0.2995(5)	0.2620(4)	0.047(3)
C(22)	0.411(1)	0.3474(5)	0.3427(4)	0.049(3)
C(23)	0.225(1)	0.3319(4)	0.3802(3)	0.035(3)
C(24)	0.038(1)	0.2658(5)	0.3338(3)	0.045(3)
C(25)	0.033(1)	0.2172(4)	0.2528(4)	0.044(3)
C(26)	0.247(1)	0.3847(4)	0.4690(3)	0.047(3)
C(27)	0.048(1)	0.3652(4)	0.5102(3)	0.039(3)
C(28)	0.092(1)	0.4244(4)	0.5994(3)	0.045(3)
C(29)	-0.102(1)	0.4081(5)	0.6447(3)	0.048(3)
C(30)	-0.049(1)	0.4683(5)	0.7336(4)	0.053(3)
C(31)	-0.243(1)	0.4559(5)	0.7797(4)	0.059(3)
C(32)	-0.191(2)	0.5187(6)	0.8669(4)	0.077(4)
C(33)	-0.387(2)	0.5083(7)	0.9118(5)	0.101(5)

Table 4.5(b): Final fractional atomic coordinates and $U_{eq}(Å^2)$ of the P-form

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)

Table 4.6(a): Anisotropic thermal parameters U_{ij} **of** the N-form.

Atom	U_{11}	u_{22}	U_{33}	$_{23}$	U_{13}	U_{12}
Cu	0.0349(9)	0.0525(8)	0.0346(7)	-0.0007(6)	0.0115(6)	-0.0082(6)
O(1)	0.049(3)	0.050(3)	0.030(3)	-0.003(2)	0.019(2)	-0.014(3)
O(2)	0.032(3)	0.054(3)	0.037(3)	-0.006(2)	0.013(2)	-0.013(3)
C(3)	0.032(4)	0.047(4)	0.03(1	0.012(3)	0.007(3)	0.009(4)
C(4)	0.036(5)	0.049(4)	0.031(4)	0.001(3)	0.008(3)	-0.004(4)
C(5)	0.030(5)	0.042(4)	0.032(4)	0.005(3)	-0.005(3)	-0.004(4)
C(6)	0 . 01(5)	0.056(5)	0 . 01(I)	0.016(3)	0.005(3)	0.002(4)
C(7)	0.056(5)	0.050(5)	0.041(4)	0.000(3)	0.018(4)	-0.018(4)
C(8)	0.059(6)	0.053(5)	0.045(4)	0.008(4)	0.011(4)	-0.013(4)
C(9)	0.035(5)	0.060(5)	0.037(4)	0.021(4)	0.003(4)	0.004(4)
C(10)	0.058(5)	0.053(5)	0.038(4)	0.003(3)	0.020(4)	-0.002(4)
C(11)	0.048(5)	0.046(4)	0.035(4)	0.005(3)	0.018(4)	-0.007(4)
C(12)	0.051(5)	0.070(5)	0.045(4)	0.018(4)	0.016(4)	-0.007(4)
C(13)	0.046(5)	0.082(6)	0.050(5)	0.023(4)	0.022(4)	-0.004(4)
(1	0.045(5)	0.068(5)	0.044(4)	0.019(4)	0.016(4)	0.008(4)
C(15)	0.046(5)	0.065(5)	0.044(4)	0.019(4)	0.020(4)	0.004(4)
C(16)	0.045(5)	0.061(5)	0.044(4)	0.019(4)	0.017(4)	0.002(4)
C(17)	0.058(5)	0.061(5)	0.041(4)	0.015(4)	0.013(4)	0.000(4)
C(18)	0.064(6)	0.059(5)	0.049(5)	0.012(4)	0.023(4)	-0.009(4)
C(1	0.091(7)	0.079(6)	0.048(5)	0.014(4)	0.026(5)	0.011(5)
C(20)	0.039(5)	0.035(4)	0.027(4)	0.012(3)	0.006(3)	0.006(3)
C(21)	0.039(5)	0.060(5)	0.032(4)	0.004(3)	0.008(4)	-0.013(4)
C(22)	0.042(5)	0.064(5)	0.032(4)	0.005(3)	0.005(4)	-0.011(4)
(3	0.037(5)	0.039(4)	0.029(4)	0.007(3)	0.010(3)	0.003(4)
C(24)	0.034(5)	0.064(5)	0.028(4)	0.000(3)	0.013(3)	-0.002(4)
C(25)	0.032(5)	0.052(4)	0.038(4)	0.002(3)	0.014(4)	-0.013(4)
C(26)	0.041(5)	0.057(4)	0.034(4)	0.002(3)	0.011(4)	-0.005(4)
C(27)	0.041(5)	0.046(4)	0.026(4)	0.002(3)	0.007(3)	0.002(4)
C(28)	0.044(5)	0.050(4)	0.032(4)	0.002(3)	0.008(3)	-0.004(4)
C(29)	0.047(5)	0.061(5)	0.030(4)	0.007(3)	0.010(4)	-0.005(4)
C(30)	0.046(5)	0.069(5)	0.034(4)	0.003(4)	0.005(4)	0.006(4)
C(31)	0.053(5)	0.075(5)	0.045(4)	0.009(4)	0.022(4)	0.002(4)
C(32)	0.089(7)	0.091(6)	0.044(5)	0.006(4)	0.030(5)	-0.006(5)
C(33)	0.101(8)	0.128(8)	0.070(6)	0.014(5)	0.046(6)	-0.008(6)

Table 4.6(b): Anisotropic thermal parameters U_{ij} of the P-form.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	0.0348(8)	0.0509(9)	0.082(1)	0.0114(7)	0.0056(6)	-0.0013(6)
O(1)	0.037(3)	0.050(3)	0.090(4)	0.006(3)	0.012(3)	0.000(2)
O(2)	0.045(3)	0.047(3)	0.094(4)	0.004(5)	0.009(3)	-0.005(3)
C(3)	0.037(5)	0.048(5)	0.079(6)	0.023(4)	0.007(4)	0.007(4)
C(4)	0.039(4)	0.043(4)	0.077(5)	0.006(4)	0.010(4)	0.007(3)
C(5)	0.032(4)	0.058(5)	0.073(5)	0.028(4)	0.010(4)	0.010(4)
C(6)	0.044(5)	0.043(5)	0.056(5)	0.012(4)	0.000(4)	0.002(4)
C(7)	0.044(5)	0.048(5)	0.090(6)	0.001(4)	0.013(4)	0.014(4)
C(8)	0.042(5)	0.055(5)	0.098(6)	-0.005(5)	0.019(4)	0.008(4)
C(9)	0.037(4)	0.054(5)	0.065(5)	0.017(4)	0.006(4)	0.005(3)
C(10)	0.048(5)	0.047(5)	0.094(6)	0.016(4)	0.006(4)	0.004(4)
C(11)	0.040(4)	0.051(5)	0.083(6)	0.009(4)	0.010(4)	0.003(4)
C(12)	0.041(4)	0.060(5)	0.097(7)	0.002(5)	0.012(4)	-0.005(4)
C(13)	0.041(4)	0.056(5)	0.084(6)	0.023(5)	-0.001(4)	-0.012(4)
C(14)	0.041(4)	0.058(5)	0.085(6)	0.020(4)	0.006(4)	0.000(4)
C(15)	0.039(4)	0.047(5)	0.086(6)	0.019(4)	0.008(4)	0.003(3)
C(16)	0.049(5)	0.052(5)	0.077(6)	0.008(4)	0.010(4)	0.002(4)
C(17)	0.064(5)	0.059(5)	0.087(6)	0.016(5)	0.001(5)	0.000(4)
C(18)	0.079(6)	0.055(5)	0.109(7)	0.012(5)	-0.003(5)	-0.015(5)
C(19)	0.104(9)	0.078(7)	0.18(1)	0.022(7)	0.013(8)	-0.007(6)
C(20)	0.041(5)	0.051(5)	0.077(6)	0.022(4)	-0.001(4)	0.003(4)
C(21)	0.042(5)	0.054(5)	0.110(7)	0.001(5)	0.008(4)	0.003(4)
C(22)	0.052(5)	0.057(6)	0.107(7)	0.008(5)	0.005(5)	0.006(4)
C(23)	0.055(5)	0.060(5)	0.069(6)	0.023(4)	0.007(4)	0.013(4)
C(24)	0.045(5)	0.070(6)	0.085(6)	0.016(5)	0.016(4)	0.011(4)
C(25)	0.046(5)	0.046(5)	0.086(6)	0.007(4)	0.006(4)	0.000(4)
C(26)	0.076(6)	0.044(4)	0.086(6)	-0.015(4)	0.005(5)	0.004(4)
C(27)	0.073(6)	0.040(4)	0.085(6)	-0.004(4)	-0.001(5)	0.002(4)
C(28)	0.071(6)	0.070(6)	0.086(6)	0.016(5)	-0.001(5)	0.014(5)
C(29)	0.084(7)	0.067(6)	0.077(6)	0.007(5)	0.002(5)	0.014(5)
C(30)	0.079(6)	0.051(5)	0.083(6)	-0.008(5)	0.004(5)	0.015(4)
C(31)	0.082(6)	0.066(6)	0.078(6)	-0.005(5)	0.009(5)	0.016(5)
C(32)	0.082(7)	0.064(6)	0.122(8)	0.003(6)	0.011(6)	0.008(5)
C(33)	0.101(8)	0.089(7)	0.16(1)	0.008(7)	0.021(7)	-0.008(6)

Table 4.7: Fractional coordinates and $U_{iso}(Å^2)$ values of hydrogen atoms in the N and P-form.

Atom	N-form				P-form			
	x	y	z	U_{iso}	x	y	z	U_{iso}
H(4)	0.528	0.246	0.120	0.046	0.345	-0.058	-0.150	0.060
H(7)	0.700	0.302	0.048	0.056	0.532	0.069	-0.104	0.068
H(8)	0.983	0.341	-0.031	0.063	0.754	0.251	-0.066	0.068
H(10)	0.823	0.046	-0.198	0.054	0.561	0.497	0.115	0.064
H(11)	0.521	0.010	-0.124	0.047	0.348	0.316	0.087	0.058
H(21)	0.562	0.315	0.234	0.051	-0.098	0.666	0.787	0.071
H(22)	0.562	0.401	0.375	0.050	-0.139	0.459	0.663	0.079
H(24)	-0.116	0.251	0.360	0.049	0.296	0.562	0.646	0.070
H(25)	-0.122	0.165	0.218	0.045	0.338	0.773	0.774	0.064
H(121)	1.279	0.201	-0.141	0.064	0.840	0.507	-0.036	0.078
H(122)	1.143	0.300	-0.153	0.064	0.893	0.460	0.066	0.078
H(131)	0.896	0.193	-0.282	0.066	0.807	0.608	0.199	0.069
H(132)	1.029	0.092	-0.270	0.066	0.762	0.662	0.088	0.069
H(141)	1.416	0.173	-0.273	0.058	0.007	0.721	0.052	0.070
H(142)	1.282	0.275	-0.286	0.058	0.050	0.669	0.161	0.070
H(151)	1.043	0.170	-0.416	0.057	0.983	0.835	0.290	0.062
H(152)	1.159	0.066	-0.402	0.057	0.942	0.888	0.180	0.062
H(161)	1.558	0.138	-0.406	0.055	0.187	0.936	0.141	0.067
H(162)	1.441	0.241	-0.420	0.055	0.226	0.889	0.254	0.067
H(171)	1.198	0.138	-0.551	0.058	0.162	0.060	0.373	0.079
H(172)	1.304	0.033	-0.536	0.058	0.125	0.107	0.259	0.079
H(181)	1.708	0.100	-0.537	0.065	0.372	0.153	0.223	0.098
H(182)	1.601	0.205	-0.553	0.065	0.409	0.110	0.342	0.098
H(261)	0.283	0.463	0.480	0.053	0.117	-0.686	-0.397	0.078
H(262)	0.409	0.371	0.502	0.053	0.100	-0.631	-0.505	0.078
H(271)	0.019	0.287	0.502	0.046	-0.152	-0.688	-0.507	0.076
H(272)	-0.113	0.385	0.480	0.046	-0.136	-0.741	-0.395	0.076
H(281)	0.127	0.502	0.606	0.048	-0.048	-0.899	-0.490	0.082
H(282)	0.255	0.406	0.628	0.048	-0.066	-0.847	-0.608	0.082
H(291)	-0.133	0.331	0.638	0.057	-0.317	-0.903	-0.602	0.083
H(292)	-0.263	0.428	0.616	0.057	-0.303	-0.947	-0.483	0.083
H(301)	-0.012	0.547	0.740	0.059	-0.219	-0.117	-0.584	0.078
H(302)	0.112	0.448	0.762	0.059	-0.247	-0.076	-0.703	0.078
H(311)	-0.276	0.378	0.774	0.066	-0.497	-0.127	-0.683	0.092
H(312)	-0.405	0.475	0.749	0.066	-0.469	-0.168	-0.564	0.092
H(321)	-0.151	0.595	0.872	0.085	-0.385	-0.337	-0.673	0.101
H(322)	-0.031	0.496	0.897	0.085	-0.433	-0.301	-0.791	0.101
H(191)	1.654	0.086	-0.682	0.078	0.476	0.345	0.380	0.133
H(192)	1.464	-0.004	-0.668	0.078	0.304	0.325	0.335	0.133
H(193)	1.356	0.101	-0.684	0.078	0.341	0.283	0.453	0.133
(3 3 1	-0.347	0.551	0.974	0.106	-0.616	-0.485	-0.763	0.130
(2)	-0.545	0.529	0.882	0.106	-0.626	-0.393	-0.635	0.130
I)	-0.425	0.430	0.908	0.106	-0.674	-0.3.56	-0.753	0.130

Table 4.8: Average $U_{eq}(Å^2)$ values in the N and P forms.

	N-form	P-form
Core	0.042(4)	0.061(6)
Phenyl ring **A**	0.047(5)	0.062(7)
B	0.042(6)	0.069(7)
Chain A	0.056(7)	0.08(2)
B	0.06(2)	0.09(2)

could be correlated with the differences in the unit cell volumes. Comparison of the unit cell volumes of the P and the N forms (Table 4.1) shows that the P-form crystallizes in a unit cell approximately 1% larger than that of the N-form. With Z=1 in both the 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. It must be mentioned that although the U_{eq} values characterizing the atoms of the P-form are higher, there is no evidence for any structural disorder.

In both the crystal structures, the respective U_{eq} values of the terminal atoms of the alkyl chains are the highest.

4.4.2 Molecular geometry

In Table 4.9(a), (b) and (c), the bond lengths, valence angles and the average bond lengths of the different groups are listed. The copper atoms lying on inversion centres in both the structures, are each surrounded by four oxygen atoms in a square planar arrangement. Figure 4.5 depicts the dimensions of the coordination polyhedron in the dimorphs. Figure 4.6 compares the dimensions of the cores of molecules in N and P-forms. It is interesting to note that in the crystal structure of the P-form (Figure 4.5(b)), lengths of the chemically equivalent bonds differ quite significantly *viz.*, Cu-O(1) and Cu-O(2), O(2)-C(3) and O(1)-C(5), C(3)-C(4) and C(4)-C(5). Such a difference suggests that in the P-form, contribution from the resonance structure shown in Figure 4.7(a) is perhaps more than 50%, thereby leading to a significant increase in the double bond character of the bonds C(3)-C(4) and O(1)-C(5). Figure 4.6(a) shows that un-

Table 4.9(a): Bond lengths(Å) in the dimorphs of Cu-C$_8$H$_{17}$.

	N-form	P-form		N-form	P-form
Cu-O(1)	1.914(5)	1.917(4)	C(15)-C(16)	1.53(1)	1.526(9)
Cu-O(2)	1.902(3)	1.888(5)	C(16)-C(17)	1.522(9)	1.51(1)
O(1)-C(5)	1.257(6)	1.25(1)	C(17)-C(18)	1.52(1)	1.53(1)
O(2)-C(3)	1.276(7)	1.292(9)	C(18)-C(19)	1.521(9)	1.49(1)
C(3)-C(4)	1.39(1)	1.354(9)	C(20)-C(25)	1.408(8)	1.372(9)
C(3)-C(20)	1.516(7)	1.51(1)	C(20)-C(21)	1.38(1)	1.38(1)
C(4)-C(5)	1.387(8)	1.41(1)	C(21)-C(22)	1.383(9)	1.36(1)
C(5)-C(6)	1.508(9)	1.487(8)	C(22)-C(23)	1.39(1)	1.39(1)
C(6)-C(11)	1.384(8)	1.37(1)	C(23)-C(24)	1.375(8)	1.403(9)
C(6)-C(7)	1.390(9)	1.41(1)	C(23)-C(26)	1.503(7)	1.54(1)
C(7)-C(8)	1.38(1)	1.391(9)	C(24)-C(25)	1.386(8)	1.37(1)
C(8)-C(9)	1.380(9)	1.41(1)	C(26)-C(27)	1.51(1)	1.52(1)
C(9)-C(10)	1.39(1)	1.37(1)	C(27)-C(28)	1.521(7)	1.56(1)
C(9)-C(12)	1.51(1)	1.512(9)	C(28)-C(29)	1.52(1)	1.53(1)
C(10)-C(11)	1.39(1)	1.400(9)	C(29)-C(30)	1.520(8)	1.50(1)
C(12)-C(13)	1.501(9)	1.51(1)	C(30)-C(31)	1.52(1)	1.53(1)
C(13)-C(14)	1.52(1)	1.520(9)	C(31)-C(32)	1.503(9)	1.52(1)
C(14)-C(15)	1.522(9)	1.52(1)	C(32)-C(33)	1.51(1)	1.49(1)

Table 4.9(b): Bond angles(°) in the dimorphs of Cu-C$_8$H$_{17}$.

	N-form	P-form		N-form	P-form
O(2)-Cu-O(1)	92.8(2)	92.3(2)	C(13)-C(14)-C(15)	113.6(6)	114.5(6)
C(5)-O(1)-Cu	126.7(4)	127.4(5)	C(14)-C(15)-C(16)	113.9(6)	113.2(6)
C(3)-O(2)-Cu	125.9(4)	127.0(5)	C(17)-C(16)-C(15)	114.0(6)	114.8(6)
O(2)-C(3)-C(4)	125.1(6)	124.6(7)	C(16)-C(17)-C(18)	113.2(6)	113.0(7)
O(2)-C(3)-C(20)	113.5(5)	113.4(6)	C(19)-C(18)-C(17)	113.0(6)	113.0(8)
C(4)-C(3)-C(20)	121.4(5)	122.0(7)	C(25)-C(20)-C(21)	118.0(6)	118.8(7)
C(3)-C(4)-C(5)	124.2(6)	124.7(7)	C(25)-C(20)-C(3)	119.6(5)	118.4(7)
O(1)-C(5)-C(4)	124.8(6)	123.8(7)	C(21)-C(20)-C(3)	122.4(5)	122.8(7)
O(1)-C(5)-C(6)	114.0(5)	114.5(7)	C(22)-C(21)-C(20)	119.4(6)	121.3(8)
C(4)-C(5)-C(6)	121.2(5)	121.7(7)	C(21)-C(22)-C(23)	122.4(6)	122.5(8)
C(11)-C(6)-C(7)	118.8(6)	118.1(7)	C(24)-C(23)-C(22)	117.3(6)	114.8(8)
C(11)-C(6)-C(5)	117.9(6)	120.1(7)	C(24)-C(23)-C(26)	124.4(6)	124.2(7)
C(7)-C(6)-C(5)	123.2(6)	121.8(7)	C(22)-C(23)-C(26)	118.2(6)	121.0(7)
C(8)-C(7)-C(6)	120.3(7)	119.8(7)	C(23)-C(24)-C(25)	121.4(6)	123.2(8)
C(9)-C(8)-C(7)	121.9(7)	121.2(7)	C(20)-C(25)-C(24)	121.3(6)	119.4(8)
C(8)-C(9)-C(10)	117.4(7)	118.4(7)	C(23)-C(26)-C(27)	118.1(5)	111.6(7)
C(8)-C(9)-C(12)	120.4(6)	124.0(7)	C(26)-C(27)-C(28)	112.4(5)	110.1(7)
C(10)-C(9)-C(12)	122.2(6)	117.6(7)	C(27)-C(28)-C(29)	115.1(5)	110.9(7)
C(11)-C(10)-C(9)	121.6(7)	120.3(7)	C(30)-C(29)-C(28)	113.0(5)	114.6(8)
C(10)-C(11)-C(6)	120.0(6)	122.2(7)	C(29)-C(30)-C(31)	114.1(6)	112.9(7)
C(13)-C(12)-C(9)	116.3(6)	118.0(7)	C(32)-C(31)-C(30)	113.4(6)	112.8(8)
C(12)-C(13)-C(14)	114.5(6)	110.8(6)	C(31)-C(32)-C(33)	113.3(7)	113.8(9)

Table 4.9(c): Average bond lengths(Å) and valence angles(°) along with the values given by Allen *et al*, [1987].

	bond lengths		values given by Allen *et al*		bond angles	
	N-form	P-form			N-form	P-form
Core:						
Cu-O	1.908(6)	1.90(1)		O-Cu-O	92.8(2)	92.3(2)
O-C_{ar}(core)	1.27(1)	1.27(2)		Cu-O-C_{ar}	126.3(4)	127.2(2)
C_{ar}-C_{ar} (core)	1.389(2)	1.38(3)		O-C_{ar}-C_{ar}	125.0(2)	124.2(4)
				C_{ar}-C_{ar}-C_{ar}	124.2(6)	124.7(7)
Phenyl ring:						
A	1.386(5)	1.39(2)	1.380(13)		120(2)	120(1)
B	1.39(1)	1.38(1)			120(2)	120(3)
Chain:						
A	1.519(9)	1.519(7)	1.530(15)		113.7(5)	113(1)
B	1.516(7)	1.53(2)			113.6(9)	113.(2)
C_{core}-C_{phenyl}	1.512(4)	1.50(1)		C_{phenyl}-C_{sp^3}-C_{sp^3}	117.2(9)	115(3)
C_{sp^3}-C_{phenyl}	1.507(4)	1.53(1)	1.513(14)			

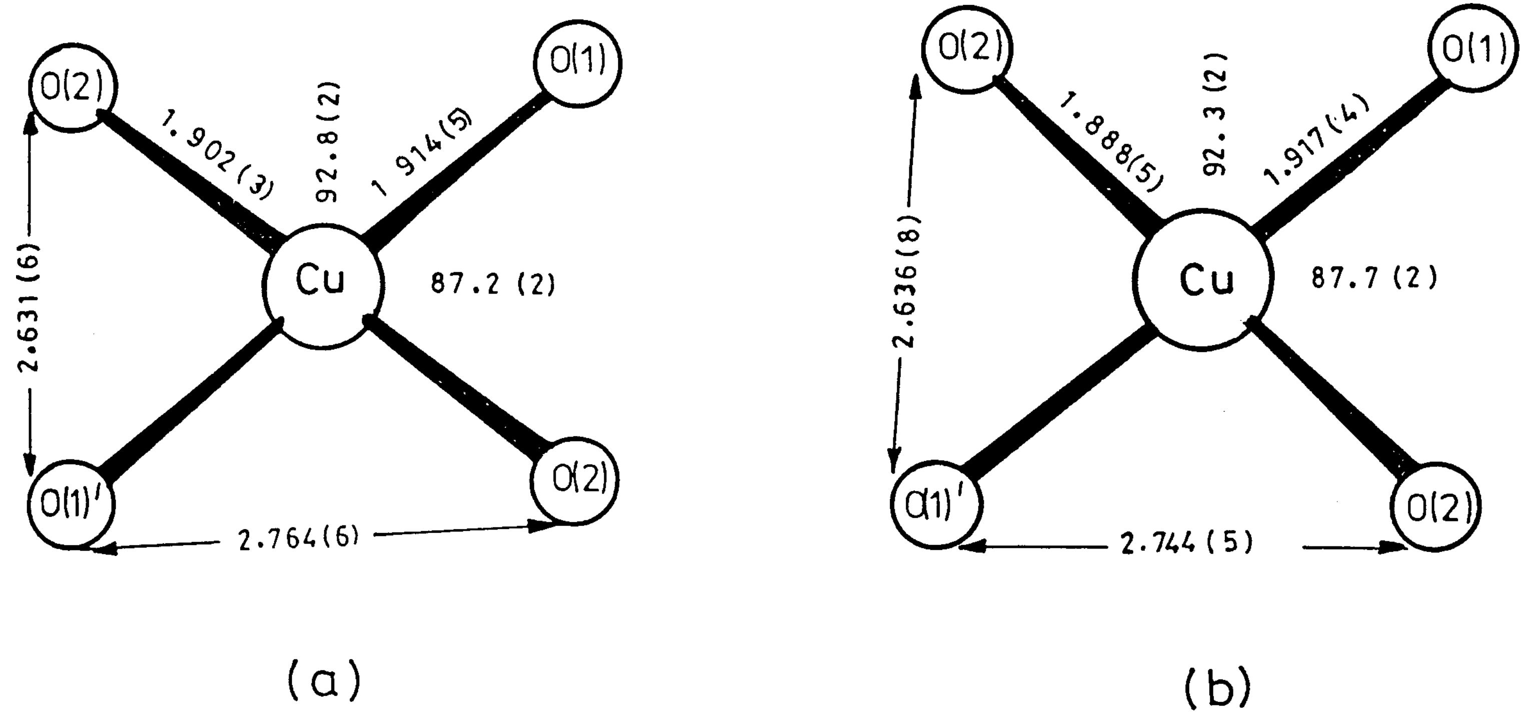


Figure 4.5: Coordination polyhedron around the copper atom in (a) N-form (b) P-form.

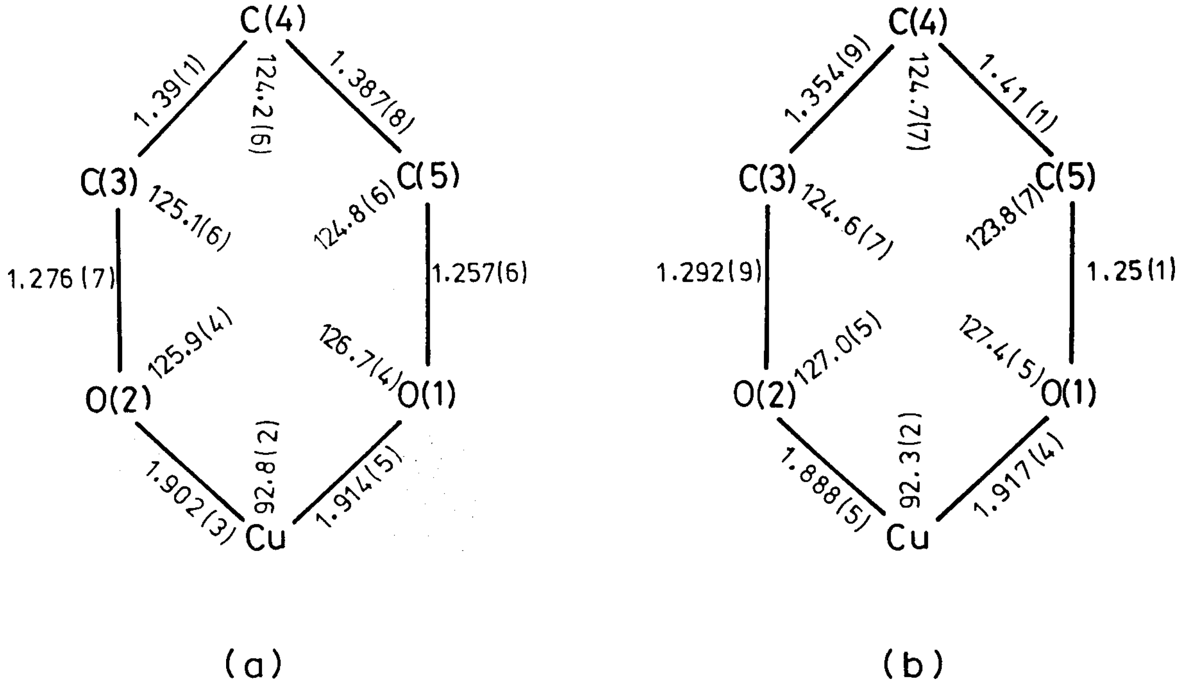


Figure 4.6: Comparison of the dimensions of the core. (a) N-form (b) P-form.

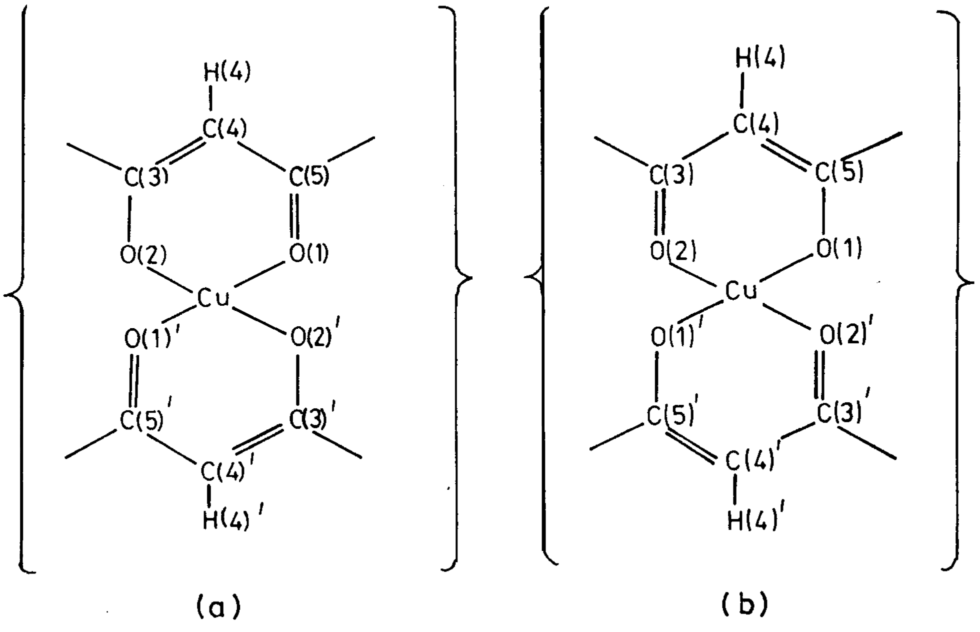


Figure 4.7: Resonance structures for the core.

like in the P-form, the difference between the chemically equivalent bond lengths in the N-form are less than the respective $3(\sigma)$ values and hence not significant. This feature could be ascribed to equal contributions from the resonance structures in Figure 4.7(a) and (b). It is also not clear why the predominance of the resonance structure in Figure 4.7(a) should occur only in the P-form.

The displacements, δ's, of the nonhydrogen atoms from the respective least squares mean planes fitted through the crystallographically independent part of the core *i.e.*, through the atoms Cu, O(1), O(2), C(3) to C(5) are compared in Figure 4.8. In both the cases, among the atoms of the core, displacement is highest for the copper atom. It is also observed that in the case of the P-form, δ's for the atoms of the core are less than the respective e.s.d's. In contrast, in the N-form, the corresponding δ's are higher than the respective e.s.d's. Thus, in the P-form, the core of the molecule appears to be more planar than in the N-form. Comparison of the δ-values of the terminal atoms of the chains indicates that reduction in the degree of planarity in the N-form is not just confined to the core but is prevalent in the entire molecule. It is found that in the N-form, the δ values 2.016(8) and 1.42(1)Å respectively of the terminal atoms C(19) and C(33) are conspicuously higher than the corresponding values of 0.29(1) and 0.10(1)Å observed in the P-form. Thus, in the P-form, the entire molecule is nearly in the plane of the core whereas in the N-form, it is not so.

Further evidence for the nonplanar character of the molecular core is obtained from calculation of the angle η between the planes through the Cu-O-C-C, in

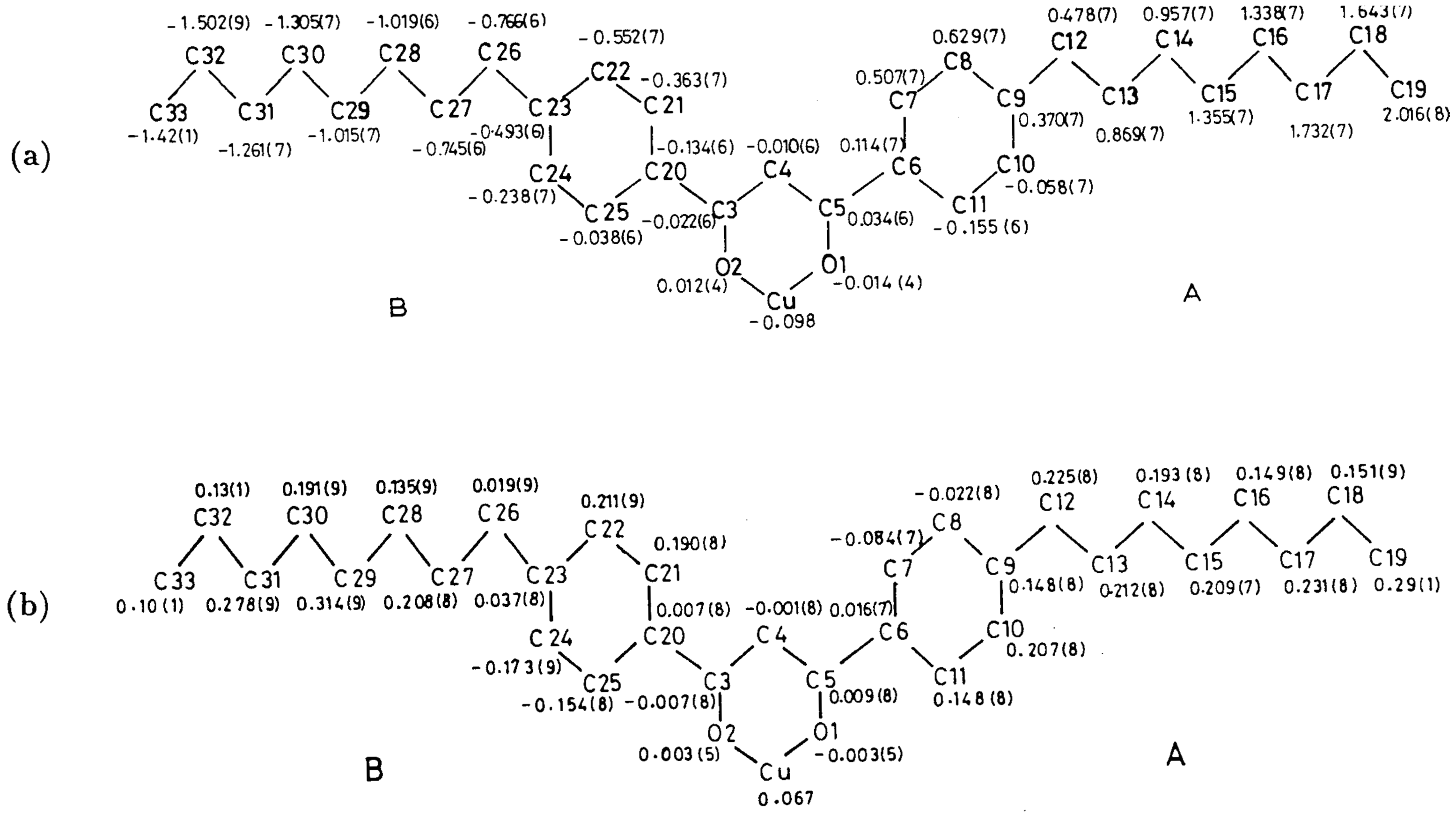


Figure 4.8: Displacements, δ's, of all the nonhydrogen atoms of the molecule from the plane through the crystallographically independent half of the core. (a) N-form (b) P-form.

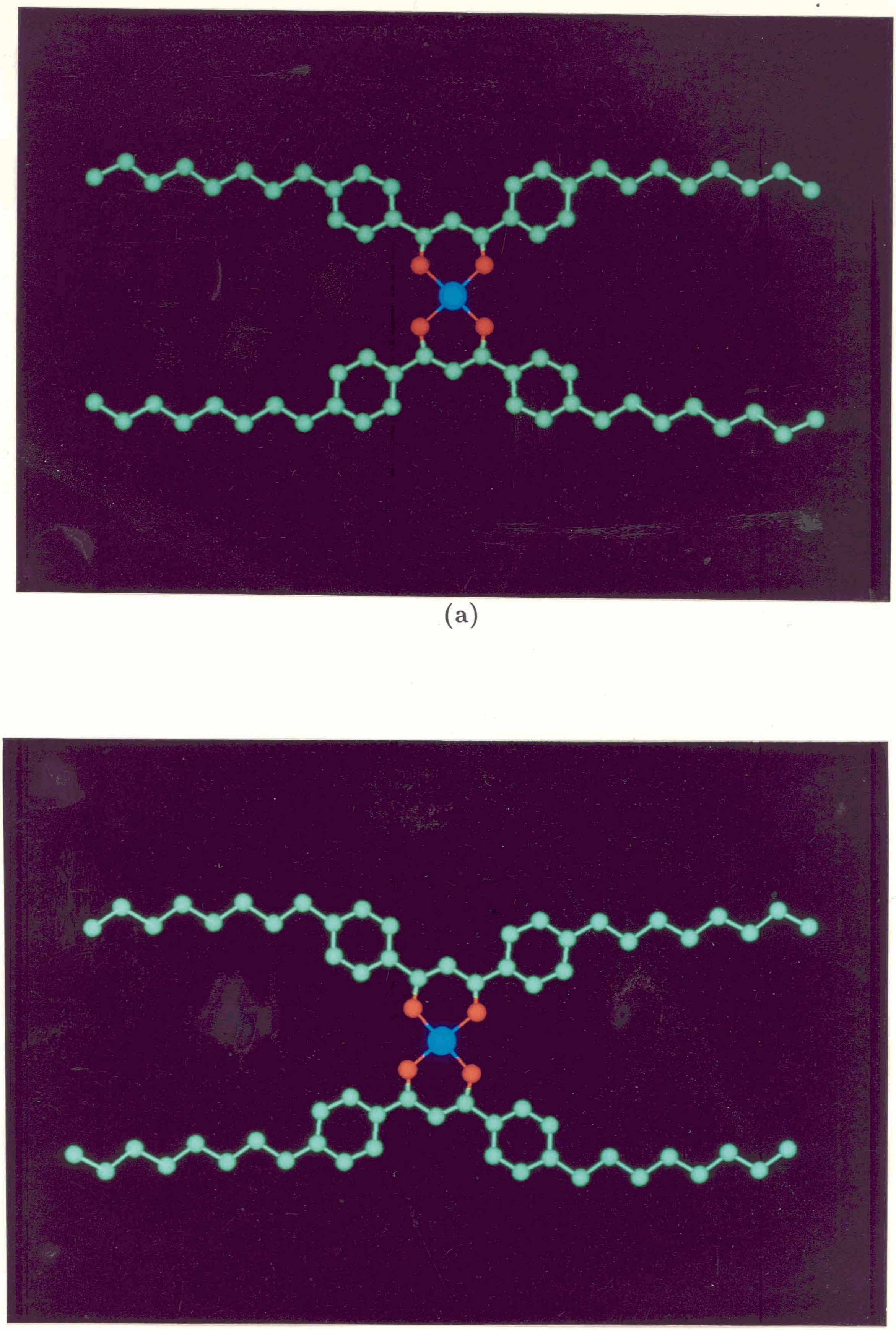
each half of the core. As in the case of Cu-OC_8H_{17} and Cu-OC_7H_{15}-C_7H_{15} (Chapter 2 and 3 of this thesis), the value of the dihedral angle, η, is nonzero, the value being 1.1 and 4.8° for the P and N forms respectively.

The tilts of the phenyl rings and the alkyl chains with respect to the core are also very different in the two forms. Whereas in the P-form, the phenyl rings and chains A and B (Figure 4.8) are tilted with respect to the core by 6, 9, 3 and 7° respectively, the corresponding angles for the N-form are enhanced to 17, 11, 16 and 12° respectively. In both the cases, the tilts of the phenyl rings are controlled primarily by steric effects. Thus, the overall tilts as well as the displacements of the phenyl rings and the chains with respect to the core are less in the P-form than in the N-form. To sum up, it may be said that in the P-form, the molecule of Cu-C_8H_{17} is more planar than in the N-form.

Figure 4.9(a) and (b) depict the conformation of the Cu-C_8H_{17} molecule in the dimorphs. In both the forms, the chains are fully extended in an all-*trans* conformation (Table 4.10). The end-to-end dimensions of the molecule calculated as the distances between the atoms C(19)...C(33) and C(33)...C(19)′ are as follows:

P-form: 30.3, 9.6Å
N-form: 30.4, 9.7Å

Here, the symbol ′ denotes the centrosymmetrically related atom. The molecular dimensions are comparable in both the forms. The rectangular disc-like geometry resembles the model-B proposed by Ohta et *al* [1986] and also the conformations observed for Cu-OC_8H_{17} (Chapter 2 of this thesis).



(a)

(b)

Figure 4.9: Molecular conformation in (a) N-form (b) P-form.

Table 4.10: Observed torsional angles(°) in the chains of the N and the P-forms.

	N-form	P-form
C(9)-C(12)-C(13)-C(14)	-179.7(5)	175.9(7)
C(12)-C(13)-C(14)-C(15)	-179.8(5)	178.8(6)
C(13)-C(14)-C(15)-C(16)	-175.6(5)	178.3(6)
C(14)-C(15)-C(16)-C(17)	179.6(5)	177.2(6)
C(15)-C(16)-C(17)-C(18)	-177.1(5)	179.4(7)
C(16)-C(17)-C(18)-C(19)	179.2(5)	177.7(8)
C(23)-C(26)-C(27)-C(28)	-179.7(5)	178.0(7)
C(26)-C(27)-C(28)-C(29)	180.0(5)	179.7(8)
C(27)-C(28)-C(29)-C(30)	179.6(5)	-177.1(7)
C(28)-C(29)-C(30)-C(31)	178.2(5)	176.0(7)
C(29)-C(30)-C(31)-C(32)	-178.2(5)	-179.0(8)
C(30)-C(31)-C(32)-C(33)	178.5(6)	175.4(8)

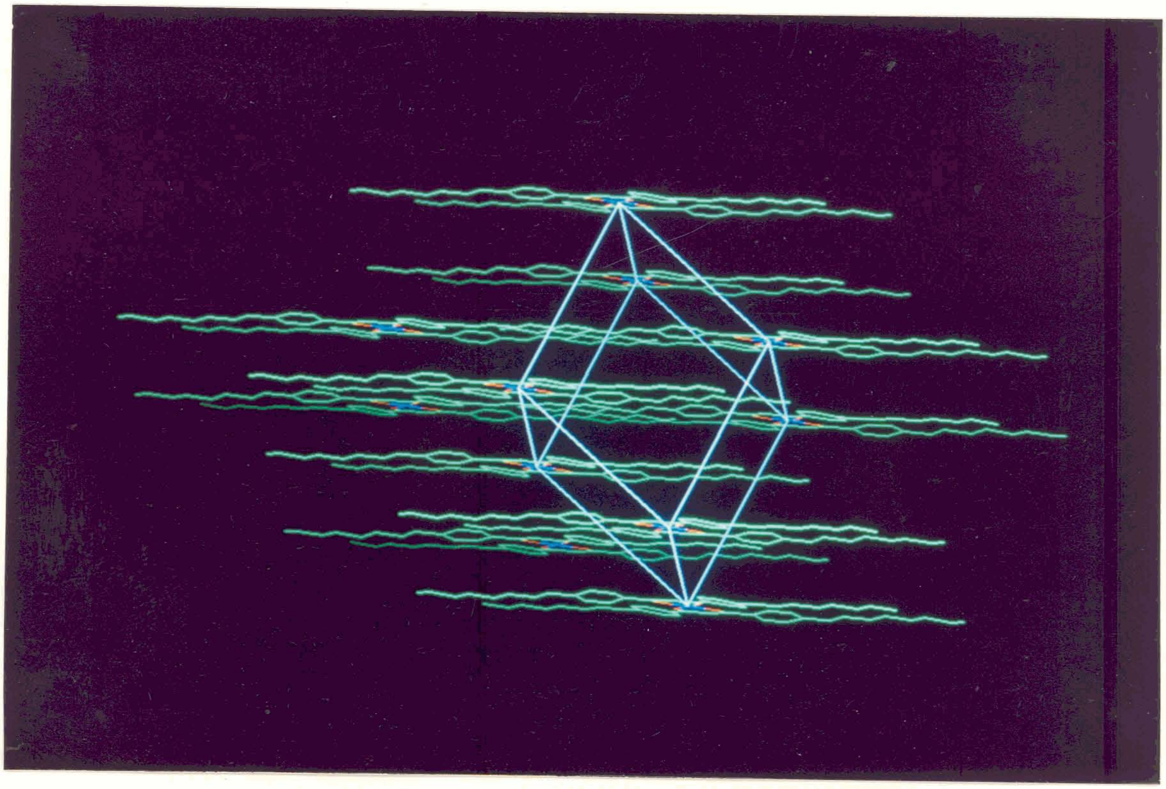


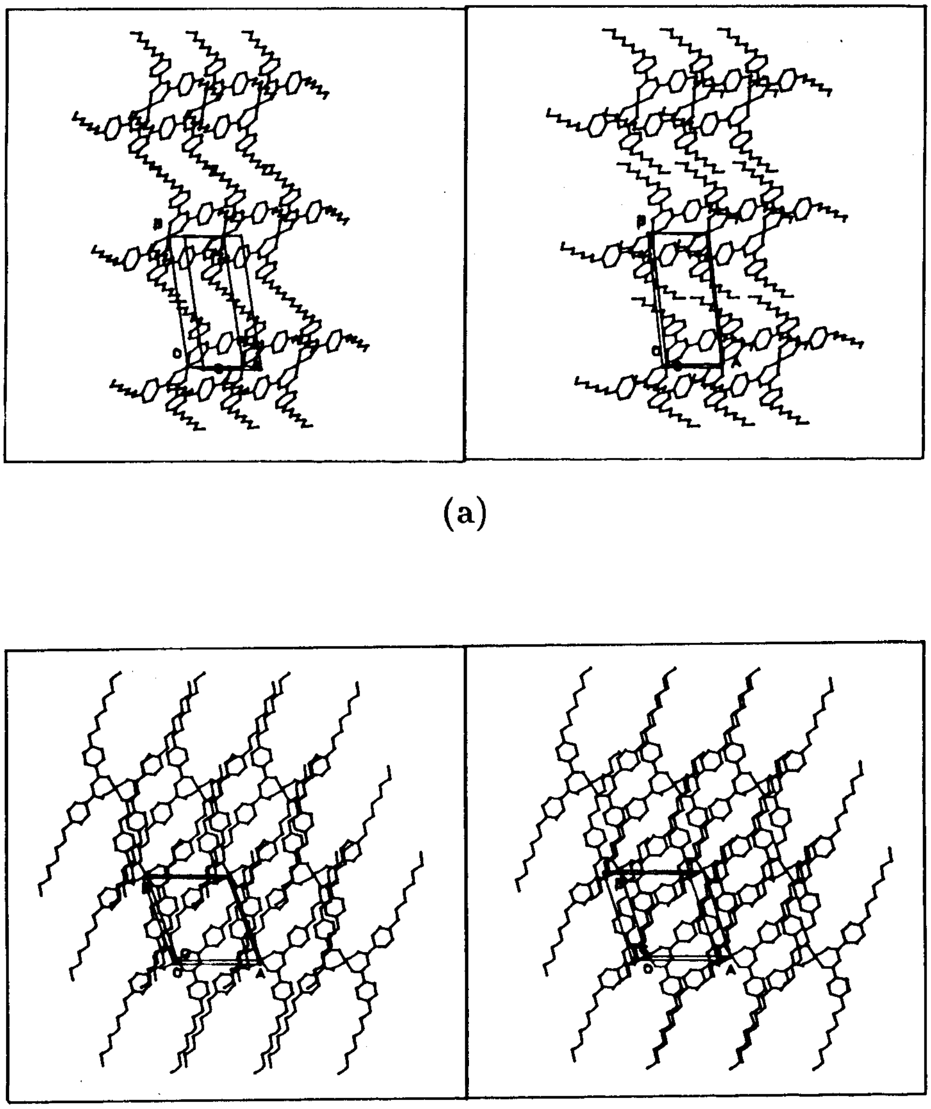
Figure 4.11: Layer structure observed in the N-form

4.4.3 Molecular arrangement

The molecular arrangement in the crystal structures of the P and the N-forms exhibit interesting differences. Figures 4.10(a) and (b) show the stereo views of the packing in the N and P form respectively as seen down the c-axis. In both the cases, the molecules are arranged essentially in layers which are perpendicular to the respective crystallographic a-axis; the molecules are, however, tilted with respect to the layer normal. The typical layer structure observed in the N-form is shown in Figure 4.11. Examination of intermolecular contact distances ≤ 4Å shows that in the P-form, each molecule in the layer is surrounded by six others situated at $\pm\vec{b}$, $\pm\overrightarrow{(b+c)}$, $\pm\overrightarrow{(2b+c)}$ *i.e.*, at ±11.6, ±15.1, ±23.7Å respectively. For the N-form, each molecule in the layer is surrounded by six others situated at $\pm\vec{c}$, $\pm\overrightarrow{(b+c)}$, $\pm\overrightarrow{(b+2c)}$ *i.e.*, at ±17.6, ±19.1 and ±33.9Å respectively.

Figure 4.12 depicts the conspicuous differences in the six-fold coordination observed in the two forms. In both the forms, interactions between adjacent molecules within the layer are essentially of the van der Waal's type. In the case of the P-form, the interactions are mainly of the type, phenyl ring...chain and core...chain. In the N-form, the interactions are of the type, phenyl ring...chain and chain..chain.

In both the forms, periodic stacking of the layers along the respective crystallographic a-direction gives rise to tilted columnar arrangements depicted in 4.13(a) and (b). The tilt of the core with respect to the column axis is 122 for the N-form and 111° for the P-form respectively (Figure 4.14). In the P-form,



(a)

(b)

Figure 4.10: Stereo view of the molecules viewed down the c-axis. (a) N-form (b) P-form.

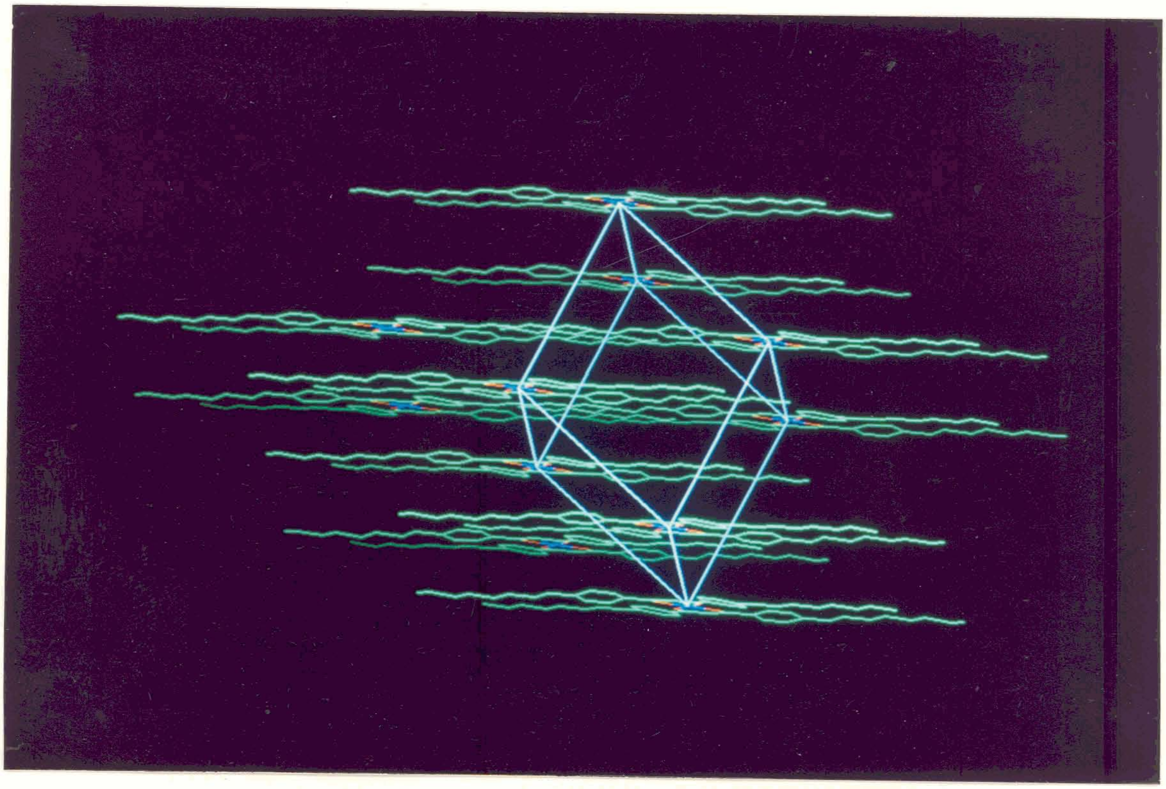


Figure 4.11: Layer structure observed in the N-form

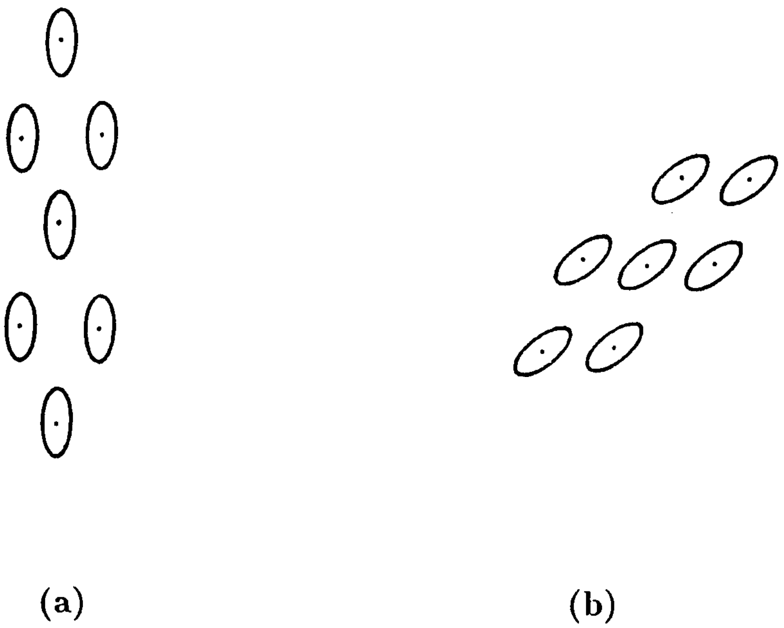
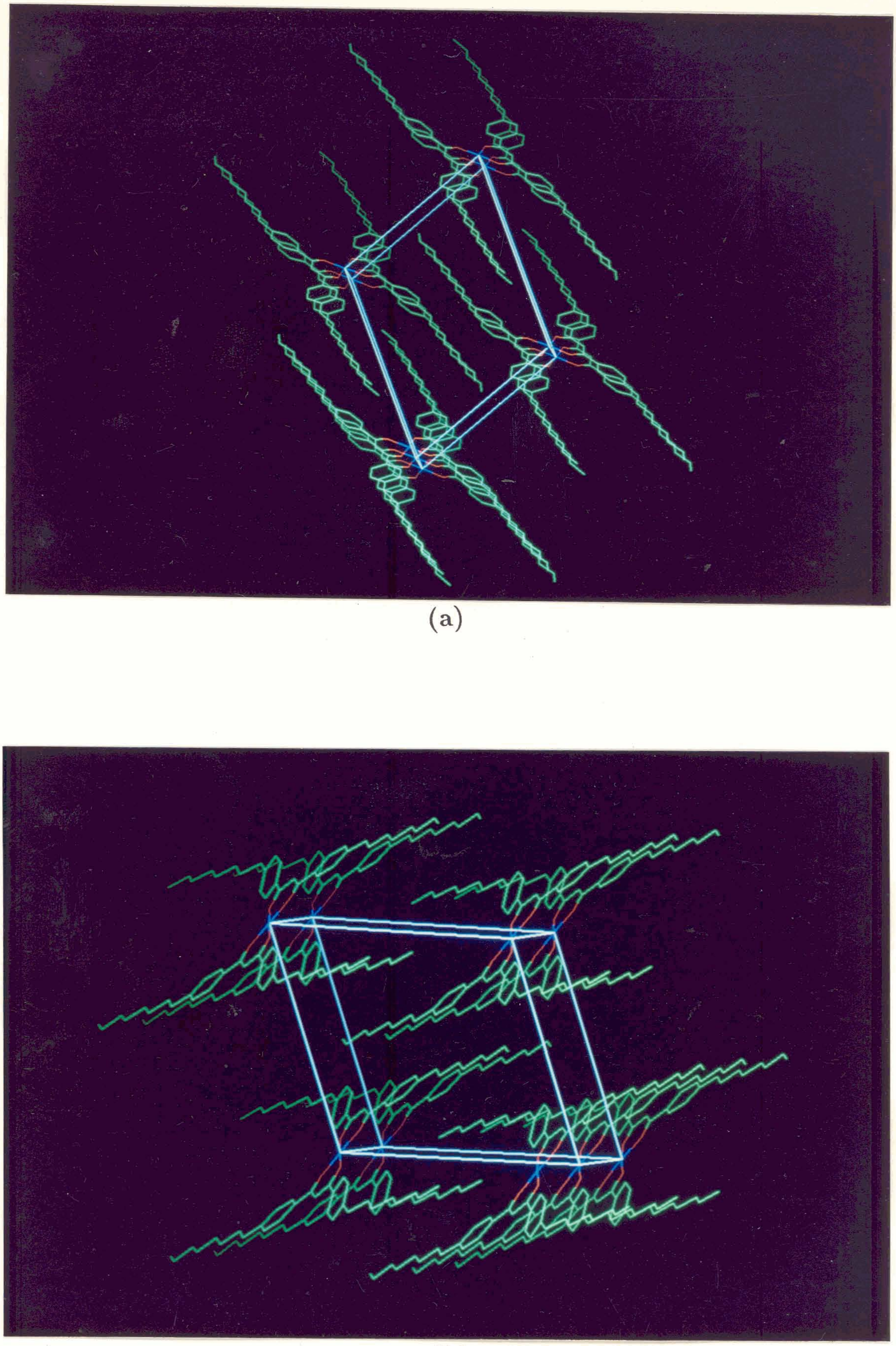


Figure 4.12: Two-dimensional representation of the hexagonal arrangement of columns in the dimorphs of Cu-C_8H_{17}. **(a)** N-form (b) P-form.



(a)

(b)

Figure **4.13:** Columnar arrangements in (a) N-form (b) P-form.

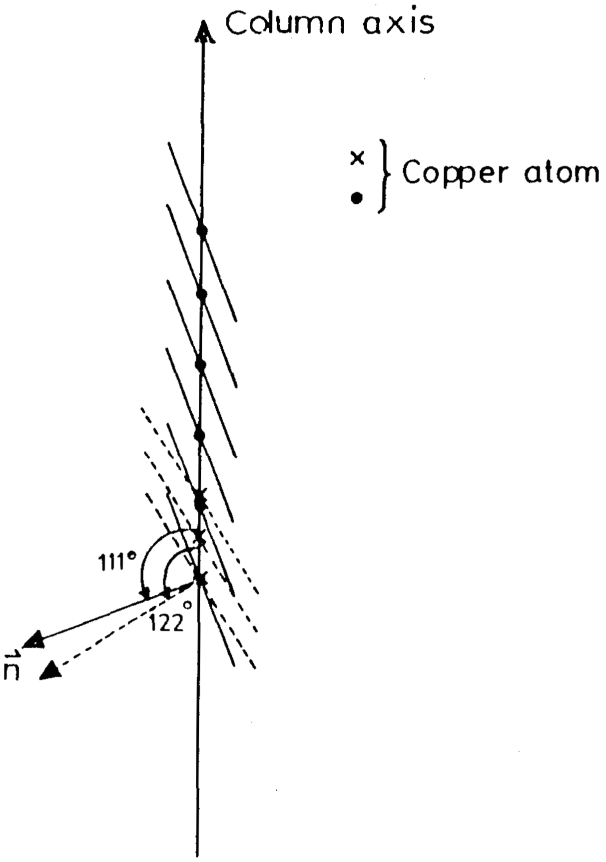


Figure 4.14: Comparison of the tilts of the core with respect to the column axis. The dashed lines represent the arrangement in the N-form.

the columnar arrangement is stabilized by non bonded interactions of the type core...phenyl ring, phenyl ring...phenyl ring, phenyl ring...chain and chain...chain which exist between adjacent molecules of the column. In the N-form, the corresponding interactions are of the following type: core...core, core...phenyl ring, core...chain, phenyl ring...phenyl ring and phenyl ring...chain.

In the N as well as the P-forms, each column is surrounded by six others as shown in Figure **4.12.** Interestingly, in the crystal lattice of the dimorphs, the volume which is a product of the area of the hexagon formed by the six coordinating columns (Figure **4.12)** and the stacking distance along the column is nearly the same *viz.*, $814\times5.8=4.7\times10^3$Å^3 for the N-form and $414\times10.3=4.3\times10^3$Å^3 for the P-form. Figure **4.12** shows that the arrangement of the columns in the two forms is strikingly different, although the 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. ESR studies of Eastman et al [1987] also suggest a columnar arrangement for Cu-C_8H_{17} in its crystalline phase. They mention about a separation of 2 to 3nm between copper atoms of adjacent columns. Our analysis shows that in the N-form, copper atoms from adjacent columns are separated by distances of the same order.

The most striking difference between the columnar arrangements in the N and the P forms concerns the Cu...Cu distance along the column axis. In the former, it is 5.8Å whereas in the latter, it is enhanced to 10.3Å. Examination of the intermolecular contact distances $\leq$ 4Å shows that in the N-form, the number of contact distances along the column is 33 and in contrast, in the layer, the number is only 14 *i.e.*, along the column, there are 2.5 times larger number of contacts $\leq$ 4Å. In the case of the P-form the situation is opposite. The number of contacts within a layer (28) is nearly twice that along the column (16). The conspicuous concentration of contact distances along the column axis is likely to be a factor closely related to the proximity of the copper atoms along the columnar axis of the N-form or *vice* versa. It must be pointed out that irrespective of the Cu...Cu distance along the column, on account of the tilt of the molecule with respect to the column axis, in both the crystal structures, the perpendicular distance between adjacent molecules along the column is ~4Å.