APPENDIX - I

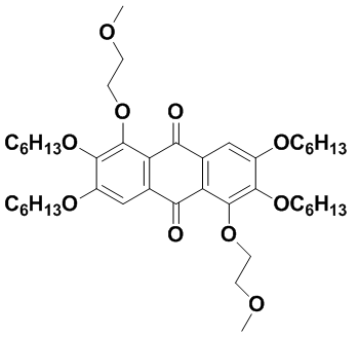
Table 1: Details of diffraction patterns of columnar phases

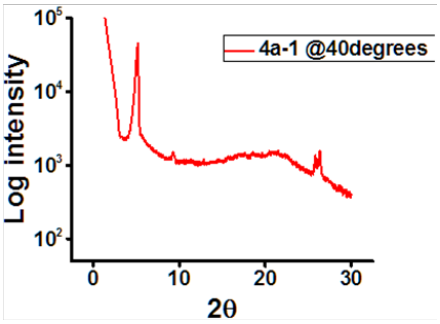
Phase	**Symmetry**	**Formula**	**conditions**
Smectic		$d_{hk} = \frac{a}{(h+k)} = 1 : \frac{1}{2} : \frac{1}{3} : \frac{1}{4} : \frac{1}{5}$	
Hexagonal	$p6mm$	$d_{hk} = \frac{a}{\sqrt{(h^2+hk+k^2)}} = 1 : \frac{1}{\sqrt{3}} : \frac{1}{2} : \frac{1}{\sqrt{7}} : \frac{1}{12}$	
Rectangular	$c2mm$ $p2gg$ $p2mg$	$d_{hk} = \sqrt{\frac{1}{\frac{h^2}{a^2}+\frac{k^2}{b^2}}}$	$hk : h+k = 2n+1$ $h0 : h = 2n+1, 0k : k = 2n+1, hk : allobserved$ $0k : k = 2n+1, hk : allobserved$
Square	$p4gm$	$d_{hk} = \frac{a}{\sqrt{(h^2+k^2)}} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{2} : \frac{1}{\sqrt{5}} : \frac{1}{\sqrt{8}} : \frac{1}{\sqrt{10}}$	$h0 : h = 2n$ $0k : k = 2n$
Cubic	$Ia\bar{3}d$	$d_{hk} = \frac{a}{\sqrt{(h^2+k^2+l^2)}} = \frac{1}{\sqrt{6}} : \frac{1}{\sqrt{8}} : \frac{1}{\sqrt{14}} : \frac{1}{16}$	$hkl : h+k+l = 2n$ $0kl : k, l = 2n$ $hhl : 2h+l = 4n$ $h00 : h = 4n$
Cubic	$pm\bar{3}n$	$d_{hkl} = \frac{a}{\sqrt{(h^2+k^2)}} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{4}} : \frac{1}{\sqrt{5}} : \frac{1}{\sqrt{6}}$	$hhl : l = 2n$ $hh0 : h = 2n$
Cubic	$Im\bar{3}m$	$d_{hkl} = \frac{a}{\sqrt{(h^2+k^2)}} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{4}} : \frac{1}{\sqrt{6}} : \frac{1}{\sqrt{8}} : \frac{1}{\sqrt{10}}$	$hkl : h+k+l = 2n$ $0kl : k+l = 2n$ $hhl : l = 2n$ $h00 : h = 2n$
Oblique	p_1	$\frac{1}{d^2} = \frac{\frac{h^2}{a^2}+\frac{k^2}{b^2}-\frac{2hk\cos r}{ab}}{\sin^2 r}$	

APPENDIX -2 : Indexing XRD pattern

2.1 Indexing Columnar hexagonal plastic phase

Compund 4a-I, Temperature 40^0C. Molecular weight : 757 g/mol.





Spacings of observed peaks are as follows:

$d_1 = 17.07\mathring{A}$, $d_2 = 9.46\mathring{A}$, $d_3 = 6.87\mathring{A}$, $d_4 = 3.44\mathring{A}$, $d_5 = 3.37\mathring{A}$.

Formula for hexagonal lattice:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \tag{1}$$

Indexing process involves assuming some peaks as (h, k, l) according to no of lattice parameters present in the formula of particular lattice. And with the calculated lattice parameters we fit the other peaks with specific (h, k, l) miller planes followed by comparing the d values calculated with observed d-spacings for the sample.

The above formula contains two lattice parameters 'a' and 'c'. So, we assume two peaks

In the above equation (1), we assume and substitute $d_1 = 17.07\mathring{A}$ as $(1, 0, 0)$

$$\frac{1}{17.07^2} = \frac{4}{3}\left(\frac{1 + 1(0) + 0}{a^2}\right) + \frac{0}{c^2}$$

$$\frac{1}{17.07^2} = \frac{4}{3}\left(\frac{1}{a^2}\right)$$

$$a^2 = \frac{4}{3}(17.07)^2$$

$$a = \frac{2}{\sqrt{3}}(17.07)$$

$$a = 19.71\mathring{A}$$

Assuming $d_4 = (0, 0, 2)$

$$\frac{1}{3.44^2} = \frac{4}{3}\left(\frac{(0)^2 + (0)(0) + (0)^2}{a^2}\right) + \frac{4}{c^2}$$
$$4c^2 = 4(3.44)^2$$
$$c = 2(3.44)$$
$$c = 6.88\mathring{A}$$

We fit other peaks by substituting different (h, k, l) values with the above calculated parameters, $a = 19.71\mathring{A}$ and $c = 6.88\mathring{A}$ in (1).

Ex:- We substitute $(h, k, l) = (1, 0, 2)$, $a = 19.71\mathring{A}$ and $c = 6.88\mathring{A}$ in (1)

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{1 + 1 + 0}{19.71^2}\right) + \frac{4}{6.88^2}$$
$$d = 3.39\mathring{A}$$

(we observed peak at $d = 3.37\mathring{A}$, so we can index the peak as (1,0,2))

Similarly, we fit other peaks and the details are as tabulated as follows:

Table 1: Peaks.

$d_{obs}(\mathring{A})$	$d_{cal}(\mathring{A})$	**Index**
17.07	17.07	100
9.46	9.85	110
6.87	6.45	200
3.44	3.44	002
3.37	3.39	102

Now the pattern is fitted into hexagonal lattice with lattice parameters $a = 19.71\mathring{A}$, $c = 6.88\mathring{A}$ From the lattice parameter 'a', we can calculate lattice area 'S_h', lattice volume 'V_h', as follows:

$$S_h = a^2 \times \sin(60^0)$$
$$= \frac{a^2 \times \sqrt{3}}{2} \qquad | \qquad \sin(60^0) = \frac{\sqrt{3}}{2}$$
$$S_h = \frac{(19.71)^2 \times \sqrt{3}}{2} = 336.437\mathring{A}^2$$

And,

$$
\begin{aligned}
V_h &= a^2 \times \sin(60^0) \times h_c \\
&= \frac{a^2 \times \sqrt{3} \times h_c}{2} \\
&= (19.71)^2 \times \frac{\sqrt{3}}{2} \times 3.37 \\
V_h &= 1143.886 \mathring{A}^3
\end{aligned}
\qquad
\begin{aligned}
a &= 19.71 \mathring{A} \\
h_c &= 3.37 \mathring{A}
\end{aligned}
$$

And we can calculate the number of molecules 'Z' occupying single slice of a column, as follows:

$$Z = \frac{V}{V_m} \tag{2}$$

$$V_m = \frac{M}{N_A \times \rho} \tag{3}$$

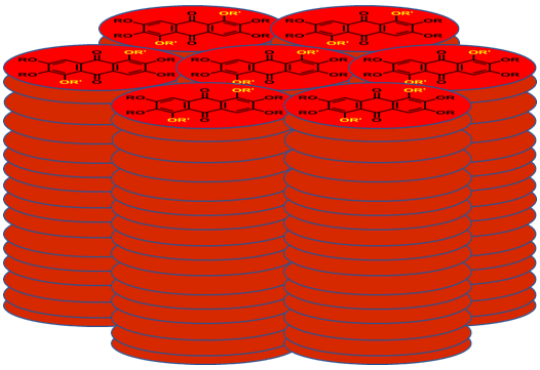
$$Z = \frac{\sqrt{3} N_A \rho a^2 h_c}{2m} \tag{4}$$

Where N_A - Avogadro number, ρ - density in kg/m^3 assumed as 1000 kg/m^3, h_c - core-core peak, a - lattice parameter, M - molecular weight

$$Z = \frac{\sqrt{3} \times 6.023 \times 10^{23} \times 1000 \times (19.71 \times 10^{-10})^2 \times (3.34 \times 10^{-10})}{2 \times 756.48 \times 10^{-3}} \tag{5}$$

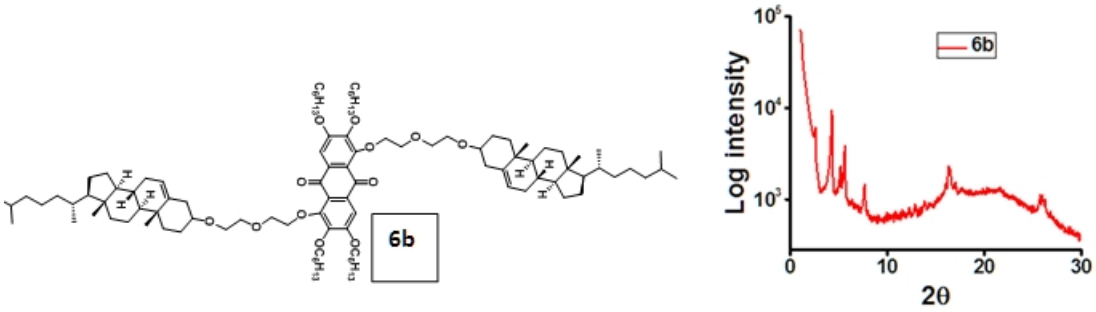
$$\mathbf{Z = 1.04}$$

Based on 'Z' value we proposed the model of compound when they assembled in hexagonal lattice as



2.2 Indexing columnar rectangular lattice (c2mm)

Compound: 6b, Temperature: 40^0C. Molecular weight= $1554.33 \times 10^{-3} kg/mol$



Spacings of observed are as follows:
$d_1 = 34.21\mathring{A}$, $d_2 = 20.74\mathring{A}$, $d_3 = 17.07\mathring{A}$, $d_4 = 15.71\mathring{A}$, $d_5 = 11.55\mathring{A}$, $d_6 = 5.40\mathring{A}$, $d_7 = 5.21\mathring{A}$, $d_8 = 3.43\mathring{A}$ (h_c- core-core peak)

Formula for rectangular lattice:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} \tag{1}$$

The above formula contains two lattice parameters 'a' and 'b'. So we assume two peaks and calculate the values of 'a' and 'b'. Then we will use these values and fit the other peaks.

We assume $d_1 = 34.21\mathring{A}$ as $(2, 0)$ and substituted in the above equation (1)

$$\frac{1}{(34.21)^2} = \left(\frac{2^2}{a^2}\right) + \left(\frac{0^2}{b^2}\right)$$
$$a = 68.42\mathring{A}$$

We assume $d_2 = 20.74\mathring{A}$ as $(1, 1)$ and substitute $a = 68.42\mathring{A}$ in the above equation (1)

$$\frac{1}{(20.74)^2} = \frac{1}{(68.42)^2} + \frac{1}{b^2}$$
$$b = 21.76\mathring{A}$$

We use 'a' and 'b' values with different (h,k) we fit the other peaks.
Example: We substitute (h, k) as $(1, 3)$ and $a = 68.42\mathring{A}$ and $b = 21.76\mathring{A}$

$$\frac{1}{(d^2)} = \left(\frac{1^2}{68.42^2}\right) + \left(\frac{3^2}{21.76^2}\right)$$

$$\frac{1}{(d^2)} = \frac{4}{(30.53)^2} + \frac{9}{(27.42)^2}$$

$$\mathbf{b = 15.74\mathring{A}}$$

We have observed peak corresponding to spacing $15.71\mathring{A}$. So we can index the peak to $(1, 3)$ miller plane. Similarly, we have indexed all the peaks observed into specific miller planes. Further, when we see the values of h, k of all the peaks they follow the condition $h + k = 2n$ which is even. So, the rectangular lattice is of centered in nature.

Table 2: Peaks.

$d_{obs}(\mathring{A})$	$d_{cal}(\mathring{A})$	**Index**
34.21	34.21	20
20.74	19.75	11
17.07	17.10	04
15.71	15.74	13
11.55	11.40	60
5.40	5.44	40
5.21	5.18	04

Further we can calculate other lattice parameters as follows $\mathbf{S_r}$ = **Lattice area:**

$$S_r = ab \tag{2}$$

$$S_r = \text{Lattice area}$$
$$a, b = \text{Lattice parameters}$$

On substituting $a = 68.42\mathring{A}, b = 21.76\mathring{A}$ in equation (2) we can get lattice area as follows

$$S_r = (68.42) \times (21.76)$$
$$S_r = 1488.8192\mathring{A}^2$$

$\mathbf{V_h}$ = **Lattice Volume:**

$$V_r = abh_c \tag{3}$$

$$V_r = (68.42) \times (21.76) \times (3.43)$$
$$V_r = 5106.6498\mathring{A}^3$$

Z = Number of molecules 'Z' occupying single slice of a column

$$Z = \frac{V}{V_m} \tag{4}$$

$$V = \text{Volume of lattice}$$
$$V_m = \text{Volume of molecule}$$

$$V_m = \frac{M}{N_A \times \rho} \tag{5}$$

Where N_A - Avogadro number, ρ - density in kg/m^3 assumed as 1000 kg/m^3, M - molecular weight

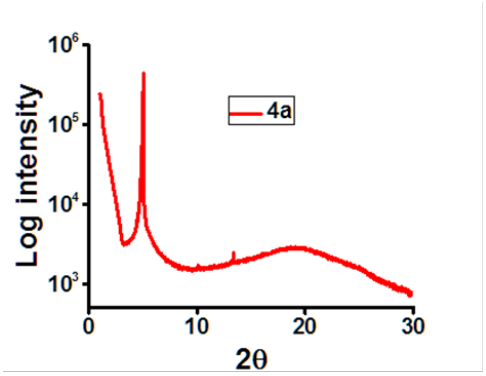
$$Z = \frac{6.023 \times 10^{23} \times 1000 \times (68.42 \times 10^{-10}) \times (21.76 \times 10^{-10}) \times (3.43 \times 10^{-10})}{1554.33 \times 10^{-3}}$$

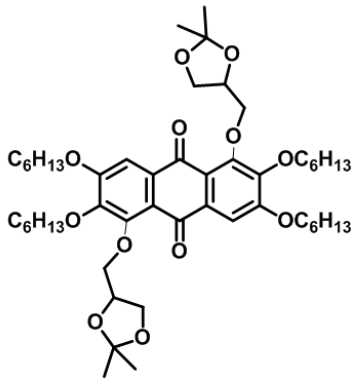
$$\mathbf{Z = 1.98}$$

Based on Z value we proposed the model of compound when they assembled in rectangular lattice as

2.3 Indexing Columnar hexagonal phase

Compound: 4a, Temperature: 130^0C. Molecular weight= $869.13\times10^{-3}kg/mol$





Spacings of observed are as follows:
$d_1 = 17.53\mathring{A}$, $d_2 = 8.76\mathring{A}$, $d_3 = 6.61\mathring{A}$, $d_4 = 4.60\mathring{A}$, $d_5 = 3.59\mathring{A}$ (h_c- core-core peak)

Formula for hexagonal lattice:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) \tag{1}$$

The above formula contains one lattice parameters 'a'.So we assume one peak as (1, 0) and calculate the values of 'a'. Then we will use these values and fit the other peaks. We assume $d_1 = 17.53\mathring{A}$ as $(1, 0)$ and substituted in the above equation (1).

We assume $d_1 = 17.53\mathring{A}$ as $(1, 0)$ and substituted in the above equation (1)

$$\frac{1}{17.53^2} = \frac{4}{3}\left(\frac{1^2+(1*(0))+0^2}{a^2}\right)$$
$$\frac{1}{17.53^2} = \frac{4}{3}\left(\frac{1}{a^2}\right)$$
$$a^2 = \frac{4}{3}(17.53^2)$$
$$a = \frac{2}{\sqrt{3}}(17.53^2)$$
$$a = 20.24\mathring{A}$$

Next step is fitting the other peaks to specific miller planes by taking the calculating value of **'a'**.

Example: We substitute (h.k) as (2, 1) and substituting values of a in the above equation

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{2^2 + (1)(2) + 1^2}{20.24^2}\right)$$
$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{7}{20.24^2}\right)$$
$$d = 6.62\mathring{A}$$

We observed peak corresponding to $d = 6.61\mathring{A}$; so we can index that peak as $(2, 1)$.
Similarly we fit the other small angle peaks and the details are as tabulated as follows.

Table 3: Peaks.

$d_{obs}(\mathring{A})$	$d_{cal}(\mathring{A})$	**Index**
17.53	17.53	10
8.76	8.76	20
6.61	6.62	21

Now the pattern is fitted into hexagonal lattice with lattice parameters $a = 20.24\mathring{A}$

We can calculate the other parameters as follows:

S_h = Lattice area:

$$S_h = a^2 \sin(60^0)$$
$$S_h = \frac{(20.24)^2 \times \sqrt{3}}{2}$$
$$S_h = 354.397\mathring{A}^2$$

V_h = Lattice Volume:

$$V_h = a^2 \sin(60^0) \times h_c$$
$$V_h = (20.24)^2 \times \sin(60^0) \times (3.59)$$
$$V_h = 1240.391\mathring{A}^3$$

Z = Number of molecules 'Z' occupying single slice of a column

$$Z = \frac{V}{V_m} \tag{2}$$

$$V = \text{Volume of lattice}$$
$$V_m = \text{Volume of molecule}$$

$$V_m = \frac{M}{N_A \times \rho} \tag{3}$$

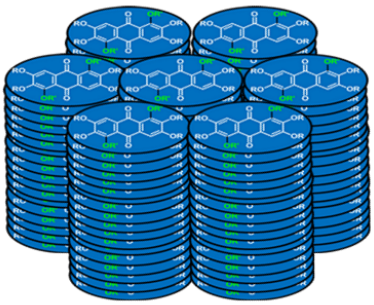
$$Z = \frac{\sqrt{3} N_A \rho a^2 h_c}{2m} \tag{4}$$

Where N_A - Avogadro number, ρ - density in kg/m^3 assumed as 1000 kg/m^3, h_c - core-core peak, a - lattice parameter, M - molecular weight

$$Z = \frac{\sqrt{3} \times 6.023 \times 10^{23} \times 1000 \times (20.24 \times 10^{-10})^2 \times (3.34 \times 10^{-10})}{2 \times 869.13 \times 10^{-3}} \tag{5}$$

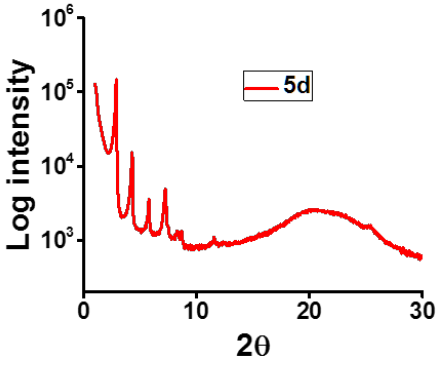
$$\mathbf{Z = 1.02}$$

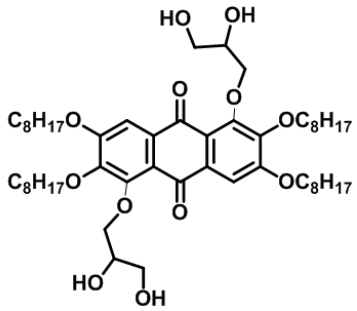
Based on Z value we proposed the model of compound when they assembled in hexagonal lattice as



2.4 Indexing columnar rectangular lattice (p2gg)

Compound: 5d, Temperature: 60^0C. Molecular weight= $901.22 \times 10^{-3} kg/mol$





Spacings of observed are as follows:
$d_1 = 30.53\mathring{A}$, $d_2 = 20.37\mathring{A}$, $d_3 = 15.24\mathring{A}$, $d_4 = 12.17\mathring{A}$, $d_5 = 10.63\mathring{A}$,
$d_6 = 10.18\mathring{A}$, $d_7 = 7.63\mathring{A}$, $d_8 = 4.34\mathring{A}$, $d_9 = 3.51\mathring{A}$ (h_c- core-core peak)

Formula for rectangular lattice:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} \tag{1}$$

The above formula contains two lattice parameters 'a' and 'b'. So we assume two peaks and calculate the values of 'a' and 'b'. Then we will use these values and fit the other peaks.

We assume $d_1 = 30.53\mathring{A}$ as $(1, 0)$ and substituted in the above equation (1)

$$\frac{1}{(30.53)^2} = \frac{1}{a^2} + \frac{0^2}{b^2}$$
$$a = 30.536\mathring{A}$$

We assume $d_2 = 20.37\mathring{A}$ as $(1, 1)$ and substitute $a = 30.536\mathring{A}$ in the above equation (1)

$$\frac{1}{(20.37)^2} = \frac{1}{(30.536)^2} + \frac{1}{b^2}$$
$$b = 27.422\mathring{A}$$

We use 'a' and 'b' values with different (h,k) we fit the other peaks.
Example: We substitute (h, k) as $(2, 3)$ and $a = 30.53\mathring{A}$ and $b = 27.42\mathring{A}$

$$\frac{1}{(d^2)} = \frac{2^2}{(30.53)^2} + \frac{3^2}{(27.42)^2}$$
$$b = 27.422\mathring{A}$$
$$\frac{1}{(d^2)} = \frac{4}{(30.53)^2} + \frac{9}{(27.42)^2}$$

$$\mathbf{d = 7.84\mathring{A}}$$

We have observed peak corresponding to spacing $7.63\mathring{A}$. So we can index the peak to $(1, 3)$ miller plane. Similarly we have indexed all the peaks observed into specific miller planes.

Table 4: Peaks.

$d_{obs}(\mathring{A})$	$d_{cal}(\mathring{A})$	**Index**
30.53	30.53	10
20.37	20.37	11
15.24	15.26	20
12.17	12.50	12
10.63	10.20	22
10.18	10.17	30
7.63	7.84	23

Further we can calculate other lattice parameters as follows

$\mathbf{S_r}$ = Lattice area:

$$S_r = ab \tag{2}$$

$$S_r = \text{Lattice area}$$
$$a, b = \text{Lattice parameters}$$

On substituting $a = 30.53\mathring{A}, b = 27.42\mathring{A}$ in equation (2) we can get lattice area as follows

$$S_r = (30.53) \times (27.42)$$
$$S_r = 837.1326\mathring{A}^2$$

$\mathbf{V_h}$ = Lattice Volume:

$$V_r = abh_c \tag{3}$$

$$V_r = (30.53) \times (27.42) \times (3.51)$$
$$V_r = 5106.6498\mathring{A}^3$$

Z = Number of molecules 'Z' occupying single slice of a column

$$Z = \frac{V}{V_m} \tag{4}$$

V = Volume of lattice

V_m = Volume of molecule

$$V_m = \frac{M}{N_A \times \rho} \tag{5}$$

Where N_A - Avogadro number, ρ - density in kg/m^3 assumed as 1000 kg/m^3, M - molecular weight

$$Z = \frac{6.023 \times 10^{23} \times 1000 \times (30.536 \times 10^{-10}) \times (27.42 \times 10^{-10}) \times (3.51 \times 10^{-10})}{901.22 \times 10^{-3}}$$

$$\mathbf{Z = 2.002}$$

Based on Z value we proposed the model of compound when they assembled in rectangular lattice as