Superlattice configurations in linear chain hydrocarbon binary mixtures – Case of n-$C_{28}H_{58}$: n-C_xH_{2x+2} ($x = 10, 12, 14, 16$)

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Abstract. Powder XRD data of mixtures of title compounds are interpreted in terms of superlattices (SL). It is suggested that SL configurations (orthorhombic–orthorhombic, orthorhombic–monoclinic, monoclinic–monoclinic) are realizable, because of discrete orientational changes in the alignment of molecules of n-$C_{28}H_{58}$ hydrocarbon, through an angle mq, where $m = 1, 2, 3 \ldots$ and angle q has an average value of 3.3°. Supporting literature evidence on the inclinations are discussed.

Keywords. Long-chain alkanes; binary mixtures; superlattices; discrete orientational changes.

1. Introduction

Powder X-ray diffraction (PXRD) studies[1–3] on mixtures of long-chain hydrocarbons show the occurrence of superlattice structures. A PXRD study was made on n-$C_{28}H_{58}$: n-$C_{18}H_{38}$ hydrocarbon-mixture system and a model of superlattice configuration was proposed[4], in terms of orthorhombic–orthorhombic (b_0–b_0), orthorhombic–monoclinic (b_0–b_m) and monoclinic–monoclinic (b_m–b_m) structures of the two layers forming the superlattice phase. With a view to determine the applicability and generality of the (b_0–b_0), (b_0–b_m), (b_m–b_m) superlattice model, further PXRD studies were carried out on four different systems of hydrocarbons. The results of the study are presented in this report.

2. Materials and methods

Linear chain hydrocarbons, the n-octacosane (n-$C_{28}H_{58}$), n-decane (n-$C_{10}H_{22}$), n-dodecane (n-$C_{12}H_{26}$), n-tetradecane (n-$C_{14}H_{30}$), and n-hexadecane (n-$C_{16}H_{34}$) were employed in the present study (for brevity the compounds are referred to as: C28, C10, C12, C14 and C16 respectively). All the compounds were from Fluka (Switzerland) with purity >99%. Mixtures of C28 : C10. C28 : C12, C28 : C14 and C28 : C16 were

prepared in molar ratios (MR) and examined by the PXRD method. There were five samples in each system, with different MR values. PXRD patterns at ambient temperature were recorded on a computer-interfaced Philips powder X-ray Diffractometer, type PW1710, at 25 mA and 40 kV, using CoKa^2 radiation (1.79285 Å). PXRD patterns shown in figure 1 are representative of the diffraction patterns recorded in case of different binary mixtures.
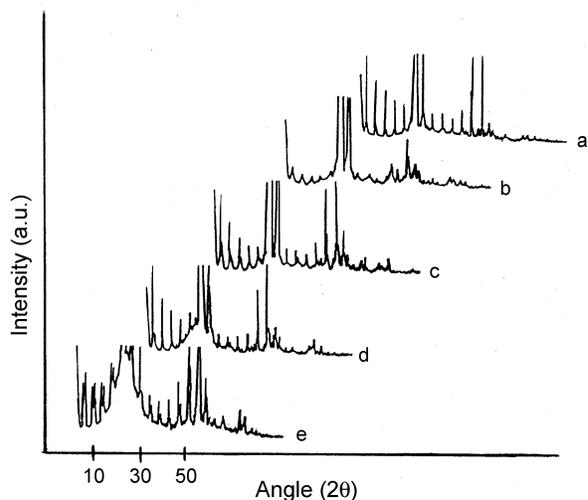
Figure 1. PXRD patterns of C28 : C10 binary mixtures; MR values: (a) 1.9067; (b) 1.5876; (c) 0.9962; (d) 0.6254; (e) 0.2746.

*For correspondence

No	pure C28 (refs 6, 7) b_0	b_m	MR	C28 : C10 d	I	MR	C28 : C12 d	I	MR	C28 : C14 d	I	MR	C28 : C16 d	I
1	37·4065	33·2104		14·6206	1475		14·3477	1945		10·5827	664		10·9930	557
2	18·7032	16·6052		10·8289	1303		10·9265	1892		10·2636	209		10·3074	278
3	12·4688	11·0701	a	8·2078	847	a	8·2230	1260	a	8·0293	373	a	10·0514	206
4	9·3516	8·3026		6·5802	697		6·5924	1011		7·7314	84		8·2642	328
5	7·4813	6·6420		5·4988	595		6·4302	548		6·4784	206		7·7947	185
1				10·8728	339		14·4297	2061		11·0235	1314		10·9848	1986
2				10·1613	296		10·9265	773		10·0559	112		10·7507	643
3			b	8·1549	207	b	10·1613	590	b	8·2785	740	b	10·1434	206
4				7·8205	177		8·2306	475		7·8571	68		8·2583	1354
5				6·5802	161		7·7657	369		6·6265	462		8·1312	361
1				10·8661	999		10·9198	1082		11·0501	1287		10·9768	2247
2				10·3212	586		10·1671	361		10·3275	301		10·1148	82
3			c	8·1850	681	c	8·2192	762	c	8·2877	827	c	8·2554	1442
4				7·8447	317		7·7794	266		7·8730	210		7·7036	32
5				7·6223	207		6·5924	630		6·6319	679		6·6117	985
1				14·5724	1560		10·9198	524		11·0161	890		10·9930	1099
2				10·8595	1043		10·2082	335		10·1582	417		10·1086	267
3			d	8·2116	980	d	8·2306	339	d	8·2754	541	d	8·2591	746
4				6·5753	620		7·8067	225		7·7855	287		7·7659	180
5				5·5206	659		6·6022	250		6·6263	417		7·6501	120
1				14·2897	2247		14·3306	1137		11·0000	1851		10·9876	694
2				10·8795	870		13·7798	1195		10·5351	440		10·2666	489
3			e	10·0631	967	e	10·9276	1073	e	10·2683	406	e	10·0898	552
4				8·2078	812		10·4974	218		8·2734	2078		8·2546	499
5				7·7488	853		8·2266	803		7·8508	360		7·8604	406

Molar ratios (MR) of the binary mixtures

	MR values				
Mixture	a	b	c	d	e
C28 : C10	1·9067	1·5876	0·9962	0·6254	0·2746
C28 : C12	1·9247	1·4005	1·0054	0·5997	0·1991
C28 : C14	2·0350	1·5870	0·9859	0·4872	0·2410
C28 : C16	1·9884	1·4729	1·0172	0·5152	0·2382

The d-values of peaks in the PXRD patterns of all the samples were estimated (while taking the intensities into considerations for indexing purpose) and compared with the long spacings of C28 in orthorhombic and monoclinic phases;[5,6] the phases are denoted by b_0 and b_m respectively. In the majority of cases, no matching was observed (table 1). PXRD data summed up by Robertson[7] showed that the hydrocarbons C10 and C16 have long-spacings 13·4 Å and 20·9 Å respectively, corresponding to the triclinic phase; C11 and C15 have long-spacings 15·9 Å and 21·0 Å respectively, corresponding to b_0 phase (characteristic to odd carbon-number linear chain hydrocarbons[8]).

In order to account for the observed d_{001} values and justify the formation of superlattices, C10, C12, C14 and C16 hydrocarbons are assumed to occur in the b_m and b_0 phases (in view of the low melting points, these hydrocarbons cannot form the close-packed triclinic structures at room temperature); the lattice parameters a and b, of different short chain hydrocarbons (C10–C16) can then have comparable values with those of C28. (The cell parameters a and b of linear chain hydrocarbons, either in b_m or b_0 phases
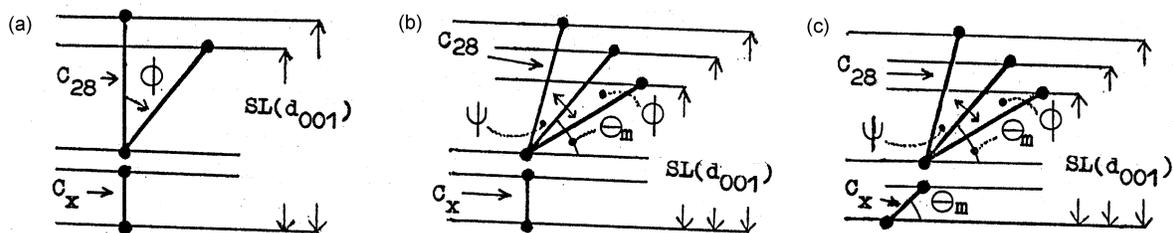
Figure 2. Superlattices in C28 : Cx (x = 10, 12, 14, 16) mixture systems. (**a**) b_0–b_0 (C28 and Cx are in the b_0 phase): Fluctuations in the orientation of C28 (from the vertical mode or b_0 phase) can lead to different b_0–b_0 forms; (**b**) b_0–b_m (Cx in b_0 phase; C28 with different orientations in b_m phase). Clockwise rotation = angle **f**; anti-clockwise rotation = angle **y**. (**c**) b_m–b_m (Cx in b phase; C28 with different orientations in b_m phase).

have almost constant values and are independent of chain length.[8,9])

3. Results and discussion

The peaks that did not match with the d-values of b_m and b_0 phases of C28 were identified in the PXRD data of each sample (table 1). Such selected d-values were compared with the d-values of three categories (figure 2) of superlattice models (b_0–b_0), (b_0–b_m), and (b_m–b_m). The d-values of the first 20 peaks of the PXRD patterns of each sample were projected as d_{001} values (by multiplying them with suitable integers) and such d-values that matched the d-values of any superlattice configurations were picked up, tabulated and the averages calculated. The corresponding probable angles of inclinations (**f** or **y**: figure 2) of the molecules were estimated. These data are shown in tables 2–5. The meaning of angles **f** and **y** are as follows. Let a C28 molecule be inclined through angle q_m with respect to lower basal plane (figure 2b). In the stable monoclinic form,[5] $q_m = 60.44°$. Let the incli- nation of C28 molecule fluctuate[4] around q_m. If the change in the orientation of molecule is in the clockwise direction (from q_m position), then the change in the angle is denoted by **f**; in case of anticlockwise rota- tion, it is denoted by **y**.

Similar to the situation seen in case of the C28– C18 system,[4] the angle with value = 3.3° was seen to play an important role in the present case also (tables 2–5). The dispersion in the values of the estimated angle q (q = **f**/u = **y**/v; where u and v are integers) in case of five systems of hydrocarbon mixtures is shown in figure 3; the average of these values is 3.3°. After noticing such persistent and constant behav- iour in the angles, angles which were not the integer multiples of 3.3°, and those which needed large integer

multipliers, were not taken into consideration and the corresponding superlattices (involving such angles) were assumed to be non-occurring (or non realizable).

The present authors believe that tables 2–5 and figure 3 are ample evidence for the existence of dis- crete molecular orientational (or inclinational) changes in long-chain hydrocarbon systems and that they are explicitly manifested in the presence of shorter chain components, probably due to the greater freedom per- mitted by the environment (owing to the restricted fluidity of the shorter chain components at the time of crystallization).

3.1 *The angle of value = 3.3°*

Through the following considerations, an attempt is made to explain the significance of the angle of value = 3.3°.

Let the initial state of molecules (for example AB) be vertical with respect to the basal plane X_1X_2 (normal to the plane of the diagram; figure 4a). In order to obtain an inclined structure (such as mono- clinic), let the plane X_1X_2 be pushed up through an angle q and labeled as $X_1'X_2$ (figure 4b). Now, with the plane X_1X_2, the molecules are also pushed up, through different distances. However, with respect to the basal plane P_b', the overall structure is not an inclined structure. In order to make the structure an inclined one, each molecule has to be pulled down, through different distances (for example molecule AB through a distance h_i), so that the basal plane P_b', is once again parallel to the initial plane P_b (figure 4c). In case of b_m phase[7] of C28, the angle **a** = 119.56° (so that q = 29.56°) and the lattice spacing (b) is 7.42 Å. It turns out that the value of h_i (= $b\sin q$) = 3.66 Å (figure 4d). This value divided by 1.27 Å (the projected bond length: b_{pl}) gives a value

Table 2.   C28 : C10 Superlattice configurations.

Parameter	$(\boldsymbol{b}_0)$ a	Observed b	c	d
(i) *Superlattice type:* $(\boldsymbol{b}_0\text{–}\boldsymbol{b}_0)$				
d_{001} (Å)	52·72	51·6331	50·4275	49·450
f	–	15·22	21·07	25·23
y	–	–	–	–
Integer multiplier	–	5	7	8
q	–	3·04	3·01	3·15
Resulting value	–	15·22	21·07	25·23

Parameter	$(\boldsymbol{b}_m)$ a	Observed b	c	d
(ii) *Superlattice type:* $(\boldsymbol{b}_0\text{–}\boldsymbol{b}_m)$				
d_{001} (Å)	48·256	47·2716	49·450	50·4275
f	–	3·19	–	–
y	–	–	4·33*	8·49*
Integer multiplier	–	1	–	–
q	–	3·19	–	–
Resulting value	–	3·19	–	–

Parameter	$(\boldsymbol{b}_m\text{–}\boldsymbol{b}_m)$ a	Observed b	c	d	e
(iii) *Superlattice type:* $(\boldsymbol{b}_m\text{–}\boldsymbol{b}_m)$					
d_{001} (Å)	46·768	47·416	45·6275	44·2780	43·552
f	–	–	3·67	7·58	9·545
y	–	1·75*	–	–	–
Integer multiplier	–	–	1	2	3
q	–	–	3·67	3·75	3·18
Resulting value	–	–	3·67	7·5	9·54

*Less probable
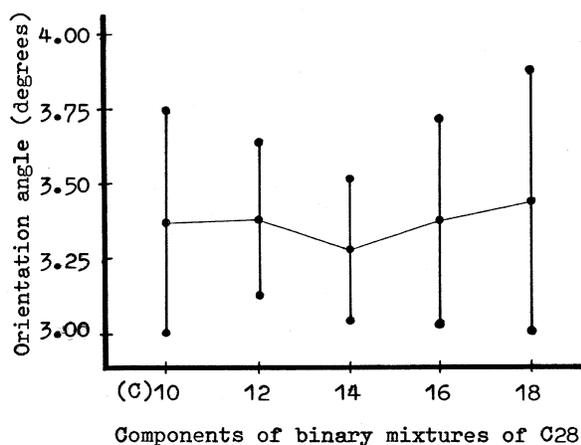
Figure 3. Extent of dispersion in the angle of orientation q (of C28 molecule), in case of binary mixtures of C28 with different shorter chain hydrocarbons.

of 2·88. It means that, in case of monoclinic structure, one C28 molecule slides through 2·88 bond lengths (b_{pl}), with respect to its neighbouring C28 molecule (placed towards the reference vertex of the triangle). Now if the angle $q = 3\cdot3°$, then the displacement, $h_i = 0\cdot42$ Å. If $3\cdot3°$ is taken to represent the smallest angular displacement, through which one C28 molecule slides (or shifts) with respect to its neighbour, then the ratio $b_{pl}/0\cdot42 = 3\cdot02$. It indicates that there are three such steps along one b_{pl} distance (1·27 Å). Probably, each step may indicate a (shallow) minimum.

In view of this argument, the value of h_i obtained in case of C28 (3·66 Å) has to be the result of a certain minimum distance multiplied by an integer. It is seen that $3\cdot66/9 = 0\cdot4066$ and it differs slightly from $0\cdot42$. If $h_i = 0\cdot4066$ is used in the equation

Table 3. C28 : C12 Superlattice configuration.

Parameter	Observed (b_0) a	b	c	d
(i) *Superlattice type:* (b_0–b_0)				
d_{001} (Å)	55·26	54·5526	53·3685	52·6758
f	–	11·33	19·12[+]	22·83[+]
y	–	–	–	–
Integer multiplier	–	3	6	7
q	–	3·78*	3·185	3·27
Resulting value	–	11·34	19·21	22·87

Parameter	Observed a	b	c	d	(b_m) e	f	g	h
(ii) *Superlattice type:* (b_0–b_m)								
d_{001} (A)	54·5528	53·3685	52·6758	51·5737	50·6057	49·3556	43·4557	41·5714
f	–	–	–	–	–	4·57*	18·82	23·51*
y	18·23	10·44[+]	6·73[+]	3·40	–	–	–	–
Integer multiplier	5	3	2	1	–	–	6	7
q	3·64	3·47	3·35	3·40	–	–	3·14	3·358
Resulting value	18·2	10·41	6·7	3·40	–	–	18·84	23·506

Parameter	Observed (b_m–b_m) a	b	c	d
(iii) *Superlattice type:* (b_m–b_m)				
d_{001} (A)	48·9783	43·4557	42·6739	41·5714
f	–	15·31*	17·13	19·60
y	–	–	–	–
Integer multiplier	–	4	5	6
q	–	3·83	3·43	3·27
Resulting value	–	15·32	17·15	19·62

*Less probable; [+]have equal chances
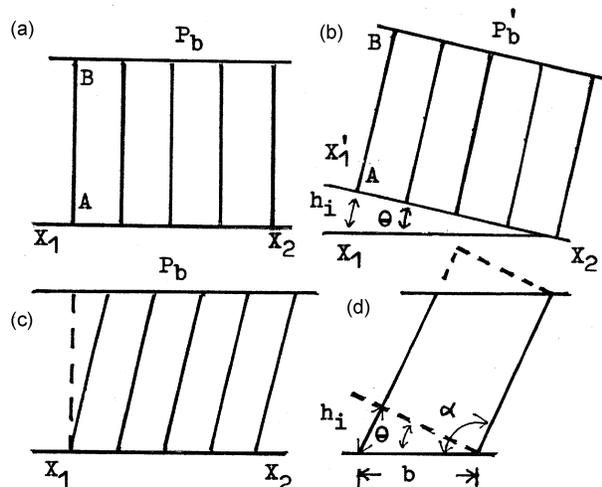
Figure 4. (**a**)–(**c**) Modifications of vertical structure to inclined structure. (**d**) Minimum displacement and related angle: $b = 7·42$ Å in b_m phase of C28.

$h_i = b\sin q$, then $q = 3·141°$, which is not very different from 3·3°. However, the distribution of angle q (figure 5) shows a peak centred about 3·15° and seems to confirm the above point of view. Small variations in the orientations of shorter chain hydrocarbons (C10 etc.), which lead to modifications in the lamellar thickness, are sufficient to cause fluctuations in the value of q (leading to the average value 3·3°), as noticed in figure 3. Strobl[10] proposed a flip-flop mechanism that could promote a screw-like motion of the hydrocarbon chain in a crystal matrix. It appears that the energy minima that are required in such a mechanism may be similar to the minima that are considered here. It may be noted that the sliding that is assumed to take place here is virtual, since superlattices are formed during the crystallization process itself. The molecules are stacked during the crystallization in a way that it may appear as if sliding of each molecule with respect to its

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Table 4. C28 : C14 superlattice configurations.

	Observed				
Parameter	$(\boldsymbol{b}_0)$ a	b	c	d	e
(i) *Superlattice type:* $(\boldsymbol{b}_0–\boldsymbol{b}_0)$					
d_{001} (Å)	57·8	56·5439	55·2947	54·5749	53·4162
f	–	16·26	21·12	24·24	29·29
y	–	–	–	–	–
Integer multiplier	–	5	6	7	9
q	–	3·25	3·52	3·46	3·25
Resulting value	–	16·25	21·12	24·22	29·25

	Observed				
Parameter	$(\boldsymbol{b}_m)$ a	b	c	d	e
(ii) *Superlattice type:* $(\boldsymbol{b}_0–\boldsymbol{b}_m)$					
d_{001} (Å)	53·33	53·4162	52·4147	51·4483	50·2795
f	–	–	3·26	6·15	9·39
y	–	0·27	–	–	–
Integer multiplier	–	–	1	2	3
q	–	–	3·26	3·05	3·13
Resulting value	–	–	3·26	6·1	9·39

	Observed				
Parameter	$(\boldsymbol{b}_m–\boldsymbol{b}_m)$ a	b	c	d	e
(iii) *Superlattice type:* $(\boldsymbol{b}_m–\boldsymbol{b}_m)$					
d_{001} (Å)	51·1877	51·4483	50·5311	52·4147	53·4162
f	–	0·89*	1·91*	–	–
y	–	–	–	4·47*	8·70*
Integer multiplier	–	–	–	–	3
q	–	–	–	–	2·9
Resulting value	–	–	–	–	8·7

*Less probable
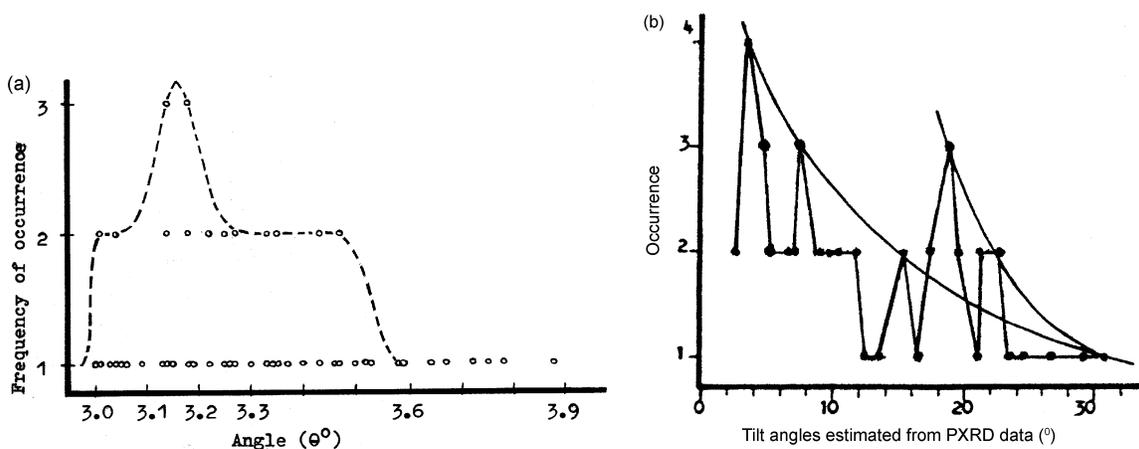
Figure 5. (**a**) Distribution of the value of angle q, in case of different binary mixtures of C28 : Cx (x = 10, 12, 14, 16, 18). (**b**) Exponential nature of distribution angles.

Table 5. C28 : C16 superlattice configuration.

Parameter	(b_0) a	b	c	d	e	f	g			
				Observed						

(i) *Superlattice type: (b_0–b_0)*

Parameter	(b_0) a	b	c	d	e	f	g
d_{001} (Å)	60·34	60·54	59·5982	58·51	57·7273	56·6065	55·4829
f	–	–	11·94*	18·80	22·51	26·97	30·86
y	–	–	–	–	–	–	–
Integer multiplier	–	–	3	6	7	8	9
q	–	–	3·98	3·14	3·22	3·37[+]	3·43
Resulting value	–	–	11·94	18·84	22·54	26·96	30·87

(ii) *Superlattice type: (b_0–b_m)*   (Observed)

Parameter	(b_m) a	b	c	d	e	f	g	h	i	j
d_{001} (Å)	55·876	55·4829	54·80	53·5288	52·5136	51·633	59·5982	58·51	57·7273	56·6065
f	–	1·31*	3·47	7·17	9·92	12·19	–	–	–	–
y	–	–	–	–	–	–	17·62	10·76	7·05	2·99*
Integer multiplier	–	–	1	2	3	4	5	3	2	–
q	–	–	3·47	3·58	3·3	3·04	3·53	3·59*	3·5	–
Resulting value	–	–	3·47	7·16	9·99	12·16	17·65	10·77	7·0	–

(iii) *Superlattice type: (b_m–b_m)*   (Observed)

Parameter	(b_m–b_m) a	b	c	d	e	f	g
d_{001} (Å)	53·39	53·5288	52·5136	51·6330	54·6096	55·4829	56·6065
f	–	–	2·87*	5·515*	–	–	–
y	–	0·65*	–	–	5·11*	7·45	13·37
Integer multiplier	–	–	–	–	–	2	4
q	–	–	–	–	–	3·72*	3·34[+]
Resulting value	–	–	–	–	–	7·4	13·36

*Less probable; [+]have equal chances
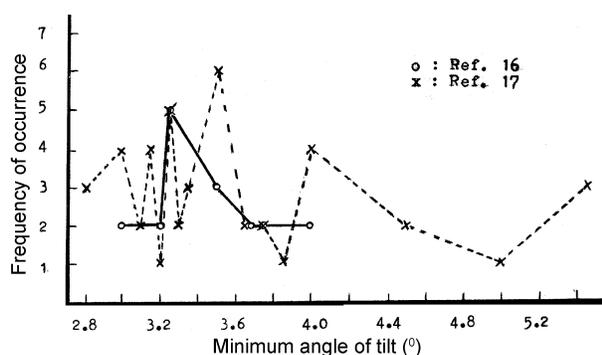
Figure 6.   Frequency of occurrence of different tilt angles; data were taken from refs 16 and 17.

neighbour, is the reason for the occurrence of such structure.

In our opinion, the present case is close to the situation that occurs during the crystallization of C28 in the usual b_m phase, with the difference that each methyl group of the longer chain slips into neighbouring shallow minimum energy positions that are found on either side of deeper minima. It appears that virtual sliding may also be envisaged as due to virtual phase transitions. It is not possible to claim, based on the present limited PXRD data, that such slips into neighbouring shallow minima may be due to quantum fluctuations. (However, others reported such quantum fluctuations in the positions of molecules, which were not allowed classically, in the case of other compounds.[11])

3.2   *Some supporting evidence*

Since any proof in support of the hypothesis about differential inclinations of long-chain molecules can establish the validity of the model of super lattices

Table 6. Angle of inclination (DPPC mixtures) (ref. [11]).

System	$T(°C)$	Pressure Π(mN/m)	Inclination (tilt) angle q	q as integer multiple (present work)
DPPC : PA (3 : 1)	30	15	25·5°	3·1875 × 8 = 25·5
DPPC : PA (1 : 1)	30	15	22·1°	3·157 × 7 = 22·1
DPPC : PA (1 : 2)	30	15	19·3°	3·22 × 6 = 19·32
DPPC : PA (1 : 4)	30	15	19·1°	3·18 × 6 = 19·08
DPPC : PA (3 : 1)	30	40	21·3°	3·55 × 6 = 21·3
DPPC : PA (1 : 1)	30	40	< 5° (?)	≈ 3·3
DPPC : PA (1 : 2)	30	40	< 5° (?)	≈ 3·3
DPPC : PA (1 : 4)	30	40	< 5° (?)	≈ 3·3
DPPC : HD (3 : 1)	30	40	25·3°	3·614 × 7 = 25·29
DPPC : HD (1 : 1)	30	40	20·8°	3·47 × 6 = 20·82
DPPC : HD (1 : 2)	30	40	17·9°	3·58 × 5 = 17·9
DPPC : HD (1 : 4)	30	40	≤ 5·0° (?)	≈ 3·3

PA = Palmitic acid; HD = Hexadecanol; DPPC = 1,2-dipalmitoyl-sn-glycero-3-phosphatidylcholine
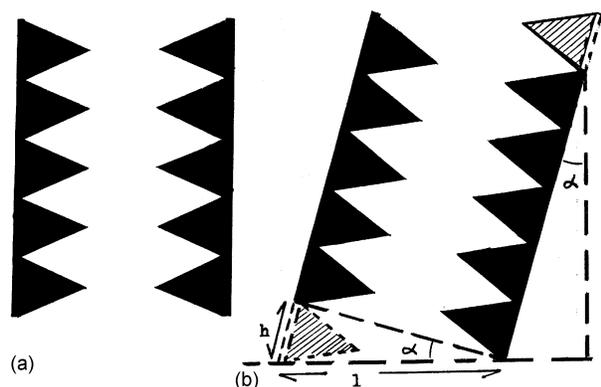
Figure 7. A schematic representation of vertical and tilted molecular chains: (**a**) saw teeth model; (**b**) relation between a and h.

in the binary systems of hydrocarbons, we surveyed the scenario of monolayer organizations studied by other researchers. The data seem to be in favour of our findings. Such supporting information and the relevant concepts are discussed in this section.

The DPPC : PA system studied by Lee *et al*[12] showed different angles of inclination q at different compositions. We found that these q values can be expressed as integer multiples of a value around 3° (table 6, last column). An angle that is very close to this value was obtained in case of super lattice configurations.[9,10] We notice similar behaviour in some of single-component systems investigated by Peters *et al*,[13] Bohm *et al*,[14] Brezesinski *et al*[15] and Levison *et al*[16] as shown in table 7 (last column).

Jang and Miller[17] measured the tilt angles of stearate molecules (present in the form of Langmuir–Blodgett films and self-assembled mono layers) at fluorite surfaces, by employing polarized Fourier transform infrared internal reflection spectroscopy. Lautz and Fischer[18] made studies on Langmuir monolayers of octadecanol, employing Brewster angle auto correlation spectroscopy. The tilt (or inclination) angles reported (tables 3 and 4 of ref. 17; figure 4 of ref. 18) are given as the product of an angle (≈ 3·3°) and an integer (n). The results are shown in figure 6. It may be observed that the distribution of angle of inclination that we derived from PXRD analysis (figure 5) is close to the situation presented in figure 6. Further, the tilt angles observed in case of behenic acid[19] were q = 21 to 29°, and in case of calcium dibehenate[20] were: q = 3 to 13°. It may be noted that 3° is the lowest[20] detected value.

In the case of octodecanol (around the triple point), a jump in the tilt angle was reported[17] from 3 to 8° and 4 to 7·5° for small changes in temperature i.e., 0·2°C and 0·1°C respectively (at two different temperatures). It is quite interesting to note that figure 4, 5 and 6 of ref. 18 showed complete absence of tilt in the range 0–3°. This result coincides with our observation that the first shallow minimum from the vertical (to the basal plane) is about 3·3°.

Orientational fluctuations of molecules are related to phase transitions in Langmuir mono layers[18]. Teer *et al*[21] and Shih *et al*[22] interpreted different phase transitions occurring in the mono layers in terms of interactions of the head groups and of aliphatic–aliphatic

Table 7. Angle of inclinations (some single component systems).

System	Ref.	T(°C)	Pressure Π(mN/m)	Inclination (tilt) angle q	q as integer multiple (present work)
DPG	12	20	5	14	$3 \cdot 5 \times 4 = 14$
		20	40	≤ 2 (?)	–
L-DPPE	13	20	10	24	$3 \cdot 44 \times 7 = 24 \cdot 08$
		20	38	0	–
DL-DPPE		20	10	22	$3 \cdot 15 \times 7 = 22 \cdot 05$
		20	38	0	–
L-DPPC	14	15	30	30	$3 \cdot 34 \times 9 = 30 \cdot 06$
		15	45	25	$3 \cdot 58 X7 = 25 \cdot 06$
DL-DPPC		15	30	27	$3 \cdot 38 \times 8 = 27 \cdot 04$
		15	45	25	$3 \cdot 58 \times 7 = 25 \cdot 06$
D-DPPC	15	20	27	29	$3 \cdot 29 \times 9 = 29 \cdot 07$
		20	41	25	$3 \cdot 58 \times 7 = 25 \cdot 06$
D-DPPC/		20	20	14	$3 \cdot 5 \times 4 = 14$
PLA$_2$		20	30	8(?)	–

DPG = 1,2-dipalmitoyl-sn-glycerol; DPPE = dipalmitoyl phosphatidyl ethanolamine; DPPC = 1,2-dipalmitoyl-sn-glycero-3-phophatidylcholine. PLA$_2$ = phospholipase A$_2$; L = levorotatory; D = dextrorotatory; DL = racemic mixture

chains. Phase transitions result from instabilities caused by competition between intermolecular interactions.[18] Luty and Eckhardt[23] developed a microscopic theory of orientational and structural instabilities associated with Langmuir mono layers, while considering a mechanism for coupling the lattice strain to molecular tilt and felt that a delicate balance between the potential and chain interactions dictates the molecular tilting characteristics. The authors[23] point out that the soft non-covalent interactions between molecular over-layers are due to shallow potential functions and cause the mode of epitaxy to be very sensitive to competition between the intermolecular interactions. The molecules relax to such orientations, where the potential energy is a minimum[24] (and also coincident configurations are at optimum). In this context, we wish to compare two adjacent hydrocarbon molecules (in a layer) with two saws (having identical triangular teeth) facing each other (figure 7a). Let the configuration be identified as one having minimum potential energy. When the saws are tilted to one side (in the same plane that contains them), then the teeth configuration is identical to the initial (minimum potential energy) one for a particular value of a, given by $\sin^{-1}(h/l)$. Since h is the width of each tooth (at its base; see figure 7b) the above expression may be written as $a = \sin^{-1}(nh/l)$. Since for small values of a, $\sin\alpha \approx a$, it may be written that $a = nh/l$. Or if $h/l = a_0$, then $a = na_0$, where $a_0 \approx 3 \cdot 3°$, as shown by the simple reasoning put forth in the earlier discussion (§3). We believe that it is this an-

gle that is manifested in inclinations (or tilt) of all aliphatic chains. We also noticed that different inclinations might exit in the super lattices of the same (binary) system. In this context, it may be recalled that Daughty *et al*[25] noticed increased tilt of molecules (with surface normal) with increasing numbers of layers (in case of an azo dye chromophore in zirconium phosphate–phosphonate) and attribute the trend to improved packing in lower layers upon deposition of additional epilayers.

4. Conclusions

Variability of the angle of inclination (q) in mono layer systems and the emergence of the $\langle q \rangle \approx 3 \cdot 3°$ and its very close proximity to the value that we noticed based on PXRD studies, indicates the possible validity of the model of superlattices that is proposed. SAXS and SANS investigations are planned to obtain greater insight into the superlattice structures of binary mixtures of hydrocarbons.

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References

1. Shashikanth P B and Prasad P B V 1999 *Bull. Mater. Sci.* **22** 65
2. Shashikanth P B and Prasad P B V 2001 *Cryst. Res. Technol.* **36** 327
3. (a) Shashikanth P B and Prasad P B V 2001 *Proc. Indian Acad.* (*Chem. Sci.*) **113** 109; (b) Shashikanth P B and Prasad P B V 2003 *Proc. Indian Acad.* (*Chem. Sci.*) **15** 67
4. Neelima P, Shashikanth P B and Prasad P B V 2004 *14th LAWPSP* (*Lubricants, Additives, Waxes and Petroleum Specialty Products*) *Symposium*, Mumbai, vol. 14, pp. W-02; 1–4
5. Aquilano D 1997 *J. Cryst. Growth* **37** 215
6. Broadhurst M J 1962 *J. Res. Nat. Bur. Stand.* **A66** 241
7. Robertson J M 1953 *Organic crystals and molecules* (Ithaca, NY: Cornell University Press) pp 167, 169
8. Boistelle R 1980 in *Current topics in materials science* (ed.) E Kaldis (Amsterdam: North-Holland) vol 4
9. Bunn C W and Alcock T C 1945 *Trans. Faraday Soc.* **41** 317
10. Stroble G R 1977 *J. Polym. Sci. Polym. Symp.* **59** 121
11. Colmenero J, Mukhopadhyay R, Alegria A and Frick B 1998 *Phys. Rev. Lett.* **80** 2350
12. Lee K Y C, Gopal A, Von Nahmen A, Zasadzinski J A, Majewski J, Smith G S, Howes P B and Kjaer K 2002 *J. Chem. Phys.* **116** 774
13. Robertson M, Peters G H, Toxavaerd S, Larsen N B, Bjørnholm T, Schaumburg K and Kjaer K 1995 *Nature*, *Struct. Biol.* **2** 395
14. Bohm C, Mohwald H, Leiserwitz L, Als-Nielsen J and Kjaer K 1993 *Biophys. J.* **64** 553
15. Brezesinski G, Dietrich A, Struth B and Mohwald H 1995 *Chem. Phys. Lipids* **76** 145
16. Dahmen-Levison U, Brezesinski G and Mohwald H 1998 *Thin Solid Films* **327** 616
17. Jang W H and Miller J D 1995 *J. Phys. Chem.* **99** 10272
18. Lautz C and Fischer T F 1997 *J. Phys. Chem.* **B101** 8790
19. Charych D H and Bednarski M D 1992 *MRS Bull.* **11** 61
20. Maoz R and Sagiv J 1984 *J. Colloid Intreface Sci.* **100** 465
21. Teer E, Knobler C M, Kautz C, Wurlitzer S, Kildea J and Fischer T M 1997 *J. Chem. Phys.* **106** 1913
22. Shih M C, Durbin M K, Malik A and Dutta P 1994 *J. Phys. Chem.* **101** 9132
23. Lutty T and Eckhardt C J 1995 *J. Phys. Chem.* **99** 8872
24. Simpson G J and Rowlen K L 1999 *J. Phys. Chem.* **B103** 1525
25. Doughty S K, Simpson G J and Rowlen K L 1998 *J. Am. Chem. Soc.* **120** 7997