$$F=2\Sigma f\cos 2\pi(hX+lZ)$$
$$\times[\cos 2\pi kY+i\sin 2\pi kY]$$
$$2\Sigma f\sin 2\pi(hX+lZ)$$
$$\times[-\sin 2\pi kY+i\cos 2\pi kY]=F\,,$$

which may be summarized by saying that if $\mathcal{F}$ is the geometrical structure factor for any k, and $\mathcal{G}$ is the geometrical structure factor calculated as if the parity of k were opposite to its true value, then for odd or even k

$$F=\Sigma f\mathcal{F},\quad (q_x+q'_x)=\Sigma xf\mathcal{G},\quad (q_x-q'_x)=\Sigma xf\mathcal{F},$$
$$(q_y-q'_y)=\Sigma yf\mathcal{G}\,,\ (q_z+q'_z)=\Sigma zf\mathcal{G}\,,\ (q_z-q'_z)=\Sigma zf\mathcal{F}\,.$$

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The Modes of Hydrocarbon Chain Packing

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The symmetry of a saturated hydrocarbon chain in extended *trans* configuration and indeterminate length is reviewed. A uniform row of such chains is defined so that the chain axes are parallel, coplanar and equidistant, and that the planes of the carbon atom zigzags of all the chains are parallel. The symmetry within such a row is stated, and all the possible symmetry relations between such rows when they are parallel, adjacent and identical is investigated. Making reasonable assumptions concerning dimensions, packing efficiency and stability, four different relations are found when the chain axes of neighboring rows are parallel, and seven different relations are found when the axes are not parallel. All the possible chain-packing subcells that could be made up of such rows are constructed, subject to the limitations that the subcells extend over no more than two rows, and that the same symmetry relation exists between all adjacent rows. Ten different subcells are thus generated when all the chain axes are parallel, and thirty-one when they are not. It is found that the eight reported chain-packing modes are all included among these. It is shown that the symmetry of three of the six reported subcells in which the chain axes are all parallel is higher than was previously assumed. An attempt to relate the frequency of occurrence of the various subcells to the van der Waals energy as calculated by the Salem method failed.

Introduction

Eight hydrocarbon-chain packing arrangements have been described from single-crystal structure determinations, six of which have all the chain axes parallel and the remaining two have the chain axes of alternate layers crossed. Another packing arrangement, the hexagonal, has been postulated from powder data but its structure is unknown. Still another, the 'ideal', has had its structure described in detail (Kitaigorodskii, 1961) but it has never been observed.

The purpose of this communication is to relate the described modes by generating them from symmetry operations between uniform rows of chains. This approach not only leads to simple classification of all the known packing modes, but it may indicate what new ones might be found.

General considerations

The lateral van der Waals forces between hydrocarbon chains within a crystal structure are rarely so strong, compared with end-packing forces, as to make the effect of the end packing completely negligible. This effect becomes evident when the total crystal symmetry is lower than the chain packing symmetry. Conversely, these forces are rarely so weak in comparison with the forces in other parts of the structure that the chains are not able to assume a uniform, compact, stable and

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precise configuration. (Liquid crystalline structures probably retain much of the compactness and gross order of the chain packing but lose the stability of a particular precise configuration.) We shall here be concerned with the variety of precise configurations hydrocarbon chains take within crystal structures. Though the forces at the ends of the chains usually determine the configuration, we shall neglect these end effects in one respect: when two parallel chains fit together in a particular configuration, the shear that may be induced by end-packing forces may cause the convex parts along one chain not to fit exactly into the concave parts along the other chain by up to several tenths of 1Å. This effect we shall ignore, just as, when discussing chain packing in a crystal structure, one usually ignores the distortions in this packing which often occur close to the chain ends.

Since each chain-packing mode is described in terms of a subcell which represents the local interrelationships between hydrocarbon chains in a structure, and ignores chain ends and groups attached thereon, we shall here for convenience assume that the chains are infinitely long. The concern here is only with saturated chains, but this also includes the saturated portions of chains between double bonds, cyclopropane rings, and the like. In the crystal structures solved to date, saturated portions of chains have generally been found to be in the extended *trans* configuration, with occasionally some minor twisting to satisfy end-group packing requirements. In this discussion we shall assume strict *trans* configuration so that one plane goes through all the carbon atoms in a chain; this will be called the *chain zigzag plane*.

The symmetry of a hydrocarbon chain

The hydrocarbon chain itself has mirror symmetry about a plane perpendicular to the chain axis and going through each atom in a CH_2 group. The chain axis is itself a twofold screw axis. Two kinds of twofold rotation axis exist perpendicular to the chain axis: one parallel to the plane of the chain zigzag going through a carbon atom, and one perpendicular to the chain zigzag going through the point halfway between two carbon atoms. This latter point is on the chain axis and is a center of symmetry. There is a translational symmetry vector along the chain axis between alternate CH_2 groups. One may consider adjacent CH_2 groups as being related by a glide down the chain axis perpendicular to the plane which includes the chain axis and is perpendicular to the plane of the chain zigzag.

The symmetry of a uniform row of chains

Let us define a *uniform row* of chains as a row of chains in which the chain axes are all parallel and equidistant within one plane which we shall call the *row plane*, and in which the planes of the chain zigzags are all parallel. This row plane will include two translational symmetry vectors: one along the chain axes, which is traditionally called **c**, and one between the chains, which we shall call **b**. If, as previously discussed, we neglect the shear due to end effects when the crystal symmetry is lower than the chain packing symmetry, **b** and **c** would be orthogonal. Let us pick the origin of our vector system at a chain center of symmetry.

When the chains are packed very closely within a row, the planes of the chain zigzags are nearly perpendicular to the row planes and the H atoms of adjacent chains fit together in such a way that the zigzags are opposed. Then the **b** translational symmetry vector traverses two interchain distances and there is centered symmetry in the row. When the planes of the chain zigzags are rotated away from being nearly perpendicular to the row plane, the interchain H-atom packing changes character in that the zigzags of neighboring chains go the same way, and thus **b** extends just to adjacent chains. The t_T and t_M chain relations of Kitaigorodskii (1961) are respectively the special cases with closest approach of the two general chain relations within a row mentioned above. In the first, twofold rotation axes between them relate neighboring chains, and in the second, twofold screw axes relate them. The symmetry of a row retains the centers of symmetry, twofold screw axes and mirror planes of the individual chains, but unless the chain zigzags are exactly parallel or perpendicular to a row plane, the row loses the twofold rotation and glide symmetry of the individual chains. A row will have additional centers of symmetry halfway between the chain axes at 0 and $\frac{1}{2}\mathbf{c}$ in the first relation, and at $\frac{1}{4}$ and $\frac{3}{4}\mathbf{c}$ in the second relation.

Symmetry relations between chain rows

We shall generate the various chain-packing modes by the parallel stacking of identical uniform rows. Adjacent rows may have the same direction of their chain axes, or their chain axes may be rotated with respect to one another about the normal to the row planes. We shall now survey all the symmetry relations that can relate two adjacent uniform rows, and subsequently use these row relations to build up unit cells which would be the subcells which describe the chain packing in hydrocarbon-chain compounds.

When we consider the possible symmetry operations that can relate uniform rows, a mirror plane is immediately ruled out since the convex parts of one row will butt against the mirror-related parts of the next row rather than fit into the concavities.

Because of the inherent symmetry of hydrocarbon chains, a center of symmetry between the rows in the plane through **b** perpendicular to **c** is equivalent to a translation symmetry vector **a** passing through that point. (Any center of symmetry between the rows leads to parallelism of the chain axes of the neighboring rows.) If this center is at $\frac{1}{2}\mathbf{c}$ away from the above plane we have the same result. If this center is at $\frac{1}{4}$ or $\frac{3}{4}\mathbf{c}$, this is equivalent to a twofold rotation axis parallel to **c** going through the center. Any other between-row position of a center is ruled out by the same packing argument that required **b** and **c** to be orthogonal, which here requires **a** to be perpendicular to **c**.

A twofold rotation axis between the rows parallel to **b** is equivalent to a mirror if it is at $\frac{1}{4}$ or $\frac{3}{4}$**c**, or to a *c*-glide perpendicular to **a** if it is at 0 or $\frac{1}{2}$**c**. A twofold screw axis between the rows parallel to **b** is equivalent to an *a*-glide perpendicular to **b** if the axis is at 0 or $\frac{1}{2}$**c** or to a *b*-glide perpendicular to **a** if it is at $\frac{1}{4}$ or $\frac{3}{4}$**c**. A twofold screw axis between the rows parallel to **c** is equivalent to a translation symmetry vector passing orthogonally through that axis. Twofold rotation or screw axes not parallel or perpendicular to **c** are possible, but we shall consider these later. The only remaining symmetry axes parallel to the uniform rows that can relate them are 4 and $\bar{4}$, where the planes of the chain zigzags are at 45° to the planes of the rows and the rotation axes go through the latter planes parallel to **c** at $\frac{1}{2}$**b**. The first of these can be ruled out because, clustered around the fourfold axis, all the convex parts butt against one another. The second is more likely but its probability of occurrence is still low since each chain is in van der Waals contact with only four others; such a configuration has not been observed and we consider it mechanically unstable in the crystalline state.

Let us now consider the remaining possible symmetry operations, restricting our attention for the moment to the cases where the **b** and **c** symmetry axes are coincident with these axes as defined within each row. An *a*-glide perpendicular to **b**, a *b*-glide perpendicular to **a** and a *c*-glide perpendicular to **a** are all possible. The last-mentioned glide is, however, considered improbable because of the criterion that each chain should be in van der Waals contact with more than four neighbors. An *n*-glide perpendicular to **a** or **b** is equivalent to a *b*- or *a*-glide respectively. An *a*- or *n*-glide perpendicular to **c**, *B*-face centering or body centering are all equivalent to twofold axes. *C*-face centering is equivalent to translational symmetry.

The only other possible symmetry relations are fourfold inversion or various screw axes parallel to **a**. All the previously described symmetry relations in which **a** is normal to the row planes imply twofold screw axes parallel to **a**, and no new relations are generated by considering this symmetry relation independently. If we insist that chains of equal total length shall end in parallel planes in the structure, as has always been found, then all threefold and sixfold screw axes parallel to **a** are eliminated from consideration. Of the various fourfold screw axes and a fourfold inversion axis, the latter and a 4_2 axis require the chain zigzag planes to be perpendicular to the row planes. This latter circumstance introduces a glide perpendicular to **a** (when a fourfold axis is possible, as is discussed in the next section) relating atoms of the same chain on opposite sides of a row plane. This glide combined with either 4_2 or $\bar{4}$ produces the other. Nevertheless there are distinctly different row relations depending on whether the 4_2 or $\bar{4}$ axes intersect the chain axes, and this shall be our distinguishing criterion. All these fourfold relations involve crossed chains and will be discussed further in the next section.

To summarize at this point: if we require that (1) the structures are made up of hydrocarbon chains in uniform rows, (2) there is some interpenetration of H atoms between rows, (3) each chain is in van der Waals contact with more than four others, (4) the symmetry axes in the rows are parallel and perpendicular to the chain axes, and (5) the chain axes of all rows are parallel, a survey of all the symmetry operations that can relate such layers shows that all the probable ones reduce to the following:

1. Simple translation;
2. A twofold rotation axis parallel to the chain axes;
3. An *a*-glide perpendicular to **b**; and,
4. A *b*-glide perpendicular to **a**.

Let us designate these as *t*, 2, a_b and b_a row relations respectively.

Further row relations with rotated axes

If we allow the symmetry axes to be arbitrarily rotated about an axis perpendicular to the row plane with respect to the direction of the chain axes, some of the symmetry operation degeneracy due to the inherent symmetry of the chains is removed. We can have the rows related by twofold rotation or screw axes parallel to some direction in the row planes, simple *n*-glide's, and various face or body centerings. Rotation or screw axes and *a*- or *n*-glides, each perpendicular to the new axes **b** or **c**, all lead to crossed chains. Glides perpendicular to **a**, *B*- and *C*-face centering, and body centering all lead to parallel chain axes. These latter situations can be described by the original set of symmetry axes and so will not be further considered.

What remain are the crossed-chain row relations in which the new **b** and **c** vectors represent the periodicity of net-point matching between rows. Since the orthogonal original vector sets in each row (call them $\mathbf{b}_0$ and $\mathbf{c}_0$) are identical but rotated with respect to one another, the new vector set (which we will call **b** and **c**) needed to describe the combined symmetry will lie in directions bisecting the rotated angle for each original axis. Thus **b** and **c** will also be orthogonal. Every net point from the new set must correspond to a net point from each of the original sets, but the converse of this statement is generally not true.

For a reasonably high degree of net-point matching between rows, we may expect that adjacent chains go through adjacent points of the new net. Thus the [011] and [01$\bar{1}$] directions of the new net would be parallel to the chain axes, and these net diagonals would have the length of a hydrocarbon chain with an even number of CH_2 groups (of length $n.c_0$ where n is an integer). Let us define a vector **d** parallel to **b** relating adjacent chains in one row. Then $\mathbf{d}=\mathbf{b}_0$ if $\mathbf{b}_0$ relates adjacent chains, and $\mathbf{d}=\frac{1}{2}\mathbf{b}_0$ if $\mathbf{b}_0$ relates alternate chains. The diagram of Fig. 1 represents the relationship between the original and the new axes.

The angle between **b** and the chain axes will be called ψ, and the quantity m is integral or half-integral depending on whether $\mathbf{d}=\mathbf{b}_0$ or $\mathbf{d}=\frac{1}{2}\mathbf{b}_0$ respectively. It follows directly from the trigonometry of Fig. 1 that:

$$m(n-m)=\mathbf{d}^2/\mathbf{c}_0^2$$
$$\text{and } \tan\psi=\sqrt{[m/(n-m)]}$$

For the moment we shall only consider the situations in which $m \geq n\text{-}m$, since interchange of m and $n\text{-}m$ is equivalent to interchange of **b** and **c**.

Let us now consider what the possible values of m and n might be in the light of the known dimensions of hydrocarbon chains: In known crystal structures, the range of the alternate C–C distances along a hydrocarbon chain ($\mathbf{c}_0$) is from 2·50 to 2·66 Å. The range of distances between chain axes (**d**) in a uniform row is 4·0 to 5·0 Å, depending on the angle the plane of the chain zigzags makes with the row plane. When this angle is close to 90°, $\mathbf{d}=\frac{1}{2}\mathbf{b}_0$ in the range of **d** from 4·0 Å up to about 4·2 Å. Beyond this latter value of **d**, the H atom intermeshing between chains changes and $\mathbf{d}=\mathbf{b}_0$. Thus, for m half-integral,

$$2{\cdot}25 \leq m(n-m) \leq 2{\cdot}82,$$

and for m integral

$$2{\cdot}82 \leqq m(n-m) \leq 4{\cdot}00.$$

The upper limit in the last expression is rather unrealistic since, near the maximum in **d**, the chain zigzag planes must be near 45° from the row planes, and the surface presented to the next row is so puckered that the density of van der Waals contacts between such rows when crossed will be minimal. In addition, the density of such contacts within a row is minimal with this orientation. We consider a more realistic upper limit for $m(n\text{-}m)$ to be 3·5. This restriction excludes two possibilities having a value of 4·0.

Within these limits, there are only four possibilities, and these are shown in Table 1, where ω is the angle between chain axes of adjacent rows and equals $180° - 2\psi$.

Table 1. *Angles of crossed-chain row relations*

n	m	$m(n-m)$	ψ	ω
3	1·5	2·25	45°	90°
4	3	3·00	60°	60°
5	4·5	2·25	71·6°	36·8°
6	5·5	2·75	73·2°	33·6°

The chain zigzag planes are nearly or exactly perpendicular to the row planes in the first, third and fourth of these possibilities, since m is half-integral. The first possibility is the only one in which the fourfold relations about **a**, mentioned in the last section, can occur. In the second possibility, the chain zigzag planes are nearly or exactly parallel to the row planes since m is integral. This particular chain orientation with respect to the rows is particularly favorable for this angle of crossing, since the array of H atoms on the surface of such a row is remarkably close to being hexagonal, and the next row can fit on top of it with a rotation of any multiple of 60° with little loss of packing efficiency as compared to no rotation. For this reason, one can expect this kind of crossed-chain row relation to be most prevalent.

When n is even, each row is A-centered and an n-glide is equivalent to an a-glide. Only one type of symmetry relation between rows is possible since an a-glide perpendicular to an axis, a twofold rotation and a twofold screw parallel to that same axis, are all equivalent.

When n is odd, each row is primitive. We can either have an a-glide perpendicular to one of the axes (which is equivalent to a twofold screw axis parallel to that axis) or we can have a twofold rotation axis relating the rows. Only if $\omega = 90°$ and if the planes of the chain zigzags are exactly perpendicular to the row planes, can n-glides occur. Then, an n-glide perpendicular to **a** will always relate atoms on opposite sides of the same chain, and if the rows are related by twofold axes, an n-glide perpendicular to the third axis is automatically generated.

The arbitrariness of the choice in assignment of **b** and **c** was previously destroyed when we considered only $m \geq n\text{-}m$, which in effect defined the **c** axis as the one parallel to the bisector of the acute chain-crossing angle. Let us now lift this restriction and restore the arbitrariness so that we need not duplicate the symmetry operations with respect to **b** and **c**. Thus we can always assume **b** as the axis perpendicular to the two others, but we now must include angles (ω) between chain axes which are supplements of the ones previously given.

To summarize for crossed-chain row relations, if we assume (1) uniform rows, (2) hydrocarbon chains of

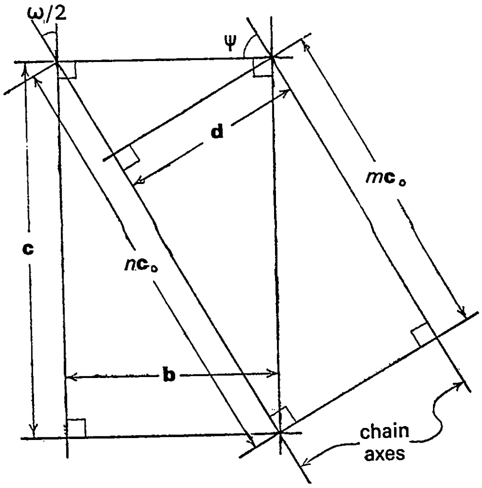

Fig. 1. Relationship between the symmetry axes within a chain row and the combined-symmetry axes of two rows with the chain axes crossed.

equal total length end in planes, (3) net-point matching between rows so that there is a net representing the combined symmetry whose points correspond to original net-points within each row, (4) adjacent chains in a row go through adjacent combined-symmetry net points, (5) the planes of the chain zigzags are nearly parallel or perpendicular to the row planes, and (6) the range of distances between chain axes within a row and the range of alternate C–C distances along a chain are those found in known crystal structures, then only four crossing angles (and their supplements) are possible: 90°, 60°, 36·8°, and 33·6°. If we use only the first four assumptions, a survey of all the symmetry operations relative to the combined symmetry vectors that can relate the rows shows that all the possible ones are implied by the following: (1) A-centering, (2) no centering but a twofold screw axis parallel to **b**, (3) no centering but a twofold rotation axis parallel to **b**, and (4) any fourfold screw or inversion axis parallel to **a**. Let us designate these as A, 2_1, 2_b, 4_1, 4_2, 4_3, and $\bar{4}$ row relations respectively.

Chain-packing subcells

So far, we have considered all the possible symmetry operations relating adjacent uniform rows of chains, subject to reasonable conditions for packing. If we intend to determine what total chain-packing symmetries (*i.e.* chain-packing subcell symmetries) might occur, we must consider the sequence of symmetry relationships from row to row. In principle, the sequence can be very complex. Nevertheless, each of the known chain-packing subcells extends over no more than two rows and involves only one kind of symmetry relation between rows. These subcells can be fully described by specifying (1) whether the angle between the chain zigzag planes and the row planes is 0°, 90° or neither, (2) the type of symmetry operation relating the rows, (3) the angle between chain axes of neighboring rows, and (4) the relative disposition of symmetry axes on each side of a given row when the chain zigzag planes are parallel or perpendicular to the row planes. When the fourth specification is needed, the positions of the symmetry axes on both sides of a row can be related to each other either by the symmetry of the rows or by the symmetry that would have been followed without the special chain zigzag orientation. If the axis positions follow the row symmetry, orthorhombic subcells are formed; if not, monoclinic subcells result. In the more general cases, t and 2 row relations lead to monoclinic subcells with **c** as the unique axis; A, 2_1 and 2_b row relations lead to monoclinic subcells with **b** as the unique axis; a_b and b_a row relations lead to orthorhombic subcells; and fourfold screw and inversion row relations lead to tetragonal subcells with **a** as the unique axis.

Let us now define a subcell notation to represent all of the structures discussed above. Monoclinic, orthorhombic and tetragonal subcells will be denoted by M, O and T respectively. A following superscript $^{\parallel}$ or $^{\perp}$ will denote the special cases of the planes of the chain zigzags parallel or perpendicular respectively to the row planes. A following subscript will denote the between-rows symmetry relation: $_1$ for t, $_2$ for 2, $_a$ for a_b,

Table 2. *Parallel-chain subcells*

Subcell symbol	Subcell symmetry (**c** along chain axes, **b** in row plane)		Previously used symbol and reported symmetry; references and comments	
M_1	$P2_1/m$	No. 11	Never observed – M (Kitaigorodskii, 1961) – called 'ideal'.	
M_2	$B2/m$	No. 12	$T_{\parallel}$ ($P\bar{1}$)	(Abrahamsson, 1959*e*) (Hayashida, 1962) (Müller & Lonsdale, 1948) (von Sydow, 1956) (Vand & Bell, 1951)
			T	(Kitaigorodskii, 1961)
O_a	$Pnam$	No. 62	$O_{\perp}$ ($Pnam$)	(Abrahamsson, 1959*e*) (Bunn, 1939) (Shearer & Vand, 1956) (von Sydow, 1956) (Vainshtein & Pinsker, 1950)
			R	(Kitaigorodskii, 1961)
O_b	$Pbnm$	No. 62	$O_{\perp}'$ ($Pbnm$)	(Abrahamsson, 1959*c*) (Abrahamsson, 1959*e*)
$M_1{}^{\parallel}$	$P2_1/m$	No. 11	$M_{\parallel}$ ($P2_1/m$)	(Abrahamsson & Westerdahl, 1963), special case of M_1
$M_2{}^{\parallel}$	$B2/m$	No. 12	Never observed – special case of M_2	
$M_2{}^{\perp}$	$A2/m$	No. 12	Never observed – special case of M_2 with change of row designation	
$O_1{}^{\parallel}$	$Pnm2_1$	No. 31	Never observed.	
$O_2{}^{\parallel}$	$Pma2$	No. 28	$O_{\parallel}'$ ($P22_12$)	(Abrahamsson & Ryderstedt-Nahringbauer, 1962)
$O_2{}^{\perp}$	$A2_122$	No. 20	$O_{\parallel}$ ($P2_12_12$)	(Abrahamsson, 1959*e*) (von Sydow, 1958)

$_b$ for b_a, $_A$ for A, $_{21}$ for 2_1, $_{2b}$ for 2_b, $_{42}$ for 4_2 and $_{\bar{4}}$ for $\bar{4}$. We shall only consider subcells on the level of complexity of those that have been reported, and since this excludes subcells involving more than two rows, we shall henceforth ignore 4_1 and 4_3 row relations. For the crossed-chain modes, we shall use a preceding numerical subscript which is the chain-crossing angle (ω) that is bisected by the **c** vector.

Parallel chain subcells

Displayed in Table 2 are all the resulting parallel chain subcells on the level of complexity of the reported ones. In several cases ($O_2^{\parallel}$ and $O_2^{\perp}$) the space groups reported by previous authors were deficient in including the total symmetry of the structures they described.

In the case of M_2, which has previously been reported as triclinic, the shear distortion, due to end forces when the overall crystal symmetry is lower than the chain packing symmetry, becomes particularly important. Reproduced in Table 3 are the relevant data for the triclinic subcell from Abrahamsson's (1959*e*) review article for nine known structures having this subcell, plus the values of $\Delta z = a_s \cos \beta_s + b_s \cos \alpha_s$. The quantity Δz is a measure of this shear distortion, since it is the distance in the $\mathbf{c}_s$ direction between the plane perpendicular to $\mathbf{c}_s$ going through the origin and the end of the [110] triclinic lattice vector. In the monoclinic representation with no shear, this is the **b** vector and $\Delta z = 0$. As can be seen in Table 3 the values of Δz range on both sides of zero, and if we exclude the data on A' n-C_{15} fatty acid (in which Δz is an order of magnitude larger than in the other compounds and thus may be suspect), zero is within a standard deviation of the mean. We consider this as an indication that the 'triclinic' subcell is ideally monoclinic but subject to fairly random distortions. The monoclinic subcell representation of this chain-packing mode does not (contrary to the cases discussed above where the previously reported symmetry was too low) add new information concerning expected systematic diffraction absences. Nevertheless, this representation may lead to easier interpretation of data, and so the monoclinic representation of Vand's subcell is described in Table 4. The relationship between the two representations is shown in Fig. 2, in which the two subcells are each seen

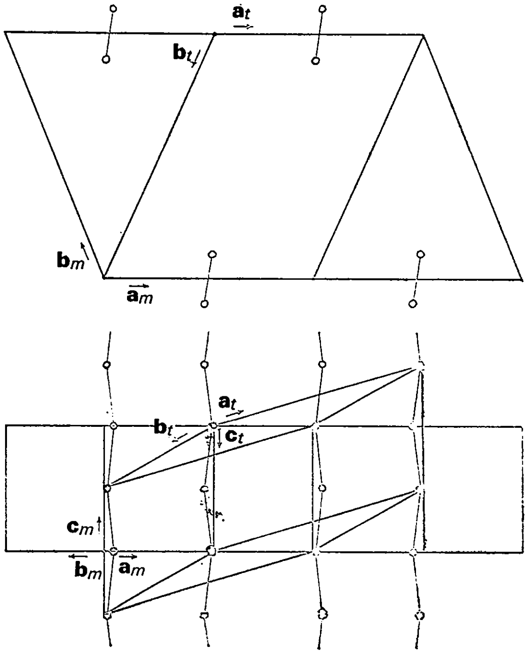

Fig. 2. Comparison between triclinic and monoclinic representations of the M_2 subcell.

Table 3. *Data for the 'triclinic' subcell*

(From Abrahamsson, 1959*e*)

Long-chain compound	a_s (Å)	b_s (Å)	α	β	Δz (Å)
Trilaurin (Vand & Bell, 1951)	4·287	5·40	74°45′	108°2′	+0·09
A' n-C_{15} (von Sydow, 1956)	4·25	5·82	66°	106°	+1·20
A n-C_{12} (von Sydow, 1956)	4·42	5·41	74°	109°	+0·05
17-Me-C_{18} (Abrahamsson, 1959*d*)	4·28	5·29	78°	109°	−0·30
16DL-Me-C_{18} (Abrahamsson, 1958)	4·49	5·40	73°	107°	+0·27
14DL-Me-C_{18} (Abrahamsson, 1959*a*)	4·47	5·16	72°	109°	+0·14
9DL-Me-C_{18} (Abrahamsson, 1956)	4·20	5·27	81°	103°	−0·12
3DL-Me-C_{18} (Abrahamsson, 1959*e*)	4·22	5·18	75°	107°	+0·11
2DL-Me-C_{18} (Abrahamsson, 1959*b*)	4·33	5·27	72°	109°	+0·22

	Including A' n-C_{15}	Excluding A' n-C_{15}
$\overline{\Delta z}$	+0·184	+0·058
$\sigma(\overline{\Delta z})$	0·139	0·066

projected down the chain axes and projected perpendicular to the common face of both subcells.

The row stacking for the various parallel-chain subcells is shown in Figs. 3, 4 and 5. One can see in Fig. 3 that the M_1, M_2, O_a and O_b chain-packing modes are related to one another by multiples of approximately 90° rotations of the planes of the chain zigzags of alternate rows with respect to the other rows. Similarly, in Fig. 4, it is obvious that 180° rotation of alternate rows relates $O_1^\parallel$ and $O_2^\parallel$, and also $M_1^\parallel$ and $M_2^\parallel$.

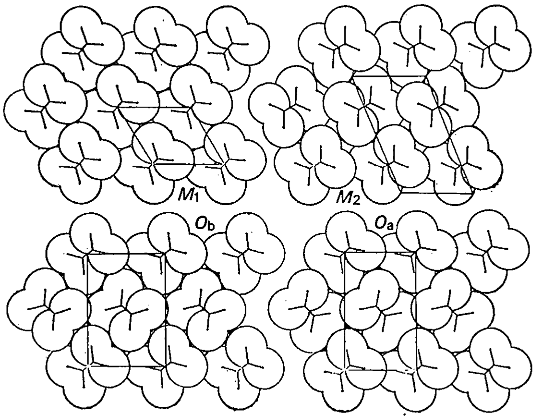

Fig. 3. Parallel chain axes, hydrocarbon chain packing modes: Chain zigzag planes at oblique angle to rows.

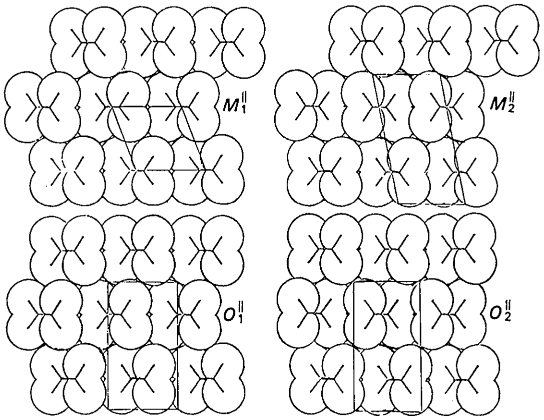

Fig. 4. Parallel chain axes, hydrocarbon chain packing modes: Chain zigzag planes parallel to rows.

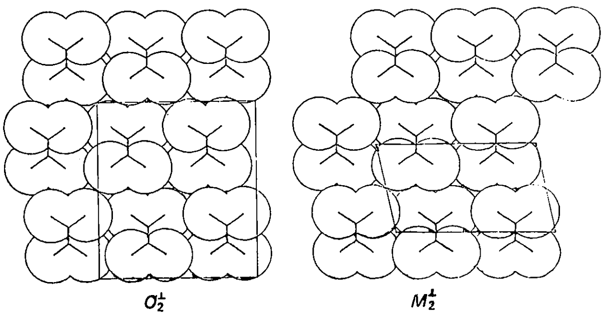

Fig. 5. Parallel chain axes, hydrocarbon chain packing modes: Chain zigzag planes perpendicular to rows.

Table 4. *Monoclinic transformation of Vand's data on the 'triclinic' subcell*
(Vand & Bell, 1951)

Subcell symmetry:	$B2/m$
Subcell dimensions:	$a_s = 8{\cdot}156$ Å $b_s = 5{\cdot}121$ $c_s = 2{\cdot}45$ $\gamma_s = 112°7'$
Carbon atom coordinates in asymmetric unit:	(0·2813, 0·1021, 0)

Crossed-chain subcells

The various crossed-chain subcells are shown in Table 5. For $n > 3$, each listed mode which distinguishes between **b** and **c** is in actuality two modes, one with ω as listed in Table 1, and the other with ω the supplement of the first. Thus 31 different subcells are tabulated here. When we wish to distinguish between these in our notation, we shall use a preceding subscript equal to the value of ω. For the orthorhombic modes, where there is a choice of subcells, the second is a special case of the first such that additional twofold rotation axes parallel to the **a** axis go through the chain axes. Further criteria based on packing efficiency that could reduce this list have not been developed, primarily because of the lack of experimental data.

Attractive van der Waals energy of reported parallel-chain modes

Salem (1962) has derived an expression for calculating the van der Waals attractive energy of long parallel chains. It is easy to use since it depends only on distances between chain axes. Correcting for small errors in Salem's calculations (such as his assuming that there are four crystallographically distinct chains in the O_a subcell rather than the correct number, two) and generalizing for any parallel-chain mode, we have:

$$W_{\text{att.}} = -620\left[\left(\sum_{r\leq R}\frac{1}{r^5}\right)+\frac{2\pi}{3AR^3}\right]$$

where r is the distance of some other chain axis from a given chain axis, R is a value of r large enough that the summation (the first term in the bracket) can be replaced by an integral (the value of which is the second term) for $r > R$, and A is the excluded cross-sectional area per chain. This calculation was programmed for an IBM 1620 computer, and it was found that, if we set $R = 20A$, 64 to 70 chains were included in the summation and the integral term contributed less than 1% to the energy.

The results are shown in Table 6. Salem implies that, though the repulsive contribution to the total energy is much more sensitive to the specific H-atom interactions in various chain-packing modes, it might not be very far wrong to assume that 'the attractive and repulsive energies [are] in a ratio of 5 to 1 at the equilibrium distance'. Thus the total van der Waals energy might tend to be proportional to the attractive component.

Table 5. *Crossed-chain subcells*

n	Subcell symbol	Subcell symmetry			
3	$T_{42}\perp$	$P4_2/nam$	No. 138		[special case of $O_{21}\perp$ (*Pnaa*)]
3	$T_{\bar{4}}\perp$	$P4_2/nba$	No. 133		[special case of $O_{2b}\perp$ (*Pn2n*)]
3	M_{21}	$P2_1/a$	No. 14		
3	M_{2b}	$P2$	No. 3		
4	M_A, $M_A\parallel$	$A2/a$	No. 15		
4	$O_A\parallel$	$Am2a$	No. 40	or	*Amaa* No. 66
5	M_{21}, $M_{21}\perp$	$P2_1/a$	No. 14		
5	M_{2b}, $M_{2b}\perp$	$P2$	No. 3		
5	$O_{21}\perp$	$Pn2_1a$	No. 33	or	*Pnaa* No. 56
5	$O_{2b}\perp$	$Pn2n$	No. 34	or	*Pnan* No. 52
6	M_A, $M_A\perp$	$A2/a$	No. 15		
6	$O_A\perp$	$A2aa$	No. 37		
Occurrence in reported structure:					
		$_{90}T_{42}\perp$	or	$_{90}M_{21}$	(Turner & Lingafelter, 1955)
		$_{60}M_A\parallel$	or	$_{60}M_A$	(Lomer, 1952)
					(Sim, 1955)
					(Vand, Lomer & Lang, 1949)

Table 6. *Attractive van der Waals energy by the Salem method*

Subcell symbol	Data source	$W_{\text{att.}}$ (kcal/mole/CH_2)
M_2	(Abrahamsson, 1959*e*), average	−2·09
O_a	(Salem, 1962)	−2·02
O_a	(Abrahamsson, 1959*e*), average	−1·94
O_b	(Abrahamsson, 1959*c*) (Abrahamsson, 1959*e*)	−1·99
$M_1\parallel$	(Abrahamsson, 1963)	−2·03
$O_2\parallel$	(Abrahamsson & Ryderstedt-Nahringbauer, 1962)	−1·14
$O_2\perp$	(Abrahamsson, 1959*e*) (von Sydow, 1958)	−0·94

Since many of the assumptions of this method are somewhat questionable, one should not take the numbers in Table 6 very seriously. Nevertheless one can conclude that, since the $M_1^{\parallel}$ and O_b modes (which have each been found only once) have the same order of magnitude of energy as the O_a mode (which is the most common), therefore, the frequency of occurrence of the various modes cannot be adequately explained on the basis of van der Waals energy alone. We are currently investigating the possibility that a factor of prime importance in explaining this frequency distribution may be the thermal energy, which may be related to the ability of each mode to undergo oscillations of the chains about the chain axes with minimal axis displacement while maintaining van der Waals contact with their neighbors.

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